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# Surface reactivity of CIGS absorber on soda-lime and flexible substrates studied by XPS: a global approach of deoxidation, ageing and alkali elements distribution

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**Abstract** — CIGS based solar cells are still part of the most popular solar cells developed. A chemical study is presented here by using XPS measurements, characterizing the surface chemistry and reactivity, with a focus on deoxidation and further ageing products, among which binary compounds and oxides can be found. Different chemical treatments are also suggested to adjust the surface composition of CIGS materials and to determine the re-oxidation delay. A specific point will be also discussed about the comparative evolution of alkali element distribution during the ageing of conventional CIGS/glass and CIGS/flexible substrate systems, requiring in this case an external alkali source.

**Index term** — CIGS, XPS, ageing, surface deoxidation, flexible substrates.

## I. INTRODUCTION

Photovoltaic cells based on CIGS (Cu(In,Ga)Se<sub>2</sub>) absorbers are among the most efficient in photo-conversion. In the worldwide competitive context of photovoltaic market, the cells architectures are in constant evolution to still gain efficiency while decreasing the production cost. In addition, new developments are considered to address new emerging market orientation, such as flexible solar cells (for transport, energy productive buildings, high technology and intelligence...) widely dominated at the moment by the organic and nanomaterial sectors [1]. Among the thin films technology, CIGS has proven to be relevant and recent evolutions are oriented towards its adaptation on flexible substrates. In this particular case, unlike the classical soda lime substrates on which was developed the initial CIGS cell design, an internal source of alkali elements is missing. Past studies [2]-[4] have clearly demonstrated that alkali presence and localization in the CIGS network (mainly at grain boundaries) is a key parameter of efficiency increase. Therefore, different routes are considered to provide alkali in

the absorber from an external source. This additional but essential step is usually performed from the front side of the absorber (post-deposition treatment). Consequently, the surface composition of CIGS is a fundamental point as it will condition the absorber/buffer layers and their interface properties in the final stack.

Indeed, whatever the substrate on which CIGS is deposited, it is well known that the performance of these solar cells is mainly governed by the bulk absorber properties. However, the interfaces with the front and back contact layers are also crucial for the performance improvement and have to be finely optimized. X-ray Photoelectron Spectroscopy (XPS) enables to obtain overall physico-chemical information by the determination of the composition and chemical environments at the surface, bulk and interfaces of CIGS layers. Specific spectroscopic signatures of deposition process and storage conditions can be highlighted and bring insight about the quality of the absorber considering different surface issues such as oxidation/deoxidation, presence of binary compounds and deeper aspects involving alkali elements distribution or absorbers ageing evolution...

This work is mainly focused on the surface reactivity. In the first part, the study of CIGS surface chemistry (classical architectures on soda lime substrates) after the reactor extraction, after further preparation by specific chemical engineering (HCl [5], NH<sub>3</sub>-H<sub>2</sub>O, HCl-KCN [6], [7] and NH<sub>3</sub>-H<sub>2</sub>O-KCN) and the chemical evolution of those surfaces in time at ambient atmosphere, is presented. Indeed, this work aims to find an effective and easy to use universal treatment (here dipping) to adjust the surface composition, control the doping and contamination levels, eliminate oxides and binary compounds. Likewise, since surface composition of the CIGS differs from the bulk one, a specific preparation has to be performed before the buffer layers deposition, in order to

obtain the best band alignment. To complete this study, the XPS monitoring of the surface evolution during 4 months is performed in order to determine the acceptable delay before implementing the next steps of the cell fabrication.

In the second part of this work, the study of CIGS deposited on flexible substrates with specific NaF and KF post-deposition treatments is presented. A focus is made on CIGS surface evolution arising from these treatments. For this purpose un-rinsed samples are first studied, to maintain a capping and protective layer and avoid unwanted alkali surface diffusion. Then, water rinsed samples are examined, just after elimination of the residual alkali charge and along time evolution, with a specific attention on the alkali elements behavior.

A cross analysis of the results on the flexible and soda-lime substrates is presented and completed by the evolution of alkali distribution in-depth.

## II. EXPERIMENTAL RESULTS

### A. Deoxidation treatment

A major issue of CIGS based solar cells concerns the control of the surface composition to ensure optimal interface properties. This surface composition can be finely adjusted using a chemical engineering procedure relying on dipping in selected solutions (HCl,  $\text{NH}_3\text{-H}_2\text{O}$ , HCl-KCN and  $\text{NH}_3\text{-H}_2\text{O-KCN}$ ). Indeed, initially, the surface composition of an as-grown sample differs strongly from the one of the bulk and is representative of the absorber elaboration process.

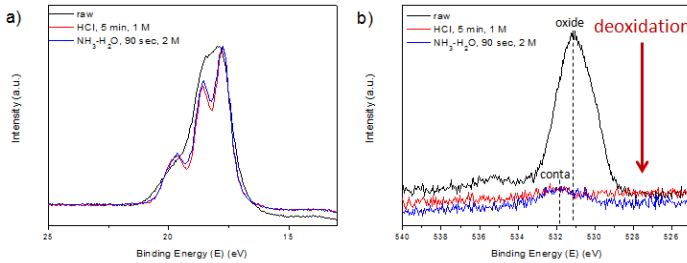


Fig. 1. a)  $\text{Ga}_{3d}\text{-In}_{3d}$  and b)  $\text{O}_{1s}$  photopeaks acquired on CIGS surfaces (on soda-lime substrate) of an aged raw sample (black) and after treatment of this surface by a subsequent HCl dipping (red) or a  $\text{NH}_3\text{-H}_2\text{O}$  (blue) dipping.

Fig. 1 a) shows the  $\text{Ga}_{3d}\text{-In}_{3d}$  photopeaks monitored on CIGS (on soda-lime) absorbers after different surface preparations. This spectral window, rarely considered in XPS studies, presents the advantage of enabling a direct comparison of the In and Ga proportions, the photoelectrons collected having similar escape depths. This represents then an original and powerful tool to GGI (namely  $[\text{Ga}]/([\text{Ga}]+[\text{In}])$  ratio) determination. Firstly, in the case of the as-grown CIGS surface, the  $\text{Ga}_{3d}\text{-In}_{3d}$  photopeak is characterized by a specific

spectrum shape, without visible spin-orbit splitting, revealing a significantly perturbed surface. After HCl treatment (1M, 5 min), a notable surface evolution is shown, with the re-emergence of the  $\text{In}_{4d}$  doublet structure. This observation is correlated to a strong decrease of the  $\text{O}_{1s}$  photopeak (Fig. 1.b)) and the analysis of the high energy resolution spectra  $\text{Cu}_{2p}$ ,  $\text{Ga}_{3d}\text{-In}_{4d}$ ,  $\text{Se}_{3d}$  evidences the surface deoxidation [5]. The corresponding overall composition before and after the chemical treatment is presented in Table I and highlights an initial Cu-poor surface ( $\text{CGI} = [\text{Cu}]/([\text{Ga}]+[\text{In}]) = 0.24$  compared to 0.86 expected from deep EDS measurement) already observed by other groups [2], [3] and the presence of Na. After HCl dipping, the specific ratios are in good agreement with the ones obtained from the overall EDS value (at 15kV accelerating voltage the whole layer probed), and an efficient elimination of the superficial oxide layer is proved. The most impacted ratio is the CGI ( $[\text{Cu}]/([\text{Ga}]+[\text{In}])$ ) and a slightly higher content than the one targeted is measured.

Similar behavior is observed when the dipping of the CIGS sample is realized in a  $\text{NH}_3\text{-H}_2\text{O}$  solution, with the re-emergence of the  $\text{In}_{4d}$  doublet structure and the deoxidation of the surface. However, it is noteworthy that the CGI ratio reaches a lower value when the sample is immersed in the  $\text{NH}_3\text{-H}_2\text{O}$  solution, leading to the conclusion that the Cu content at the surface is modulated by the choice of the dipping solution.

Concerning the CIG/Se ( $[\text{Cu}]+[\text{Ga}]+[\text{In}]/[\text{Se}]$ ) ratio, mainly governed by the Se content, discrepancies are also observable with EDS values but the consistency within the XPS set of values evidences a constant global stoichiometry. It is worth noting that EDS values are only indicative as the probed depth is not the same as the one of XPS (around 1.5  $\mu\text{m}$  vs 10 nm), as well as the accuracy of quantitative data. Indeed, the fine analysis of the  $\text{Se}_{3d}$  photopeaks evidences the presence of superficial  $\text{Se}^0$  (Figure 2) for both formulations employed lowering the CIG/Se.

TABLE I  
SUMMARY OF THE XPS SPECIFIC RATIOS OF CIGS SURFACES  
FOR THE DIFFERENT CHEMICAL TREATMENTS STUDIED

Sample	GGI	CGI	CIG/Se
As-grown	$0.20 \pm 0.03$	$0.24 \pm 0.03$	$0.62 \pm 0.03$
HCl	$0.32 \pm 0.03$	$0.91 \pm 0.03$	$0.49 \pm 0.03$
$\text{NH}_3\text{-H}_2\text{O}$	$0.32 \pm 0.03$	$0.74 \pm 0.03$	$0.47 \pm 0.03$
HCl-KCN	$0.31 \pm 0.03$	$0.68 \pm 0.03$	$0.63 \pm 0.03$
$\text{NH}_3\text{-H}_2\text{O-KCN}$	$0.31 \pm 0.03$	$0.62 \pm 0.03$	$0.63 \pm 0.03$
EDS	$0.28 \pm 0.05$	$0.86 \pm 0.05$	$1.17 \pm 0.04$

Finally, the additional use of KCN dipping is considered. This treatment has proven to efficiently eliminate elementary Se ( $\text{Se}^0$ ) [8]. By using either HCl-KCN or  $\text{NH}_3\text{-H}_2\text{O-KCN}$  treatments (HCl or  $\text{NH}_3\text{-H}_2\text{O}$  dipping following by a 5 minutes dipping in KCN solution at 1M), similar results are

obtained with the thinning of the  $\text{Se}_{3d}$  peak (Figure 2), due to the disappearance of the  $\text{Se}^0$  contribution at 56 eV. Consequently, the spin-orbit splitting of  $\text{Se}_{3d}$  peak is fully recovered.

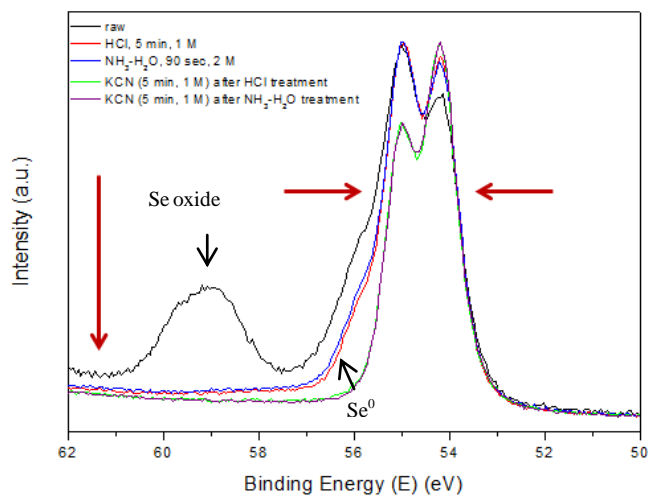


Fig. 2.  $\text{Se}_{3d}$  photopeaks acquired on CIGS surfaces of an aged as grown sample (black) and after different chemical treatments of this surface (HCl,  $\text{NH}_3\text{-H}_2\text{O}$ , HCl-KCN and  $\text{NH}_3\text{-H}_2\text{O-KCN}$ ).

The use of KCN leads to CGI ratio lower than the one obtained for HCl,  $\text{NH}_3\text{-H}_2\text{O}$  and the overall EDS value. This confirms that the Cu content at the surface is directly modulated by the nature and formulation of the dipping solution.

### B. Ageing at ambient atmosphere

Starting from those pristine surfaces, samples have been aged in air for 4 months to study their reoxidation kinetics. Whatever the treatment, oxidation is only observed after almost 2 days air storage as illustrated by the evolution of  $\text{O}_{1s}$  and  $\text{Se}_{3d}$  peaks (Fig. 3).

The oxide contribution to the  $\text{O}_{1s}$  signal ( $531.00 \pm 0.05$  eV) increases in time and the Se oxide contribution ( $59.00 \pm 0.05$  eV) is detected on the 4 days spectrum. During ageing, the surface progressively becomes again Cu-poor and the Na also migrates to the surface. In addition, Cu oxide becomes detectable only after 4 months. Longer time evolution experiments are ongoing to determine if this trend continues. Note that the CGI remains higher than the one measured on the as-grown surface after 4 months (0.32 instead of 0.29).

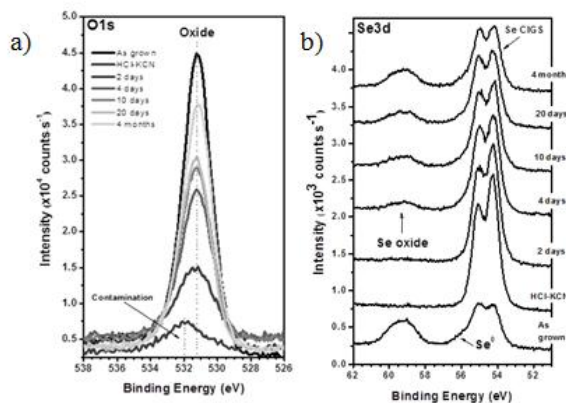


Fig. 3. Time evolution of CIGS deoxidized surfaces: a)  $\text{O}_{1s}$  and b)  $\text{Se}_{3d}$  (after HCl+KCN treatment) photopeaks acquired just after treatment until 4 months air ageing. The as-grown spectra are shown for comparison.

### C. CIGS thin films on flexible substrates

For CIGS deposition on flexible substrates (such as polyimide), alkali are introduced from the top side by additional post-treatments, evaporated under Se flux. Consequently, chemical modifications are expected on CIGS surface, but also concerning alkali incorporation and migration during ageing.  $\text{Cu}(\text{In,Ga})\text{Se}_2$  layers have been deposited at IPVF on 800 nm DC sputtered molybdenum layer on polyimide foils (Upilex 50S). CIGS films have been grown with a multi-stage co evaporation process developed at low temperature ( $<400^\circ\text{C}$ ).

Both as deposited samples, which present the initial CIGS chemical surface, and freshly rinsed ones (extra-pure water), to reproduce the process stage before the buffer layer deposition, have been investigated. Specific spectroscopic signatures and alkali incorporations are observed, depending on the nature of the alkali.

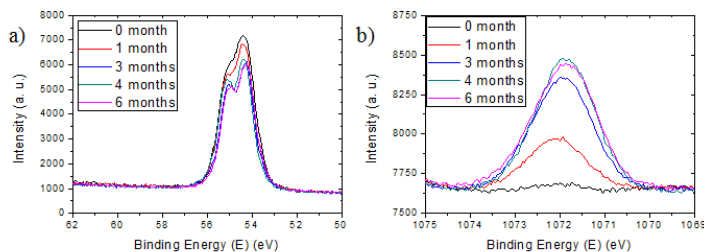


Fig. 4. a)  $\text{Se}_{3d}$  and b)  $\text{Na}_{1s}$  photopeaks evolution over air ageing for a rinsed CIGS sample deposited on flexible substrate with NaF post-deposition treatment.

For rinsed CIGS sample, unusual surface evolutions are evidenced during air ageing, with the absence of oxidized Se contribution (Fig. 4 a)) even after 4 months. This behavior is strongly different to the one observed on conventional CIGS/soda-lime (section B) and concomitant with a surprising reemergence of the spin-orbit splitting. Regarding the alkali behavior, the increase with time of  $\text{Na}_{1s}$  photopeak (Fig. 4 b)) evidences its migration to the surface, similar to the soda-lime system. No reemergence of the counter-ion was observed in this particular case.

The un-rinsed sample presents similar characteristics, with an equivalent Na migration and also no evolution of the counter-ion over ageing time. Moreover, the  $\text{Se}_{3d}$  photopeak doesn't present any oxide traces, even after 6 months of ageing.

The exact depth distribution of alkali is investigated by XPS profiling over the first hundreds of nanometers ( $\text{Ar}^+$  sputtering 2000 eV, zalar rotational mode) and completed by GD-OES qualitative profiling. Different distributions are pointed out for NaF and KF as the incorporation of the counter ion depends on its mobility.

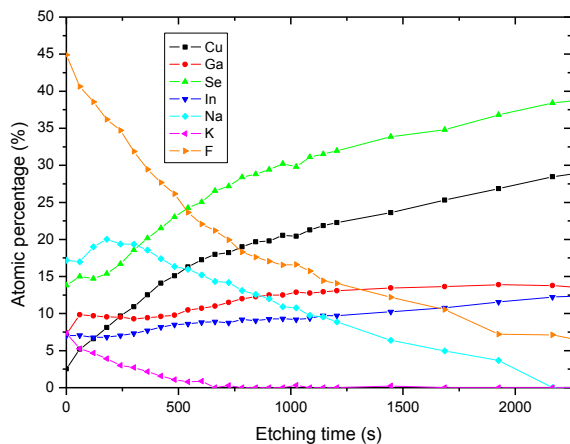


Fig. 5. XPS atomic percentage evolution over etching time for the different elements present in the CIGS sample.

For a sample with two alkali post-treatments deposition (in a first time, NaF, followed by a KF deposition), it is shown that the counter ion of alkali element is localized deeper in the layer (Fig 5.) while two kinetics are observed for the two different alkali elements. Indeed, the KF post-deposition treatment is performed after the NaF post-deposition treatment, which is in good agreement with the evolution of the XPS atomic percentages observed here.

### III. CONCLUSION

Comparison of the surface reactivity of CIGS between soda-lime and flexible substrates was underlined in this study. While deoxidation treatment is necessary to restore as pristine CIGS surface in the case of soda-lime substrates, a specific surface chemistry is shown for the CIGS elaborated on flexible substrates. In addition, a different surface reactivity is observed, as evidenced by the absence of Se oxide even after 4 months ageing. Concerning alkali, their depth distribution differs with the source (soda-lime, NaF or KF post-treatment) but ageing leads to a migration of alkali elements toward the surface in all cases. Ongoing experiments will provide the complementary information to fully determine the position of alkali elements in CIGS absorber layers and their mobility to optimize the elaboration process on flexible substrate.

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