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# BAND GAP ENERGY OF CHALCOPYRITE THIN FILM SOLAR CELL ABSORBERS DETERMINED BY SOFT X-RAY EMISSION AND ABSORPTION SPECTROSCOPY

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## ABSTRACT

The chemical and electronic structure of high-efficiency chalcopyrite thin film solar cell absorbers significantly differs between the surface and the bulk. While it is widely accepted that the absorber surface exhibits a Cu-poor surface phase with increased band gap ( $E_g$ ), a direct access to the crucial information of the depth-dependency of  $E_g$  is still missing. In this paper, we demonstrate that a combination of x-ray emission and absorption spectroscopy allows a determination of  $E_g$  in the surface-near bulk and thus complements the established surface- and bulk-sensitive techniques of  $E_g$  determination. As an example, we discuss the determination of  $E_g$  for a Cu(In,Ga)Se<sub>2</sub> absorber [(1.52 ± 0.20) eV].

## INTRODUCTION

Thin film solar cells based on Cu(In<sub>1-x</sub>Ga<sub>x</sub>)(S<sub>y</sub>Se<sub>1-y</sub>)<sub>2</sub> ("CIGSSe") chalcopyrite absorbers are promising candidates to supersede the current state-of-the-art Si wafer-based photovoltaics. CIGSSe solar cells have already reached efficiencies close to 20 % on a laboratory scale [1] and 13.4 % on large areas (3459 cm<sup>2</sup> [2]). For chalcopyrite absorbers in high-efficiency cells, the surface composition significantly deviates from the stoichiometric Cu : (In+Ga) : (S+Se) = 1 : 1 : 2 bulk composition. Surface-sensitive characterization techniques generally indicate a Cu-poor surface composition [3-7]. In consequence, the formation of an ordered defect compound at the absorber surface was suggested [8,9]. Defect chalcopyrites with a composition ranging from 1 : 2 : 3.5

[8,10] over 1 : 3 : 5 [11-14], 1 : 5 : 8 [14, 15], 1 : 7 : 11 [16] to 1 : 11 : 17 [16] were proposed, and corresponding (bulk) samples were synthesized. Optical characterization of these bulk materials shows that the defect (Cu-poor) chalcopyrites have larger band gap energies ( $E_g$ ) compared to their stoichiometric counterparts [10-13, 14-16]. For solar cell absorbers, direct determination of the surface band gap by UV photoelectron spectroscopy (UPS) and inverse photoemission (IPES) showed that  $E_g$  is indeed widened at the Cu-poor surface of absorbers with stoichiometric bulk composition [4-7].

To date, the thickness and extent of the region with widened band gap is not known. No measurement technique so far established in the chalcopyrite community is able to *directly* probe  $E_g$  in the surface-near bulk and thus form the bridge between very surface-sensitive UPS and IPES measurements (i.e., the electronic surface band gap) and bulk-sensitive optical measurements (i.e., the optical bulk band gap). Note that band gap profiles based on composition gradients determined by (destructive) depth profiling techniques cannot play this role, since they do not consider the influence of Cu depletion on  $E_g$  [17].

While x-ray emission spectroscopy (XES) probes occupied electronic states, x-ray absorption spectroscopy (XAS) probes unoccupied states. Thus, by combining these two techniques, it is possible to probe  $E_g$  (in the presence of a core hole, i.e. not in the ground state).

## EXPERIMENTAL

This investigation is based on a S-free Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> "CIGSe"/Mo/glass test structure. The chalcopyrite absorber film (approx. 2 μm thick) was 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. 18 for more details). In order to minimize sample contamination due to air exposure, the samples were individually packed in dry nitrogen immediately after preparation. The sample exposure time to ambient air (before the first characterization) could thus be limited to less than 5 min.

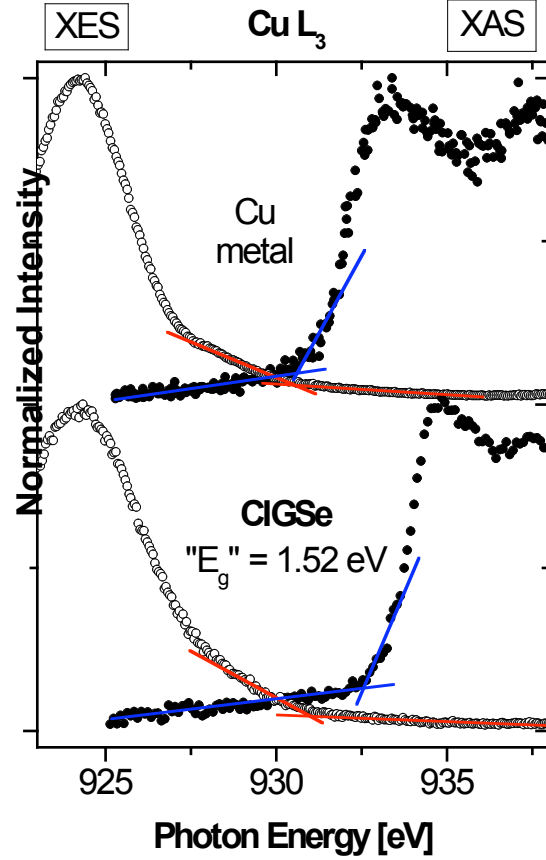
XES/XAS spectra were collected in the SXF endstation of Beamline 8.0 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (endstation base pressure below 5·10<sup>-8</sup> mbar). The XAS spectra were recorded in the total fluorescence yield mode using a channeltron mounted in front of the sample, and the XES spectra were taken with the permanently installed SXF spectrometer.

## RESULTS AND DISCUSSION

Fig. 1 shows the Cu L<sub>3</sub> XES and XAS spectra of the investigated CIGSe sample. For comparison, spectra of metallic Cu are also shown. Since XES and XAS probe occupied and unoccupied states, respectively, the combination of both spectra gives information about E<sub>g</sub>. Note that the band gap that can be determined from these measurements represents the band gap in the presence of a core hole (in our case a Cu 2p<sub>3/2</sub> core hole). This band gap "E<sub>g</sub>" 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<sub>g</sub>" represents a lower limit to the ground state band gap.

"E<sub>g</sub>" was determined as the intersection of the baseline with a linear extrapolation of the leading XES and XAS edges. For the CIGSe absorber an "E<sub>g</sub>" of [1.52 ± 0.20] eV is found, while the Cu metal reference shows no "gap" between the respective XES and XAS spectra (as expected).

The derived CIGSe "E<sub>g</sub>" value is considerably bigger than the bulk band gap: according to its bulk composition of X = 0.21, as determined by energy dispersive X-ray analysis, the bulk band gap energy was approximated [17] to 1.12 eV. Since the core-hole influence turns the derived "E<sub>g</sub>" values into a lower-



**Fig. 1.** Cu L<sub>3</sub> x-ray emission (XES, left) and absorption (XAS, right) spectra of the investigated CIGSe (bottom spectra) sample. For comparison, the spectra of metallic Cu (top spectra) are also shown. The linear approximation of the leading edges for the determination of "E<sub>g</sub>" (a lower bound for the true band gap value – see text) is indicated by the solid blue and red lines. The given band gap energy "E<sub>g</sub>" has an error of ± 0.20 eV.

bound approximation for the ground state band gap, the observation of an increased "E<sub>g</sub>" value unambiguously indicates an increased ground state band gap as well.

In order to understand the observed difference, the information depth of the XES and XAS measurements has to be quantified. Since the photons involved in XAS (in total fluorescence yield mode) have similar attenuation lengths as those in XES, we limit our respective considerations to the latter:

The intensity of the emission from a material A of limited thickness  $I^A(x)$  can be written as

$$I^A(x) = I_{\text{ref}}^A \left( 1 - e^{-\frac{x}{\lambda^*}} \right) \quad (1),$$

where  $I_{\text{ref}}^A$  denotes the reference emission intensity of material A with infinite thickness (“infinite” corresponds to a material thickness that results in a saturated emission intensity). Furthermore, we define the effective attenuation length  $\lambda^*$  by

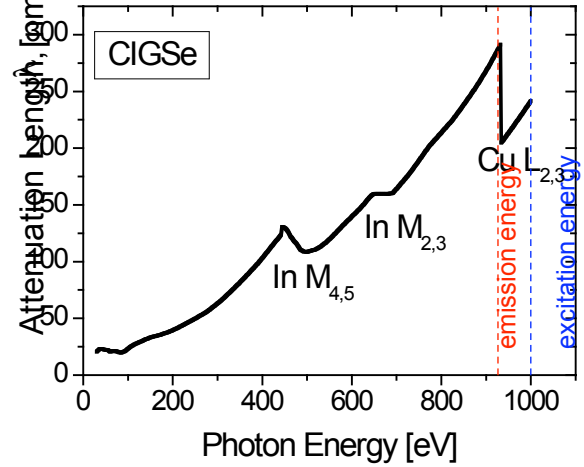
$$\frac{1}{\lambda^*} = \left( \frac{1}{\lambda_{\text{exc}} \cdot \sin \alpha} \right) + \left( \frac{1}{\lambda_{\text{em}} \cdot \sin \beta} \right) \quad (2),$$

where  $\lambda_{\text{exc}}$  and  $\lambda_{\text{em}}$  are the attenuation lengths in material A for the excitation and emission energy, respectively.  $\alpha$  and  $\beta$  are the angles of excitation and emission relative to the sample surface, respectively (in our case  $\alpha = \beta = 45^\circ$ ). This effective attenuation length takes into account that, for an XES or XAS event to be recorded, a photon-in-photon-out process needs to take place.

Fig. 2 shows the attenuation length  $\lambda$  (from Ref. [19]) as a function of photon energy for a CIGSe sample (with  $X = 0.21$  and thus a density of  $5.73 \text{ g/cm}^3$  [17] and  $\alpha = \beta = 45^\circ$ ).  $\lambda$  ranges from approx. 20 nm for low photon energies to 200-300 nm for higher photon energies. At approx. 450, 670, and 930 eV, pronounced features can be observed, which can be ascribed to In  $M_{4,5}$ , In  $M_{2,3}$ , and Cu  $L_{2,3}$  absorption edges. Since we use the Cu  $L_3$  emission and absorption to determine “ $E_g$ ”,  $\lambda_{\text{exc}}$  (at 1000 eV) and  $\lambda_{\text{em}}$  (at 925 eV) are 242 and 287 nm, respectively. Using Eq. (2),  $\lambda^*$  can then be calculated to 93 nm. Assuming that the information depth is defined as the thickness from which 90% of the overall signal is collected, we can use Eq. (1) to determine an approximate information depth of 213 nm. Note that this is an approximate value, since the specific morphology of the surface is not taken into account. As is well known, corrugations of CIGSe surfaces can easily amount to several tens of nanometers.

The observed difference between the “ $E_g$ ” value determined from our XES and XAS measurements [ $1.52 \pm 0.20$  eV] and the  $E_g$  based on the bulk composition (1.12 eV) can thus be discussed on the basis of different information depths. The fact that the band gap widening is detected with XES and XAS (i.e., with an information depth of  $\sim 213$  nm) indicates that the Cu-poor, band gap-widened surface phase must be significantly extended into the bulk of the investigated CIGSe absorber.

Comparing the derived information depth of 213 nm with the information depths (a few  $\mu\text{m}$  or a few nm) of established techniques of  $E_g$  determination (optical spectroscopy and UPS/IPES, respectively), it is now possible to derive band gap information from the



**Fig. 2.** Attenuation length (from Ref. [19]) as a function of photon energy, computed for the bulk composition of the investigated CIGSe sample.

intermediate depth regime between optical bulk band gaps and electronic surface band gaps. Note that, by using different absorption edges (if available) for the “ $E_g$ ” determination by XES/XAS, it is even possible to vary the XES/XAS information depth in discrete steps, provided the probed element has a significant contribution to both, the valence band maximum *and* conduction band minimum (as in the present case of Cu).

In the near future, we are planning to extend our experiments to absorbers with different X- and Y-composition, including wide-gap chalcopyrites such as  $\text{CuInS}_2$  and  $\text{CuGaSe}_2$ , in order to systematically investigate the depth-dependence of  $E_g$  as a function of composition.

## SUMMARY & CONCLUSION

We have shown that the combination of x-ray emission (XES) and x-ray absorption (XAS) spectroscopy is uniquely suited to gain direct access to electronic band gaps in the surface-near bulk region (in the present case with an information depth of approx. 213 nm). As an example, we have determined the surface-near electronic band gap for a  $\text{Cu(In,Ga)Se}_2$  absorber to be  $(1.52 \pm 0.20)$  eV. The combination of XES and XAS thus closes the “information gap” between established surface- and bulk-sensitive techniques to determine the band gap, opening a new route for the depth-dependent investigation of the electronic structure of chalcopyrite thin film solar cell absorbers.

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