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Alkali Postdeposition Treatment-Induced Changes of the Chemical and Electronic Structure of Cu(In,Ga)Se₂ Thin-Film Solar Cell Absorbers: A First-Principle Perspective

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Supporting Information

ABSTRACT: The effects of alkali postdeposition treatment (PDT) on the valence band structure of Cu(In,Ga)Se₂ (CIGSe) thin-film solar cell absorbers are addressed from a first-principles perspective. In detail, experimentally derived hard X-ray photoelectron spectroscopy (HAXPES) data [Handick, E.; et al. ACS Appl. Mater. Interfaces 2015, 7, 27414–27420] of the valence band structure of alkali-free and NaF/KF-PDT CIGSe are directly compared and fit by calculated density of states (DOS) of CuInSe₂, its Cu-deficient counterpart CuIn₅Se₈, and different potentially formed secondary phases, such as KInSe₂, InSe, and In₂Se₃. The DOSs are based on first-principles electronic structure calculations and weighted according to element-, symmetry-, and energy-dependent photoionization cross sections for the comparison to experimental data. The HAXPES spectra were recorded using photon energies ranging from 2 to 8 keV, allowing extraction of information from different sample depths. The analysis of the alkali-free CIGSe valence band structure reveals that it can best be described by a mixture of the DOS of CuInSe₂, CuIn₅Se₈, and different potentially formed secondary phases, such as KInSe₂, InSe, and In₂Se₃. The effects of light alkalis on the properties of CIGSe absorbers and related solar cells have been studied extensively over the years.3–5 According to several experiments, NaF-PDT results in improved open circuit voltage (Vₜₜₜₜ) and fill factor (FF). Upon (additional) KF-PDT, even higher Vₜₜₜₜ and FF were achieved. Moreover, employing a KF-PDT allows the deposition of thinner CdS buffer layers, which leads to reduced optical losses in the buffer, resulting in increased short circuit currents.3–5,7 The KF-PDT-induced changes in surface composition (mainly Cu and Ga depletion and presence of K but not F) and surface morphology3,11–16 have been associated with the formation of a K-containing surface species.3,5,13–17 To correlate this secondary phase formation...
at the absorber surface with changes in the electronic structure of the CIGSe absorber layer after KF-PDT, direct and inverse photoemission measurements have been used in previous studies.\textsuperscript{14,17} The main finding has been that the KF-PDT process induces shifts of the valence band maximum (VBM) and the conduction band minimum away from the Fermi level, manifesting itself in a widening of the band gap at the absorber surface.\textsuperscript{13,17} According to previous studies,\textsuperscript{13,17} the VBM lowering cannot only be explained by a decrease in p–d interband repulsion related to the degree of Cu deficiency \textsuperscript{18} but is also rather indicative of the formation of a K−In−Se type surface species. The measured surface band gap of 2.5 eV\textsuperscript{17} is consistent with the theoretical value for the secondary phase compound KInSe\textsubscript{2}.\textsuperscript{19,20}

Due to hybridization of the electronic states that form the valence band, a detailed analysis of respective photoelectron spectroscopy spectra can be challenging, in particular, if the spectra of the constituent phases are not known a priori. Here, we provide the missing information by means of first-principles simulations, which we use to model the experimental spectra published in refs \textsuperscript{17, 21} (see Figure S1, Supporting Information (SI) for convenience). Briefly, we consider hard X-ray photoelectron spectra (HAXPES) data of the valence band region for three CIGSe samples (alkali-free, K-poor, and K-rich) measured with excitation energies of 2, 6, and 8 keV. The latter two samples were prepared employing a combined NaF/KF-PDT with a higher KF deposition rate for the last sample (for more details, see refs 3, 13, 17). The data of the alkali-free and K-rich CIGSe samples clearly show distinct changes in the spectral shape (see Figure S1), with the spectra of the K-poor CIGSe most likely being a linear combination (with relative shifts) of the first two data sets. Note that the employed excitation energies also influence the spectral shape due to changes in relative photoionization cross sections of the states forming the valence band as well as by a different probing depth (if the composition changes throughout the probed volume, which is defined by the exponential attenuation of the photoelectron signal within the sample). For photoelectrons from the valence band region, the kinetic energy increases similar to the excitation energy from 2, over 6, to 8 keV, resulting in an inelastic mean free path (IMFP) increase from 4, over 10, to 12 nm, respectively, for the valence band regime.\textsuperscript{13,22}

In this work, we develop first-principles models that aim to reduce the measured HAXPES valence band spectra of the CIGSe absorber (surface) for which no PDT (i.e., alkali-free) or NaF/KF-PDT was performed as part of the preparation process. The ultimate goal is to reveal the chemical and electronic absorber structure and how it is impacted by alkali PDT. Of particular relevance would be any insight into the electronic absorber structure and how it is impacted by alkali PDT. The ultimate goal is to reveal the chemical and electronic absorber structure and how it is impacted by alkali PDT. Of particular relevance would be any insight into the electronic absorber structure and how it is impacted by alkali PDT. Of particular relevance would be any insight into the electronic absorber structure and how it is impacted by alkali PDT. Of particular relevance would be any insight into the electronic absorber structure and how it is impacted by alkali PDT. 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Of particular relevance would be any insight into the electronic absorber structure and how it is impacts of the CIGSe absorber even in cases where the absorber is treated with moderate or low amounts of K. To do so, we derive simulated HAXPES valence band spectra by using first-principles density functional theory (DFT) electronic structures of crystalline Cu−In−Se phases with different compositions as well as those of potentially formed (K−In)−Se secondary phases. We omit Ga in our simulations, because it is depleted at KF-PDT CIGSe surfaces.\textsuperscript{3,13} We assume that the absorber surface could consist of six possible compounds: CuIn\textsubscript{5}Se\textsubscript{6}, CuIn\textsubscript{3}Se\textsubscript{8}, KIn\textsubscript{2}Se\textsubscript{2} (having a monoclinic or chalcopyrite crystal structure),\textsuperscript{16} InSe\textsubscript{2} and In\textsubscript{2}Se\textsubscript{3}. The computed crystal structures and lattice constants are given in Figure S2 and Table S1, respectively. Besides the ordered defect compound phase CuIn\textsubscript{5}Se\textsubscript{6}, the CuIn\textsubscript{3}Se\textsubscript{8} phase has been considered as a Cu-deficient compound near surfaces and grain boundaries. However, despite intensive research,\textsuperscript{23,24} a precise structural model for the CuIn\textsubscript{5}Se\textsubscript{6} phase remains elusive, possibly due to inherent randomness\textsuperscript{3} in the position of the Cu vacancies and In antisites (i.e., In on Cu sites). Consequently, modeling the electronic structure of the CuIn\textsubscript{5}Se\textsubscript{6} phase is challenging. However, the stoichiometry of CuIn\textsubscript{5}Se\textsubscript{6} is a weighted sum of the stoichiometry of CuInSe\textsubscript{2} and of CuIn\textsubscript{3}Se\textsubscript{8}; we will represent the density of states (DOS) of this phase accordingly. The simulated HAXPES spectra of the different compounds are obtained by summing up partial atom- and orbital-resolved densities of states (PDOSs) weighted by the corresponding theoretical free-atom photoionization cross sections.\textsuperscript{5,26} Finally, we use linear combinations of these simulated spectra to fit the experimental spectra. On the basis of the fit results, we then attempt to identify the chemical origin of the main spectral valence band features and draw conclusions with respect to sample composition and how it changes upon KF-PDT.

2. METHODS

Our calculations were performed in the framework of DFT employing the HSE06\textsuperscript{27,28} functional, as implemented in the FHI-aims code.\textsuperscript{29} Electron wave functions were calculated by the full potential all-electron method. We employed primitive cells in all cases. The $8 \times 8 \times 8$ k-point mesh was used for each structure.

The atomic orbital basis employed in FHI-aims provides a straightforward way to decompose the total density of states (DOS) into its atom- and orbital-projected contributions (PDOSs). To compare theoretical results with experimental HAXPES spectra, PDOSs were weighted with atom- and orbital-dependent photoionization cross sections. Finally, we use linear combinations of these simulated spectra to fit the experimental spectra. On the basis of the fit results, we then attempt to identify the chemical origin of the main spectral valence band features and draw conclusions with respect to sample composition and how it changes upon KF-PDT.

3. RESULTS AND DISCUSSION

We first present the calculated valence band DOSs and the simulated HAXPES spectra for all potentially present phases and analyze the origin of the most prominent spectral features. This is followed by showing the fits to the experimental spectra and the discussion of the results.
3.1. Densities of States of Relevant Cu Compounds.

We start with the alkali-free CIGSe sample (i.e., no NaF/KF-PDT). The untreated absorber surface cannot be described as a stoichiometric CuInSe_2 but is found to have a significant Cu deficiency (indicating a surface stoichiometry between CuIn_3Se_5 and CuIn_5Se_8), confirming previous reports.\(^{14,30-32}\) Such Cu-deficient CIGSe surfaces have been attributed to the formation of ordered defect/vacancy surface compounds (i.e., CuIn_3Se_5 and/or CuIn_5Se_8)\(^{33,34}\) or surface reconstruction (i.e., a Cu-free In-Se-type surface termination) in the past.\(^{35}\) One of the aims of this work is to contribute to this ongoing discussion. The more Cu-deficient CuIn_5Se_8 phase, first proposed by Zhang et al.\(^{18}\) and afterward used, e.g., in the defect studies by Kiss et al.\(^{36}\) and Ghorbani et al.,\(^{37}\) has a stannite-type crystal structure with a periodic repetition of defect clusters of two Cu vacancies and an In-on-Cu antisite.

As mentioned above, there exists no simple model for CuIn_3Se_5. However, we will represent the CuIn_3Se_5 DOS as a weighted sum of CuInSe_2 and CuIn_5Se_8 DOS for the comparison with HAXPES valence band spectra of the alkali-free CIGSe below.

The valence band DOSs for CuInSe_2 and CuIn_5Se_8 are shown in Figure 1a,b, respectively. It can be seen that they are dominated by Cu \(d\) and Se \(p\) states, which are distributed quite differently in the two materials. For CuInSe_2, the two main peaks in DOS arise from bonding and antibonding states between Cu \(d\) and Se \(p\). In the ordered defect compound CuIn_5Se_8, the deficiency of Cu obviously leads to the deficiency of Cu-Se bonds. As a result, the region of hybridized Cu \(d\) and Se \(p\) states narrows so that the two prominent peaks in the total DOS merge and the total bandwidth decreases, in agreement with ref 18. Figure 1c,e shows the CuInSe_2 PDOSs multiplied by the photoionization cross sections for electrons having a kinetic energy of 2 and 6 keV, respectively, thus approximating the corresponding HAXPES spectra. The total relative intensities of the two main peaks are equal for the spectra without photoionization cross section weighting and with 2 keV cross section correction (Figure 1a,c). In Figure 1c, the shoulder near the VBM comprises nearly equal Se \(p\) and Cu \(d\) contributions and the peak between \(-2.5\) and \(-1.5\) eV is prominently formed by Cu \(d\) orbitals. For the 6 keV cross section-weighted DOS (Figure 1e), the contribution of the Cu \(d\) orbital is significantly reduced and the \(p\)- and \(s\)-derived contributions increase in intensity. As a result, the Cu \(p\)- and Se \(p\)-derived low-energy DOS becomes relatively more intense. For CuIn_5Se_8 (see Figure 1b,d,f), the uncorrected total DOS and the 2 keV cross section-weighted DOS are very similar, as in the case of the CuInSe_2. For the 6 keV cross section correction, the Cu \(d\) contribution again is reduced and the \(p\)- and \(s\)-derived orbitals increase in intensity.

3.2. Densities of States of Relevant (K−In−Se) Compounds.

The microscopic character of the surface modification of the CIGSe absorber material after the KF-PDT has been discussed extensively during recent years.\(^{3,4,12,17}\) Possible reasons for the surface modifications could be the formation of K−In−Se\(^{8,13,15-17,20,38}\) and/or In−Se-type layers.\(^{16,17,38}\) In this work, we consider KInSe_2 in two different lattice structures (monoclinic and chalcopyrite-type) as well as In_2Se_3 and InSe as being layers that most likely form at the absorber surface.

Our previous calculations\(^{23}\) suggested that K can fill up pre-existing Cu vacancies during KF-PDT, but on the basis of formation enthalpies, the resulting alloy would undergo phase separation to CuInSe_2 and KInSe_2 phases if the process is kinetically feasible. Reordering of the Cu and K would then naturally lead to the formation of chalcopyrite KInSe_2. Experimentally, the stable KInSe_2 phase is monoclinic, with a layered atomic structure.\(^{23}\) As the calculated formation
enthalpies for the two phases are similar, differing only by 0.13 eV, both phases are considered in the following discussion.

The valence band DOSs for both KInSe₂ polymorphs are shown in Figure 2a,b. They are dominated mainly by the Se p features, with a minor In p contribution seen between 0 and −4 eV. There is no significant contribution from K-derived orbitals to the valence band DOSs, reflecting the ionic character of K in the compound. The photoionization cross section-weighted DOSs for 2 keV and both types of KInSe₂ are (almost) exclusively due to the Se p orbital; see Figure 2c,d. For the 6 keV correction shown in Figure 2e,f In p and In s/Se s contributions become more pronounced. However, since the two KInSe₂ structures contain similar InSe skeletons with ionized K atoms only providing extra electrons, the (weighted)
DOSs for the two polymorphs are very similar, making it difficult to differentiate between them in the HAXPES spectra. This also means that it is possible to use either one when fitting the experimental spectra below. Since the formation of monoclinic, layered KInSe2 is energetically more favorable (see Section 3), this phase was used in the considerations below.

We consider in this work the α-phase of In2Se3 and the γ-phase of InSe. According to our calculations, they have lower formation enthalpies than other In−Se phases and similarly to the case of KInSe2 polymorphs, we do not expect significant differences between phases of the same stoichiometry. In2Se3 DOSs (without and with photoionization cross section correction) are shown in Figure 3a,c,e, and those for InSe, in Figure 3b,d,f. They are dominated by pronounced peaks between −4.5 and −1.5 eV, which are due to the Se p orbital similar to the potassium indium selenides considered above. Within the energy range from −6 to 0 eV, the main contributions in the DOS are due to the Se p and In p orbitals. The hybridization of the orbitals (bond formation) is, however, not strong as can be inferred from the very different intensities of the two contributions. The hybridization results in shoulders on both sides of the DOS main peak in the case of KInSe2, whereas only one shoulder at the higher binding energy side appears in the case of InSe. In the 2 keV photoionization cross section-weighted DOS, the Se p feature dominates without any significant contributions from other orbitals. The 6 keV corrected DOSs look mainly the same, with a small increase of the In p and Se p contributions.

### 3.3. Comparison of Computed DOSs with HAXPES Spectra

Even without fitting one can immediately recognize obvious resemblances between the computed and photoionization cross section-weighted DOSs of CuInSe2 or CuIn5Se8 phases and the experimental HAXPES spectra of the alkali-free CIGSe sample shown in Figure S1. Similarly, the experimental spectra of the K-rich samples show strong similarities with the computed and weighted KInSe2 as well as InSe DOSs. These observations form the “basis set” for the materials used in the fitting procedure, aiming at representing the experimental HAXPES spectra by a combination of calculated, photoionization cross section-corrected DOSs.

The total corrected DOSs are modeled as linear combinations of the respective DOSs for all contributing phases. i.e.

\[
g_{\text{tot}}(E) = \sum_i a_i g_i(E - b_i)
\]

where \(g_i\) is the cross section-corrected DOS for sample component \(i\) and \(a_i\) is its concentration. The shifts \(b_i\) along the energy axis \(E\) account for the expected different energy level positions with respect to the experimental spectrum. The coefficients \(a_i\) and \(b_i\) were determined by minimizing the mean square error between experimental and simulated intensities. The goodness of the fitting was obtained relative to the normalized mean square error of the fit as

\[
G = 1 - \frac{\|g_{\text{ref}}(E) - \langle g_{\text{ref}}(E) \rangle_E\|}{\|g_{\text{ref}}(E) - \langle g_{\text{ref}}(E) \rangle_E\|_2}
\]

where \(g_{\text{ref}}\) is the HAXPES data vector, \(\langle \cdot \rangle_E\) gives the mean value of the data, and \(\|\cdot\|\) indicates the 2-norm of a vector. Thus, the closer \(G\) is to unity, the better is the fit. To obtain as meaningful fits as possible, we kept the fitting parameters to a minimum and assumed that each experimental spectra is constituted of a maximum of two phases, leading to four fitting parameters for each fit.

#### 3.3.1. Alkali-Free CIGSe Absorber

We assume that the alkali-free CIGSe absorber (surface) is composed of CuInSe2, CuIn5Se8, InSe, and/or In2Se3 phases and the respective HAXPES spectra can be represented as a linear combination of these components. Results of the fits of the experimental spectrum corresponding to the 2 keV excitation energy using the photoionization cross section-corrected DOSs for different components are shown in the left hand side column of Figure

---

**Figure 4.** Photoionization cross section-corrected DOSs and experimental HAXPES spectra for the alkali-free CIGSe sample measured with excitation energies of 2 (a, c, e) and 6 keV (b, d, f). The components used for the fit are given on the left. The fraction of the calculated, corrected DOS components to give the best fit (for the respective compound combination) are displayed as filled areas under the curves. The respective goodness of the fit together with other fit parameters are stated in Table 1.
HAXPES data (Figure 4a,b) is best for the CuInSe2 simulation approach. The shapes and the widths of the valence band spectra, give the overall good agreement to experiments, including the experimental resolution limit the accuracy of our band calculations and DFT energy level structures, as well as to the respective goodness of the fit (as defined in eq 2) is also stated.

The components (A, B) used in the fit are given in the first column. The ratios of the resulting component intensities (I(A)/I(B)) and the band offsets, i.e., the VBM difference (VBM(B) − VBM(A)) are given next. G, the goodness of the fit together with other fit parameters is stated in Table 2.

Figure 5. Photoionization cross section-corrected DOSs and experimental HAXPES spectra for K-poor CIGSe samples measured with excitation energies of 2 (a, c, e) and 6 keV (b, d, f). The components used for the fit are given on the left of the column. The fraction of the calculated, corrected DOS components to give the best fit (for the respective compound combination) are displayed as filled areas under the curves. The respective goodness of the fit with other fit parameters is stated in Table 2.

4. Numerical data of the fits are given in Table 1. The experimental spectra shown in Figure 4a,b are best fit when a valence band offset of −0.3 and −0.5 eV is used between CuInSe2 and CuIn5Se8, i.e., the VBM of CuIn5Se8 is at lower energy. The band offset is similar to a suggested value of −0.55 eV for the interface between CuInSe2 and the ordered vacancy compound (ref 33). The uncertainties related to DOS calculations and DFT energy level structures, as well as to the experimental resolution limit the accuracy of our band offset determination and we give them using only one digit. However, the qualitative consistency of the band offsets and the overall good agreement to experiments, including the shapes and the widths of the valence band spectra, give confidence to our modeling approach, both with respect to the selected phases (and their atomic structures) and the HAXPES simulation approach.

The quality of the respective fits of the 2 and 6 keV HAXPES data (Figure 4a,b) is best for the CuInSe2−CuIn5Se8 combination. According to Table 1, the CuIn5Se8/CuInSe2 composition ratio for the 2 keV excitation is 27:73 and for the 6 keV excitation 37:63. Thus, the Cu-deficient phase has a larger relative contribution for the more surface sensitive HAXPES data, in agreement with previous findings. The fit component ratios can be used to calculate chemical formulae as follows: The different atomic percentages in the CuInSe2 and CuIn5Se8 phases are weighted by the derived component ratios and normalized to five Se atoms. The 2 and 6 keV composition ratios then result in Cu1.08In2.97Se5 and Cu1.26In2.99Se5 stoichiometries, respectively. Thus, closest to the surface, the stoichiometry is very close to that of CuIn5Se8, and deeper into the material, the Cu content increases (valence electron IMFPs for 2 and 6 keV excitations are 4 and 10 nm, respectively). For the CuInSe2+InSe (Figure 4c,d) and CuIn5Se8−InSe (Figure 4e,f) combinations, the quality of the fit is lower, especially around the intensity maxima and close to VBM. Note that the linear combination of In2Se3 and InSe is also stated.

Figure 5. Photoionization cross section-corrected DOSs and experimental HAXPES spectra for K-poor CIGSe samples measured with excitation energies of 2 and 6 keV. The components used for the fit are given in the first column. The ratios of the resulting component intensities (I(A)/I(B)) and the band offsets, i.e., the VBM difference (VBM(B) − VBM(A)) are given next. G, the goodness of the fit (as defined in eq 2) is also stated.

Table 1. Fitting Results for the Alkali-Free CIGSe Sample Measured with Excitation Energies of 2 and 6 keV.

<table>
<thead>
<tr>
<th>phases in fit</th>
<th>2 keV data</th>
<th>6 keV data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>intensity ratio</td>
<td>band offset (eV)</td>
</tr>
<tr>
<td>CuInSe2</td>
<td>CuIn5Se8</td>
<td>27:73</td>
</tr>
<tr>
<td>CuInSe2</td>
<td>InSe</td>
<td>47:53</td>
</tr>
<tr>
<td>CuIn5Se8</td>
<td>In2Se3</td>
<td>53:47</td>
</tr>
</tbody>
</table>

The components (A, B) used in the fit are given in the first column. The ratios of the resulting component intensities (I(A)/I(B)) and the band offsets, i.e., the VBM difference (VBM(B) − VBM(A)) are given next. G, the goodness of the fit (as defined in eq 2) is also stated.
combined with those of the KInSe2, InSe, or In2Se3 secondary phase components (cf. the first, second, and third row in Figure 5).

All simulated spectra have similar appearances due to the major Cu1.14In2.95Se5 contribution describing well the main features. As given in Table 2, all material combinations show rather similar fit qualities although the fits using the KInSe2 phase are the best. The mutual band offsets given indicate that VBMs of the secondary phases are below the VBM of the substrate, reflecting the effect of Cu 3d levels pushing the VBM upward in the substrate. The substrate contributions dominate in the fits, and they increase clearly from 2 to 6 keV excitation, i.e., on enhancing the information depth. Overall, the fitting confirms the surface modification and likely formation of a secondary phase with a pronounced (K−)In−Se bond contribution, but its contribution in the spectra is too small to reliably determine its composition.

### Table 2. Fitting Results for the K-Poor CIGSe Sample Measured with Excitation Energies of 2 and 6 keV

<table>
<thead>
<tr>
<th>phases in fit</th>
<th>2 keV data</th>
<th>6 keV data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1.14In2.95Se5</td>
<td>KInSe2</td>
<td>Cu1.14In2.95Se5</td>
</tr>
<tr>
<td>Cu1.14In2.95Se5</td>
<td>In2Se3</td>
<td>Cu1.14In2.95Se5</td>
</tr>
</tbody>
</table>

The components (A, B) used in the fit are given in the first column. The ratios of the resulting component intensities (I(A)/I(B)) and the band offsets, i.e., the VBM difference (VBM(B) − VBM(A)) are given next. G the goodness of the fit (as defined in eq 2) is also stated.

### Table 3. Fitting Results for the K-Rich CIGSe Sample Measured with Excitation Energies of 2 and 8 keV

<table>
<thead>
<tr>
<th>phases in fit</th>
<th>2 keV data</th>
<th>6 keV data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1.14In2.95Se5</td>
<td>KInSe2</td>
<td>Cu1.14In2.95Se5</td>
</tr>
<tr>
<td>Cu1.14In2.95Se5</td>
<td>In2Se3</td>
<td>Cu1.14In2.95Se5</td>
</tr>
</tbody>
</table>

The components (A, B) used in the fit are given in the first column. The ratios of the resulting component intensities (I(A)/I(B)) and the band offsets, i.e., the VBM difference (VBM(B) − VBM(A)), are given next. G the goodness of the fit (as defined in eq 2) is also stated.

Figure 6. Photoionization cross section-corrected DOSs and experimental HAXPES spectra for K-rich CIGSe samples measured with excitation energies of 2 (a, c, e) and 8 keV (b, d, f). The components used for the fit are given on the left of the column. The fraction of the calculated, corrected DOS components to give the best fit (for the respective compound combination) are displayed as filled areas under the curves. The respective goodness of the fit together with other fit parameters are stated in Table 3.

### 3.3.3. K-Rich CIGSe Absorber

The HAXPES spectra and their fits for the K-rich CIGSe absorber are shown in Figure 6. Note that excitation energies of 2 and 8 keV were used for these samples instead of the 2 and 6 keV used for the alkali-free and K-poor CIGSe sample discussed above. The shapes of the 6 and 8 keV photoionization cross section-corrected DOSs for the different phases we consider are very similar, but the DOSs corrected for the 8 keV photoionization cross sections have only about 50% of the 6 keV intensity (see Table S2). The substrate is again Cu1.14In2.95Se5. Compared to the K-poor results, the intensities of the spectra below VBM have considerably increased but appear to retain an otherwise similar shape. A linear combination of the photoionization cross section-corrected DOSs of Cu1.14In2.95Se5 and KInSe2

combined with those of the KInSe2, InSe, or In2Se3 secondary phase components (cf. the first, second, and third row in Figure 5).

All simulated spectra have similar appearances due to the major Cu1.14In2.95Se5 contribution describing well the main features. As given in Table 2, all material combinations show rather similar fit qualities although the fits using the KInSe2 phase are the best. The mutual band offsets given indicate that VBMs of the secondary phases are below the VBM of the substrate, reflecting the effect of Cu 3d levels pushing the VBM upward in the substrate. The substrate contributions dominate in the fits, and they increase clearly from 2 to 6 keV excitation, i.e., on enhancing the information depth. Overall, the fitting confirms the surface modification and likely formation of a secondary phase with a pronounced (K−)In−Se bond contribution, but its contribution in the spectra is too small to reliably determine its composition.
yields clearly the best match with the 2 keV as well as the 8 keV experimental spectra of the K-rich CIGSe absorber. Moreover, the derived band offsets between these two phases are consistent in all cases, as shown in Tables 2 and 3, further supporting the reliability of our fitting procedure. By comparison, the fits with InSe and In2Se3 cannot reproduce the shapes of the measured spectra. Most striking is, however, the inconsistency of the derived band offsets switching from being negative for the alkali-poor to positive for the alkali-rich sample set. Considering that both phases are supposed to have being negative for the alkali-poor to positive for the alkali-rich sample set. Considering that both phases are supposed to have

4. CONCLUSIONS

We have analyzed HAXPES spectra of CIGSe solar cell absorbers exposed to NaF/KF-PDT using linear combinations of simulated spectra for Cu-deficient CIGSe phases of different stoichiometries and of potentially formed secondary phases, such as KInSe2, InSe, and In2Se3. HAXPES data of K-poor and K-rich samples measured with X-ray excitation energies of 2, 6, and 8 keV were used for comparison. Samples without PDT were used as alkali-free CIGSe references. Although the crystalline structure of the surfaces of the samples is not known, our method allows us to derive a first-principles description of the electronic structure of their valence bands. Our analyses give robust trends and enable us to draw conclusions for the different samples and for the 2 and 6 (8) keV HAXPES data having different probing depths. The most important findings are: (i) The surface of alkali-free CIGSe is Cu depleted. The HAXPES valence band spectra are best described by a mixture of the (photoionization cross section) corrected DOS of stoichiometric CuInSe2 and Cu-deficient CuInSe2 with the resulting stoichiometry at the surface corresponding roughly to CuInSe2 being less Cu-deficient further away from the surface. The combinations involving Cu-free In−Se compounds did not result in reasonable fits of the measured valence band spectra (without additional Cu-containing phases). This could indicate the presence of an ordered defect/vacancy surface compound. 

(ii) The valence band structure of K-rich samples agrees well with a superposition of corrected KInSe2 and Cu-deficient phase DOSs. (iii) The valence band of K-poor samples can also be explained by a combination of KInSe2 and the Cu-deficient phase. However, explaining the valence band structure by a corrected DOS combination of In−Se-type species (and here, in particular, In2Se3 and KInSe2 results in a similar fit quality, indicating that the formation of a pronounced K−In−Se-type species might depend on the K amount available during PDT. In any case, (K)In−Se-type surface phases have different optoelectronic properties than those of (Cu-deficient) CIGSe. To what extent this will affect the electronic structure at the emitter/absorber heterointerface in the thin-film device layer stack is a subject of ongoing studies and discussions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b18216.

HAXPES spectra for K-free, K-poor, and K-rich samples; photoionization cross sections for Cu-, In-, Se-, and K-derived valence orbitals; crystal structures of the calculated phases (PDF)

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Notes

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