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Deep surface Cu depletion induced by K in high efficiency Cu(In,Ga)Se₂ solar cell absorbers

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Abstract:
In this work we used K-rich glass substrates to provide potassium during the co-evaporation of CIGS absorber layers. Subsequently, we applied a post-deposition treatment (PDT) using KF or RbF to some of the grown absorbers. It was found that the presence of K during the growth of the CIGS layer led to cell efficiencies beyond 17%, and the addition of a PDT pushed it beyond 18%. The major finding of this work is the observation of discontinuous 100-200 nm-deep Cu-depleted patches in the vicinity of the CdS buffer layer, correlated with the presence of K during the growth of the absorber layer. The PDT had no influence on the formation of these patches. A second finding concerns the composition of the Cu-depleted areas, where an anti-correlation between Cu and both In and K was measured using scanning transmission electron microscopy (STEM). Furthermore, a steeper Ga/(In+Ga) ratio gradient was measured for the absorbers grown with the presence of K, suggesting that K hinders the group III element inter-diffusion. Finally, no Cd in-diffusion to the CIGS layer could be detected. This indicates that if Cd_Cu substitution occurs, either their concentration is below our instrumental detection limit, or its presence is contained within the first 6 nm from the CdS/CIGS interface.

1. Introduction

Heavy alkali doping of the CIGS absorber with K, Rb, and Cs has recently allowed a rapid improvement in the conversion efficiency of record devices, mainly enhanced by a sharp increase in V_{oc} and FF values of the devices [1–5]. While the doping of CIGS using exclusively Na led to efficiencies of around 20% (19.7%(Solar Frontier 2013[6]) - 19.8%(Solibro 2013 [7]) - 20.0%(NREL 2008 [8])- 20.3%(ZSW 2011[9]) - 20.4%(EMPA 2013[10]), the latest K, Rb or Cs post deposition treatment (PDT) of the CIGS absorber have pushed the record efficiencies beyond
22% (22.3% (Solar Frontier 2015 [11]) 22.6% (ZSW 2016 [3])). Except for Solar Frontier using a Zn(O,S) buffer layer, all of these processes use a CdS buffer layer.

The exact role of the alkali impurities is still under discussion but many similarities between Na and K have already been reported. When Na is available during the growth of the CIGS absorber, it is known for hindering metal inter-diffusion, leading to a steeper Ga gradient [12], which is also observed for K [1,13]. Additionally, Na is known to increase the free carrier concentration, either by lowering the number of InCu\textsuperscript{2+} (or GaCu\textsuperscript{2+}) donor-like defects [14], or by compensating V\textsubscript{Se} recombination centers present at the grain boundaries, in combination with O\textsubscript{2} [15,16], or by forming NaCu at high temperature that would increase the final concentration of V\textsubscript{Cu} acceptors by Na out-diffusion during the cool down [17]. Concerning the addition of K, the boost of the electrical characteristics is also attributed to an increase in net doping by the passivation of the grain boundaries and bulk InCu\textsuperscript{2+} (or GaCu\textsuperscript{2+}) donor-like defects [2,5,18], or by the increase of V\textsubscript{Cu} concentration induced by K out-diffusion during the cool down[17]. However, unlike Na, the gain is also attributed to the passivation of the interface with the buffer layer. This allows the use of a thinner buffer, consequently reducing optical losses. Such an interface passivation may be explained by the formation of an intermediate layer (e.g. KIn\textsubscript{x}Se\textsubscript{y}) [1,19–21], or by the creation of a buried PN homojunction, enhanced by either the Cd\textsubscript{Cu} substitution [22], or else by a Cu-depletion at the surface of the absorber layer. Such a Cu-depletion would increase the local band bending and thus create a higher potential barrier for holes to recombine at the interface [2,23]. It is however not clear yet if these different explanations about the passivation of the CIGS/buffer layer interface depends on the alkaline incorporation strategy [24,25].

Our study has been designed to measure the consequences of the different strategies to add alkalis on the local chemical composition of the absorber. Scanning Transmission Electron Microscopy (STEM) combined with Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive X-ray (EDX) are used to map compositional variations in our high-efficiency CIGS absorbers. X-ray diffraction (XRD) and Raman spectroscopy are employed to support our STEM conclusions. We discuss the consequences of having K out-diffusing from the substrate during the growth of the absorber, and compare it to different PDT. Additionally, we analyze the different CdS/CIGS interfaces looking for Cd diffusion to the CIGS absorber from the CdS buffer layer.

2. Experimental methods

To observe the modifications induced by the different alkali PDT, we have prepared a total of 4 samples. The first 3 samples were deposited on K-rich/Na-poor glass and were subjected to no PDT, KF-PDT, and RbF-PDT, respectively. To test whether K from the substrate plays a
Therefore the average bulk compositions placement of th lab 2000 by Kleve.

The preparation of the samples was standardized as follows. Prior to the CIGS deposition, the substrates were cleaned with an ammonia solution and coated with a 400 nm Mo bi-layer via DC magnetron sputtering. For the ‘Ref’ sample only, a 20nm $\text{Al}_2\text{O}_3$ layer was deposited by atomic layer deposition prior to the Mo. Therefore, the alkali out-diffusion from the glass is prevented but the subsequent CIGS would also nucleate on a NaF coated Mo layer as for the other samples. For all the samples, NaF was deposited as a precursor layer on top of the Mo back contact. The CIGS layers were all made in the same co-evaporation system, using the same deposition profile (see Figure 2) but in separated batches. The metal co-evaporation follows a Cu-poor, Cu-rich, Cu-poor deposition strategy, where the CIGS film will start Cu-poor, becomes Cu-rich during part of the deposition time and ends Cu-poor. A Cu-poor final composition is necessary to avoid segregation of $\text{Cu}_{2-x}\text{Se}$ secondary phases, which results in severe shunting of the solar cells. In the beginning of the co-evaporation, a Ga-rich layer is deposited, which leads to an increased band gap close to the back contact, and the change goes into the position of the conduction band. This increase aims at preventing electrons generated in the bulk of the film from reaching the back contact, which has a high surface recombination velocity. The temperature set point was 550°C for the samples ‘no- PDT’, ‘KF-PDT’ and ‘Ref’; and 600°C for the ‘RbF-PDT’. The PDTs was performed at 350°C under weak Se atmosphere, directly after the absorber deposition without breaking the vacuum. Subsequently, for the no-PDT samples a 40 nm CdS buffer layer was grown by Chemical Bath Deposition (CBD) (samples immersed in beaker with room temperature solution then placed in a 60°C water bath for 8 min) within 5 min after the substrates were taken out from the vacuum. This buffer layer thickness was reduced to 30 nm for samples treated by a PDT (solutions separately pre-heated to 60°C, mixed, sample immersed and beaker placed in a water bath at 60°C for 4 min).

Transmission Electron Microscopy (TEM) work was carried out on a FEI Tecnai F30 ST operated at 300 kV accelerating voltage, equipped with a Tridiem 863 energy filter for the Electron Energy Loss Spectroscopy (EELS). TEM lamellae have been prepared using a FEI Strata DB235 equipped with a Ga-based Focused Ion Beam (FIB), using the in-situ lift-out method [26]. The relative thickness of the lamella was maintained between $t/\lambda = 0.15 - 0.5$. The data sets presented in this article have been processed using a Multivariate Statistical Analysis tool (MSA) elaborated by Lucas et al. [27] in order to screen out noise corruption of the data. The final composition of the films was measured by X-Ray Fluorescence (XRF) performed in a Spectro X-lab 2000 by Kleve. The quantification in EELS is precise, but its accuracy relies heavily on the placement of the background and signal windows prior to the quantification calculation [28]. Therefore the average bulk compositions in EELS were corrected based on the X-ray
Fluorescence (XRF) results. In addition, this article refers to Cu/III and Ga/III ratios. They are both calculated from the quantification maps of Cu, Ga and In; and correspond to Cu/(In+Ga) and Ga/(In+Ga), respectively. The quantifications are always derived from the PCA treated datasets. All the chemical maps (except the STEM EDX one) are plotted using Digital Micrograph (GMS2.32) from Gatan.

The Transmission Kikuchi Diffraction (TKD) was acquired on a Zeiss Merlin using its EBSD system (Nordlys Max detector, AZtec HKL software). X-ray diffractograms were measured on a X’pert Pro instrument from PAN (\(\lambda_{Kα}: 1.5406 \text{ Å}\)). The Raman analysis was done with a InVia(2013) spectrometer from Renishaw. For the rear-face measurement, we peeled off the CIGS absorbers using superglue; the analysis was conducted immediately after the peeling (< 1 h).

3. Results

Table 1 – Summary of the samples presented in the article

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Substrate</th>
<th>PDT</th>
<th>Voc [mV]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>Eta [%]</th>
<th>NaF [nm]</th>
<th>CdS [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref</td>
<td>K-rich glass +Al₂O₃</td>
<td>none</td>
<td>506</td>
<td>32.69</td>
<td>70.59</td>
<td>11.67</td>
<td>15</td>
<td>40</td>
</tr>
<tr>
<td>no-PDT</td>
<td>K-rich glass</td>
<td>none</td>
<td>700</td>
<td>32.16</td>
<td>75.62</td>
<td>17.03</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>KF-PDT</td>
<td>K-rich glass</td>
<td>KF</td>
<td>717</td>
<td>33.43</td>
<td>75.83</td>
<td>18.18</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>RbF-PDT</td>
<td>K-rich glass</td>
<td>RbF</td>
<td>713</td>
<td>33.19</td>
<td>77.92</td>
<td>18.44</td>
<td>25</td>
<td>30</td>
</tr>
</tbody>
</table>

Sample description

Table 1 presents a summary of the different samples discussed in this work. The samples grown on K-rich substrates with no barrier reach the highest efficiencies, ranging from 17 to 18.4% (without anti-reflective coating), with \(V_{oc}\) values above 700 mV. Among these three samples, the PDT ones show a slightly higher \(V_{oc}\) (+17 and +13 mV for the ‘KF-PDT’ and ‘RbF-PDT’, respectively), but mainly a boost in \(J_{sc}\) (+1.3 and +1.0 mA/cm² for the ‘KF-PDT’ and ‘RbF-PDT’, respectively). The sample ‘Ref’, equipped with an additional Al₂O₃ alkali-barrier, performs poorly in comparison. Its efficiency is around 11.7%, and its \(V_{oc}\) value is at 506 mV. We note that the thickness of NaF is slightly lower for this sample (15 nm instead of 25 nm), and the CdS is around 40 nm. With the presence of the Al₂O₃ barrier, a thicker NaF layer led to delamination of the CIGS layer during the CBD.

Absorber layer composition

As measured with STEM-EELS, the three samples with no alkali barrier (‘no-PDT’, ‘KF-PDT’ and ‘RbF-PDT’) show distinct Cu-depleted patches at the surface of the absorber (from 100 nm to
200 nm deep), which are accompanied with a significantly higher signal of both In and K (Figure 3 and Figure 5). The K-edge is sufficiently strong to be detected when summing spectra from a large area, but is too weak for reliable quantification on a pixel-by-pixel basis; therefore only the concentrations of Cu, In and Ga are reported here. The Cu/III ratios calculated at the border of such a patch drop abruptly down from 0.9 outside the patch to a constant level of approximately 0.4 in the patch. The Ga/III ratio also abruptly decreases, but less, changing from 0.40 to 0.35. It is interesting to note that the Cu-depleted patches do not form a continuous layer. In addition, their locations can often not be related to the presence of grain boundaries, but seem to be grown epitaxially on existing grains. For these three samples, the Ga/III profile throughout the absorber conserves a strong gradient, corresponding to the deposition profile. Results from both STEM EDX and STEM EELS show that, in the vicinity of the back-contact, the values of the Ga/III ratio range from 0.55 to 0.75 (Figure 5 and Figure 6). The higher Ga content at the back is further supported by the Raman measurements (Figure 7 (b)) where the “A1 CIGS” peak of these samples shift towards the higher frequencies, as described by Witte et al. [29]. Likewise the Transmission Kikuchi Diffraction (TKD) (Figure 8) shows the presence of smaller crystals nearby the Mo, becoming larger further away.

On the other hand, the sample ‘Ref’ does not show any sign of Cu-depleted, K-rich patches close to the buffer layer (Figure 3). Additionally, its chemical composition is constant throughout the thickness of the absorber layer with a Cu/III and Ga/III around 0.9 and 0.4, respectively (Figure 6).

The Raman analysis of the front side (Figure 7, (a)) shows a strong peak appearing at 156 nm$^{-1}$ only for the samples having the Cu-depleted patches. The literature suggests that this peak may be attributed to the presence of an Ordered Vacancy Compound (OVC) in the CIGS layer [30–32]. For the same samples, Grazing Incidence X-ray Diffraction (GIXRD) analysis reveals extra shoulders at higher angles for two of the CIGS peaks (Figure 9). An indium peak can be seen in the two last diffractograms (samples ‘no-PDT’ and ‘KF-PDT’), which emanates from soldering of indium for contacting made on the edge of the sample and is not relevant for the analysis. As indicated in the figure, these two samples are measured with a slightly lower incidence angle ($\alpha = 0.1$ instead of 0.3); indeed the shoulders are not as pronounced for these two samples and a lower angle favors their visibility. Interestingly, the $\theta$-2$\theta$ measurements (not shown here) indicate that while the texture of the CIGS film is essentially [112] for the sample ‘Ref’, it adopts a [220/204] preferential texture for the three other samples, independently of the PDT. A [220/204] texture has been correlated to higher absorber quality, with more homogeneous opto-electronic properties and lower density of non-radiative recombination centers [33].
The reason for the formation of Cu-depleted patches at the surface of the CIGS absorber is not fully understood, but it seems that it is a consequence of the Cu-poor stage at the end of the co-evaporation in combination with presence of K.

**Cd–CIGS transition**

For all the samples, the CdS buffer layers measure between 30 - 40 nm in thickness. As Cd$_{Cu}$ substitution defects may be expected in the CIGS, we plotted the Cd profile across different CIGS/CdS interfaces looking for signs of Cd diffusion (cf. Figure 4). First, the PDT samples, ‘KF-PDT’ and ‘RbF-PDT’, lead to sharp interfaces (less than 6 nm), similarly as for the samples without any PDT. Second, the presence or absence of K during the growth of the absorber also leads to comparable transition profiles. Third, the influence of a Cu-depleted patch below the buffer layer does not lead to significant difference in the Cd profile either. Thus, in every case, the CIGS/Cd interface is consistently measured to be less than 6 nm in thickness, and no sign of Cd diffusion can be detected further into the CIGS layer. A Cu signal may sometimes be observed into the CdS buffer layer in the STEM maps (Figure 3, Figure 5 and Figure 6). This is an artifact generated by the ion bombardment during the sample polishing.

4. Discussion

1. Cu depletion
The Cu-deficient patches at the surface of the absorber layer appear to be a direct consequence of both the presence of K during the growth, and the Cu-poor stage at the end of the co-evaporation recipe. The addition of a PDT does not significantly change the local composition profiles as measured with STEM EELS (Figure 4). The low Cu/III values raise questions about the new possible stoichiometry of those areas. EELS quantification indicates that, on average, the Cu/III ratio drops down from about 0.9 to 0.4. This leads to a compound close to Cu$_2$(In,Ga)$_3$Se$_x$. The shoulders visible in the GIXRD (noted Ψ) indicate the presence of this Cu-depleted phase, as previously observed by Szaniawski [34] and Souilah [35]. Using the pseudo-ternary diagram from the latter to estimate the corresponding amount of Se in the second phase, we obtain a stoichiometry of 2:5:8.5. This result indicates a slightly stronger Cu-depletion than in the study of Stokes [36] (2:4:7) but still less depleted than the commonly reported 1:3:5 stoichiometry. The high amount of In in the Cu-depleted areas supports the presence of 2V$_{Cu}$ + In$_{Cu}$ neutral defect pairs [37]. However, the surprisingly high signal of K in the same regions indicates that the K is not only located at the grain boundaries of the CIGS, but is integrated in the main lattice during the growth of the absorber, possibly located on the V$_{Cu}$. In addition, its actual
concentration is most probably above several thousands of ppm to overcome the EELS detection limit as estimated from our measurements.

Referring to theoretical calculations, both surface Cu vacancies and alkali impurities are expected to have a large and favorable influence on the conduction band offset (CBO) and the valence band offset (VBO) between the CIGS absorber and the CdS buffer layer [23]. The stronger band bending would repel holes and shift the pn-junction deeper into the CIGS absorber, lowering the recombination rate of the charge carriers at the CIGS/buffer interface [38]. In our experiments, we can correlate the highest solar cell efficiencies with the combination of the K-rich glass and the addition of PDT (with a thin CdS layer). Since the Cu-depleted area does not cover the entire surface region uniformly, the function of the Cu-poor patches and their influence on electrical properties of the solar cell devices is not entirely clear and further analysis is ongoing. At this point the results indicate that the patches are not detrimental to device performance and may even contribute in a positive way by reducing the recombination at the CIGS/buffer interface by widening of the band gap as discussed above.

Based on STEM EELS, we cannot conclude on a possible Cd$_{Cu}$ substitution. All the buffer layer/CIGS interfaces appear to be about 6 nm-thick. So if there is a Cd in-diffusion to the CIGS, either Cd concentration is below the detection limit of the technique, or the substitution actually occurs at the extreme surface of the absorber, i.e. in the sub-nanometer range; which is beyond the spatial resolution of the present analysis. Thus, our measurements do not allow us to exclude that the Cd$_{Cu}$ substitution exists at all, but we are able to conclude that any Cd-rich surface layer in the CIGS absorber is thinner than 6 nm.

As mentioned in the result section, the formation of the Cu-depleted patches is not fully understood. Unlike the observation of Stokes et al. [36] our analysis shows that the Cu-poor layer is discontinuous. Here we propose a mechanism based on our results. Towards the end of the second stage of the co-evaporation, the excess of Cu would lead to an almost stoichiometric CIGS 1:1:2 with Cu$_{2-x}$Se precipitates at the surface and in the grain boundaries. During the last stage of the co-evaporation, the Cu$_{2-x}$Se is gradually consumed, compensating for the lack of Cu received in the growth front (Cu/III = 0.6, Figure 2 (right)). Throughout this stage, the well-spread Cu-rich phase would be slowly reduced to clusters. Concurrently, the Cu already integrated in the existing CIGS lattice would also try to diffuse to the growth front, but would be restrained by the presence of K. Indeed, at high temperature, a large amount of K is expected to be soluble in the CIGS, leading to a high concentration of K$_{Cu}$ limiting the presence of V$_{Cu}$ [17], which in turn would reduce the Cu ion mobility [39]. Therefore, while the fractions of surface nearby Cu-rich clusters would receive enough Cu to maintain the 1:1:2 phase, the surroundings would see a higher concentration of K$_{Cu}$ which would further prevent Cu in-diffusion to the OVC, leading to the parallel growth of two different phases without lateral
inter-diffusion. However, the final Cu/III ratio is expected to be around 0.6 according to the deposition profile (Figure 2), but is consistently measured to be around 0.4 (Figure 4). This may also be explained by the high solubility of K at high temperature which would prevent a complete incorporation of Cu in the lattice, lowering the Cu/III ratio accordingly.

2. Ga/III gradient
With this study, we confirm that the presence of K hinders the In/Ga inter-diffusion, leading to a higher concentration of Ga in the vicinity of the back contact. This higher Ga content is reflected by the smaller crystal size there [40,41] (cf. Figure 8). Referring to the co-evaporation profile Figure 2 (right), the Ga/III ratio starts around 0.8 then drops to 0.35 afterwards. While for the ‘ref’ sample the measured Ga/III ratio close to the Mo layer is around 0.40, it is about 0.55 and 0.75 for the ‘RbF-PDT’ and the ‘KF-PDT’, respectively (Figure 6 and Figure 5). We also estimated similar Ga/III values using the “A1 CIGS” peak shift of Raman spectroscopy measurements acquired from the rear-side (Figure 7, b) [42]. We obtained results around 0.45 for the sample ‘Ref’; and 0.55 and 0.70 for the samples ‘RbF-PDT’ and ‘KF-PDT’, respectively, which is in excellent agreement with the STEM results.

3. Solar cell efficiencies
The ‘Ref’ sample performs poorly. The low V_{oc} could indicate a lack of NaF precursor; however, a thicker precursor layer led to delamination of the thin film during the CBD step, suggesting that the CIGS was already saturated in alkali. It therefore seems reasonable to conclude that the performance results from the absence of one or several of the major features observed in the highest efficiency ones: the Cu-depleted patches, the Ga/III gradient, and possibly the [220/204] preferential texture. All the cells post-treated with an alkali could receive a thinner CdS buffer layer which explains the higher values of J_{sc} measured in these cases. The use of an alkali-PDT also correlates with an increase of the V_{oc} as seen in Table 1. However, the key parameter influencing the electrical characteristics of the devices is the presence or absence of K during the growth of the CIGS absorber layer, which modifies its structure and composition.

5. Conclusion
With this study, we show that the presence of K during the growth of the absorber layer strongly modifies both its structure and its composition, and we obtain solar cell efficiencies beyond 17% with these features. The efficiency can be further improved to 18.4% with an additional PDT (all without ARC). While the In/Ga inter-diffusion is slowed down by the presence of K, leading to a steeper Ga/III gradient, Cu-depleted patches also appear at the surface of the CIGS. From a theoretical perspective, the two separate effects are both expected to have positive consequence on the electrical performance of the devices. The TEM EELS results reveal that the Cu-depletion correlates with an increase in In and K. This would
therefore support both the creation of $2V_{\text{Cu}} + \text{In}_{\text{Cu}}$ neutral defect pairs and the presence of $K_{\text{Cu}}$ defects. Finally, the Cd/CIGS interface is comparable for all of the samples, thus no evidence of Cd in-diffusion to the CIGS could be detected. This allows us to conclude that if Cd$_{\text{Cu}}$ substitutions happen, they are either located at the extreme surface, or below the detection limit of our measurement setting.

6. Acknowledgements

Authors are thankful Lars Riekehr for assistance with the STEM-EDS measurements. We acknowledge funding from the Swedish Energy Agency, EU-project ARCIGS-M and the Swedish Science Council.

![Figure 1: Sketch illustrating the outline of the different samples. The PDT is performed directly after the CIGS co-evaporation.](image-url)
Figure 2 – Detailed co-evaporation profile of the CIGS layer, showing the substrate temperatures plotted together with the individual flux variation of Cu, In and Ga (left); and the estimated Cu/III and Ga/III ratios, both instantaneous and integrated (right). The Se source was kept constant during the co-evaporation to ensure a good saturation level.
Figure 3 STEM EELS of the CIGS absorber in the vicinity of the CdS buffer layer showing the Annular Dark Field (ADF), Cu, Ga, Cd, In and K maps for the sample ‘ref’, ‘no-PDT’, ‘KF-PDT’ and ‘RbF-PDT’, respectively. Ratio maps have been used for the ‘KF PDT’ sample to cancel the thickness irregularity. Contribution from Cd can be seen in the In maps (bright buffer layer), and C contamination might contribute slightly to the K maps, raising the signal intensity over the whole area. While the hollow black arrows indicate the locations of the Cu/III, Ga/III and K/(Cu+In+Ga) composition profiles shown in Figure 3, the plain blue (or dotted green) arrows indicate the locations of the Cd composition profile also displayed in Figure 3.
Figure 4 Compilation of the Cu/III, Ga/III and K profiles (left) and Cd signal intensity profiles (right) of the sample ‘ref’, ‘no-PDT’, ‘KF-PDT’ and ‘RbF-PDT’, respectively. The Cd profiles are extracted from the area indicated by the plain blue (or dotted green) arrows in Figure 3. The Cu/III, Ga/III and K/(Cu+In+Ga) profiles are integrated from the area indicated by the black arrow in Figure 3.
Figure 5 STEM EDS of the sample ‘KF-PDT’ showing the maps of Cu, In, Cu/III and Ga/III. The black horizontal line is an artefact from the measurement system; no data were saved for this line.
Figure 6 - STEM EELS of the whole CIGS absorber showing the Cu/III ratios maps for the sample ‘Ref’ (A), and ‘RbF-PDT’ (B). At the bottom, the compared Cu/III and Ga/III ratio profiles. The hollow black arrows on the maps represent the integration areas used to extract the composition profiles.
Figure 7 Raman spectrum acquired (a) on the front side of the samples, (b) on the backside after peeling off the cells. All spectra are background corrected and normalized to the A1 CIGS peaks.
Figure 8 - TKD analysis showing both the Euler plot and the band contrast images for the samples ‘KF-PDT’ and ‘RbF-PDT’.
Figure 9 GI-XRD of the different samples. The symbol $\Delta$ shows the CIGS 1:1:2 peaks, and the $\Psi$ the peak shifted of the OVC regions.
Figure 10 STEM EELS of the sample ‘KF-PDT’ showing the Cu-signal dependence on the lamella thickness. On the left, the Cu and the relative thickness maps, the black and dashed green arrows represent the integration areas used to plot the graph on the right. The signal intensity is only distorted by the thickness variation which justifies the use of ratio maps (namely Cu/III, Ga/III and K/(Cu+In+Ga)) for this sample to display chemical composition maps exempt of thickness variation bias.

7. Literature


W. Witte, R. Kniese, M. Powalla, Raman investigations of Cu(In,Ga)Se₂ thin films with


