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# **RbF-related post-deposition treatments on Cu(In,Ga)(S,Se)<sub>2</sub> absorbers: The role of the chalcogen atmosphere**

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## **Abstract**

An intriguing area in the field of alkali fluoride post-deposition treatment (PDT) on Cu(In,Ga)(S,Se)<sub>2</sub> (CIGSSe) absorbers is the effect of the chalcogen atmosphere on the absorber's surface during the PDT process. In this work, we focus on RbF-PDTs and we study i) the effect of Se and S atmosphere and ii) the impact of In and RbF co-evaporation under S on the vibrational and chemical properties of the absorber's surface. Using micro-Raman and X-ray photoelectron spectroscopy, we examine three different PDT processes: RbF under S atmosphere (RbF(S)-PDT), In and RbF co-evaporation under S atmosphere (In+RbF(S)-PDT) and In and RbF co-evaporation under Se atmosphere (In+RbF(Se)-PDT). Our results show that under Se atmosphere the formation of a Cu-poor chalcopyrite phase is enhanced, while under S atmosphere Cu-poor chalcopyrite phases are hindered. In addition, the In+RbF(S)-PDT leads to the formation of a Rb:In<sub>x</sub>S<sub>y</sub> compound at the surface of the absorber. This almost Cu-free surface compound seems to impede Cu inclusion during the In+RbF(S)-PDT in the indium sulfide spinelle lattice thanks to the occupation of its cationic vacancies by Rb.

**Keywords:** Cu(In,Ga)(Se,S)<sub>2</sub>; Post-deposition treatment; RbF; photoemission spectroscopy; Raman



# 1. Introduction

Recently, the development of heavy alkali fluoride PDTs [1–3] has boost the light-to-power conversion efficiency of  $\text{Cu}(\text{In,Ga})\text{Se}_2$  (CIGSe) and  $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$  (CIGSSe)-based solar cells, passing the best multi-crystalline silicon devices [4]. Up until now the highest solar cell efficiency has been obtained using RbF-PDT [2] or CsF-PDT [4], on CIGSe and CIGSSe absorbers, respectively. One principal feature of the heavy (K, Rb, Cs) alkali-PDTs is the segregation of the alkali element at the external (CIGSSe/buffer or/and CIGSSe/back contact) and internal (grain boundaries) interfaces of the absorber [5–10]. As a consequence, the heavy-alkali PDTs induce modifications on *i*) the structural and chemical properties of the grain boundaries [5–8] and *ii*) the composition and morphology of the surface [8–10]. In this work, we focus on the surface of the absorber.

The CIGSe and CIGSSe record cells were achieved with PDTs performed under elemental Se evaporation (CIGSe/RbF record cell [2]) or using a selenization process followed by sulfurization (CIGSSe/CsF record cell [3]). In a previous study [11,12] we have demonstrated that changing the chalcogen atmosphere from Se to S during KF post deposition treatment has a crucial effect on the CIGSe surface composition. Moreover, the copper content prior to the PDT and the addition of indium during the PDT seem to play an important role on the effectiveness of the PDT [13]. In [8,14–17], the authors indicated that KF and RbF-PDT performed under Se atmosphere lead to the formation of a thin alkali- $\text{In}_x\text{Se}_y$  layer at the surface of the absorber that is beneficial for the solar cell performance. RbF-PDTs under elemental Se atmosphere are widely used and a growing body of literature has examined the composition of the absorber's surface before and after Se-based PDTs [8,9,13,17,18]. However, for the RbF-PDT under elemental S atmosphere, recently reported in [19], the formation of a thin alkali- $\text{In}_x\text{S}_y$  layer is still under question.

Alkali fluoride PDTs on CIGSe absorbers have been widely investigated [2,7–20]. However, PDT conditions on absorbers with sulfur (leading to world record cell efficiencies) are not extensively studied. In this article, we study sulfur-selenide CIGSSe absorbers synthesized by Avancis GmbH and we examine *i*) how the chalcogen atmosphere (S versus Se) during the In+RbF PDT influences the surface composition and *ii*) how the addition of In during the RbF PDT under S atmosphere

modifies the vibrational and chemical structure of the absorber's surface. Within this framework, the three investigated PDT procedures are: *i*) RbF under S atmosphere *ii*) In and RbF co-evaporation under S atmosphere and *iii*) In and RbF co-evaporation under Se atmosphere. The vibrational and chemical modifications of the surface are examined by micro-Raman and X-ray photoelectron spectroscopy (XPS), respectively.

## 2. Experimental section

### 2.1 Samples preparation

CIGSSe absorbers were produced at the AVANCIS pilot line by the stacked elemental layer-rapid thermal process (SEL-RTP) [21,22] on soda lime glass substrates covered by a SiN alkali-barrier. Note that only a small Ga amount is present at the surface after RTP. The Mo back contact contained an intermediate selenization barrier. The precursor consisted of DC magnetron sputtered Cu-In-Ga:Na layers and a thermally evaporated Se film on top. RTP was conducted in an infrared heated furnace with high heating rates and with addition of a sulfur containing gas.

Prior to the PDT, the CIGSSe samples were etched with potassium cyanide (KCN) solution in order to remove possible oxide phases from the surface. The absorbers then underwent three different PDT: *i*) RbF under sulfur atmosphere, *ii*) In and RbF co-evaporation under sulfur atmosphere and *iii*) In and RbF co-evaporation under selenium atmosphere. In the following, the bare CIGSSe sample and the three treated samples are labeled: CIGSSe-REF, CIGSSe-RbF(S), CIGSSe-In+RbF(S) and CIGSSe-In+RbF(Se), respectively. All PDTs were performed under vacuum ( $10^{-4}$  Pa) and at 350°C substrate temperature. The deposition rate of In and RbF was 0.5 Å/s and 0.3 Å/s, respectively. The duration of the In and RbF co-evaporation (for the CIGSSe-In+RbF(S or Se) samples) and of the RbF alone (CIGSSe-RbF(S) sample) was ten minutes, followed by ten minutes annealing stage at 350°C. After the end of the PDT process, all the samples were dipped in ammonia solution (1 mol/L) for one minute in order to remove the remaining fluoride phases from the extreme surface. The characteristics of the four investigated samples, one bare and three treated absorbers, are shown in Table I.

## 2.2 Characterization methods

The vibrational structure of the near surface region (around 150 nm) was studied by micro-Raman spectroscopy at 457 nm excitation wavelength, in a Renishaw InVia Reflex microscope equipped with an Argon laser source. The laser power and acquisition time were optimized to avoid possible degradation or heating of the analyzed surface.

XPS analysis was performed in a Kratos Nova spectrometer using monochromatic Al K $\alpha$  (1486.58 eV) X-ray source. The measurements were performed at pressure lower than  $10^{-7}$  Pa with 20 eV pass energy. All samples were dipped in diluted ammonia solution (1 mol/L) for one minute and dried with nitrogen before the transfer in the XPS analysis chamber.

Ga 2p<sub>3/2</sub>, Cu 2p<sub>3/2</sub>, In 3d<sub>5/2</sub>, Rb 3d, Se 3p, S 2p, In M<sub>4</sub>N<sub>45</sub>N<sub>45</sub>, C 1s and O 1s peaks and extended valence band (from -3 to 24 eV) were measured for all the samples (not all shown). After the background subtraction; linear for In 3d<sub>5/2</sub>, Cu 2p<sub>3/2</sub>, S 2p and Se 3p, the peaks were fitted with Gaussian-Lorentzian line shape. The indium chemical environment was determined by calculating its modified Auger parameter ( $\alpha'$ (In)), given by the following expression [23]:

$$\alpha'(\text{In}) = E_{\text{bin}}(\text{In } 3d_{5/2}) + E_{\text{kin}}(\text{In } M_4N_{45}N_{45})$$

where  $E_{\text{bin}}(\text{In } 3d_{5/2})$  and  $E_{\text{kin}}(\text{In } M_4N_{45}N_{45})$  are the binding energy of the In 3d<sub>5/2</sub> core level and the kinetic energy of the In M<sub>4</sub>N<sub>45</sub>N<sub>45</sub> Auger line, respectively. The modified Auger parameter is independent of charging effects, band bending and is very sensitive to the chemical environment [23,24].

## 3. Results and discussion

### 3.1 Surface analyses

The Raman spectra of the four investigated absorbers are depicted in Fig. 1. All samples show a clear phase separation between the Cu(In,Ga)Se<sub>2</sub> (CIGSe) and the Cu(In,Ga)S<sub>2</sub> CIGS chalcopyrite structure. The A<sub>1</sub> vibrational mode of the CIGSe and CIGS chalcopyrite compound is found at 178 cm<sup>-1</sup> and 290 cm<sup>-1</sup>, respectively [25,26]. The CIGSSe-REF and CIGSSe-RbF(S) exhibit the same vibrational structures,

without any Raman band indicating the presence of Cu-poor chalcopyrite compound. Given that the Raman penetration depth is around 150 nm and that the amount of Rb supplied during the PDT is extremely low, the presence of Rb-related phases at the absorbers surface can be only confirmed by the XPS analysis (Fig 2a). Hence, the identification of possible Rb-related phases will be discussed in the XPS section.

The CIGSSe-In+RbF(Se) Raman spectrum presents two distinct features compared to the other absorbers: *i)* the Raman peak at  $157\text{ cm}^{-1}$  and *ii)* the region from  $200\text{ cm}^{-1}$  to  $260\text{ cm}^{-1}$  with broad Raman bands. The peak at  $157\text{ cm}^{-1}$  is attributed to the  $A_1$  vibrational mode of a Cu-poor chalcopyrite phase that corresponds to the  $\text{Cu}(\text{In,Ga})_3\text{Se}_5$  defect compound, namely ordered vacancy compound (OVC) [27]. The broad Raman bands from  $200\text{ cm}^{-1}$  to  $260\text{ cm}^{-1}$  correspond to the  $B_2$  and E modes of the stoichiometric CIGSe and OVC phase [25,27]. Unfortunately, the deconvolution of the  $200\text{ cm}^{-1}$  to  $260\text{ cm}^{-1}$  region into four distinct peaks is not feasible due to the fact that the  $B_2$  and E Raman bands of the CIGSe and OVC phase are broad. As a result, the identification of the exact position of these Raman modes is not possible.

In contrast, no clear OVC peak was detected in the CIGSSe-In+RbF(S) Raman spectrum, suggesting that either there is no OVC at the surface or the OVC is too thin to be detected by the Raman analysis. The CIGSSe-In+RbF(S) surface also shows broad bands from  $240\text{ cm}^{-1}$  to  $270\text{ cm}^{-1}$  and from  $300\text{ cm}^{-1}$  to  $340\text{ cm}^{-1}$  compared to CIGSSe-REF and CIGSSe-RbF(S) [28].  $\text{In}_2\text{S}_3$  crystallizes in the defective spinel structure with ordered vacancies and according to [29], the Raman spectrum of  $\text{In}_2\text{S}_3$  has main peaks at 244, 266, 307 and  $327\text{ cm}^{-1}$ . The broad bands from  $240\text{ cm}^{-1}$  to  $270\text{ cm}^{-1}$  and from  $300\text{ cm}^{-1}$  to  $340\text{ cm}^{-1}$  are attributed to a thin layer of indium sulfide which could contain a low amount of Rb. Thus, the peaks in the two regions are weak and broad without shift compared to  $\text{In}_2\text{S}_3$ . Therefore an indium sulfide compound likely forms at the CIGSSe surface after the In+RbF(S) PDT.

By comparing the Raman analysis of the In+RbF PDTs under Se or S we see two different behaviors, depending on the chalcogen atmosphere. The OVC is only detected on the CIGSSe-In+RbF(Se) absorber surface while the CIGSSe-In+RbF(S) does not show any Cu-poor Se-related phase, suggesting that either there is no OVC or the OVC is too thin to be detected. The change in surface composition between CIGSSe-In+RbF(Se) and CIGSSe-In+RbF(S) could be explained by the different

thermodynamically stable phases between the selenide and sulfide phases. Studies on the  $\text{Cu}_2\text{Se}-\text{In}_2\text{Se}_3-\text{Ga}_2\text{Se}_3$  and  $\text{Cu}_2\text{S}-\text{In}_2\text{S}_3-\text{Ga}_2\text{S}_3$  phase diagrams [30] have shown that  $\text{CuIn}_3\text{S}_5$  chalcopyrite-related phase is not stable, in contrast  $\text{CuGa}_3\text{S}_5$ ,  $\text{CuGa}_3\text{Se}_5$  and  $\text{CuIn}_3\text{Se}_5$  compounds are thermodynamically stable. For the In-rich-Cu-poor sulfide compounds the thermodynamically stable phase is the  $\text{CuIn}_5\text{S}_8$  thiospinelle structure. However, none of the possible ( $\text{CuGa}_3\text{S}_5$ ,  $\text{CuIn}_5\text{S}_8$ ) Cu-poor sulfide compounds are detected in the Raman spectrum of the CIGSSe-In+RbF(S) absorber. Hence, it seems that the excess of In during the In+RbF(S) PDT forms a  $\text{Rb}:\text{In}_x\text{S}_y$  compound rather than a Cu-poor sulfide phase. This phenomenon could lead to a thinner OVC, not detectable by the Raman analysis, in the CIGSSe-In+RbF(S) sample compared to the CIGSSe-In+RbF(Se).

XPS spectra of the four samples are shown in Fig 2. Rubidium is detected at the surface for all treated absorbers (Fig. 2a). The Cu  $2p_{3/2}$  photoemission peaks displayed in Fig. 2b allow to determine the evolution of the Cu content at the surface before and after each PDT. Slight Cu depletion is detected for the CIGSSe-RbF(S) absorber, while an important decrease of Cu content is observed for the CIGSSe-In+RbF(Se) and CIGSSe-In+RbF(S) samples, compared to the reference. One result to emerge from this data is that almost no Cu is detected in the case of CIGSSe-In+RbF(S).

The CIGSSe-REF, CIGSSe-RbF(S) and CIGSSe-In+RbF(Se) XPS In  $3d_{5/2}$  peaks displayed in Fig. 2c are fitted using two contributions (In-A and In-B), indicating two different indium chemical environments. This observation is in line with the In  $M_4N_{45}N_{45}$  signals (Fig. 2d) that also show both In-A and In-B contributions. The In-A contribution (blue peak) corresponds to the indium of the chalcopyrite structure and the In-B (orange peak) observed at higher binding energy, corresponds to an indium oxide [29]. The calculated  $\alpha'$ (In-A) and  $\alpha'$ (In-B) Auger parameters are close to 852.4 eV and 851.3 eV respectively, and they are consistent with the values found in the literature for the chalcopyrite and oxide chemical environment of In [12,14,31–35] (Fig. 3). For the sake of clarity only  $\alpha'$ (In-A) values are gathered in the Wagner-plot (Fig. 3) where similar chemical environments are located on the same diagonal.

Conversely, the In  $M_4N_{45}N_{45}$  Auger line and In  $3d_{5/2}$  peak of CIGSSe-In+RbF(S) can be fitted with only one contribution. In addition, the In  $M_4N_{45}N_{45}$  Auger line shows a very different shape, compared to the other three samples, indicating a different chemical environment of In. This observation is in good accordance with the detected



$\alpha'$ (In-A) of CIGSSe-In+RbF(S) (851.9 eV) that significantly differs from the  $\alpha'$ (In) values of the other three absorbers and it cannot be attributed to any reported In-based chalcopyrite or oxide structure. In the literature,  $\alpha'$ (In) values close to 852.0 eV often refer to  $\text{In}_2\text{S}_3$  phases [32].

The Se 3p-S 2p spectra in Fig. 2e allow to estimate the sulfur content of the different samples. As expected, RbF treatments performed under S atmosphere (CIGSSe-RbF(S) and CIGSSe-In+RbF(S)), induce an increase of the sulfur content at the surface. For the CIGSSe-RbF(S) absorber, the Se 3p doublet (fitted by the green peaks) is still detected after the PDT. In contrast, CIGSSe-In+RbF(S) presents only the S 2p doublet. The fact that the Se 3p photopeak is not detected at the CIGSSe-In+RbF(S) surface, indicates the presence of a Se-free topping layer. It is well known that 95% of the XPS signal *i.e.* the information depth (ID), corresponds to  $3 \cdot \text{IMPF}$  (Inelastic Mean Free Path). The IMPF of Se 3p photoelectron peak in  $\text{In}_2\text{S}_3$  is around 2.6 nm [36] and thus the thickness of the sulfide-based topping layer should be at least 8 nm.

The valence band (VB) of the CIGSSe-REF and CIGSSe-RbF(S) (Fig. 4) exhibit the characteristic features of the chalcopyrite structure with an intense band (from 0 to 6 eV) related to the Cu 3d – Se 4p (S 3p) hybridization and a second one around 7 eV related to the In 5s – Se 4p (S 3p) hybridization [37,38]. The intensity of the CIGSSe-RbF(S) VB is slightly lower than the CIGSSe-REF VB due to the lower Cu content at the surface. This observation is in good accordance with the Cu  $2p_{3/2}$  signal intensity (Fig. 2a).

Conversely, the VB shape of CIGSSe-In+RbF(S) undergoes an important evolution, suggesting a drastic decrease of the Cu content at the surface. Moreover the VB maximum (VBM) with respect to the reference is shifted by 0.13 eV towards higher binding energy. Similar VB shape and VBM shift have been already observed in Cu-poor selenide phases [38] and they were attributed to a chalcopyrite-related compound. This result is also consistent to the observed Cu-poor OVC compound detected with the Raman analysis and the  $\alpha'$ (In-A) value reported above, that indicate a chalcopyrite-related phase.

### 3.2 Discussion

CIGSSe-In+RbF(S) does not show the same features as the other three absorbers. First according to the  $\alpha'$ (In-A) Auger parameter value, the indium chemical environment does not belong to any chalcopyrite-related structure. Moreover, the valence band exhibits a totally different shape compared to those of the chalcopyrite structure and the VBM strongly shifts (0.94 eV) towards higher binding energies with respect to the reference CIGSSe-REF. Taken together, the change of the valence band shape and the indium Auger parameter  $\alpha'$ (In-A) value show the formation of a non-chalcopyrite-related topping layer. Since the VBM, valence band shape and  $\alpha'$ (In-A) value are close to the  $\text{In}_2\text{S}_3$  values [32,35] and as Rb is detected, conversely to Se and Cu, it can be reasonably assumed that the topping layer is a  $\text{Rb:In}_x\text{S}_y$ -related compound. One can also notice that there is a negligible amount of In oxides at the surface and that no clear OVC peak was detected by the Raman analysis.

In+RbF PDTs performed under Se or S atmosphere induce a considerable evolution of the Cu content at the surface. However, CIGSSe-In+RbF(Se) shows a clear indication of an OVC formation during the PDT. This observation is in line with the XPS analyses indicating a strong decrease of the Cu  $2p_{3/2}$  signal and VB shape that corresponds to a Cu-poor chalcopyrite-related structure, such as the OVC observed by the Raman spectroscopy. Additionally, the  $\alpha'$ (In-A) value of CIGSSe-In+RbF(Se) shows that the In chemical environment remains identical to the one of the chalcopyrite structure and no  $\text{Rb:In}_x\text{Se}_y$  topping layer is observed, conversely to the CIGSSe- In+RbF(S) absorber where the presence of a Cu-free  $\text{Rb:In}_x\text{S}_y$  topping layer is detected after the PDT .

The CIGSSe-RbF(S) absorber shows similar characteristics to the untreated reference absorber and exhibits a slight Cu depletion at the surface after the PDT. Moreover, since the  $\alpha'$ (In-A) value and the VB shape correspond to the chalcopyrite structure, we could assume that the rubidium is mainly present at the CIGSSe GBs and it does not participate to the formation of a topping layer.

A schematic representation of the different phases that form at the surface of our investigated samples is shown in Fig. 5 and summarized in Table II.

The  $\text{Rb:In}_x\text{S}_y$  layer is formed only during In+RbF PDT under elemental sulfur atmosphere and almost no Cu is detected at the surface. In the CIGSSe-based solar

cell community, finding a CdS alternative junction partner is an issue for more than 15 years [39,40]. Today the most promising candidates are the Zn(O,S) [41–45] and the  $\text{In}_x\text{S}_y$  compounds [46–52]. One of the  $\text{In}_2\text{S}_3$  weaknesses is related to its spinel structure where 1/3 of the tetrahedral (Td) sites are vacant allowing to host third elements as Cu or Na. In a previous study, we demonstrate that when Cu occupy the Td sites, a  $\text{CuIn}_5\text{S}_8$  phase forms [46,47,53]. This phase formation leads to band gap narrowing, and deteriorates the photovoltaic performance [46,47]. Occupation of the cationic vacancies with Rb in  $\text{Rb:In}_x\text{S}_y$  compound may impede Cu inclusion in indium sulfide matrix and consequently formation of the detrimental  $\text{CuIn}_5\text{S}_8$  phase. So  $\text{Rb:In}_x\text{S}_y$  could be possibility used prior to  $\text{In}_2\text{S}_3$  dry buffer layer deposition. However its property to impede the Cu diffusion from the CIGSSe absorber towards the  $\text{In}_2\text{S}_3$  dry buffer layer still have to be demonstrated. Further investigations are also required such as the  $\text{Rb:In}_x\text{S}_y$  band gap, structure, electronic and optical properties and how these characteristics change with the deposition process, temperature, flux and thickness of the deposited layer.

## 4. Conclusions

In this paper we have investigated the impact of the chalcogen atmosphere (S and Se) during the RbF-PDT on  $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$  or CIGSSe. The most striking results to emerge from our study are i) the fact that, under S atmosphere the formation of an OVC compound is hindered, ii) the OVC is mainly present on the absorber's surface treated with  $\text{In}+\text{RbF}$  under Se atmosphere and iii) the  $\text{CIGSSe-In}+\text{RbF}(\text{S})$  sample exhibits VB shape and indium chemical environment that do not belong to the chalcopyrite structure. This latter feature indicates the formation of a Cu-free  $\text{Rb:In}_x\text{S}_y$  compound at the surface of the  $\text{CIGSSe-In}+\text{RbF}(\text{S})$  absorber. The present findings suggest that the  $\text{Rb:In}_x\text{S}_y$  formation seem to hinder Cu inclusion in indium sulfide matrix and could possibility be used prior to the  $\text{In}_2\text{S}_3$  alternative buffer layer deposition process.

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**Table I:** Summary of the surface treatments and PDTs on the four investigated samples: bare CIGSSe (CIGSSe-REF), RbF under S vapor PDT (CIGSSe-RbF(S)), In and RbF co-evaporation under Se vapor PDT (CIGSSe-In+RbF(Se)) and In and RbF co-evaporation under S vapor PDT (CIGSSe-In+RbF(S))

Sample	PDT	PDT atmosphere	NH <sub>3</sub> rinsing after PDT
CIGSSe-REF	no	no	yes
CIGSSe-RbF(S)	RbF	S	yes
CIGSSe-In+RbF(Se)	In and RbF	Se	yes
CIGSSe-In+RbF(S)	In and RbF	S	yes

**Table II:** Summary of the observed phases at the surface, based on the Raman and XPS analysis for each PDT

Sample	Detected phases	
	From the Raman analysis (150 nm interaction depth)	From the XPS analysis (< 10 nm information depth)
CIGSSe-REF	Chalcopyrite	Chalcopyrite
CIGSSe-RbF(S)	Chalcopyrite	Chalcopyrite
CIGSSe-In+RbF(Se)	Chalcopyrite Ordered Vacancy Compound (chalcopyrite-related phase)	Ordered Vacancy Compound (chalcopyrite-related phase)
CIGSSe-In+RbF(S)	Chalcopyrite	Rb:In <sub>x</sub> S <sub>y</sub>