Limitations of Near Edge X-ray Absorption Fine Structure as a tool for observing conduction bands in chalcopyrite solar cell heterojunctions

Benjamin Johnson*, Jo Klaer, Saoussen Merdes, Mihaela Gorgoi, Britta Höpfner, Antje Vollmer, Iver Lauermann

Helmholtz-Zentrum Berlin, Albert-Einstein-Str. 15, 12489 Berlin, Germany

ARTICLE INFO

ABSTRACT

A non-optimized interface band alignment in a heterojunction-based solar cell can have negative effects on the current and voltage characteristics of the resulting device. To evaluate the use of Near Edge X-ray Absorption Fine Structure spectroscopy (NEXAFS) as a means to measure the conduction band position, Cu(In,Ga)S$_2$ chalcopyrite thin film surfaces were investigated as these form the absorber layer in solar cells with the structure ZnO/buffer/Cu(In,Ga)S$_2$/Mo/glass. The composition dependence of the structure of the conduction bands of CuIn$_x$Ga$_{1-x}$S$_2$ has been revealed for $x = 0$, 0.67 and 1 with both hard and soft NEXAFS and the resulting changes in conduction band offset at the junction with the buffer layer discussed. A comprehensive study of the positions of the absorption edges of all elements was carried out and the development of the conduction band with Ga content was observed, also with respect to calculated densities of states.

© 2013 Elsevier B.V. All rights reserved.

Valence and conduction band (VB and CB) alignments at heterojunctions play important roles in the functionality of semiconductor heterojunction devices such as the chalcopyrite thin layer solar cell based on the structure n$^+$-ZnO/i-ZnO/buffer/Cu(In,Ga)S$_2$/Mo/glass and others: buffer/Cu(In,Ga)Se$_2$ and buffer/CdTe or a-Si/c-Si [1–3]. The sulfide-based device with a CdS buffer layer has reached an efficiency of about 13% [4]. More specifically, whether or not the CB offset at the buffer/absorber junction is optimized, that is, whether the CB edge of the absorber is closer to the Fermi level than the CB of the buffer (spike) or vice versa (cliff) can influence the current–voltage characteristics of the device. The reduced effective band gap of the cliff configuration can limit the photovoltage while the position in the junction where p = n moves closer to the defect-rich buffer/absorber interface leading to increased charge carrier recombination [1].

Knowledge of these offsets is, therefore, critical to understanding the performance of the resulting solar cell. While the VB offset, ΔE_{VB}, can be determined with established methods, such as combined XPS/UPS [5,6] or Constant Final State Yield spectroscopy [7], a determination of CB edge positions and offsets, ΔE_{CB}, has proved more difficult. The most common method is simply the assumption that the CB minimum is the energy of the VB plus the band gap.

However, the determination of the surface band gap, which is relevant for the band offset, is more involved. Two of the main methods for the direct determination of the CB minimum are inverse photoelectron spectroscopy (IPES) and Near Edge X-ray Absorption Fine Structure (NEXAFS). They have given reliable results in some situations [8–11], although both have unresolved difficulties and the results must be carefully analyzed. IPES requires high intensity electron irradiation of the sample which often leads to charging of less conductive materials. In the case of NEXAFS these include transition probabilities, spectrum broadening and excitonic or core–hole effects. The latter may cause shifts in the measured position of the absorption edges which do not correspond to the ground state of the material. This is because the position of the absorption edge in NEXAFS represents the energy difference between the initial state (core level) and the final empty state (conduction band) in the material's excited state. The attraction between the core–hole and the excited electron may make the energy difference between the core level and conduction band state appear artificially smaller than it is in the ground state of the material. Also, because the absorption edge represents an energy difference, the energy of the initial state (core level) must be considered to determine whether differences in binding energy could influence the calculated energy of the final conduction band state. Here, while considering only the position of the absorption edge, we assume at first a constant initial state (core level binding) energy, although in several cases we explicitly consider specific measured binding energies. This assumption of constant binding energies will have immediate

* Corresponding author. Tel.: +49 30 8413 4523.
E-mail address: benjamin.johnson@alumni.tu-berlin.de (B. Johnson).

relevance when considering differences between the $CuInS_2$ and $Cu(In,Ga)S_2$ samples because they are stoichiometrically similar.

Complicating matters still further, a junction, by its very existence, implies a buried interface which is often difficult to examine using surface sensitive methods and important processes such as chemical shifts during junction formation must often be neglected in order to determine an offset value [12–14].

As will be seen, only a semi-quantitative assessment of the NEXAFS measurements was made because of the difficulties in establishing an absolute calibration of the energy scales. We, therefore, keep our focus on examining the validity of NEX-AFS as a tool for monitoring CB edge positions rather than an actual determination of ΔE_{CB}. For this reason bare solar cell grade $CuIn_xGa_{1-x}S_2$ ($x = 0$, 0.67 and 1) or "CIGS" layers grown by rapid thermal processing (RTP) [15] were studied after being etched in a standard solution of 5% KCN for 3 min to remove the secondary Cu_xS phase [16]. Inferences about the junction with CdS are then made by using the results of other measurements and we remain mainly on qualitative footing.

The samples were loaded into the vacuum chamber ($\sim 10^{-9}$ mbar) immediately after preparation and no subsequent sputtering of surfaces was undertaken in order to clean them. The measurements were performed at the BESSY II synchrotron in Berlin, Germany. The absorption edges in the soft X-ray regime (50–2000 eV) were made on the Optics beam line with the SurICat end station and detected using total electron yield (sample current) mode so that the information depth exceeded the 1–4 nm reached with XPS. Estimates of the NEXAFS information depths reach into the tens of nanometers and, like the information depths in PES, are dependent on electron kinetic energy and vary between absorption edges. The structure in the mirror current from the refocusing mirror of the beamline (I_0) caused by X-ray absorption from elements on the mirror was used as a reference so that all of the spectra from each individual element enjoyed a common, albeit not necessarily absolute, energy scale and real shifts between the absorption edges can be considered. Although the elements on the mirror are unknown, their absorption features occur at energies which do not change during the time scale of the measurements.

The hard X-ray edges (2000–10,000 eV) were measured at the KMC-1 beam line with the HIKE end station using X-ray emission with a Bruker fluorescence detector. The information depths reach into the micrometer range and are much less surface sensitive than the soft X-ray measurements. Because no refocusing optics exist and the analogue of the mirror current, the N_2-ionization current, was not useful in calibrating the energy scale each edge was measured successively on each sample with a low scan count in order to avoid broadening or shifts of the absorption edge. This is caused by the monochromator not scanning the exact energy window with every sweep (monochromator reproducibility) and could not be corrected for on this beamline. While the resulting spectra are somewhat noisy, it again enables the comparison of the spectra on an energy scale common to all curves for each element.

In the analysis of NEXAFS spectra the definition of the "position" of the edge itself can be problematic and the literature provides several different methods of determining the position of the edge. These include fitting the the crest of the curve immediately after the absorption edge with the initial-state core level [9], extrapolation of the absorption edge to the background [10,11], the maximum of its first derivative [17] as well as consideration of a fitted density of states calculation. In addition, the second derivative can also be used, although this is often in an attempt to differentiate two peaks separated by an energy close to that of the experimental resolution [18]. In more complex attempts, often reserved for EXAFS data, a polynomial background can be subtracted after which a spline fit is used for normalization [19].

In this study we have chosen to observe mainly overall shifts in the peaks which amounts to the position of the absorption edge at its half-maximum. This method gives us satisfactory trends and other factors must be clarified before the results would profit from any increased accuracy derived from the methods mentioned above. We also consider the position of peaks after the absorption edge as in [9] although we have not carried out in-depth fits using the measured core levels.

Fig. 1 shows the soft X-ray NEXAFS measurements on the Cu L_3, In $M_{4,5}$, Ga L_3 and S L_3 absorption edges from $CuInS_2$ (red), $CuIn_{0.67}Ga_{0.33}S_2$ (blue) and $CuGaS_2$ (green). Although the edges are shown before the subtraction of the corresponding core level binding energies, the subtraction did not always change the results and will be considered in cases where the subtraction led to significant differences. The shifts seen in Fig. 1 correspond then, at least qualitatively, to shifts in the CB states of the CIGS with varying [Ga]/[In+Ga] ratios. It can immediately be seen that Cu L_3 (see inset) and S L_3 edges are shifted and correspond to an opening of the CIGS band gap with increasing Ga concentration while the In $M_{4,5}$ and Ga L_3 edges display no shift (the noisy CIGS spectrum from Ga is due to the low surface Ga content of $\sim 8\%$). It is evident that several measurements of different absorption edges are needed in order to understand the development of the CB and one measurement, while not incorrect, may not illustrate fully the differences between the systems.

Before focusing on the shifts in Fig. 1(a) and (d) it is helpful to consider the VB edge positions (measured with UPS, not shown) and bulk band gaps, E_g, of CIGS shown in Table 1 for an estimate of where the CB edges of the three materials may be expected. The E_g values do not necessarily reflect values for solar cell-grade surfaces due to stoichiometric gradients which may cause differences between bulk and surface characteristics [20,21]. The values in the table show a CIS CB edge 0.8 eV above the Fermi level with the $CuIn_{0.67}Ga_{0.33}S_2$ CB edge 0.1 eV further up and the CGS 1.1 eV beyond that.

Fig. 1(a) shows the Cu L_3 edges with a crest shift between the CIS and CIGS measurements of 150 ± 30 meV, similar to that found in Table 1. Further supporting this as a real shift in the CB is the fact that the CIS and $CuIn_{0.67}Ga_{0.33}S_2$ crystal lattices are similar meaning other factors influencing the position of an absorption edge, such as excitonic effects, can be disregarded as they will be the same in both materials. The fine structure after the absorption edge is similar for CIS and CIGS showing a similarity of the conduction bands and further supports the similarities of both lattices. One exception is the characteristic drop in intensity in the CIGS spectrum just after the crest and is even more pronounced in the CGS sample. However, the fine structure of the CGS is different than the other two materials and the shift between CIGS and CGS is anomalously small, 0.25 eV, as compared to the 1.1 eV expected from the bulk band gap estimation. The measurement itself may affect the position of the CGS Cu L_3 absorption edge differently than that of CIS and CIGS. Analysis after the subtraction of the Cu $2p_{3/2}$ core level binding energy (not shown) corrected this discrepancy somewhat so that the shift between CIGS and CGS was 0.40 eV while leaving the shift between

Table 1
Measured valence band edge positions (energy below Fermi level, E_f), bulk band gaps (E_g) and resulting estimated conduction band edge positions (energy above E_f) for $CuInS_2$, $CuIn_{0.67}Ga_{0.33}S_2$ and $CuGaS_2$.

Sample	VB edge ($E_f - E_{VB}$)	Band gap	CB edge ($E_f + E_{CB}$)
$CuInS_2$	0.7 eV	1.5 eV	0.8 eV
$CuIn_{0.67}Ga_{0.33}S_2$	0.7 eV	1.6 eV	0.9 eV
$CuGaS_2$	0.4 eV	2.4 eV	2.0 eV