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DEPTH-RESOLVED BAND GAP IN $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ THIN FILMS

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The surface composition of $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ (“CIGSSe”) thin films intrinsically deviates from the corresponding bulk composition, which also modifies the electronic structure and thus the optical properties. We have used a combination of photon and electron spectroscopies with different information depths to gain *depth-resolved* information on the band gap energy (E_g) in CIG(S)Se thin films. We find an increasing E_g with decreasing information depth, indicating the formation of a surface region with significantly higher E_g . This E_g -widened surface region extends further into the bulk of the sulfur-free CIGSe thin film compared to the CIGSSe thin film.

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Thin film solar cells based on $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)(\text{S}_Y\text{Se}_{1-Y})_2$ (“CIGSSe”) chalcopyrite absorbers reach efficiencies close to 20 % on a laboratory scale [1] and 13.4 % on large areas (3459 cm^2 [1]). An intrinsic feature of high-efficiency Cu chalcopyrite absorbers is a significant deviation of their surface composition from the stoichiometric $\text{Cu} : (\text{In}+\text{Ga}) : (\text{S}+\text{Se}) = 1 : 1 : 2$ bulk composition. Surface-sensitive characterization techniques generally show a Cu-poor surface with an increased band gap, such that the formation of an ordered defect compound at the absorber surface was suggested [2,3]. Indeed, optical characterization of Cu-poor bulk materials show that the defect (Cu-poor) chalcopyrites have larger band gap energies (E_g) compared to their stoichiometric counterparts [4-7].

To shed light on the depth-dependence of the band gap, we have used a combination of photon and electron spectroscopies with different information depths to gain *depth-resolved* E_g information of CIGSSe thin films. Furthermore, we have investigated the impact of S in the CIGSSe on the formation of the Cu-poor, E_g -widened region and its extension into the absorber bulk.

Two classes of samples were investigated: S-free CIGSe/Mo/glass and S-containing CIGSSe/Mo/glass structures. Chalcopyrite absorber films (approx. $2 \mu\text{m}$ thick) were prepared at 550°C using multi-source thermal co-evaporation onto Mo-coated soda-lime glass substrates [8], resulting in absorber layers with no intentional composition gradients. To minimize sample contamination between CIG(S)Se deposition and first characterization, the air exposure time was limited to less than 5 min.

The here-reported depth-resolved E_g values were determined in order of decreasing surface sensitivity of the experimental probes. Thus, the samples were first characterized by *surface-sensitive* x-ray and UV photoelectron spectroscopy (XPS, UPS) and inverse photoemission (IPES). Next, the electronic structure of the *surface-near bulk* was investigated by x-ray emission/absorption spectroscopy (XES/XAS). Finally, optical reflection spectra of the CIG(S)Se samples were recorded to derive the optical *bulk* band gap.

For the UPS (XPS) measurements (base pressure below $1 \cdot 10^{-10}$ mbar), He I and He II ($\text{Mg } K_\alpha$) excitation and a Specs PHOIBOS 150MCD electron analyzer were used. IPES was performed with a low-energy electron gun (STAIB) and a Dose-type detector with a SrF_2 window and Ar: I_2 filling. For UPS and IPES, the surfaces were cleaned by an Ar^+ treatment (ion energy 50 eV, sample current $< 1 \mu\text{A}/\text{cm}^2$) for 90 min. It is well known that prolonged sputtering of CIGSSe with 500 eV Ar^+ leads to the formation of metallic In and Cu [9, 10], but no such effects were observed in our experiments using 50 eV Ar^+ -ions.

XES/XAS was performed in the SXF endstation of Beamline 8.0 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. XAS spectra were recorded in the total fluorescence yield mode using a channeltron detector. The XES energy scale was carefully calibrated using reference compounds and elastically scattered photons in various orders of the XES spectrometer. The XAS energy scale was corrected according to the reference absorption spectrum of a Cu sample [12].

Optical reflection spectra were measured using a conventional UV-Vis-NIR spectrophotometer (Varian, Cary 5000) equipped with an integrating sphere and the CIG(S)Se bulk composition was determined by energy dispersive x-ray spectroscopy (EDS) using an Amray 1810T Digital Scanning Electron Microscope.

The spectra recorded for the CIGSe and CIGSSe samples by the various 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 CIG(S)Se layer. In the spectral region with pronounced interferences, the CIG(S)e absorber must consequently be transparent. Hence, in first approximation, the photon energy at which the oscillations in the reflection spectrum disappear corresponds to E_g . To further refine this approach, we note that the true E_g is actually smaller 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. 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 $R(E)$ can then be constructed. The absorption coefficient is proportional to $\ln[(R(E)-R_{\min})^{-1}]$ (modified from [13]), where R_{\min} is the 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 Cu chalcopyrites are direct semiconductors, the approximated absorption coefficient is plotted as $(\alpha h\nu)^2$

vs. the photon energy $h\nu$ to determine E_g (see insets in Fig. 1, left). We find an optical *bulk* band gap energy of $[1.14 (1.38) \pm 0.05]$ eV for the CIGSe (CIGSSe) absorber. These values are in good agreement with the respective E_g values extracted from our EDS compositions: we find $X = 0.21$ for the CIGSe sample and $X = 0.24, Y = 0.40$ for the CIGSSe sample. Assuming a stoichiometric Cu : (In+Ga) : (S+Se) ratio of 1 : 1 : 2, these values translate into (bulk) band gap energies [14] of 1.12 and 1.37 eV, respectively.

Fig. 1 (center) shows the Cu L_3 XES and XAS spectra of the investigated CIGSe and CIGSSe samples and a metallic Cu reference. Since XES and XAS probe occupied and unoccupied states, respectively, the combination of both spectra gives information about “ E_g ”. This band gap “ E_g ” is an approximation for the ground state band gap due to the potential existence of core excitonic features in the XAS spectra. If a core exciton is present, the XAS onset is observed at lower photon energies, and hence “ E_g ” represents a lower limit to the ground state band gap. Consequently, an increased “ E_g ” is direct evidence for an increased ground state band gap as well (irrespective of the presence of core-exciton effects). “ E_g ” was determined as the intersection of the baseline with a linear extrapolation of the leading XES and XAS edges. While the Cu metal reference shows no “gap” between the respective XES and XAS spectra (as expected), the *surface-near electronic bulk* “ E_g ” for the CIGSe (CIGSSe) absorber is found to be $[1.52 (1.64) \pm 0.20]$ eV.

Finally, the corresponding surface-sensitive UPS and IPES spectra of the investigated CIG(S)Se 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 the Ar^+ treatment. Similar to XES and XAS, UPS and IPES give information about the occupied and unoccupied states, respectively. Hence, by combination of both techniques it is possible to measure the *electronic surface band gap*. Again, linear extrapolation of the leading edges of the UPS and IPES spectra is used to determine the surface band gap E_g . For the clean surface of the CIGSe (CIGSSe) absorber we find a band gap energy of $[1.62 (1.92) \pm 0.15]$ eV.

In order to understand the observed variations in E_g , the information depth of the different spectroscopic techniques and the formation of a Cu-poor surface phase (as observed in our XPS measurements, not shown) have to be considered. Under the assumption that $\alpha \approx 10^4 \text{ cm}^{-1}$ for photon energies slightly above E_g (as reported for CuInSe_2 [15]) the information depth of the optical reflection measurement is ≈ 2000 nm, which is in the range of the thickness of the investigated CIG(S)Se layers (note that we define the information depth to be the thickness from which 90% of the overall signal is

collected, and that all of our spectroscopies are governed by an exponential attenuation function). This explains the good agreement between the E_g values estimated from the optical reflection and the bulk composition, since both probe the entire CIG(S)Se volume. In contrast, the information depth of XAS in total fluorescence yield mode and XES (here ≈ 200 nm [16]) is roughly an order of magnitude smaller than the CIG(S)Se thickness. (Note that because of a lower density [14], the CIGSSe XES/XAS information depth is $\approx 10\%$ larger than that in a CIGSe film [16].) According to the approximate “universal curve” [17], the inelastic mean free path of the detected photoelectrons for the UPS (He I) measurements of the investigated CIG(S)Se 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. Thus, the E_g values determined by the different spectroscopies paint a depth-resolved picture of the band gap energy in the investigated CIG(S)Se samples.

The findings discussed in conjunction with Fig. 1 are summarized schematically in Fig. 2, in which the differently determined E_g values (optical reflection, left; XES/XAS, center; UPS/IPES, right) for the investigated CIGSe (CIGSSe) samples are presented in the upper (lower) schemes. Note that only the UPS/IPES techniques can derive the position of the Fermi energy within the band gap. Therefore, we have presented the schemes such that the VBM is at the same energy. For both, the CIGSe and the CIGSSe sample we find an increasing band gap energy with decreasing information depth, which indicates the formation of a surface region with significantly higher E_g . The difference of the E_g -values determined by XES/XAS and UPS/IPES, respectively, is smaller for the CIGSe sample compared to that for the CIGSSe sample. At first sight, this might be explained by the slightly larger CIGSSe XES/XAS information depth. A closer look, however, suggests that this is very unlikely because of the exponential attenuation function. Thus, we rather interpret that finding as an indication that the E_g -widened (i.e., Cu-poor) region is more pronounced for the CIGSe absorber, which might shed new light on the lower-than-expected performance of wide-gap chalcopyrite thin film solar cells.

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References

- [1] M.A. Green, K. Emery, Y. Hishikawa, and W. Warta, *Prog. Photovolt: Res. Appl.* **16**, 61 (2008).
- [2] J.R. Tuttle, D. S. Albin, and R. Noufi, *Solar Cells* **30**, 21 (1991). D. Schmid, M. Ruckh, F. Grunwald, and H.-W. Schock, *J. Appl. Phys.* **73** (6) (1993) 2902.
- [3] M. Morkel, L. Weinhardt, B. Lohmüller, C. Heske, E. Umbach, W. Riedl, S. Zweigart, and F. Karg, *Appl. Phys. Lett.* **79**, 4482 (2001).
- [4] H.Z. Xiao, L.-Chung Yang, and A. Rockett, *J. Appl. Phys.* **76**, 1503 (1994).
- [5] T. Tanaka, Y. Demizu, T. Yamaguchi, and A. Yoshida, *J. Appl. Phys.* **81**, 7619 (1997).
- [6] L. Durán, C. Guerrero, E. Hernández, J.M. Delgado, J. Contreras, S.M. Wasim, and C.A. Durante Rincón, *J. Phys. Chem. Sol.* **64**, 1907 (2003).
- [7] I.V. Bodnar', V.A. Polubok, V. Yu. Rud', Yu. V. Rud', and M.S. Serginov, *Semiconductors* **38**, 197 (2004).
- [8] M. Gossila and W.N. Shafarman, *Thin Solid Films* **480-481**, 33 (2005).
- [9] L. Weinhardt, M. Morkel, Th. Gleim, S. Zweigart, F. Karg, C. Heske, and E. Umbach, *Proc. EPVSEC-17, Munich, Germany, (October 22-26, 2001)*, p. 1261.
- [10] D. W. Niles, K. Ramanathan, F. Hasoon, R. Noufi, B. J. Tielsch, and J. E. Fulghum, *J. Vac. Sci. Technol. A* **15**, 3044 (1997).
- [12] The reference Cu L_{2,3} absorption spectrum was measured using an experimental endstation equipped with an electron analyzer. Before and after the XAS measurement a Au 4f photoemission spectrum was recorded such that the Cu L_{2,3} XAS energy scale could be calibrated using the start and end photon energy of the XAS measurement.
- [13] V. Kumar, Sachin Kr. Sharma, T.P. Sharma, and V. Singh, *Opt. Mater.* **12**, 115 (1999).
- [14] M. Bär, W. Bohne, J. Röhrich, E. Strub, S. Lindner, M. C. Lux-Steiner, Ch.-H. Fischer, T. P. Niesen, and F. Karg, *J. Appl. Phys.* **96**, 3857 (2004).
- [15] W. Hörig, H. Neumann, H. Sobotta, B. Schmann, and G. Kohn, *Thin Solid Films* **48**, 67 (1978).
- [16] B.L. Henke, E.M. Gullikson, and J.C. Davis, CXRO database for x-ray attenuation length of a solid: http://henke.lbl.gov/optical_constants/atten2.html.
- [17] D. Briggs and M.P. Seah, *Practical Surface Analysis by Auger and X-ray Spectroscopy*, John Wiley & Sons Ltd., New York (1983).

Figure captions

Fig. 1 Left: Optical reflection spectra of CIGSe (top) and CIGSSe (bottom) thin films, together with the respective envelopes of the interference extrema and the constructed mean values (red dotted lines). Insets: E_g -determination (± 0.05 eV) using approximated absorption coefficient for the CIGSe (top) and CIGSSe (bottom) sample.

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 and of a metallic Cu reference (top). The band gap energies “ E_g ” (a lower bound for the true band gap values – see text) are determined by linear extrapolation of the leading edges (± 0.20 eV), indicated by the solid green and red lines..

Right: UV photoelectron spectroscopy (UPS, left) and inverse photoemission (IPES, right) of the CIGSe (top) and CIGSSe (bottom) samples. Spectra are shown for the as-introduced (thin solid lines) and for the cleaned samples (dots). Solid green and red lines indicate the linear extrapolation of the leading edges to determine E_g (± 0.15 eV).

Fig. 2 Schematic representation of the determined CIGSe (top) and CIGSSe (bottom) band gap energies 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. CBM (VBM) denotes the conduction band minimum (valence band maximum).

Figures

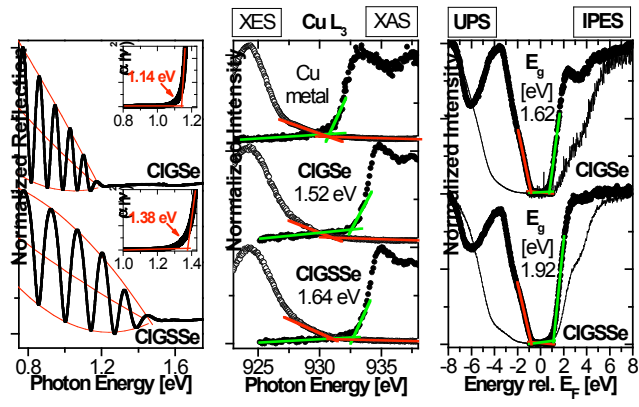


Fig. 1

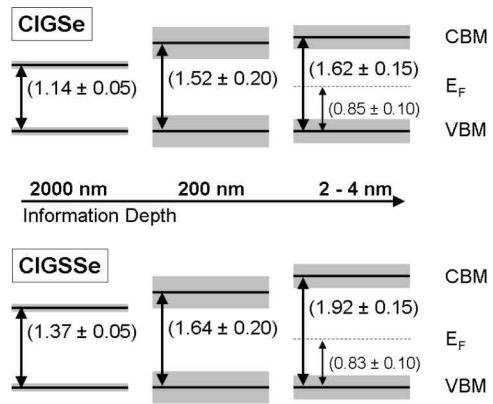


Fig. 2