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

Solène Béchu^{1*}, Muriel Bouttemy¹, Jackie Vigneron¹, Daniel Lincot², Jean-François Guillemoles², Arnaud Etcheberry¹

1. Institut Lavoisier de Versailles (ILV), Université Paris-Saclay, CNRS-UVSQ, 45 av. des Etats-Unis, Versailles 78035, France.

2. CNRS-IPVF, 18 boulevard Thomas Gobert, 91120 Palaiseau, France.

Abstract

Cu(In,Ga)Se₂ absorbers were immersed in deionized water for different times and specific chemical evolutions were monitored thanks to X-Ray Photoemission Spectroscopy. Cu(In,Ga)Se₂ 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)Se₂ (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. Theelen 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

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

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

42 **2. Methods and Experimental Setup**

43 *2.1. CIGS samples*

44 The CIGS samples were supplied by ZSW (Zentrum für Sonnenenergie- und Wasserstoff-
45 Forschung, Germany).⁹ CIGS was co-evaporated on Mo (600 nm)/glass (3 mm) substrates. The
46 CIGS layers were provided with expected GGI bulk ratio close to 0.3, a CGI of 1.0 and a
47 thickness of 2.1 μm . Surfaces were prepared to eliminate any traces of oxides,⁷ Se^0 and side
48 phases.⁸ The CIGS/water interaction was provided through immersion in 60 mL of ultra-pure
49 de-ionized water (18.2 M Ω , without degassing **with a concentration of dissolved O_2 of $5.5 \pm$**
50 **0.6 mg L^{-1}**) for several weeks. Experiments were performed in the dark.

51 *2.2. Experimental*

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

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

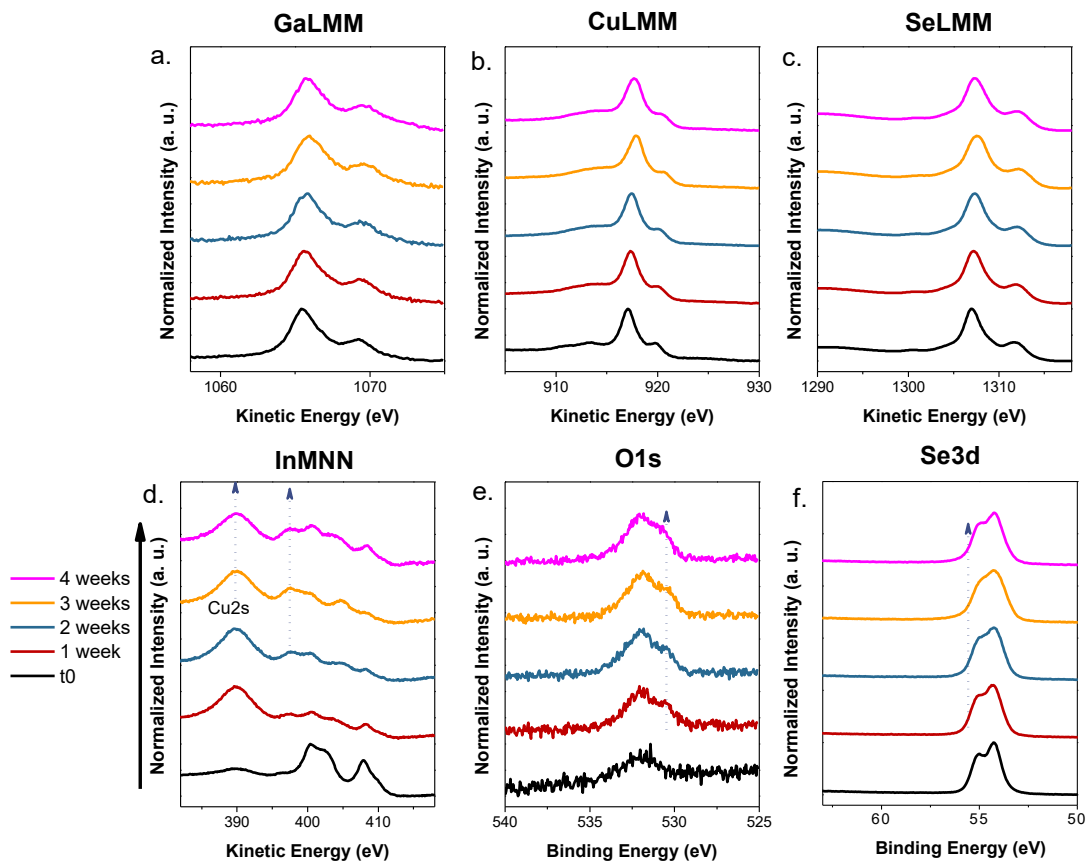
66 3. Results & Discussions

67 3.1. Immersion of fresh CIGS surfaces

68 Regarding the chemical environment of fresh CIGS surface, for each constitutive element,
69 initially only CIGS one is visible, either on the XAES lines (Figure 1, t_0 spectra), or on the
70 photopeaks. The Ga transition ($\text{GaL}_3\text{M}_{45}\text{M}_{45}$, Figure 1 a., t_0 spectrum) is representative of a sole
71 CIGS environment at 1065.7 ± 0.1 eV (Kinetic Energy, KE), without traces of Ga-O
72 contribution (1062.5 ± 0.1 eV, KE). Similar behaviors are observed for Cu and Se transitions
73 ($\text{CuL}_3\text{M}_{45}\text{M}_{45}$ and $\text{SeL}_3\text{M}_{45}\text{M}_{45}$, Figure 1 b and c., t_0 spectra) positioned at 917.2 ± 0.1 eV and
74 1307.2 ± 0.1 eV, KE respectively. The absence of oxide phases is supported by the fact that no
75 shoulder is visible at lower KE (914.1 ± 0.1 eV) for Cu and no oxidized contribution at 1300.6
76 ± 0.1 eV, KE for Se. The Se3d photopeak (Figure 1 f., t_0 spectrum) is also presented here
77 because of the large chemical shift due to Se-O bounds and clear distribution at low binding
78 energy, with the Se^0 contribution. A sole $\text{Se}3\text{d}_{5/2}$ CIGS environment is observed at 54.1 ± 0.1
79 eV (Binding Energy, BE) and no oxide or Se^0 contributions are observed (58.8 ± 0.1 and 55.1
80 ± 0.1 eV, BE respectively).¹¹ The $\text{InM}_{4/5}\text{N}_{45}\text{N}_{45}$ X-Auger region without traces of oxides is
81 presented in Figure 1 d. (t_0 spectrum), with the main CIGS contribution at 400.5 ± 0.1 eV, KE,
82 while the In-O one should be located at 398.6 ± 0.1 eV, KE. On this specific region, another
83 photopeak is of primary importance, the Na1s one, at 415.2 ± 0.1 eV, KE. Na is a key element
84 to enhance CIGS performances.¹² In present soda-lime conventional configuration, Na migrates
85 from the substrate to CIGS front side. On t_0 spectrum, no Na traces are found thanks to
86 deoxidation/cleaning process. Its reemergence and its associated kinetic can be found in
87 literature.^{5,6} Finally, the O1s photopeak region (540-525 eV, BE, Figure 1 e.) provides
88 information about the inherent carboneous contamination (531.7 ± 0.1 eV, BE) but also on
89 oxide phase (531.0 ± 0.1 eV, BE). For the t_0 spectrum, only inherent contamination is visible.

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

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



110

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

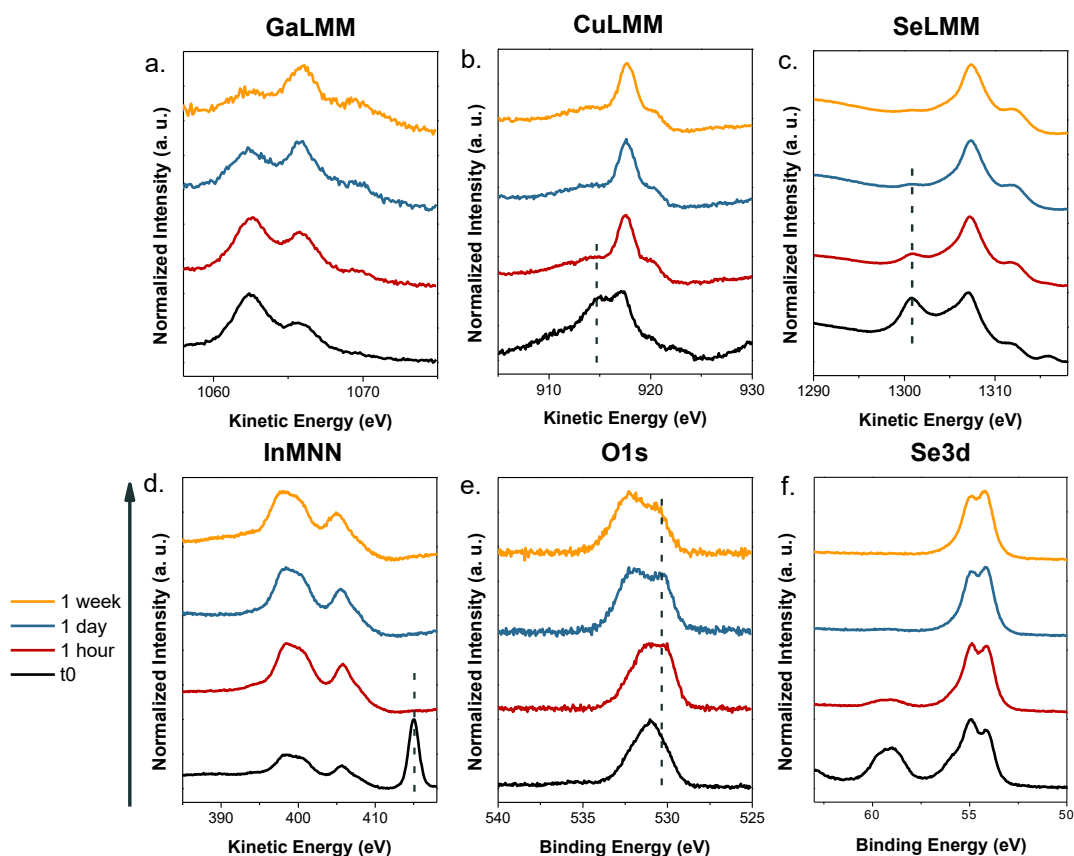
114

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

126

127 3.2. Immersion of aged CIGS surfaces

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



135

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

139

140 After one hour immersion, the Cu oxide contribution fully disappears (Figure 2 b.) as well as
141 the Na initially present on aged surface (Figure 2 d.). Moreover, a decrease of Se oxide Auger
142 feature is observed (Figure 2 c.), in agreement with the disappearance of the oxide contribution
143 in the Se3d spectral window (Figure 2 f.). After one day immersion, the entire SeO_x contribution
144 has disappeared. Concerning Ga, peak ratios between CIGS and oxide contributions (Figure 2
145 a.) progressively reverse in favor of the CIGS environment. After **one-week** immersion, **Cu and**
146 **Se** oxides have totally disappeared and the surface presents In_{ox} , residual Ga_{ox} and Se^0 (Figure
147 2 d. and e.) All these evolutions are correlated with the decrease of the O1s oxide contribution
148 at 531.0 ± 0.1 eV (BE) (Figure 2 e.). As expected, the In oxide contribution doesn't present any
149 evolution over water immersion (Figure 2 d.). Finally, this experiment informs about the
150 dissolution kinetics of the surface oxide layer on aged CIGS sample: $\text{Cu}_{\text{ox}} > \text{Se}_{\text{ox}} > \text{Ga}_{\text{ox}}$, In_{ox}
151 being almost insoluble.

152

153 3.3. ICP-OES measurements

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

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

171

172 4. Conclusion

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

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- 233

234 **Table 1: GGI and CGI ratios evolution of CIGS surfaces aged in H₂O environment, calculated from the Ga2p_{3/2}, Cu2p_{3/2}**
235 **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

236

237

238

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

	Concentration ($\mu\text{g L}^{-1}$) $\pm 10 \mu\text{g L}^{-1}$				
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

241