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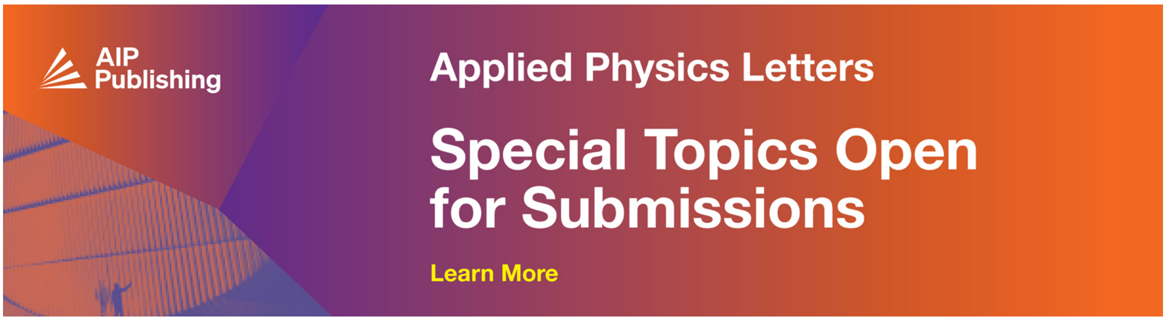

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Experimental indication for band gap widening of chalcopyrite solar cell absorbers after potassium fluoride treatment

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The implementation of potassium fluoride treatments as a doping and surface modification procedure in chalcopyrite absorber preparation has recently gained much interest since it led to new record efficiencies for this kind of solar cells. In the present work, Cu(In,Ga)Se_2 absorbers have been evaporated on alkali containing Mo/soda-lime glass substrates. We report on compositional and electronic changes of the Cu(In,Ga)Se_2 absorber surface as a result of a post deposition treatment with KF (KF PDT). In particular, by comparing standard X-ray photoelectron spectroscopy and synchrotron-based hard X-ray photoelectron spectroscopy (HAXPES), we are able to confirm a strong Cu depletion in the absorbers after the KF PDT which is limited to the very near surface region. As a result of the Cu depletion, we find a change of the valence band structure and a shift of the valence band onset by approximately 0.4 eV to lower binding energies which is tentatively explained by a band gap widening as expected for Cu deficient compounds. The KF PDT increased the open circuit voltage by 60–70 mV compared to the untreated absorbers, while the fill factor deteriorated. © *2014 AIP Publishing LLC*.

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The potential of chalcopyrite solar cells and modules as a versatile, low-cost thin film technology has long been proven and is confirmed by recent developments and efficiency improvements[1–4] which are accompanied by the build-up of production capacities in the GW regime.[5] By achieving 20.9% maximum conversion efficiency, the anterior gap to polycrystalline silicon technologies could finally be surpassed. While the importance of sodium for the doping, growth, and interdiffusion kinetics in chalcopyrite absorbers has long been discussed and established,[6–8] less attention has been paid to the implementation of other alkaline metals in the past. It was recently found that similar to sodium, potassium can be introduced into the chalcopyrite absorber during growth[9] or in a post deposition treatment (PDT).[2,10] Laemmle *et al.* showed that a KF PDT could effectively enhance the net charge carrier concentration in absorbers grown on alkaline free alumina substrates.[10] A sequential PDT with first NaF followed by KF of Cu(In,Ga)Se2 (CIGS) absorbers grown by a three-stage process on polyimide foil has been independently established by Chirila *et al.* and led to efficiencies up to 20.4%.[2] They found an influence of the KF treatment not only on the bulk of the absorber but also more importantly a modification of the CIGS surface. In particular, they found a modified interface with a pronounced Cu depletion and assumed a better incorporation of Cd into the absorber surface during the buffer deposition to be the reason for the efficiency improvement. In a recent publication, Pianezzi *et al.* suggested stronger type inversion as a result of the KF PDT being responsible for reduced interface recombination and better device performance.[11] We find evidence for a lowered valence band edge at the KF treated CIGS surface and add the idea of an increased band gap region whose effect will be discussed in this work.

We concentrate on the influence of KF PDTs on the surface of evaporated CIGS absorbers and investigate the changes in surface composition and valence band structure, relating them also to device performance. The surface sensitivity of X-ray photoelectron spectroscopy (XPS) makes it an ideal tool to study compositional changes at the absorber surface. Using brilliant synchrotron-based radiation with tunable excitation energy, this tool becomes even more powerful as it allows the variation of the information depth. We use a standard laboratory Mg Kα X-ray source in combination with the high kinetic energy XPS end station (HIKE) at the KMC-1 beamline at the BESSY II synchrotron facility for the acquisition of XPS data. For further information on the HIKE setup, the interested reader is referred to Ref. 12. Special attention is paid to changes in the band structure of the absorber at the surface, as minor changes at the absorber/buffer interface can have tremendous effects on the device performance, especially in view of potential interface recombination. Here, we compare the valence band structure of samples with and without KF PDT from data acquired at the HIKE endstation and data obtained with ultraviolet photoelectron spectroscopy (UPS).

CIGS was deposited on Mo/soda-lime glass by a standard three-stage process at a maximum temperature of 560 °C and with a [Cu]/([Ga] + [In]) (CGI) ratio of 0.80 and a [Ga]/([Ga] + [In]) (GGI) of 0.31. For more details on the absorber process, see Ref. 13. Our KF PDT approach was a slightly modified combination from Refs. 2 and 9, but with an *ex situ* KF deposition on unheated substrates: After absorber deposition, KF was evaporated *ex situ* in a separate evaporation

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TABLE I. Average open circuit voltage (V_{OC}), short circuit current density (j_{SC}), fill factor (FF), and efficiency (η) of two untreated Cu(In,Ga)Se_2 references, KF treated samples with rinsed in DI water (targeted KF thickness 15 nm and 25 nm) and KF treated samples with an additional HCl etch (15 nm and 25 nm).

Sample	V_{OC} (mV)	j_{SC} (mA/cm^2)	FF (%)	η (%)
No KF	595	31.3	72.6	13.6
No KF	611	31.2	73.7	14.1
15 nm KF	668	30.3	62.7	12.7
25 nm KF	668	29.4	60.4	11.9
15 nm KF + HCl	641	30.9	56.8	11.3
25 nm KF + HCl	663	30.2	58.6	11.8

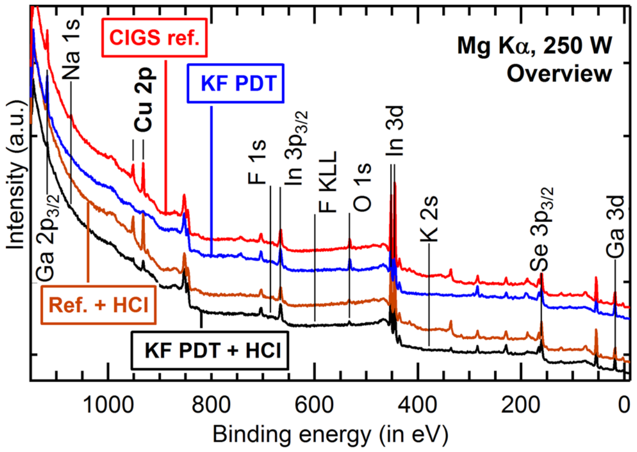

FIG. 1. XPS overview spectra recorded with Mg Kα excitation of differently treated CIGS samples. From top to bottom: reference without KF PDT rinsed with DI water, KF treated sample rinsed with DI water, reference without KF PDT etched in HCl, KF treated sample etched in HCl.

chamber with a targeted thickness of 15 nm and 25 nm, respectively. Samples were then transferred into an absorber deposition setup and the KF was diffused into the absorber for 12.5 min at 350 °C in presence of Se. After KF PDT, the samples were rinsed in de-ionised (DI) water before further processing with a wet-chemical standard CdS buffer, a sputtered i-ZnO/ZnO:Al front contact and evaporated Ni/Al contacts. Area of the completed solar cells was either 0.5 cm^2 or 1.0 cm^2. IV-characteristics were measured under simulated AM1.5 illumination and compared to CIGS references with KF treatment built from the same absorber batch. The average solar cell parameters of the resulting devices are summarized in Table I. While in our case the KF PDT did not lead to an efficiency improvement, mainly because of a ~10% decrease in fill factor, the treatment did positively affect the open circuit voltage V_{OC} and led to an increase of 60–70 mV for all KF PDT samples, independent of the applied KF thickness.

The observed V_{OC} increase compares to—but is slightly less than—the V_{OC} increase of up to 111 mV observed by Laemmle *et al.*[10] However, it is quite remarkable that for the samples presented in this work, the V_{OC} increases despite the fact that samples were prepared on glass which acts as an alkaline source already during growth, in contrast to Laemmle's work which was conducted on alkaline free substrates. For our samples, capacitance voltage measurements demonstrate that the observed V_{OC} increase cannot be attributed to an enhancement in the charge carrier density in the bulk of the absorber material, in line with Ref. 11.

For the surface analysis, absorber samples from the same batch as the solar cells were prepared with a 25 nm KF layer and identical process parameters for the in-diffusion as described above. Samples were characterized by XPS with the Mg Kα X-ray source and compared to an untreated CIGS reference. Pronounced K 1s, F 1s, and Na 1s signals could be detected on the KF PDT treated samples. Afterwards, samples were transferred into an oxygen free glovebox. To remove residual KF, a KF treated sample was rinsed with DI water together with an untreated reference. All liquids were bubbled with ultrapure nitrogen to make them oxygen-free. Samples were then transferred directly back into the XPS chamber and measured without air exposure with laboratory XPS and UPS. In addition, these two samples were transferred into and analysed in the HIKE end station using synchrotron radiation with an energy of 2100 eV. Fig. 1 shows XPS survey spectra using laboratory Mg Kα excitation, with comparable In and Se signal intensities for the two samples after DI water rinsing. From the extinction of the K 1s and F 1s signals, we conclude that rinsing in water is an effective way to remove residual KF FROM the surface, although traces of K could still be found in prolonged detail spectra (not shown) on the KF treated sample.

The most distinct difference was observed for the Cu signals, which are strongly decreased for the KF treated sample. In Fig. 2, detail spectra of the In 3d$_{5/2}$ and the Cu 2p$_{3/2}$ core levels of the untreated and a KF treated sample after water rinsing are shown. The Cu/In peak area ratio of the two samples is compared in Figs. 2(c) and 2(d). As can be seen, when using the laboratory X-ray source with 1253.6 eV excitation, this ratio is diminished to less than 10% after the KF PDT. With an excitation energy of 2100 eV the Cu/In peak area ratio of the KF PDT sample is still much lower than the reference (~55% of the reference value), but the decrease is not as strong as with the laboratory based X-ray source. There are two main differences between the two measurements: first, the laboratory X-ray source averages

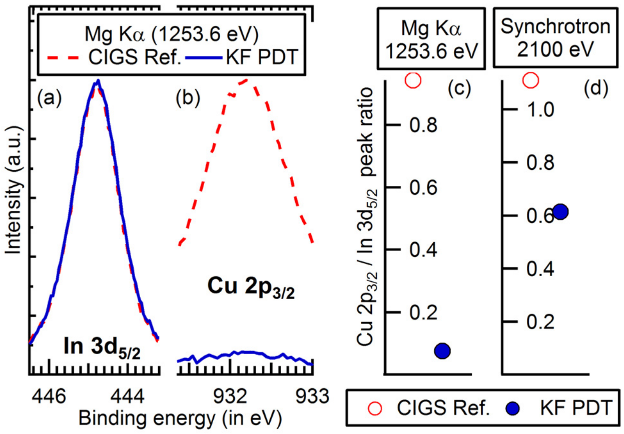

FIG. 2. (a) In 3d$_{5/2}$ and (b) Cu 2p$_{3/2}$ XPS spectra with Mg Kα excitation (1253.5 eV) of the CIGS absorber with and without KF PDT after rinsing in DI H_2O. (c) and (d) Comparison of the Cu 2p$_{3/2}$/In 3d$_{5/2}$ XPS peak intensity ratio for both samples for different excitation energies: (c) Mg Kα excitation (1253.6 eV), (d) synchrotron excitation (2100 eV).

over many more local inhomogeneities due to a larger beam spot compared to the synchrotron source; second, the escape depth of the involved photoelectrons differs, as higher excitation energies lead to an increasing inelastic mean free path (IMFP). The IMFP calculated with the TPP2M formula of Tanuma *et al.*[14] increases from 0.8 nm (1253.6 eV) to 2.2 nm (2100 eV) for the Cu 2p peak, and from 1.7 nm to 2.9 nm for In 3d photoelectrons. Based on these findings, we confirm that as a consequence of the KF PDT, the CIGS absorber surface becomes nearly completely depleted of Cu in a region that stretches only few nanometers into the absorber.

We found a valence band shift for samples after the KF PDT of 0.3 eV–0.4 eV measured in the laboratory UPS setup, where the valence band edge is referenced to the Fermi energy. Furthermore, samples prepared with KF PDT showed increased Ga and O signals that can be attributed to an increased partial oxidation of Ga at the absorber surface. These gallium oxides could be removed with an HCl etch (1%, 1 min) as was confirmed with the laboratory XPS setup (Fig. 1). However, the analysis of KF treated absorbers and solar cells after a removal of the Ga oxides through HCl etching showed that the observed effects of the KF PDT remained the same, namely, a V_{OC} increase of ~60 mV, an Cu depletion at the surface and a shift of the valence band edge measured with the laboratory XPS and UPS setup, respectively.

The HIKE setup also allows the measurement of the valence band region with sufficient resolution. Scans across the binding energy from 22 eV to 0 eV are displayed in Fig. 3. In order to compare the onset of the valence band structure of both samples directly excluding charging and band bending effects, the position of the In $4d_{5/2}$ core level at 17.6 eV (Ref. 15) is used as energy reference for both spectra. The inset in Fig. 3 shows the magnified valence band edge (VBE) region for the untreated and the KF treated sample. A clear shift of the valence band onset of 0.37 eV is observed as a consequence of the KF PDT. We interpret the lowering of the valence band edge as a widening of the absorber band gap near the surface as a consequence of the Cu-depletion. This interpretation has also consequences on the electronic behavior of the devices and will be discussed in more detail in the following. In contrast to this, no shift of the effective band gap (1.12 eV +/− 0.01 eV) is observed in quantum efficiency measurements, which confirms the assumption that the observed band gap widening is not a bulk effect but limited to the surface.

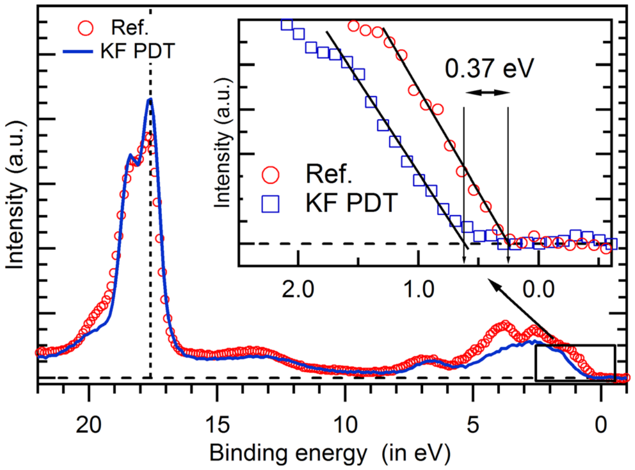

FIG. 3. XPS spectra with synchrotron excitation (2100 eV) of CIGS absorbers after rinsing with DI water. Red circles: CIGS absorber without KF PDT. Blue line: CIGS absorber after KF PDT. The energy scale of the spectra is referenced to the In $4d_{5/2}$ core level at 17.6 eV (dashed vertical line). The inset is a magnification of the valence band onset with a linear extrapolation and shows a 0.37 eV shift of the onset for the KF treated sample.

It is a well-established fact that CIGS thin films with the considered CGI of 0.8 generally show a Cu-poor surface composition in XPS measurements.[16,17] Liao and Rockett[18] and Mönig *et al.*[19] attributed this to a reconstructed surface where the very topmost atom layers (monolayers) are completely depleted of Cu. Hence, if we assume a Cu-depleted surface already for the untreated CIGS reference sample, the further decrease of the Cu signal after the KF PDT would mean that the Cu depleted region is extended further into the absorber. Taking into account the difference between the laboratory and synchrotron measurements and the different inelastic mean free paths of the photoelectrons, we expect this region now to be a few nanometers wide. Although a clear decrease of the Cu concentration at the surface of the KF PDT treated samples could be verified, a more detailed depth profiling of the composition needs more sophisticated analysis and measurement methods and is still pending. The fact that we are able resolve changes in the position of the VBE relative to the core levels contributes to the hypothesis that the KF PDT alters the composition of a surface region which is extended into the bulk instead of being restricted only to the topmost atomic layer.

Jaffe and Zunger showed that the VBE of bulk $CuInSe_2$ is characterized by bonding and anti-bonding states formed by Cu-*d* and Se-*p* orbitals.[20] The strong *p-d* repulsion pushes the VBE to towards the conduction band and results in lower band gaps as compared to corresponding II-VI semiconductors. Removal of Cu atoms diminishes this repulsion and the VBE collapses as a consequence, resulting in higher band gaps for compounds with a higher amount of Cu vacancies.[21]

The potentially beneficial effect of an ordered vacancy compound (OVC) on the electronic properties of chalcopyrite solar cells has been widely discussed in the past.[22] In particular, the increased distance of the valence band edge to the Fermi level and consequently the reduced concentration of holes as recombination partners at the CIGS surface may effectively impede interface recombination.

Here, we show evidence for a valence band shift at the absorber surface as a result of the Cu depletion induced by the KF treatment. We interpret this shift as a band gap widening under the assumption of a constant position of the conduction band edge. The formation of a Cu-deficient phase near the absorber surface as a consequence of the KF PDT could lead to a reduced interface recombination in line with the discussion above. Pianezzi *et al.*[11] found an improved Cd incorporation into the absorber after KF PDT, and type inversion resulting from this might further reduce interface recombination.

CIGS devices with highest efficiency are normally prepared with a Cu-poor final composition and a GGI between 0 and 0.3. They are generally considered to be dominated by recombination in the bulk, which seems to contradict the suggested strong influence of the absorber surface on device performance. Highest efficiency devices, where the dominating recombination takes place in the bulk should therefore benefit less from surface modifications in first order. To the contrary, a beneficial effect is still observed for these devices[2,3,9] and might be explained by the following argument: Potassium can be expected to diffuse along grain boundaries analogous to sodium. Then, the described Cu depletion phenomena might also play a similar role at grain boundaries (GBs) within the absorber. As a consequence, KF PDT might help to reduce bulk recombination via stronger Cu depleted GBs. The beneficial effect of a Cu depletion at the GBs was already suggested by Persson and Zunger.[21] Devices dominated by interface recombination with Cu rich absorbers, wide gap chalcopyrites, or even kesterite absorbers could benefit even stronger from the described effect and should therefore be within the focus of further investigations. Findings of a shift towards higher performances for KF PDT treated samples with increased Ga contents seem to support this hypothesis.[3]

The efficiency of the presented devices is with 14% not very high and we suspect detrimental recombination also at the absorber surface. Therefore, the observed strong increase in the V_{OC} of the KF treated devices is in line with the suggested reduced interface recombination as outlined above. Nevertheless, the overall efficiency of these devices does not profit from the KF PDT due to a decrease in fill factor. We suspect surface oxidations of the absorbers as discussed above to be the origin of this decrease. The oxidation of KF PDT treated samples is believed to be enhanced as a result of the *ex situ* KF preparation and the extremely hygroscopic nature of KF which enables the efficient capture of moisture during the short air exposure necessary for sample transfer. For samples with increased air exposure time (hours to days), we observed even more severely decreased fill factors well below 30%. We conclude that for future investigations an *in situ* KF PDT as introduced in Ref. 2 would be preferable.

Summarizing the results, we could show that a potassium fluoride post deposition treatment (KF PDT) of $Cu(In,Ga)Se_2$ absorbers grown on Na-containing substrates has a strong impact on their surface conditions in compositional as well as electronic terms. We confirmed with XPS that the KD PDT induces a strong Cu depletion at the very near absorber surface region. This surface modification has a direct influence on solar cell performance leading to an open circuit voltage increase of 60–70 mV. We attribute this to an altered band structure and efficiently reduced interface recombination losses. The band structure modification could be resolved through HAXPES measurements with an excitation at 2100 eV, showing a clear lowering of the valence band edge by 0.37 eV for KF treated samples. These findings emphasize the potential of KF PDT in the development of chalcopyrite and related solar cells and give insight into the underlying mechanisms behind it. We believe that the surface tuning opportunity might open new fields for further improvements of a variety of different material classes including wide-gap and Cu-rich grown chalcopyrite absorbers.

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