ELECTRONIC SUPPLEMENTARY INFORMATION

Selenization of CuInS₂ by Rapid Thermal Processing – An Alternative Approach to Induce a Band Gap Grading in Chalcopyrite Thin-Film Solar Cell Absorbers?

Roberto Félix,*^a Alfons Weber,^a Ole Zander,^a Humberto Rodriguez-Álvarez,^a Björn-Arvid Schubert,^a Joachim Klaer,^a Regan G. Wilks,^{a,b} Hans-Werner Schock,^a Roland Mainz^a and Marcus Bär^{a,b,c,d}

^aRenewable Energy, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

^bEnergy Materials In-Situ Laboratory Berlin (EMIL), Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Straße 15, D-12489 Berlin, Germany

^cHelmholtz-Institute Erlangen-Nürnberg for Renewable Energy, Forschungszentrum Jülich, Egerlandstr. 3, D-91058 Erlangen, Germany

^dPhysical Chemistry II, Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany

*corresponding author: roberto.felix duarte@helmholtz-berlin.de

Sample	Se amount [mg]	Duration [min]	Temperature [°C]
CIS	-	-	-
i	-	30	500
ii	5	5	300
iii	5	5	400
iv	5	5	500
v	5	30	470
vi	5	30	500
vii	5	30	530

Table S1. List of samples and RTP treatment parameters

Table S1 (same as Table 1 in the text) summarizes the parameters used in the selenization rapid thermal processing (RTP) treatments of $CuInS_2$ (CIS) absorbers and labels the resulting samples.



Fig. S1: XPS survey spectra of the investigated sample series.

Fig. S1 shows Mg K_{α} x-ray photoelectron spectroscopy (XPS) survey spectra of the KCN-etched CIS absorbers before and after RTP treatments, along with respective peak identification. The XPS survey spectrum of the bare CIS absorber displays the photoemission and Auger lines of the absorber elements (i.e., Cu, In, and S) as expected. Se- and traces of Na-related lines can also be observed in the spectra of all RTP-treated samples. An enhancement of Na diffusion from the Mo-coated soda-lime glass (SLG) back contact to the CIS surface is observed due to the elevated temperature of the RTP treatments, a well-reported phenomenon.^{1,2}



Binding Energy (eV)

Fig. S2: (a) - (d) XPS detail spectra of the Na 1s, Cu $2p_{3/2}$, In $3d_{3/2}$, and S 2s/Se 3s regions of the following samples in the series: CIS, (i), (ii) and (iii), normalized to background intensity. (e) - (h) XPS detail spectra of the Na 1s, Cu $2p_{1/2}$, In $3d_{3/2}$, and S 2s/Se 3s regions of the following samples in the series: (iv), (v), (vi) and (vii), normalized to background intensity. All spectra were measured using Mg K_a excitation. Vertical offsets are added for clarity.

The elemental surface composition of the absorber was derived by evaluating the intensity of the Cu $2p_{3(1)/2}$, In $3d_{3/2}$, S 2s and Se 3s core level peaks, shown in Fig. S2, along with the corresponding fits.



Fig. S3: (a) Se 3d XPS detail spectra and (b) Se $L_3M_{45}M_{45}$ (LMM) XAES lines of all RTP-treated samples, including fits, normalized to maximum intensity. (c) Magnified difference of the measured Se LMM spectra from (b) and their corresponding fits. Spectra in (a) include curve fits and were measured using Mg K_a excitation. The numbers in (a) represent the Se_{II}/(Se_I + Se_{II}) ratio of the spectra. Spectra in (b) were measured using Al K_a excitation and are shown with fits consisting of the sum of a weighted Se LMM reference line (—) and the weighted background line of the CIS absorber (—) in the same energy region. The red lines in (c) are Se LMM reference lines energetically shifted to achieve a maximum overlap with the difference lines [i.e., Se LMM spectrum minus "sum" fit from (b)]. Vertical offsets are added for clarity.

Fig. S3(a) shows the XPS Se 3d spectra and curve fits of the RTP-treated samples, along with respective curve fits. All spectra needed two sets of peaks in order to obtain satisfactory agreement between the curve fits and the measured data. The Se $3d_{5/2}$ peak of the two sets are located at the following binding energy (BE): ~ 53.8 ± 0.1 eV (Se_I) and ~ 55.1 ± 0.4 eV (Se_{II}). These BE values are consistent for Se $3d_{5/2}$ XPS core levels of chalcopyrite selenides (Se_I) and elemental Se (Se_{II}), respectively.³ Interestingly, the Se_{II} contribution is higher in the RTP control sample [i.e., sample (i)] and in samples produced by 5 min RTP treaments [samples (ii) – (iv)] then in samples produced by 30 min RTP treaments [samples (ii) – (iv)]. The corresponding Se_{II}/(Se_I + Se_{II}) ratios are stated close to each Se 3d spectrum in Fig. S3(a).

Fig. S3(b) shows the measured Se $L_3M_{45}M_{45}$ (LMM) XAES line of all RTP-treated samples, together with a weighted spectrum of the Se LMM line of a sulfur-free CIGSe absorber (serving as a CISe reference) and (when necessary) the weighted background line of the KCN-etched CIS absorber in the same energy region. The magnified differences of the measured Se LMM lines and the fits produced by the sum of the weighted references are also shown in Fig. S3(c). The Se LMM lines of samples treated for periods of 30 min and supplied with Se [i.e., samples (v) – (vii)] are finely matched by the reference Se LMM line in Fig. S3(b). The difference lines in Fig. S3(c) corresponding to these samples can be ascribed to statistically distributed noise. This finding is expected, considering that Se is the overwhelming chalcopyrite anion at the surface of these samples. Moreover, only minor traces of the Se_{II} component is found in the curve fit analysis of the Se 3d line of these samples.

In contrast, the shape of the measured Se LMM line of the rest of the samples [i.e., (i) - (iv)] in the RTP-treatment series cannot be satisfactorily matched by the sum of the two weighted reference lines (i.e., the Se LMM and the CIS background lines), as seen in Fig. S3(b). The difference between the measured spectra and the fit lines for these samples [i.e., (i) - (iv)] in fact, resemble energetically shifted Se LMM line shapes. These results, as well as the two sets of Se 3d peaks, suggest that the surface Se exists in two different chemical environments in these RTP-treated samples. The identity of these Se chemical species is addressed in Fig. 3 of the text.



Fig. S4: (a) Cu $L_3M_{45}M_{45}$ and (b) In $M_{45}N_{45}N_{45}$ XAES lines of the selenized CIS absorbers, normalized to maximum intensity. The solid and dashed lines are shown to help distinguish the energetic shifts in the XAES lines of the untreated CIS absorber and sample (v), respectively.

The In $M_{45}N_{45}N_{45}$ (MNN) and Cu LMM XAES lines of the selenized samples are displayed in Fig. S4(a) and S4(b), respectively. Similar evaluations of these XAES lines did not unambiguously reveal the presence of multiple XAES lines, as in the case of the Se LMM lines. Neither was there any indication of a second component found in the curve fits of the Cu 2p and In 3d spectra shown in Fig. S2. However, a shift in the energy of the In MNN and Cu LMM lines is found for samples shown to possess a higher Se content at their surfaces, which is a plausible indication of changes in chemical environments of Cu and In.



Fig. S5: (a) He I UPS spectra of the investigated sample series. Linear extrapolations of the respective leading edge are shown in red lines. (b) VBM positions of the investigated sample series as determined from (a).

Fig. S5(a) shows the UPS spectra of the samples along with linear fits of the VB leading edges, presented in ascending order of surface [Se]/([S]+[Se]). The VBM positions of the investigated sample series as determined from (a) are shown in Fig. S5(b).



Fig. S6: Normalized reflectance spectra of the investigated sample series prior to (a) and after (b) Kubelka-Munk transformation (K) analysis as a function of photon excitation energy. Linear extrapolations of the respective leading edges are shown in red lines. (c) Optical E_g values of the investigated sample series as determined from (b).

Fig. S6(a) and S6(b) show normalized reflectance spectra of the investigated sample series prior to and after Kubelka-Munk transformation (K) analysis,⁴ respectively, as a function of photon excitation energy, hv. Linear approximations of the leading edges are also included in the figure. Fig. S6(c) shows the extrapolated optical E_g values as a function of the surface chalcopyrite [Se]/([S]+[Se]) ratios of the absorbers.

References for Supplementary Information

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