**In vacuo XPS investigation of Cu(In,Ga)Se$_2$ surface after RbF post-deposition treatment**

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**Abstract**

Latest record efficiencies of Cu(In,Ga)Se$_2$ (CIGSe) solar cells were achieved by means of a rubidium fluoride (RbF) post-deposition treatment (PDT). To understand the effect of the RbF-PDT on the surface chemistry of CIGSe and its interaction with sodium that is generally present in the CIGSe absorber, we performed an X-ray photoelectron spectroscopy (XPS) study on CIGSe thin films as-deposited by a three-stage co-evaporation process and after the consecutive RbF-PDT. The sample transfer from the deposition to the XPS analysis chamber was performed via an ultra-high vacuum transfer system. This allows to minimize air exposure, avoiding oxide formation on the CIGSe surface, especially for alkali-treated absorbers. Beside an expected reduction of Cu- and Ga-content at the surface of RbF-treated CIGSe films, we find that Rb penetrates the CIGSe and, contrary to fluorine, it is not completely removed by subsequent ammonia etching. The remaining Rb contribution at 110.0 eV binding energy, which appears after the RbF-PDT is similar to the one detected on a co-evaporated RbInSe$_2$ reference sample and together with a new Se 3d contribution may hence belong to an Rb-In-Se secondary phase on the CIGSe surface. In addition, Na is driven towards the surface of the CIGSe absorber as a direct result of the RbF-PDT. This proves the ion-exchange mechanism in the absence of moisture and air/oxygen between heavy Rb atoms incorporated via PDT and lighter Na atoms supplied by the glass substrate. A remaining XPS

signal of Na 1s is observed after etching the vacuum transferred RbF-CIGSe sample, indicating that Rb and/or F are not as much a driving force for Na as oxygen usually is.

**Keywords**

Cu(In,Ga)Se$_2$; alkali treatment; RbF; XPS; in vacuo.

**Introduction**

The pursuit of efficiency improvements through alkali post deposition treatments (PDTs) of Cu(In,Ga)Se$_2$ (CIGSe)-based solar cells has started with the discovery of Na impact on CIGSe based device performance [1], later adding heavier alkali metals such as K [2], Rb or Cs [3]. Na included in CIGSe either by means of a NaF-PDT or diffused from the underlying soda lime glass (SLG), was shown to decrease the number of electrically active donors, thus reducing the compensation level and consequently increasing the built-in-voltage [4]. The increased free carrier concentration in NaF-CIGSe leads to higher values of open circuit voltage and fill factor of these solar cells. K in turn facilitates the inversion of the surface region and grain boundaries (GBs) and also forms a Cu-free, K-containing layer in the CIGS surface region [5, 6]. The actual mechanism leading to the improved junction quality is either related to enhanced in-diffusion of cadmium or sulfur, a better CdS coverage or due to surface passivation. In all cases, higher reactivity of the surface induced by the K-PDT [7] allows the thinning of CdS buffer layer and the reduction of optical losses [2]. Still, only a combination of Na- and K-PDT seems to gain higher electrical performance than the use of a single alkali element [8]. This rule is also relevant for the RbF-PDT, which ensured the achievement of the former record efficiency (22.6 %) for co-evaporated CIGSe devices on barrier-free SLG [3]. The competing mechanisms induced by the RbF-PDT suggest that the lighter alkali elements are being driven out of the absorber. At the same time the significant performance gain is not sufficiently understood and attributed only to 'a better diode quality' [3]. Regarding these

RbF-CIGSe devices, a theoretical study [9] proposes that lighter alkali elements behave as impurities and contribute to an increased p-type doping, whereas heavier alkali elements are more prone to forming secondary phases that passivate the surface. Moreover, the same authors suggest that Rb and Cs can only diffuse in Cu-poor material via the Cu vacancies, whereas Na and K diffuse relatively easily in both stoichiometric and Cu-poor $CuInSe_2$. As an experimental confirmation of the mentioned calculations, an investigation by electron microscopy and nano-X-ray fluorescence clearly showed that Rb diffuses along the GBs and accumulates mainly at random high angle GBs, at dislocation cores, and at the interface between the absorber and the back contact [10]. These non-ideal GBs and dislocation cores are thougt to be passivated by the RbF-PDT, which also positively modifies the $CIGS/MoSe_2$ interface. On the other hand, an atom probe tomography investigation [11] suggested that the Rb segregation and coverage make the GBs Cu deficient, inducing a better hole barrier, and thus possibly improves the minority carrier collection at GBs and the overall cell performance.

Despite these theoretical and experimental achievements a full understanding of the mechanism of RbF treatment is still lacking. In this sense we provide here an in-vacuo X-ray photoelectron spectroscopy (XPS) investigation of the CIGSe surface resulting after RbF-PDT. The formation of an Rb-containing secondary phase is investigated by comparing the bare CIGSe, the RbF-CIGSe and the etched RbF-CIGSe surfaces to a co-evaporated $RbInSe_2$ reference sample.


**Experimental**

The polycrystalline CIGSe thin films were deposited by a modified three stage co-evaporation process [12] onto $5\times5$ cm$^2$ large Mo coated SLG substrates. A final Cu-poor content was realized in the last stage by turning off the Cu flux and turning the In and Ga evaporation rate back on. Both Cu-poor CIGSe samples investigated in this study have a bulk composition of

[Cu]/([In] + [Ga]) = 0.9, as determined by X-ray fluorescence. For one of the samples (referred to as RbF-CIGS) an in situ RbF-PDT was applied right after the CIGSe preparation. The treatment was performed in the same ultra-high vacuum (UHV) evaporation chamber in the presence of RbF and Se molecular beams for 10 min at a substrate temperature of 280 °C. All CIGSe films are supplied with sodium from the underlying barrier-free SLG by diffusion during the CIGSe deposition at temperatures up to 530 °C. After having finished the CIGSe preparation and PDT process, both samples were moved into an UHV based suitcase equipped with a battery powered ion getter pump. The special design of the vacuum suitcase allowed us to easily attach it to both the physical vapor deposition (PVD) chamber and the loading chamber of a combined UHV preparation and spectroscopy system [13]. So, the bare CIGSe and RbF-CIGSe samples were transferred from the preparation to the analytic chamber at a base pressure of ~$1 \cdot 10^{-7}$ mbar.

As XPS facility, a standard laboratory system was used based on a non-monochromated X-ray source from SPECS with Mg anode providing an excitation energy of 1253.6 eV. All XPS measurements were done at room temperature at a base pressure of $5 \cdot 10^{-8}$ mbar. More details on XPS measurement and analysis are presented elsewhere [13]. The energy analyzer was calibrated in this study by fixing the $Cu2p_{3/2}$ transition at a binding energy (BE) of 932.2 eV, ensuring that possible charging of the samples during XPS measurement does not affect the analysis. After the in vacuo XPS investigation of the two samples, the RbF-CIGSe sample was etched in aqueous $NH_3$ solution, thus mimicking the chemical cleaning process that is normally performed before the deposition of the buffer and window layers of the CIGSe solar cell. The $NH_3$ etching was done in an $N_2$-purged glove box connected to the XPS instrument so that a minimum oxygen contamination was assured.

For later comparisons a $RbInSe_2$/Mo/glass reference sample was air transferred to the same XPS instrument. Co-evaporation of $RbInSe_2$ was performed in the same PVD chamber as for

the CIGSe absorbers. The monoclinic crystal structure (not shown here) of our RbInSe$_2$ thin film is in a good agreement to the literature [14].

**Results and discussions**

XPS survey spectra of as deposited and RbF-treated CIGSe surfaces excited with Mg K$\alpha$ radiation are illustrated in Figure 1. Besides the core levels and Auger emissions of Cu, In, Ga, and Se for bare CIGSe, and additional Rb, F, and Na for RbF-CIGSe, no oxygen contamination was registered. The missing oxygen signals indicate that the vacuum transfer of both samples from the PVD chamber to the XPS instrument was successful. The carbon traces on vacuum transferred samples are most likely the result of hydrocarbon vapors emanated by lubricants of the vacuum pumps (so-called adventitious carbon).
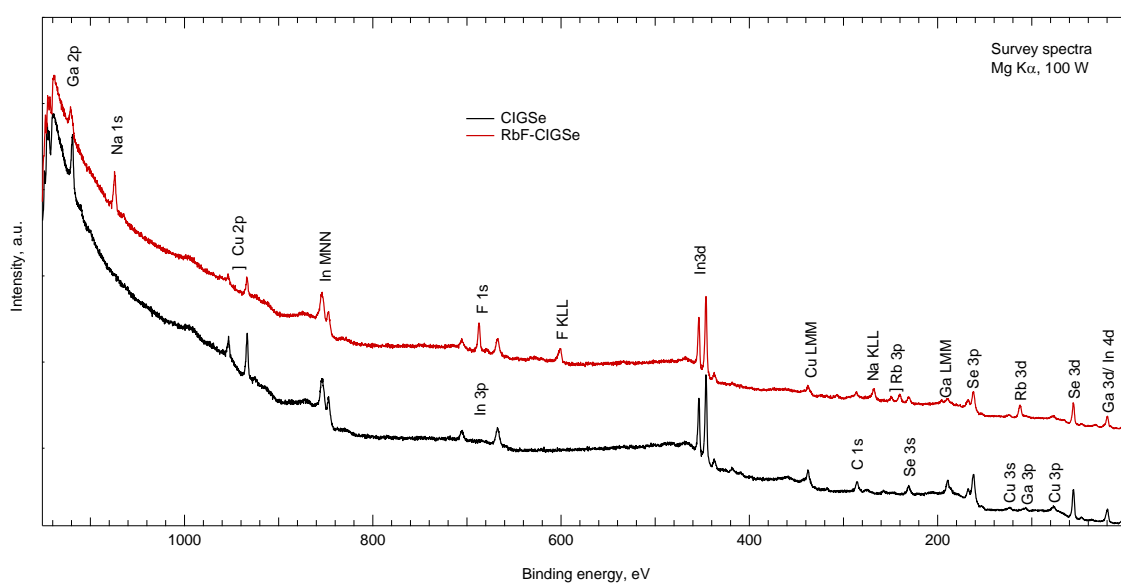


*Figure 1. XP survey spectra of two vacuum transferred CIGSe absorbers prepared under the same conditions: before the RbF-PDT and after the RbF-PDT.*

At first sight, both spectra look very similar indicating a reproducible and high-quality sample preparation. However, the detailed spectra of the core levels (Fig. 2) suggest that the RbF-PDT changes the surface of CIGSe absorber towards more Cu-poor, In-rich, and Ga-poor compositions. A similar impact of RbF-PDT onto CIGSe was described by other authors [15, 16]. Cu and Ga depletion alone would suggest that a thin RbF layer covers the CIGSe, however the In enrichment could be an indication of either a chalcopyrite with a lower Ga content or another indium-selenide based compound at the surface of the absorber.
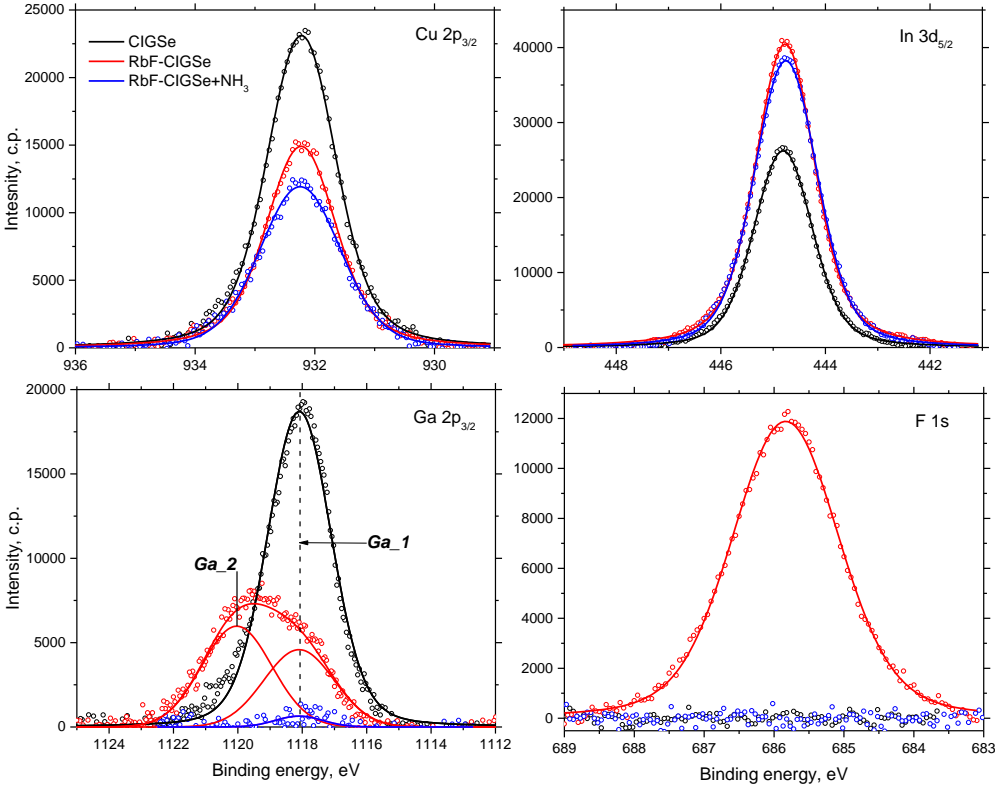
*Figure 2. Detailed XP spectra of the Cu 2p$_{3/2}$, In 3d$_{5/2}$, Ga 2p$_{3/2}$, and F 1s of the CIGSe absorbers before the RbF-PDT, after the RbF-PDT, and after the NH$_3$ etching of RbF-CIGSe.*

The obvious emergence of a new *Ga_2* bond in Ga 2p$_{3/2}$ core level at 1120.0 eV BE as result of the RbF-PDT and its removal by the NH$_3$ etching is similar to the appearance and disappearance of an additional Auger feature in the Ga LMM spectrum with etching (not shown here). Usually such a behavior is attributed to oxidation of the CIGSe surface [17], but here several facts contradict this reasoning, indicating the formation of a GaF$_3$ phase. Firstly, after the vacuum transfer there is no oxygen detected on the CIGSe surface. Secondly, the BE of the detected F 1s core level is very close to the literature value (685.8 eV) attributed to GaF$_3$ [18]. And finally, the ammonia etching completely removes both, the GaF$_3$ features from the Ga2p$_{3/2}$ and the fluorine core level (Fig. 2). Consequently, the Ga depletion after RbF-PDT (reduced *G_1* signal) may be due to the significant amount of GaF$_3$ formed at the surface of the Cu-poor CIGSe thin film. Formation of GaF$_3$ was also observed as a result of a KF-PDT by Lepetit [5]. Still, the presence of GaF$_3$ as a secondary phase after RbF-PDT should not impact the later performance of CIGSe solar cell, since it is entirely removed by ammonia solution before the formation of the p-n junction.

Although no changes are observed in the In 3d$_{5/2}$ core level spectra (Fig. 2), those of Se 3d and Rb 3d are more informative (Fig. 3). The Se 3d core level from bare CIGSe sample is characterized by two contributions (*Se_1* and *Se_2*) at BE values of 54.0 eV and 54.6 eV which can be attributed respectively to the main and second In-Se bonds in CIGSe [19].
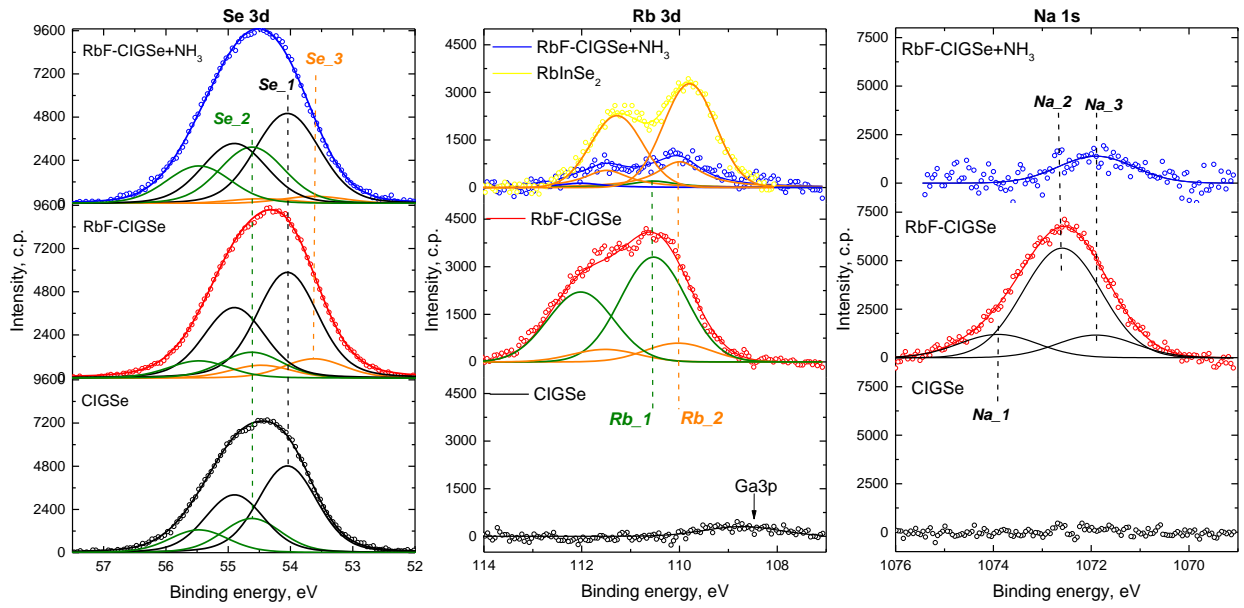
*Figure 3. Detailed XP spectra of the Rb 3d, Se 3d, and Na 1s of the CIGSe absorbers before the RbF-PDT, after the RbF-PDT, and after the NH₃ etching of RbF-CIGSe.*

It was previously suggested that the second In-Se bond might be related to the Se environment at the outermost surface of the CIGSe [5], therefore, all changes in the outermost surface would affect this *Se_2* contribution specifically. As expected, the following RbF-PDT of CIGSe induces the decrease of the *Se_2* contribution and the rise of a third contribution (*Se_3*) identified at 53.6 eV BE (Fig. 3). Since this BE of the Se $3d_{5/2}$ core level has been reported in the literature for InSe, $In_6Se_7$ [20] and $In_2Se_3$ [19], we can attribute the new *Se_3* contribution to a new In-Se bond different to those that characterize CIGSe. The lack of new contributions in the In $3d_{5/2}$ core level that would support the formation of a new In-Se bond can be simply explained by an undamaged Se environment surrounding the In atoms in CIGSe and the rest of the mentioned phases. As a confirmation, the BE values of In $3d_{5/2}$ core level of the InSe, $In_2Se_3$, and $In_6Se_7$ compounds are shown to be similar to those of CIGSe by the same authors [19, 20].

Along with the Se 3d modifications, in the Rb 3d core level spectra we can easily distinguish two features that are differently affected by the ammonia wash (Fig. 3). It is very probable that during the PDT some of the Rb atoms are incorporated in the CIGSe lattice and, in addition to the RbF phase visible as *Rb_1* emission at 110.5 eV BE, an additional phase denoted by *Rb_2* at 110.0 eV BE will form. The $NH_3$ etching then removes most of the *Rb_1* (RbF), whereas the second *Rb_2* contribution is more stable in the ammonia solution. To clarify the nature of the new feature, we compared the Rb 3d core level of RbF-CIGSe to the one of our co-evaporated $RbInSe_2$ reference sample (Fig. 3). The idea was to verify the theoretical prediction that heavier alkali metals such as Rb are more prone to forming alkali-containing secondary phases in CIGSe [9]. Interestingly, the Rb 3d core level spectrum of $RbInSe_2$ reference sample is very close to the similar one registered from the etched RbF-CIGSe surface (*Rb_2*). Comparing the behavior of the *Rb_2* feature to that of *Se_3*, and bearing in mind the In enrichment of the RbF-CIGSe sample, we can assume here that a new phase containing Rb, Se, and In is formed at the CIGSe surface. Such a secondary phase containing Rb, In, and Se was theoretically suggested by Malitckaya [9] and also suggested by Avancini [15], who registered an Rb accumulation on the CIGSe surface with increasing amounts at longer RbF-PDT. Since our etching procedure did not remove this Rb-In-Se compound (Fig. 3) we may assume that this secondary phase is left at the CdS interface in the CIGSe solar cell and is partially or completely responsible for the improvements in the performance of RbF-treated CIGSe devices [3].

Another interesting feature of the vacuum transfer is that it allows us to follow the Na behavior in the absence of oxygen. It is already well known that as a result of air exposure the sodium from the underlying soda-lime glass diffuses towards the CIGSe surface [21]. In vacuum, however, we did not register sodium traces on the surface of bare CIGSe (Fig. 3) indicating the need of oxygen and/or moisture as a chemical driving force for the diffusion of Na through CIGSe. After the RbF-PDT and without air contamination, a wide Na 1s emission

appears at ~1072.0 eV BE. The behavior of this wide Na 1s core level after the etching indicates the presence of three different contributions. *Na_1* and *Na_2* features at 1073.9 eV and 1073.6 BE (with Auger parameters of 2061.4 eV and 2010.1 eV) respectively, have appeared as result of RbF-PDT and are easily removed by the following NH$_3$ etching. At the same time, the *Na_3* feature at 1071.9 eV (2059.4 eV Auger parameter) was only partially washed by the NH$_3$ etch (Fig. 3), which is contrary to air transferred CIGSe where we generally observe that all sodium is washed away by the NH$_3$ etching. The remaining Na traces indicate either an NH$_3$-resistant compound or a deeper localization in the CIGSe such as at GBs. Based on the Auger parameters calculated using the Na KLL emission (not presented) all three contributions can be attributed to different Na- and F-containing compounds [22]. Therefore, by excluding moisture and air/oxygen from the system we actually proved the previously suspected [2, 3, 15] ion exchange mechanism between heavy Rb atoms incorporated via PDT and lighter Na atoms supplied by the glass substrate. After Rb partially substitutes Na atoms, the so-called 'free' Na diffuses towards the absorber's surface and then binds to the fluorine available in large amounts in RbF-CIGSe. Thus, in a vacuum transferred RbF-CIGSe, the Rb and/or fluorine seems to replace oxygen as one of the chemical driving forces for the diffusion of Na. Still, compared to air exposure the RbF-PDT insufficiently drives out the Na buried at GBs. In a future attempt to completely understand the Na diffusion in CIGSe it would be essential to evaluate these absorbers in a non-oxygen and non-fluorine system after the Rb-PDT.

**Conclusions**

In order to appreciate the impact of RbF-PDT, the surface modification of CIGSe absorber was spectroscopically investigated in vacuo. The vacuum transfer of both treated and untreated CIGSe was successful, as no oxygen traces were found on the samples' surface.

RbF-treated CIGSe is characterized by a Cu-poor, Ga-poor, and In-rich surface. In addition, a new Se contribution at 53.6 eV BE in the Se 3d core level suggests the formation of a new In-Se bond, different from those known for CIGSe. Another new contribution at 110.0 eV BE in the Rb 3d core level spectra indicates a new $NH_3$-resistent compound very similar to the Rb 3d signal of the $RbInSe_2$ reference sample. By connecting the new features of the Rb 3d and Se 3d core level spectra and considering the observed In enrichment, we propose that during the RbF-PDT a Rb-In-Se compound is formed on the CIGSe surface. The following ammonia wash does not remove this new compound completely. The remaining Rb-In-Se might explain the reported improvement of device performance for RbF-CIGSe [3].

As side effects of the RbF-PDT we observe the formation of $GaF_3$ on the CIGSe surface and the diffusion of Na from the bulk towards the surface. The $GaF_3$ compound should not influence the CIGSe device performance as it is easily washed only by $NH_3$. As for Na, it seems to be expelled from CIGSe bulk by the heavier Rb atoms, diffuses towards CIGSe surface, and then forms different Na- and F- containing compounds. The rubidium and/or fluorine is a chemical driving force for Na, taking to some extent the role of oxygen for Na diffusion. Moreover, when RbF-CIGSe is not exposed to air, the Na traces remain visible for XPS after the ammonia washing and may participate in the junction formation. This would be an interesting issue worth investigating in the close future.

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