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Evolution of Cu(In,Ga)Se2 surfaces under water immersion monitored by X-Ray Photoelectron Spectroscopy

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Abstract

$Cu(In,Ga)Se_2$ absorbers were immerged in deionized water for different times and specific chemical evolutions were monitored thanks to X-Ray Photoemission Spectroscopy. $Cu(In,Ga)Se_2$ related dissolution products were studied in water through Induced Coupled Plasma Optical Emission Spectroscopy. From those analyses, specific surface network disorganization was observed, with Cu migration towards the surface, leading to different kinetics of oxidation and dissolution for each element that could be quantified.

1. Introduction

Understanding the ageing mechanism of solar absorbers is a key point for the future of the photovoltaic market. Regarding the $Cu(In,Ga)Se_2$ (CIGS) solar cells technology, which reaches efficiencies up to 23.4%,[1] one key parameter to control during ageing is interfaces. Very few studies report on the properties modifications of CIGS solar devices following pure water exposure. Theeleen and al. demonstrated that, over water dipping, the chemical repartition of element drastically evolves, leading to strong modifications of electrical properties of CIGS solar cells.[2] They also studied the ageing of different layers (Al:ZnO, Mo) necessary to the device fabrication during water immersion.[3,4] However, to our knowledge, the chemical evolutions induced by water on CIGS surface were not systematically explored. Indeed, immersion in water asks the question of the surface chemical behavior in front of an infinite water reservoir but also raises interrogations about differences with air ageing with a high moisture level, which induces possible interactions with a very thin water film, more or less continuous.[5,6]

In the present study, X-Ray Photoemission Spectroscopy (XPS) is employed to follow the chemical evolution of CIGS surfaces during different water immersion times, as it can provide

the evolution of the chemical environment as well as a quantitative analysis of the surface composition. This last point is of primary importance in the case of CIGS as it will influence the band alignment with the buffer layer and can be monitored through two main ratios: the GGI ([Ga]/([Ga]+[In])) and the CGI ([Cu]/([Ga]+[In])).

In this paper, long time evolution during pure water immersion of CIGS surfaces is presented. Modifications of the initial free oxide reference surface is studied by a regular monitoring of chemical environments during 4 weeks, principally on the base of Augers lines comparison, whose features enable to more easily evidence oxidation states. The examination is completed by the corresponding key ratios determined with the associated photopeaks. Surfaces studied are either reference ones, *i.e.* without oxides or binary phases (such as elementary selenium, Se^0), thanks to chemical engineering or aged surfaces (strongly oxidized).[7,8]

2. Methods and Experimental Setup

2.1. CIGS samples

The CIGS samples were supplied by ZSW (Zentrum für Sonnenenergie- und Wasserstoff-Forschung, Germany).[9] CIGS was co-evaporated on Mo (600 nm)/glass (3 mm) substrates. The CIGS layers were provided with expected GGI bulk ratio close to 0.3, a CGI of 1.0 and a thickness of 2.1 µm. Surfaces were prepared to eliminate any traces of oxides,[7] Se^0 and side phases.[8] The CIGS/water interaction was provided through immersion in 60 mL of ultra-pure de-ionized water (18.2 MΩ, without degassing with a concentration of dissolved O_2 of 5.5 ± 0.6 mg L^{-1}) for several weeks. Experiments were performed in the dark.

2.2.Experimental

XPS surface chemical analyses were performed with a Thermo Electron K-Alpha$^+$ spectrometer using a monochromatic Al-Kα X-Ray source (1486.6 eV). The X-Ray spot size was 400 µm. High energy resolution spectra were acquired using a Constant Analyzer Energy (CAE) mode of 10 eV and 0.05 eV as energy step size. X-Ray Auger Electron Spectroscopy (XAES) lines were studied with a CAE mode of 50 eV and 0.1 energy step size. Data were processed using the Thermo Fisher scientific Avantage© data system with a Shirley-assimilated background subtraction and XPS compositions were deduced using the sensitivity factors, the transmission factor and inelastic mean-free paths from Avantage© library. The fits were performed with Gaussian/Lorentzian mix, determined on deoxidized samples. In this paper, ratios were calculated based on major photopeaks: $Ga2p_{3/2}$, $Cu2p_{3/2}$ and $In3d_{5/2}$ and Se3d.

Dosages of Ga, In, Cu, Se and Na elements in water after different interaction times were performed by Induced Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with an Agilent spectrometer. Calibrations were performed with set of standard solutions with a concentration range from 5 to 5000 µg L^{-1} in HNO_3 (4%).[10]

3. Results & Discussions

3.1.Immersion of fresh CIGS surfaces

Regarding the chemical environment of fresh CIGS surface, for each constitutive element, initially only CIGS one is visible, either on the XAES lines (Figure 1, t_0 spectra), or on the photopeaks. The Ga transition ($GaL_3M_{45}M_{45}$, Figure 1 a., t_0 spectrum) is representative of a sole CIGS environment at 1065.7 ± 0.1 eV (Kinetic Energy, KE), without traces of Ga-O contribution (1062.5 ± 0.1 eV, KE). Similar behaviors are observed for Cu and Se transitions ($CuL_3M_{45}M_{45}$ and $SeL_3M_{45}M_{45}$, Figure 1 b and c., t_0 spectra) positioned at 917.2 ± 0.1 eV and 1307.2 ± 0.1 eV, KE respectively. The absence of oxide phases is supported by the fact that no shoulder is visible at lower KE (914.1 ± 0.1 eV) for Cu and no oxidized contribution at 1300.6 ± 0.1 eV, KE for Se. The Se3d photopeak (Figure 1 f., t_0 spectrum) is also presented here because of the large chemical shift due to Se-O bounds and clear distribution at low binding energy, with the Se^0 contribution. A sole $Se3d_{5/2}$ CIGS environment is observed at 54.1 ± 0.1 eV (Binding Energy, BE) and no oxide or Se^0 contributions are observed (58.8 ± 0.1 and 55.1 ± 0.1 eV, BE respectively).[11] The $InM_{4/5}N_{45}N_{45}$ X-Auger region without traces of oxides is presented in Figure 1 d. (t_0 spectrum), with the main CIGS contribution at 400.5 ± 0.1 eV, KE, while the In-O one should be located at 398.6 ± 0.1 eV, KE. On this specific region, another photopeak is of primary importance, the Na1s one, at 415.2 ± 0.1 eV, KE. Na is a key element to enhance CIGS performances.[12] In present soda-lime conventional configuration, Na migrates from the substrate to CIGS front side. On t_0 spectrum, no Na traces are found thanks to deoxidation/cleaning process. Its reemergence and its associated kinetic can be found in literature.[5,6] Finally, the O1s photopeak region (540-525 eV, BE, Figure 1 e.) provides information about the inherent carboneous contamination (531.7 ± 0.1 eV, BE) but also on oxide phase (531.0 ± 0.1 eV, BE). For the t_0 spectrum, only inherent contamination is visible.

To investigate the CIGS/pure water interaction evolutions, a dedicated experiment focused on the interactions between water and CIGS surfaces by immerging the absorber in infinite deionized water for 4 weeks. The sample was regularly extracted for XPS analysis and then replaced in the aqueous medium. Long-time interactions with water lead to non-expected

effects on CIGS surfaces. The first one concerns the Cu signal. Indeed, after one week of ageing, an important increase of Cu content is noted at the surface with a CGI value which triples (Table 1) and consequently the emergence of a notable Cu2s photopeak (388.7 ± 0.1 eV KE, Figure 1 d.) on the In-MNN Auger region. It is strengthened over times as shown by the increase of CGI ratio value (Table 1). Moreover, the Auger parameter varies from 1849.4 ± 0.1 eV (typical of CIGS environment) to 1850.0 ± 0.1 eV, showing a modification of the chemical environment of Cu over time, also supported by the FWHM evolution of the Cu $2p_{3/2}$ photopeak which increases gradually from 0.98 ± 0.03 to 1.07 ± 0.03 eV after 4 weeks ageing. The second modification concerns the fast oxidation of In element, as observed with the appearance of In oxide contribution at 398.5 ± 0.1 eV, KE (Figure 1 d.). This is accompanied with a decrease of the GGI ratio, which is divided by two after one-week ageing (Table 1). This modification of the surface content is due to important Cu migration upon the absorber, which is in contradiction with surfaces exposed to ambient atmosphere.[6] After the four weeks of ageing, an important surface degradation appears on samples, with a possible surface delaminating. Thus, the ageing procedure in pure water has been stopped, the representativeness of surface analyses being questionable.

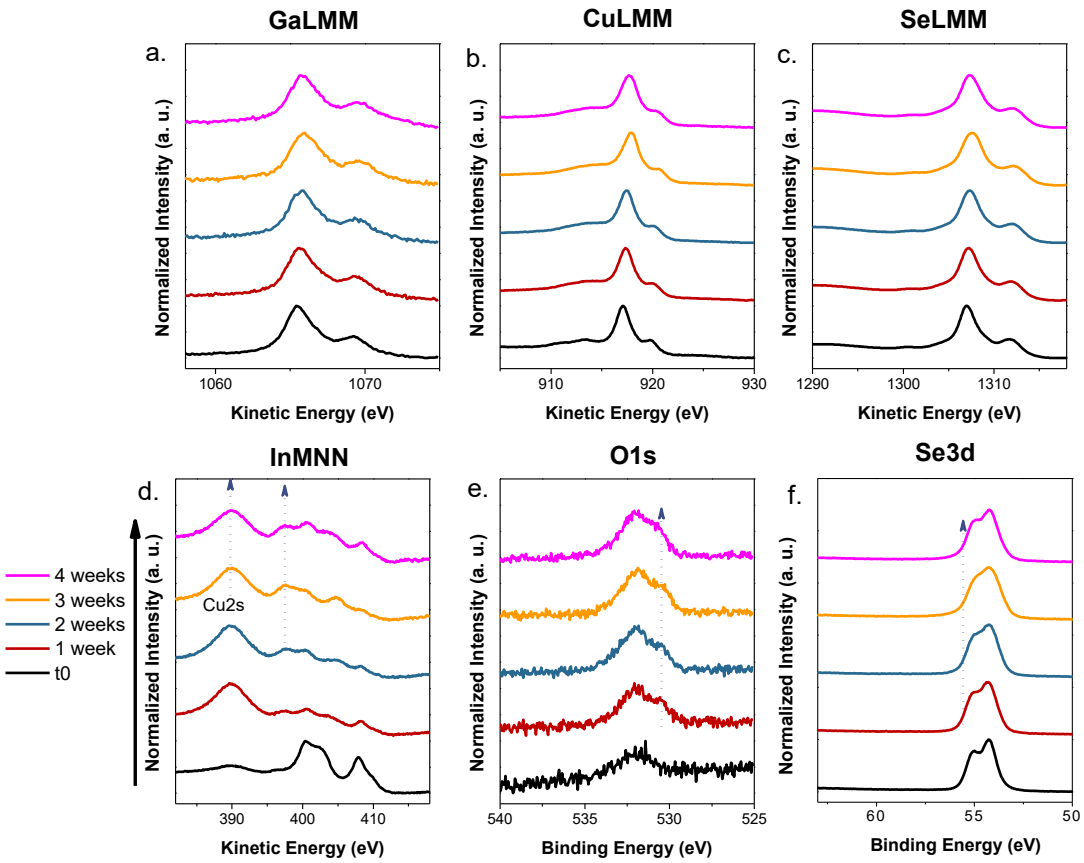

Figure 1: Normalized evolution of high energy XPS spectra of reference CIGS surface (HCl + KCN treated) over 4 weeks of water-ageing: GaLMM (a.), CuLMM (b.), SeLMM (c.), InMNN (d.) Auger regions and O1s (e.) and Se3d (f.) photopeaks. The differences observed are represented with an arrow.

According to the In behavior over time, the possibility that the other elements of CIGS network also oxidize in water is rather probable even if no traces of oxides are evidenced by surface analyses. The explanation is linked to the respective differential solubility of oxide compounds in water. This hypothesis is also supported by the fact that a Se^0 contribution is visible after one-week ageing (Figure 1 f.), growing up with time. For II-VI materials, the oxidation is a two-step process, with in a first time, the appearance of Se^0 contribution which act as an corrosion intermediate and, in a second time, the oxide growth.[13] We proved before that the Se ageing mechanism for CIGS surface follow this II-VI's scheme.[6,11] An explanation to the fact that no Ga, Cu or Se oxide are found, is, in a first time, that CIGS surface undergoes as a spontaneous anodic dissolution mechanism in water environment and, in a second time, that differential dissolution of these oxides occurs.

3.2.Immersion of aged CIGS surfaces

To evaluate the solubility of the different oxides present on CIGS surface, aged CIGS samples (at ambient atmosphere), then covered by all the possible oxide phases, were also immersed in deionized water (1 hour, 1 day and 1 week) and their surface evolution checked by XPS measurements (Figure 2). Based on Pourbaix's diagram,[14] InO_x dissolution in pure water is low even practically non-existent with a minimum solubility ($10^{-9.8}$ g-ion L^{-1}). GaO_x dissolution is slow but happens in pure water or dilute mineral acids and CuO_x and SeO_x dissolutions are expected to be faster.

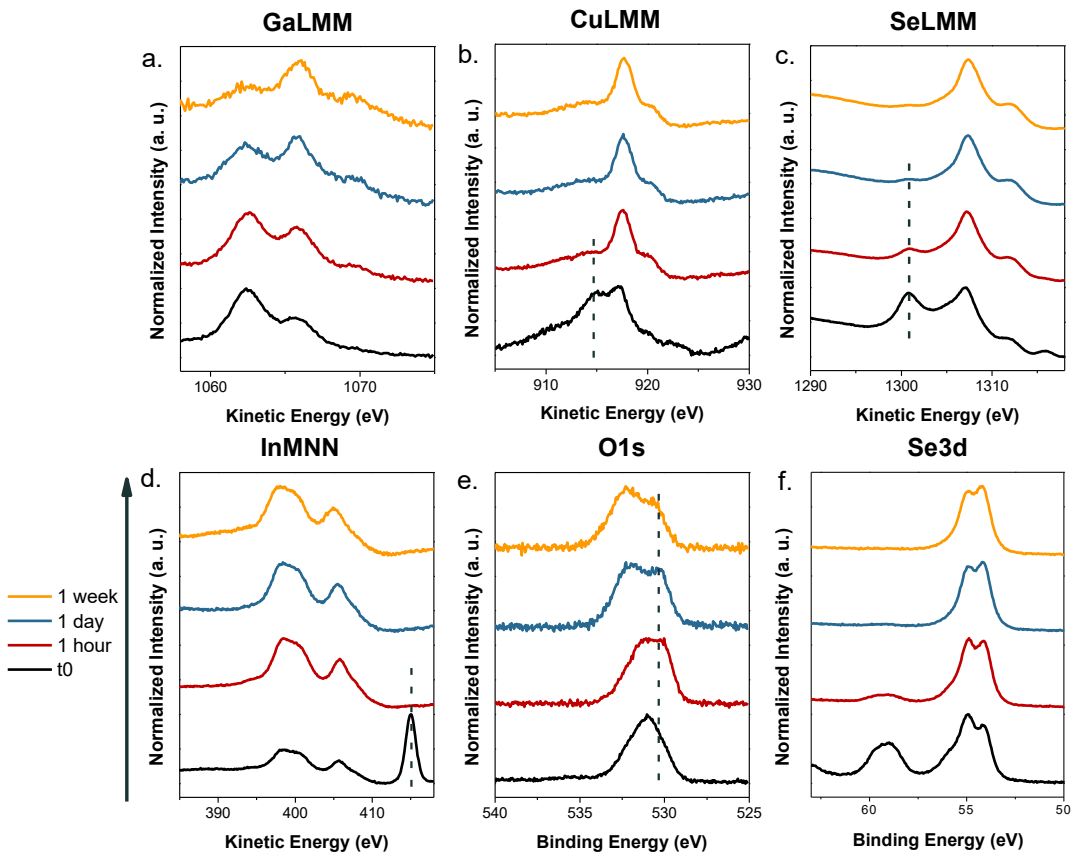

Figure 2: Normalized evolution of high energy XPS spectra of aged CIGS surface (HCl + KCN treated) over different immersion times in deionized water: GaLMM (a.), CuLMM (b.), SeLMM (c.), InMNN (d.) Auger regions and O1s (e.) and Se3d (f.) photopeaks. The differences observed are represented with an arrow.

After one hour immersion, the Cu oxide contribution fully disappears (Figure 2 b.) as well as the Na initially present on aged surface (Figure 2 d.). Moreover, a decrease of Se oxide Auger feature is observed (Figure 2 c.), in agreement with the disappearance of the oxide contribution in the Se3d spectral window (Figure 2 f.). After one day immersion, the entire SeO_x contribution has disappeared. Concerning Ga, peak ratios between CIGS and oxide contributions (Figure 2 a.) progressively reverse in favor of the CIGS environment. After one-week immersion, Cu and Se oxides have totally disappeared and the surface presents In_{ox}, residual Ga_{ox} and Se^0 (Figure 2 d. and e.) All these evolutions are correlated with the decrease of the O1s oxide contribution at 531.0 ± 0.1 eV (BE) (Figure 2 e.). As expected, the In oxide contribution doesn't present any evolution over water immersion (Figure 2 d.). Finally, this experiment informs about the dissolution kinetics of the surface oxide layer on aged CIGS sample: Cu_{ox}> Se_{ox}> Ga_{ox}, In_{ox} being almost insoluble.

3.3.ICP-OES measurements

Dissolution of Se, Cu and Ga oxides in water was evidenced for CIGS surfaces. Study was thus completed with the dosage of the water solutions in which CIGS samples were immersed using ICP-OES (Table 2). Considering the amounts measured in the different solutions, the dissolution of Se, Cu and Ga is demonstrated, with different kinetics consistent with the oxide solubilities presented in the previous paragraph. Cu is the first element detected by ICP-OES indicating that Cu_{ox} dissolution occurs in a short timescale, after one week of ageing in water. The global balance between oxide formation and dissolution leads to CGI value increase. After one week, only traces are detected in solution and the Cu surface enrichment progressively continues to increase (Table 1). Se and Ga traces appear in solution only after 2 and 3 weeks of ageing in water respectively, in good agreement with previous observations on aged surface evolution in water, with no traces of Se_{ox} neither Ga_{ox}.

Concerning Na, a really high concentration is measured even after one week. To determine the contribution of the glass substrate from the sides not covered by CIGS and correct the amount of Na detected only by migration through the absorber layer, samples presenting the same dimension but consisting in glass covered with Mo only have been immersed in water. From this experiment, the Na concentration in water solution per week measured is 200 µg L^{-1}. The CIGS deposited on top of Mo acts thus as a pump for sodium and releases Na.

4. Conclusion

In aqueous media, CIGS surface presents many chemical evolutions. Each CIGS constitutive element presents its own oxidation kinetic as well as its own dissolution kinetic in water, leading to a drastic disorganization of the CIGS network. The resulting surface is representative of several environments: the CIGS one and the oxidized one. However, some of the oxides dissolve directly inside water due to their solubilities. Two specific features are observed for the elements of column III, as In_{ox} growths rapidly and remains stable in time, without dissolution (in coherence with Pourbaix's diagram) while the oxidized contribution of Ga appears with a slower kinetic, as well as its dissolution. Regarding Se behavior, spontaneous oxidation and dissolution at open-circuit potential in water are noticed and supported by the presence of the corrosion intermediate Se^0. Evolution of Cu is similar to the Se one, leading to a migration of Cu towards the CIGS surface, in contradiction with the trends observed during ageing at ambient atmosphere. This disorganization is accompanied with a major dissolution of Na, coming from the CIGS bulk as well as a surface delamination over time.

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References

1. Nakamura M, Yamaguchi K, Kimoto Y, Yasaki Y, Kato T, Sugimoto H. Cd-free Cu (In,Ga)(Se,S)2 thin film solar cell with a new world record efficacy of 23.35%. *IEEE J Photovoltaics* . 2019:1-5. doi:10.1109/JPHOTOV.2019.2937218

2. Theelen M, Foster C, Steijvers H, Barreau N, Vroon Z, Zeman M. The impact of atmospheric species on the degradation of CIGS solar cells. *Sol Energy Mater Sol Cells*. 2015. doi:10.1016/j.solmat.2015.05.019

3. Theelen M, Dasgupta S, Vroon Z, et al. Influence of the atmospheric species water, oxygen, nitrogen and carbon dioxide on the degradation of aluminum doped zinc oxide

layers. *Thin Solid Films*. 2014;565:149-154. doi:10.1016/J.TSF.2014.07.005

4. Theelen M. Impact of atmospheric species on copper indium gallium selenide solar cell stability: an overview. *J Photonics Energy*. 2016;6(1):015501. doi:10.1117/1.JPE.6.015501

5. Calvet W, Ümsür B, Steigert A, et al. *In situ* investigation of as grown Cu(In,Ga)Se_2 thin films by means of photoemission spectroscopy. *J Vac Sci Technol A*. 2019;37(3):031510. doi:10.1116/1.5089412

6. Loubat A, Béchu S, Bouttemy M, et al. Cu depletion on Cu(In,Ga)Se_2 surfaces investigated by chemical engineering: An x-ray photoelectron spectroscopy approach. *J Vac Sci Technol A*. 2019;37(4):041201. doi:10.1116/1.5097353

7. Loubat A, Eypert C, Mollica F, et al. Optical properties of ultrathin CIGS films studied by spectroscopic ellipsometry assisted by chemical engineering. *Appl Surf Sci*. 2017;421:643-650. doi:10.1016/j.apsusc.2016.10.037

8. Lehmann J, Lehmann S, Lauermann I, et al. Reliable wet-chemical cleaning of natively oxidized high-efficiency Cu(In,Ga)Se2 thin-film solar cell absorbers. *J Appl Phys*. 2014;116(23):233502. doi:10.1063/1.4903976

9. Dimmler B, Schock HW. Scaling-up of CIS technology for thin-film solar modules. *Prog Photovoltaics Res Appl*. 1996;4(6):425-433. doi:10.1002/(SICI)1099-159X(199611/12)4:6<425::AID-PIP153>3.0.CO;2-Y

10. Skoog DA, West DM, Hollar JF. Fundamentals of Analytical Chemistry. Sixth edition. *J Chem Educ*. 1992;69(11):A305. doi:10.1021/ed069pA305.1

11. Canava B, Vigneron J, Etcheberry A, Guillemoles J., Lincot D. High resolution XPS studies of Se chemistry of a Cu(In, Ga)Se2 surface. *Appl Surf Sci*. 2002;202(1-2):8-14. doi:10.1016/S0169-4332(02)00186-1

12. Hedström J, Ohlsen H, Bodegård M, et al. ZnO/CdS/Cu(In,Ga)Se2 thin film solar cells with improved performance. In: *Proceedings of the 23rd IEEE Photovoltaic Specialists* . Louisville, KY, USA: The Institute of Electrical and Electronics Engineers, Inc; 1993:364-371.

13. Chassaing E, Grand P-P, Ramdani O, Vigneron J, Etcheberry A, Lincot D.

Electrocrystallization Mechanism of Cu–In–Se Compounds for Solar Cell Applications. *J Electrochem Soc*. 2010;157(7):387-395. doi:10.1149/1.3374590

14. Pourbaix M. *Atlas d'Equilibres Electrochimiques*. Paris: Gauthier-Vilars; 1963.

Table 1: GGI and CGI ratios evolution of CIGS surfaces aged in H_2O environment, calculated from the $Ga2p_{3/2}$, $Cu2p_{3/2}$ and $In3d_{5/2}$ regions after HCl + KCN chemical treatment.

	GGI	CGI
t_0	0.28 ± 0.03	0.98 ± 0.05
1 week	0.15 ± 0.03	3.09 ± 0.05
2 weeks	0.14 ± 0.03	3.14 ± 0.05
3 weeks	0.14 ± 0.03	3.21 ± 0.05
4 weeks	0.14 ± 0.03	3.49 ± 0.05

Table 2: Evolution of element concentrations in aged waters measured by ICP-OES for a "reference" CIGS surface. Na value is not corrected.

	Concentration (µg L^{-1}) ± 10 µg L^{-1}				
Ageing time	Cu	Ga	In	Se	Na
1 week	236	/	/	/	641
2 weeks	264	/	/	161	1459
3 weeks	269	33	/	316	2480
4 weeks	278	118	/	355	2658