Bolko von Roedern, MS 3212
National Center for Photovoltaics
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

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Dear Bolko,

This is the second quarterly report of our third 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 is painted. The work focuses on (a) deriving the bench mark picture for world-record cells, (b) analyzing state-of-the-art cells from industrial processes, and (c) aiding in the troubleshooting of cells with substandard performance.

In the last months, we have investigated different chalcopyrite absorbers from NREL (group of R. Noufi) and IEC (group of W. Shafarman). An intrinsic feature of Cu chalcopyrites is that their surface composition significantly deviates from the stoichiometric Cu : (In+Ga) : (S+Se) = 1 : 1 : 2 composition in the absorber bulk. Surface-sensitive characterization techniques almost always indicate a Cu-poor surface composition [1-5]. In consequence, the formation of an ordered defect compound at the absorber surface was suggested [6,7]. Defect chalcopyrites with a composition ranging from 1 : 2 : 3.5 [6,8] over 1 : 3 : 5 [9-12], 1 : 5 : 8 [12, 14], 1 : 7 : 11 [14] to 1 : 11 : 17 [14] were proposed and corresponding (bulk) samples were synthesized. The optical characterization of these bulk materials show that the defect (Cu-poor) chalcopyrites have larger band gap energies (E_g) compared to their stoichiometric counterparts [8-11, 12-14]. For solar cell absorbers, direct determination of the surface band gap by UV photoelectron spectroscopy (UPS) and inverse photoemission (IPES) recently showed that E_g is indeed widened at the Cu-poor surface of absorbers with stoichiometric bulk composition [2-5].

To investigate whether the composition of the chalcopyrite absorber has an impact on the formation of the Cu-poor, E_g-widened region and its extension into the absorber bulk, different chalcopyrite thin film solar cell absorbers have been investigated. We have used various photon and electron spectroscopies with different information depths in order to gain *depth-dependent* E_g information. For all investigated samples we find an increasing band gap energy with decreasing information depth and the formation of a surface region with significantly higher E_g. In addition, we find that the E_g-widened sur-

face region extends further into the bulk of the absorber for the sulfur-free CIGSe absorber (i.e., the absorber with smaller bulk band gap) than for the CIGSSe absorber.

Detailed Description of the Activities:

This investigation is initially based on two kinds of samples: S-free CIGSe/Mo/glass and S-containing CIGSSe/Mo/glass test structures. The chalcopyrite absorber films (approx. 2 μm thick) were prepared using multi-source thermal co-evaporation without intentional composition gradients. The Mo-coated soda-lime glass substrate was held at 550°C during absorber formation (see Ref. 15 for more details). In order to minimize sample contamination due to air exposure, the samples were individually packed in two plastic bags filled with dry nitrogen and some desiccant immediately after preparation. The sample exposure time to ambient air (before the first characterization) could thus be limited to less than 5 min. Once at UNLV, the samples were unpacked in a glovebag/glovebox under dry nitrogen atmosphere and directly introduced into our ultra-high vacuum (UHV) surface characterization system.

The samples were investigated by different spectroscopic techniques in order of greatest surface sensitivity. The samples were first characterized by UPS and IPES, since these (electron-based) techniques are most surface sensitive among the applied spectroscopies and thus would be most influenced by any surface contamination. For the UPS measurements, He I excitation and a Specs PHOIBOS 150 electron analyzer with a multi-channeltron detector were used. For the IPES experiments, a low-energy electron gun (STAIB) and a Dose-type detector with a SrF_2 window and Ar: I_2 filling were used. The UPS and IPES experiments were performed in UHV with a base pressure below $1 \cdot 10^{-10}$ mbar.

Next, the electronic structure of the surface-near bulk of the samples was investigated by x-ray emission/absorption spectroscopy (XES/XAS) at the SXF endstation of Beamline 8.0 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. For the transport to the ALS, the samples were again carefully packed and sealed in an inert atmosphere. Once at the ALS, the samples were mounted in and transferred through ambient air into the UHV analysis chamber of the SXF endstation (base pressure below $5 \cdot 10^{-8}$ mbar). The XAS spectra were recorded in the total fluorescence yield mode using a channeltron mounted in front of the sample, and the XES spectra were taken with the permanently installed SXF spectrometer at Beamline 8.0.

Finally, the samples were transferred back to UNLV (in air) and optical reflection spectra of the CIGSe and CIGSSe samples were measured using a conventional UV-Vis-NIR spectrophotometer (Varian, Cary 5000).

The spectra recorded for the CIGSe and CIGSSe samples by the different spectroscopic techniques are shown in Fig. 1. The different spectra (optical reflection, left; XES/XAS, center; UPS/IPES, right) allow a determination/estimation of the E_g of the investigated samples with three different information depths, as will be described in the following. As shown in Fig. 1 (left), the optical reflection spectra exhibit pronounced interference patterns. These (Fabry-Perot) oscillations are caused by interference of light reflected at the absorber/air and absorber/substrate interfaces and thus depend on the thickness d of the absorber and its absorption coefficient α. For photon energies higher than E_g, no oscillations are observed since the photons are completely absorbed in the CIGSe (CIGSSe) layer. In the spectral region with pronounced interferences the CIGSe (CIGSSe) absorber must consequently be transparent. Hence, in first approximation, the photon energy at which the oscillations in the reflection spectrum disappear corresponds to the E_g. To further refine this approach, we note that the E_g is actually shifted to lower energies since the absorption coefficient only gradually increases above E_g and since the thickness d of the absorber is sufficiently small that some light reflected at the absorber/substrate interface (although attenuated) will still be able to interfere with light reflected at the absorber/air interface.

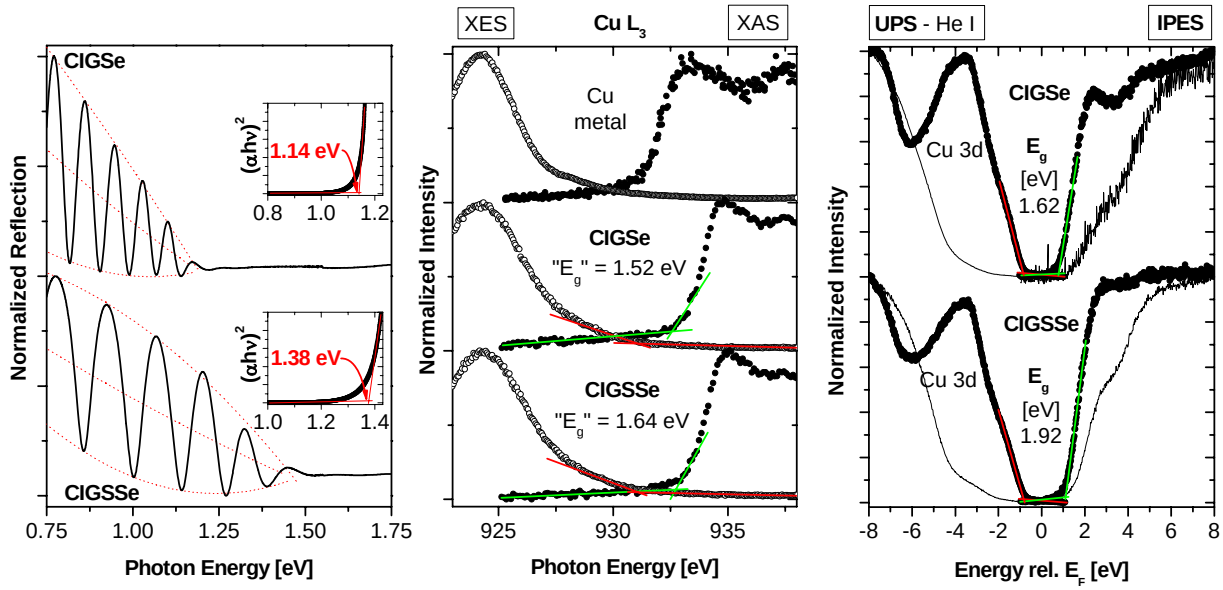

Fig. 1 Left: Optical reflection spectra of the investigated CIGSe (top) and CIGSSe (bottom) sample. The respective envelopes of the interference extrema and the constructed mean values (red dotted lines) are also shown. Insets: Approximated absorption coefficient for the CIGSe (top) and CIGSSe (bottom) sample plotted as $(\alpha h\nu)^2$ vs. the photon energy hν. The given band gap energies have an error of ± 0.05 eV.
Center: Cu L_3 x-ray emission (XES, left) and absorption (XAS, right) spectra of the investigated CIGSe (middle spectra) and CIGSSe (bottom spectra) samples. For comparison, the spectra of metallic Cu (top) are also shown. The linear approximation of the leading edges for the determination of "E_g" (a lower bound for the true band gap value – see text) is indicated by the solid green and red lines. The given band gap energies "E_g" have an error of ± 0.20 eV.
Right: UV photoelectron spectroscopy (UPS, left) and inverse photoemission (IPES, right) measurements of the investigated CIGSe (top spectra) and CIGSSe (bottom spectra) samples. For each sample, two sets of spectra are shown, one for the as-introduced (thin solid lines) and one for the cleaned samples (dots). The linear approximation of the leading edges for the determination of E_g is indicated by the solid green and red lines. The given band gap energies E_g have an error of ± 0.15 eV.

Thus, our approach to determine E_g from the "oscillation-free" reflectance R is as follows. We assume that the interferences oscillate around the "true" reflectance value and thus approximate R by the mean of the interference maxima and minima. Based on the respective envelopes of the extrema (fitted by 2nd order polynomials; see Fig. 1, left) the mean spectral characteristic of R can be constructed. The absorption coefficient was estimated by applying Eq. (1) [16], where R_{max} (R_{min}) is the maximal (minimal) reflectance in the considered spectral range (note that this approach gives reasonable results since the absolute value of α is not relevant for the estimation of E_g). Since it is well known that Cu chalcopyrites are direct semiconductors, the approximated absorption coefficient is plotted as $(\alpha h\nu)^2$ vs. the photon energy hν to determine E_g (see insets in Fig. 1, left). We find a band gap energy of [1.14 (1.38) ± 0.05] eV for the CIGSe (CIGSSe) absorber.

$$2\alpha d = \ln\left[\frac{(R_{max} - R_{min})}{(R - R_{min})}\right] \qquad (1)$$

Fig. 1 (center) shows the Cu L_3 XES and XAS spectra of the investigated CIGSe and CIGSSe samples. For comparison also the spectra of metallic Cu are shown. Since XES and XAS probe occupied and unoccupied states, respectively, the combination of both spectra gives information about E_g. However, the band gap values based on these measurements are approximate and represent a lower limit due to the potential existence of core exciton features in the XAS spectra. E_g was determined as the in-

tersection of the baseline with a linear extrapolation of the leading XES and XAS edges. The E_g for the CIGSe (CIGSSe) absorber is found to be [1.52 (1.64) ± 0.20] eV.

Finally, the corresponding surface-sensitive UPS and IPES spectra of the investigated CIGSe and CIGSSe samples are shown in Fig. 1, right. For each sample, two sets of spectra are shown: One for the as-introduced and thus surface-contaminated sample and one after cleaning the sample surface by an ion-stimulated desorption process with 50 eV Ar^+ ions. Similar to the XES and XAS measurements, UPS and IPES give information about the occupied and unoccupied states, respectively. Hence, by combination of both techniques it is possible to measure the band gap at the *surface*. Again, linear extrapolation of the leading edges of the UPS and IPES spectra is used to determine the valence band maximum (VBM) and conduction band minimum (CBM), respectively, resulting in the surface band gap E_g = CBM - VBM. For the clean surface of the CIGSe (CIGSSe) absorber we find a band gap energy of [1.62 (1.92) ± 0.15] eV.

In order to understand the observed variations in E_g, the information depth of the different spectroscopic techniques has to be considered. Under the assumption that $\alpha \approx 10^4$ cm^{-1} for photon energies slightly above E_g (as reported for $CuInSe_2$ [17]) the information depth of the optical reflection measurement is ≈ 2000 nm, which is in the range of the thickness of the investigated CIGSe (CIGSSe) layers (note that for this and the following considerations the information depth is defined as the thickness from which 90% of the overall signal is collected). XAS (in total fluorescence yield mode) and XES have similar information depths (≈ 200 nm) (based on [18]). According to the "universal curve" [19], the inelastic mean free path (IMFP) of the detected photoelectrons for the UPS (He I) measurements of the investigated CIGSe (CIGSSe) samples is ≈ 10 Å, which results in an information depth of ≈ 2 nm. The information depth of our IPES measurements is approx. twice that of the UPS technique.

Fig. 2 shows a summary of our results. It shows a schematic presentation of the determined band gap energies of the investigated CIGSe (CIGSSe) sample using the three different spectroscopic approaches (optical reflection, left; XES/XAS, center; UPS/IPES, right) as a function of the information depth. For the investigated CIGSe (CIGSSe) samples we find an increasing band gap energy with decreasing information depth and, in particular, the formation of a surface region with significantly higher E_g. The smaller difference of the band gap energies determined by XES/XAS and UPS/IPES for the CIGSe sample compared to that for the CIGSSe sample suggests that the E_g-widened (i.e., Cu-poor) region is more pronounced for the CIGSe absorber.

Currently we are extending our experiments also to wide-gap chalcopyrites such as $CuInS_2$ and $CuGaSe_2$ in order to test the hypothesis that the E_g-widened surface region is less pronounced for absorbers with larger bulk band gaps. This might explain the lower performance of devices based on wide-gap chalcopyrite absorbers compared to the world record efficiencies reported for their low-gap counterparts.

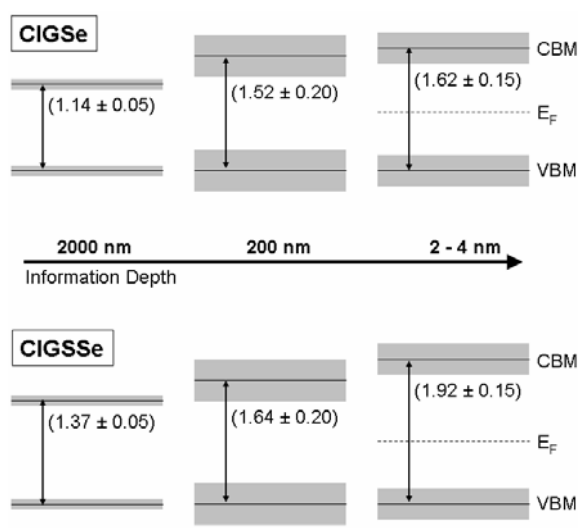

Fig. 2 Schematic presentation of the determined band gap energies of the investigated CIGSe (top) and CIGSSe (bottom) samples using the three different spectroscopic approaches (optical reflection, left; x-ray emission and absorption, center; UV photoelectron spectroscopy and inverse photoemission, right). The respective information depths of the applied spectroscopies are also shown. The gray area represents the measurement error.

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

Sincerely,

C. Heske
Associate Professor
Department of Chemistry
University of Nevada, Las Vegas

CC: C. Lopez

Department of Chemistry
4505 Maryland Parkway • Box 454003 • Las Vegas, Nevada 89154-4003
Tel (702) 895-2694 • FAX (702) 895-4072