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# Surface Off-Stoichiometry of CuInS<sub>2</sub> Thin-Film Solar Cell Absorbers

Marcus Bär, Joachim Klaer, Roberto Félix, Nicolas Barreau, Lothar Weinhardt, Regan G. Wilks, Clemens Heske, and Hans-Werner Schock

**Abstract**—In this paper, X-ray photoelectron and X-ray-excited Auger electron spectroscopy was used to investigate the chemical surface structure of CuInS<sub>2</sub> thin-film solar cell absorbers. We find that the [In]/[Cu] surface composition can vary between 1.6 ( $\pm 0.4$ ) and 3.7 ( $\pm 0.7$ ), depending on relatively minor variations in the absorber formation process and/or whether additional wet-chemical treatments are performed. These variations are primarily due to differences in the Cu surface concentration. The corresponding change of the modified In Auger parameter is interpreted as being indicative of a change in the chemical environment of In as a function of Cu off-stoichiometry.

**Index Terms**—Chalcopyrite thin-film solar cell, surface composition, wet-chemical treatment, X-ray photoelectron spectroscopy.

## I. INTRODUCTION

**T**HIN-FILM solar cells that are based on the Cu(In,Ga)(S,Se)<sub>2</sub> chalcopyrite alloy are promising candidates to overcome the obstacles for thin-film photovoltaics (PV) to successfully compete with the dominating Si-wafer-based PV technology. On the laboratory scale, ZnO/CdS/Cu(In,Ga)Se<sub>2</sub>/Mo solar cell devices already reach efficiencies in excess of 20% [1], [2], similar to cells that are based

on polycrystalline Si wafers [3]. These high efficiencies are, however, only reached when using S-free chalcopyrite absorbers with band gaps  $E_g$  in the range of 1.1–1.2 eV [1], [2]. Increasing the band gap by raising the Ga/(In+Ga) ratio of the chalcopyrite absorber and/or by incorporating sulfur does not result in higher efficiencies, although the optimal band gap for absorption of AM 1.5 irradiation is approximately 1.4 eV [4]. One ternary member of the chalcopyrite alloy family, which is CuInS<sub>2</sub> (CIS), possesses a band gap ( $E_g = 1.54$  eV [5]) close to this value. However, the performance of respective solar cell devices (up to 12.5% [6]) falls behind with respect to the expectations and in comparison with cells that are based on chalcopyrites with a lower band gap [7].

In a recent publication [8], we could show that spatially separated regions of varying color (bluish/dark and grayish/light) on the surface of as-deposited CIS absorbers are dominated by CuS and Cu<sub>2</sub>S surface phases, respectively. After their removal by KCN etching, the CIS surface was found to be Cu-deficient (w.r.t. the corresponding bulk composition) in both regions, with a more pronounced off-stoichiometry in the region that is initially covered by Cu<sub>2</sub>S. The variations in composition were shown to have a significant impact also on the respective electronic surface structure. In order to expand on these findings, we have extended our study to include more samples and additional wet-chemical treatments as another means to influence the chemical surface structure of CIS.

## II. EXPERIMENTAL DETAILS

### A. Thin-Film Deposition

The investigated CIS layers were prepared by rapid thermal processing (RTP) of sputter-deposited Cu and In precursor films on Mo (0.5  $\mu\text{m}$ )/soda-lime glass substrates in an excess sulfur atmosphere [6]. This process forms Cu<sub>2-x</sub>S phases on top of the CIS, which are generally removed prior to solar cell fabrication using a KCN etch (see the next section for more details). For the CIS samples characterized here, minor variations in the processing parameters (in particular, the available sulfur amount and the presence/absence of an additional In<sub>2</sub>S<sub>3</sub> precursor layer; see Table I) were deliberately introduced, while all other deposition parameters (see [6] for more details) remained unchanged. Based on our prior results [8], the sample color (bluish/dark or grayish/light) was used to determine whether the surface of the as-deposited CIS layers was terminated by CuS or Cu<sub>2</sub>S secondary surface phases, respectively. A list of the investigated samples, together with the observed surface termination, used

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TABLE I  
LIST OF INVESTIGATED SAMPLES AND THEIR SURFACE TREATMENTS

Sample number	Surface termination before KCN	Wet-chemical treatment	Sulfur amount [mg]	In <sub>2</sub> S <sub>3</sub> prec.
1	CuS	—	50	no
2	CuS	—	50	yes
3	Cu <sub>2</sub> S	—	50	no
4	Cu <sub>2</sub> S	—	40	yes
4a	Cu <sub>2</sub> S	NH <sub>4</sub> OH	·	·
4b	Cu <sub>2</sub> S	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	·	·
4c	Cu <sub>2</sub> S	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	·	·
5	Cu <sub>2</sub> S	—	50	yes

absorber deposition process parameters, and employed additional wet-chemical treatments, is given in Table I.

For reference, we also investigated an In<sub>2</sub>S<sub>3</sub> layer that was prepared by evaporating elemental In and S layers onto a Mo/glass substrate and subsequent annealing in a sulfur atmosphere [9].

### B. Wet-Chemical Treatments

To remove Cu<sub>2-x</sub>S surface phases from the CIS thin-film solar cell absorbers (prior to characterization), all samples were etched in an aqueous solution of KCN (3 min in 1.5 mol/L KCN + H<sub>2</sub>O at room temperature). Subsequently, additional pieces of sample 4 were treated using different wet-chemical solutions.

- 1) Sample 4a was immersed in 5 mL NH<sub>4</sub>OH (28-30%, VWR) + 45 mL H<sub>2</sub>O for 60 s at room temperature.
- 2) Sample 4b was treated in a solution of 0.25 g NaOH (Fisher) + 0.25 g Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (Alfa Aesar) + 50 mL H<sub>2</sub>O for 120 s at room temperature.
- 3) Sample 4c was immersed in a solution of 0.1 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Alfa Aesar) + 1 mL of 17.8 mol/L H<sub>2</sub>SO<sub>4</sub> (EMD) + 49 mL H<sub>2</sub>O for 90 s at room temperature.

In the following, we will refer to these wet-chemical treatments simply as “NH<sub>4</sub>OH,” “Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>,” and “K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.” After these treatments, the samples were rinsed in 50 mL of H<sub>2</sub>O, followed by 30 s under running H<sub>2</sub>O from a washing bottle. Note that less than 15 min passed between KCN etch and the additional wet-chemical treatments. While the “NH<sub>4</sub>OH” treatment mimics the induction period of the standard CdS buffer layer deposition in a chemical bath [10], the “Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>” and “K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>” wet-chemical solutions act as reducing and oxidizing agents [11], respectively. The latter two chemical treatments are applied to investigate whether they can be used to deliberately tune the chemical surface structure (in particular, the [In]/[Cu] ratio) of CIS thin-film solar cell absorbers.

### C. Characterization Techniques

To avoid (re)contamination after KCN etching and/or the applied wet-chemical treatments, the samples (still covered with a H<sub>2</sub>O film) were directly transferred into the load lock chamber of an N<sub>2</sub>-purged glove box, where they were vacuum-dried and directly transferred into the ultrahigh vacuum surface analysis chamber (base pressure < 5 × 10<sup>-10</sup> mbar). The samples were then investigated by an X-ray photoelectron (XPS) and

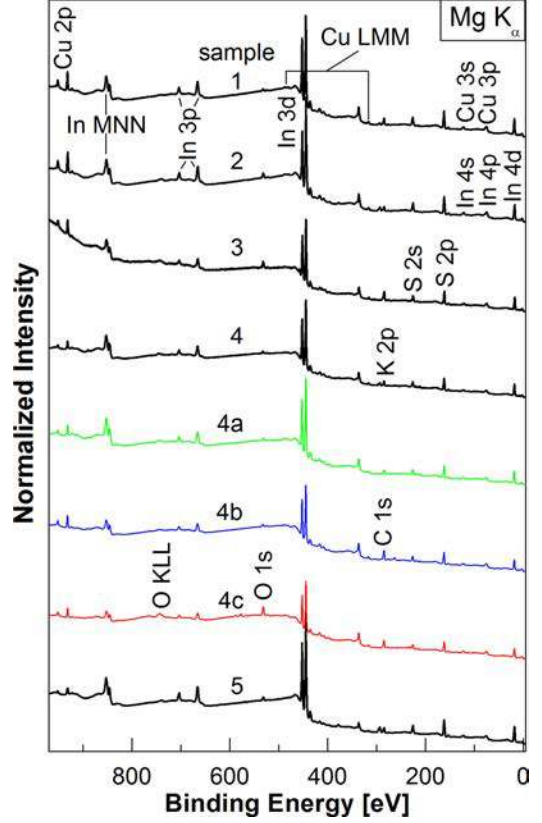


Fig. 1. XPS survey spectra of the CIS samples 1–5. Furthermore, the respective spectra of the additional wet-chemically treated samples 4a–4c are shown. The most prominent photoemission and Auger lines are indicated.

X-ray-excited Auger electron (XAES) spectroscopy. For the XPS/XAES measurements, Mg  $K_{\alpha}$  excitation and an SPECS PHOIBOS 150MCD electron analyzer (calibrated according to [12]) were used. The presented survey (detail) spectra were recorded using a step width of 0.5 eV (0.02 eV) and a pass energy of 50 eV (20 eV).

## III. RESULTS AND DISCUSSION

In Fig. 1, the XPS survey spectra of the investigated KCN-etched CIS samples are shown. The spectra look very similar, and, as expected, all XPS and XAES signals that are ascribed to copper, indium, and sulfur can be observed. In addition, carbon- and oxygen-related signals of varying intensity can be identified, which is mainly attributed to different degrees of surface contamination during transfer of the samples into the UHV analysis chamber. We note that the O 1s/C 1s intensity ratios vary between the samples, suggesting that carbon incorporated into the CIS material and/or a CIS surface oxidation induced by a wet-chemical treatment (as discussed in connection with Fig. 2) cannot be excluded. The close inspection of the spectra also reveals a clear K 2p signal for some (but not all) CIS samples. No accompanying N-related lines are detected, and therefore the presence of K on the CIS surface is presumably the result of a chemical interaction between the K<sup>+</sup> ions in the KCN etch solution and the CIS surface (rather than residual etchant). Note that a presence of K on the CIS surface after a KCN etch was

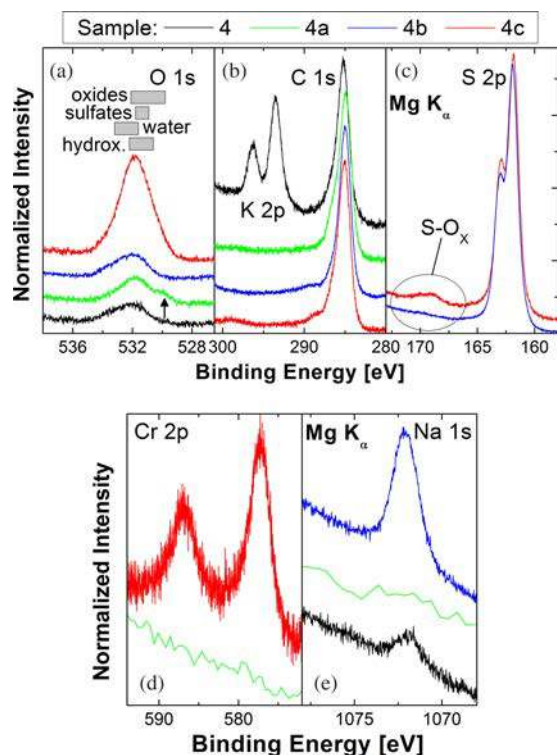


Fig. 2. XPS detail spectra of (a) O 1s, (b) K 2p and C 1s, (c) S 2p, (d) Cr 2p, and (e) Na 1s XPS line(s). The gray energy ranges for different oxygen-containing species shown in (a) are based on reference values taken from [14].

reported before [8], [13]. The varying intensities of the K 2p signals, however, may indicate that the potassium is not strongly bound to the CIS surface and, thus, may easily be influenced by variations in the rinsing procedure after the KCN etch step. Finally, a variation of the In 3d/Cu 2p intensity ratio can be observed for the different CIS sample surfaces. The implications of these changes will be discussed in detail in conjunction with Fig. 3.

Next, we will discuss the changes of the chemical CIS surface structure induced by each wet-chemical treatment. Fig. 2 shows XPS detail spectra highlighting the identified differences. Compared to the KCN-etched,  $\text{NH}_4\text{OH}$ -treated, and  $\text{Na}_2\text{S}_2\text{O}_3$ -treated samples, the O 1s line intensity after the  $\text{K}_2\text{Cr}_2\text{O}_7$  treatment is significantly increased [see Fig. 2(a)]. Although the spectral shape indicates the presence of several oxygen-containing species, the preceding sample exposure to water (by means of etch, treatment, and/or rinsing solutions) suggests that the main contributions to the O 1s line can be ascribed to adsorbed water and/or hydroxyl ( $-\text{OH}$ ) compounds. This conclusion is also confirmed by comparing the binding energy (center of gravity) of the O 1s peaks to the reference values that are indicated by gray bars (from [12] and [14]) in Fig. 2(a). Despite the rather unspecific range of reference positions for different oxygen-containing compounds that are depicted in Fig. 2(a), the low-energy shoulder of the O 1s line of the  $\text{NH}_4\text{OH}$ -treated CIS sample (indicated by an arrow), which coincides with the energetic position of oxides, may indicate an oxidized CIS surface (despite the well-known “cleaning effect” of aque-

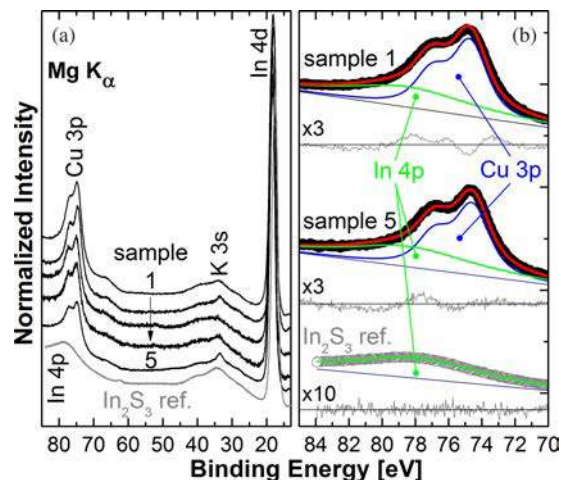


Fig. 3. (a) XPS detail spectra of the shallow core levels (normalized to the In 4d peak) of CIS samples 1–5 and an  $\text{In}_2\text{S}_3$  reference. (b) Fits (red) of the overlapping Cu 3p (blue) and In 4p (green) lines; an example is shown for CIS sample 1 and 5 and the  $\text{In}_2\text{S}_3$  reference. The experimental data (black or gray) can be presented as a sum of a Cu 3p (blue) and In 4p (green) contribution. The respective residues (difference between experimental data and fit) are shown for reference on a magnified scale.

ous ammonia [15], [16]). An explanation as to why the O 1s photo emission line intensity increases significantly after the  $\text{K}_2\text{Cr}_2\text{O}_7$  treatment is offered by the S 2p spectra in Fig. 2(c). As revealed by the comparison with the spectrum of the  $\text{Na}_2\text{S}_2\text{O}_3$ -treated CIS surface, the  $\text{K}_2\text{Cr}_2\text{O}_7$  treatment apparently induces an oxidation of sulfur (see indicated  $\text{S}-\text{O}_x$  feature, with  $x \geq 3$  [13]). This is also compatible with the energetic position of the respective O 1s line (indicated by the gray “sulfates” energy range in Fig. 2(a)) and is not surprising, given the oxidizing nature of the  $\text{K}_2\text{Cr}_2\text{O}_7$  treatment solution [11]. Note that the S 2p spectra of the KCN-etched sample, as well as of the  $\text{NH}_4\text{OH}$ -treated sample (not shown), do not indicate the presence of any  $\text{S}-\text{O}_x$  bonds.

Fig. 2(b) shows the K 2p and C 1s photoemission lines. As with the O 1s spectra in Fig. 2(a), the shapes and positions of the C 1-s peaks indicate the presence of several carbon species on the investigated CIS surfaces (such as C–H, C–C, and C–O bonds [14]). The K 2p XPS signal confirms that potassium can be found only on the CIS sample after the KCN etch, while it is removed by all subsequent wet-chemical treatments. This supports the suggestion made in the previous section that it is only weakly bound to the CIS surface. Interestingly, the  $\text{K}_2\text{Cr}_2\text{O}_7$  treatment does not cause the K 2p photoemission line to reappear. However, it causes the deposition of chromium on the CIS absorber surface, as is evident from the Cr 2p XPS lines in Fig. 2(d). The  $\text{Na}_2\text{S}_2\text{O}_3$  treatment induces an increase of the sodium surface content, as depicted in Fig. 2(e). A small Na 1s signal is also seen for the KCN-etched sample; it disappears (or is significantly reduced in intensity) after the  $\text{NH}_4\text{OH}$  treatment. Note that the (reference) spectra of the  $\text{NH}_4\text{OH}$  treated sample in Fig. 2(d) and (e) stem (due to lack of respective detail spectra) from the according survey spectrum shown in Fig. 1 and, therefore, have a larger energy step size.



Fig. 3(a) presents detail spectra of the Cu 3p, In 4p, and In 4d XPS region. The spectra are all normalized to the intensity of the In 4d signal (but offset for clarity), and thus, the observed intensity variations of the Cu 3p line can directly be translated into a variation of the [In]/[Cu] surface ratio of the investigated CIS samples. Note that only the spectra of samples 1–5 are shown; in addition, the  $\text{In}_2\text{S}_3$  spectrum is included for reference. The changing intensities of the K 3s photoemission lines agree with the aforementioned finding that varying amounts of potassium can be adsorbed after the KCN etch.

The position of the Cu 3p line coincides with that of the broad In 4p line. This makes the quantification of the [In]/[Cu] ratio on the basis of these photoemission lines challenging. Nevertheless, the use of the Cu 3p and In 4d lines for quantification is still the best option, because the respective photoelectrons have high (and very similar) kinetic energies and are, thus, less affected by surface contamination/oxidation and adsorbates. Here, the quantification of the Cu 3p and In 4d line intensities was performed by a simultaneous fit of the corresponding spectra of all samples with Voigt profiles<sup>1</sup> and a linear background. For the Cu 3p spin-orbit doublet, the respective Gaussian and Lorentzian widths were coupled for each individual XPS line, and for all samples, the intensity ratio was fixed according to the corresponding  $(2j+1)$  multiplicity, and the doublet separation was set to 2.3 eV [14]. The In 4p contribution was taken into account by an additional Voigt profile (width fixed to that of the  $\text{In}_2\text{S}_3$  reference and position and intensity set relative to the respective In 4d lines). Examples of the resulting fits are shown (for the spectra of sample 1 and 5, as well as for the  $\text{In}_2\text{S}_3$  reference) in Fig. 3(b). For the sake of clarity, the Voigt profiles for the two Cu 3p spin-orbit components are only shown as their sum.

To determine the [In]/[Cu] surface ratio, the fitted In 4d and Cu 3p intensities were corrected by the corresponding photoionization cross sections [19]. The computed surface composition of all investigated CIS samples is summarized in Fig. 4. Sample surfaces that are dominated by CuS and  $\text{Cu}_{2-x}\text{S}$  phases prior to KCN etching are shown on the left and the right, respectively. The *intrinsic* [In]/[Cu] variations between samples 1 and 5 range from  $1.8 (\pm 0.4)$  to  $3.7 (\pm 0.7)$ . Taking the *extrinsically induced* variations due to additional wet-chemical treatments into account, we find that the [In]/[Cu] ratio can easily be tuned between  $2.7 (\pm 0.5)$  for sample 4, over  $2.5 (\pm 0.5)$  for the  $\text{NH}_4\text{OH}$ -treated sample 4c,  $1.7 (\pm 0.4)$  for the  $\text{Na}_2\text{S}_3\text{O}_3$ -treated sample 4b, to  $1.6 (\pm 0.4)$  for the  $\text{K}_2\text{Cr}_2\text{O}_7$ -treated sample 4c. In all cases, the surface is significantly Cu-deficient compared to the expected [In]/[Cu] = 1 (bulk) composition of CIS thin-film solar cell absorbers. Such off-stoichiometries were observed before for chalcopyrite thin-film surfaces and have been attributed to the formation of Cu-poor 1:3:5 [20]–[22] or 1:5:8 [23] surface phases or, for epitaxial film surfaces, to a Cu-depleted surface possibly due to a surface reconstruction [24].

Considering the small changes in the CIS formation process variables (listed in Table I), it is not very likely that they are

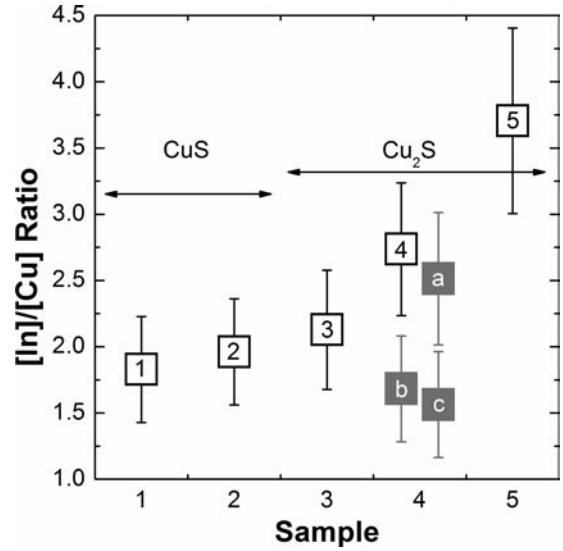


Fig. 4. Determined [In]/[Cu] surface composition for the investigated CIS samples 1–5. Furthermore, the respective ratios for the additional wet-chemically treated samples 4a–4c are shown (labeled a and c). Samples dominated by CuS and  $\text{Cu}_{2-x}\text{S}$  secondary surface phases prior KCN etching are shown on the left and the right, respectively.

exclusively responsible for the observed pronounced *intrinsic* variation of the [In]/[Cu] surface ratio. *In situ* studies of the sulfurization mechanism of Cu-In films show that the Cu-rich digenite ( $\text{Cu}_{2-x}\text{S}$ ) phase is the dominant phase at higher temperatures, with a transition to S-rich CuS observed at lower temperatures [25]. This indicates that the competition between these two copper sulfide phases might be another crucial parameter. As already discussed briefly in [8], a nonhomogeneous temperature distribution in the RTP chamber will allow parts of the sample to cool faster, resulting in surface areas dominated by CuS. Considering that the transition from  $\text{Cu}_{2-x}\text{S}$  to CuS consumes sulfur and liberates copper, one could further speculate that not enough sulfur is available for a (complete) conversion of  $\text{Cu}_{2-x}\text{S}$  to CuS when the (initially) hotter parts of the sample reach the  $\text{Cu}_{2-x}\text{S} \rightarrow \text{CuS}$  transition temperature. Consequently, the resulting varying degree of copper liberation during that process could crucially determine the final surface composition of the deposited (KCN-etched) CIS material.

In order to investigate whether the observed pronounced variations of the surface stoichiometry also induce an identifiable change in the chemical environment of the involved elements, we have computed the modified Auger parameter  $\alpha^*$ .  $\alpha^*$  is computed by adding the binding energy (BE) of a photoemission line to the kinetic energy (KE) of an Auger line of the same element and is, hence, a measure for the chemical environment independent of potential band bending and/or sample charging. Calculating  $\alpha^*$  for Cu [ $\text{BE}(\text{Cu } 2p_{3/2}) + \text{KE}(\text{Cu } L_{3M_{45}M_{45}})$ ] and S [ $\text{BE}(\text{S } 2p_{3/2}) + \text{KE}(\text{S } L_{23M_{23}M_{23}})$ ] reveals no significant changes for  $\alpha^*(\text{Cu}) = (1849.0 \pm 0.1) \text{ eV}$  (which is close to literature data for  $\text{CuInSe}_2$ : 1849.3–1849.8 eV [13]) and  $\alpha^*(\text{S}) = (312.3 \pm 0.1) \text{ eV}$  (no literature data available). In contrast,  $\alpha^*(\text{In})$  [ $\text{BE}(\text{In } 3d_{3/2}) + \text{KE}(\text{In } M_{45}N_{45}N_{45})$ ] changes from  $(859.97 \pm 0.05) \text{ eV}$  for sample 4 c { [In]/[Cu] ratio of  $1.6 (\pm 0.4)$  } to

<sup>1</sup>For the fits, the software fityk (version 0.8.2, <http://fityk.nieto.pl/>) described in detail in [17] was employed, using Voigt profiles similarly defined as in [18]. The ratio of the Lorentzian and Gaussian widths was allowed to change freely in the fit procedure; the best fit was achieved for a ratio of  $\sim 1$ .

(859.67  $\pm$  0.05) eV for sample 4 {[In]/[Cu] ratio of 2.7 ( $\pm$  0.5)}, as shown in Fig. 5. The significant shift in  $\alpha^*$  (In) as a function of [In]/[Cu] ratio suggests that the chemical environment of In changes with the degree of Cu off-stoichiometry at the surface of CIS thin-film solar cell absorbers. A similar (but smaller) shift of the modified Auger parameter to lower values when transitioning from Cu-rich to Cu-poor surface compositions was also observed by Scheer *et al.* [22].

#### IV. SUMMARY AND CONCLUSION

We have used surface-sensitive XPS and XAES measurements to characterize the off-stoichiometry of CIS thin-film solar cell absorber surfaces, with particular focus on the [In]/[Cu] surface composition. We find that the chemical surface structure can easily be influenced by minor variations in the CIS deposition process, as well as by selected wet-chemical treatments. This makes it possible to tune the [In]/[Cu] surface ratio from 1.6 ( $\pm$  0.4) to 3.7 ( $\pm$  0.7). Furthermore, we find that the modified In Auger parameter varies from 859.97 to 859.67 ( $\pm$  0.05) eV, indicating that the chemical environment of In is influenced by the degree of Cu off-stoichiometry. Future work will be needed to study how these pronounced changes of the chemical surface structure of CIS thin-film solar cell absorbers influence the electronic surface properties, allowing us to understand/predict the impact on resulting solar cell devices.

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Authors' photographs and biographies not available at the time of publication.