

## Study of Crystallographic Properties and Elemental Migration in two-stage prepared Cu(In,Al)Se<sub>2</sub>

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### Abstract

CuInAl metallic precursor films were selenised at different temperatures and the migration of the elements investigated. GD-OES was used to determine the elemental depth profiles, and XRD analysis gave an insight into the phase transformations taking place. These combined techniques made it possible to study the diffusion and reaction processes taking place during the selenisation stage. Post selenisation annealing was also investigated, which led to partial incorporation of the Al into the CuInSe<sub>2</sub> lattice.

### Introduction

The most efficient thin film solar cell to date is based on a Cu(In,Ga)Se<sub>2</sub> (CIGS) absorber layer [1]. However, CIGS devices suffers from a drop of its open-circuit voltage ( $V_{OC}$ ) for  $Ga/(In+Ga) > 0.3$  [2]. As a consequence, the best devices are made with an effective band gap  $E_G \approx 1.15$  eV [3] some distance away from the 1.35 eV optimum [4]. An alternative to CIGS is Cu(In,Al)Se<sub>2</sub> (CIAS), obtained by replacing Ga by Al. Band gaps identical to CIGS can be obtained with less lattice strain in CIAS, and its band gap ranges between 1.0 eV (CuInSe<sub>2</sub>) and 2.7 eV (CuAlSe<sub>2</sub>), against 1.0 to 1.7 eV for CIGS. This should make CIAS a suitable candidate for both single and tandem junction cells. CIAS devices of efficiencies up to 16.9% can be obtained by co-evaporation [5]. The two-stage process, however, yields lower performance, due notably to an observed migration of the Al towards the back contact of the film during the selenisation of the CuInAl metallic precursors [6, 7]. To better understand this segregation, the diffusion and reaction of the different elements of the CIAS film were studied in detail, before focusing on the particular behaviour of Al.

### Experimental

CuInAl metallic precursors were deposited on 850 nm thick Mo-coated soda lime

glass (SLG) substrates by RF-magnetron sputtering from elemental targets. The substrates were continuously rotated underneath the targets so as to deposit a succession of very thin ( $\approx 1$  nm thick) elemental layers. The resulting precursors were  $\approx 650$  nm thick. A 100 nm thick Cu layer ("cap") was added at the end of the sequence. Samples were subsequently coated with  $\approx 2$   $\mu$ m of Se and selenised in a tube furnace, in an atmosphere of 6 mbar of Ar. The heating profiles are described in Table 1.

Table 1: Selenisation steps summary. The average ramping rate was  $\approx 18$  °C/min, the dwell time for each step 30 min, and the cooling rate 1 °C/min.

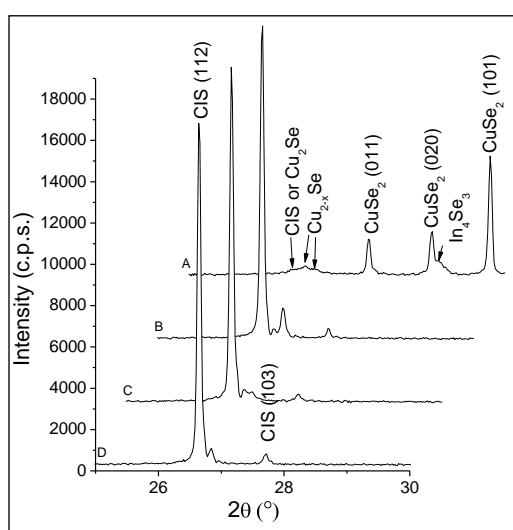
Name	Selenisation steps
A	130 °C/250 °C
B	130 °C/250 °C/350 °C
C	130 °C/250 °C/450 °C
D	130 °C/250 °C/540 °C

A 1 hour post-selenisation anneal at 570 °C in a 10 mbar Ar atmosphere and with no extra Se, was later applied in some cases. The crystalline phases present in the samples were analysed by X-ray diffraction (XRD) and the distribution of the elements throughout the bulk was characterised by glow discharge optical emission spectroscopy (GD-OES) with a Horiba Jobin Yvon GD-Profilier 2 using a 13.56 MHz radio frequency generator. Measurements were carried out at 350 Pa of Ar and at 20 W in pulsed mode at 3 kHz (pulse duration of 0.1 ms).

### Results

The precursor films consisted in a bulk matrix containing Cu, In and Al, followed by a 100 nm thick Cu cap. The atomic composition of the precursors' bulk (i.e. without the top Cu layer) was 50% Cu, 44% In and 6% Al. The Cu cap has been reported to limit the oxidation of the film, in particular Al [6]. However, the bulk

composition being nearly stoichiometric, this Cu layer was likely to yield, in case of complete diffusion into the bulk, to a relatively Cu-rich bulk composition, and therefore to the presence of remaining copper selenide phases at the end of reaction. The XRD spectra of the 4 selenised samples are shown in Figure 1 and the phases identified summarized in Table 2. Low crystallinity phases are not indicated in the figure for clarity. The XRD analyses showed the presence of the berzelianite  $\text{Cu}_{2-x}\text{Se}$  in all selenised samples. In sample A, the binary selenides  $\text{CuSe}_2$  and  $\text{In}_4\text{Se}_3$  and possibly the chalcopyrite  $\text{CuInSe}_2$  (CIS) were detected.



**Figure 1: XRD spectra of samples A, B, C and D after selenisation**

CIS could not be clearly distinguished from  $\text{Cu}_2\text{Se}$  because of the low crystallinity of the phases, and therefore no definitive affirmation can be made. The spectrum also showed the presence of small  $\alpha\text{-In}_2\text{Se}_3$ ,  $\text{Cu}_{16}\text{In}_9$  and elemental In reflections indicative of incomplete conversion at this low temperature.

Table 2: XRD crystalline phases

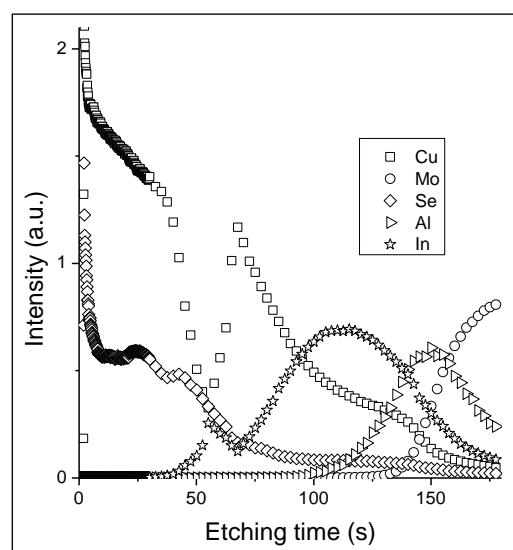
Name	XRD phases
A	$\text{CuSe}_2$ , $\text{Cu}_{2-x}\text{Se}$ , $\text{In}_4\text{Se}_3$ , $\text{Cu}_2\text{Se}^*$ , $\text{CuInSe}_2^*$ , $\alpha\text{-In}_2\text{Se}_3^*$ , $\text{Cu}_{16}\text{In}_9^*$ , $\text{In}^*$
B	$\text{Cu}_{2-x}\text{Se}$ , $\text{CuInSe}_2$ , $\text{Cu}_{16}\text{In}_9^*$ , $\text{In}^*$
C	$\text{Cu}_{2-x}\text{Se}$ , $\text{CuInSe}_2$ , $\text{Cu}_{16}\text{In}_9^*$ , $\text{In}^*$
D	$\text{Cu}_{2-x}\text{Se}$ , $\text{CuInSe}_2$

\* Traces only or low crystallinity phase

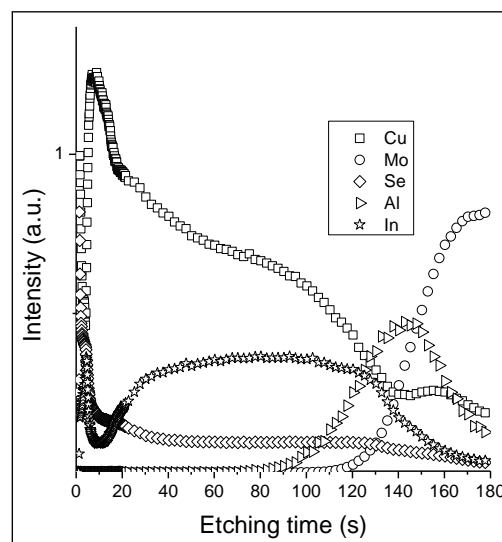
For a maximum temperature of  $350^\circ\text{C}$  (sample B),  $\text{In}_4\text{Se}_3$  and  $\text{CuSe}_2$  reflections have disappeared, while CIS has become more crystalline, and  $\text{Cu}_{2-x}\text{Se}$  and some

$\text{Cu}_{16}\text{In}_9$  and In reflections remain. The same phases were observed at  $450^\circ\text{C}$  (sample C), and finally only CIS and  $\text{Cu}_{2-x}\text{Se}$  were visible at  $540^\circ\text{C}$ . No Al-containing phase was observed in any of these samples.

To gain understanding of the physical and chemical processes behind the observed phases, depth profiles of the samples were performed by GD-OES. Even if the measurement was not calibrated for quantitative analysis, GD-OES is stable with respect to matrix effects.



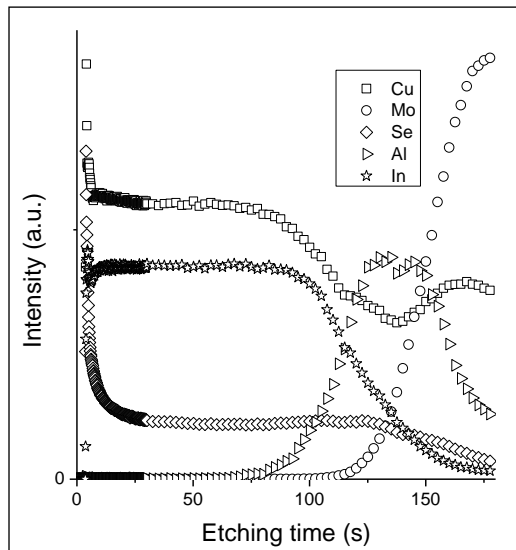
**Figure 2: GD-OES depth profile of sample A, selenised at  $130^\circ\text{C}$ - $250^\circ\text{C}$**



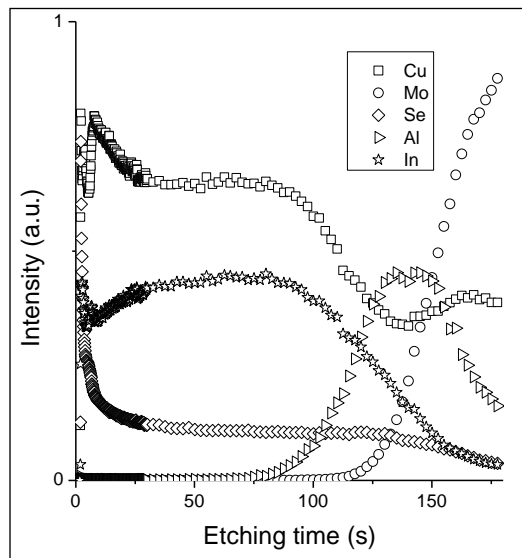
**Figure 3: GD-OES depth profile of sample B ( $130^\circ\text{C}$ - $250^\circ\text{C}$ - $350^\circ\text{C}$ )**

In sample A (Figure 2), the profile of the element Cu shows partial diffusion from the cap into the bulk, resulting in a sloped profile, with however a notable “notch” around  $t=55\text{s}$ . The amount of Se is higher at the front, where it originated from, and

decreases towards the back. The element In is mostly at the back of the film, but a small amount has diffused to the depth where the notch in Cu is observed. Most remarkable is the aggregation of the Al at the back of the film, already at this relatively low temperature. Compared with A, sample B (Figure 3) shows an enhanced interdiffusion of all the elements with the exception of Al, which remains located at the back of the film. Note that the notch in the Cu profile is no longer present.



**Figure 4: GD-OES depth profile of sample C (130°C-250°C-450°C)**



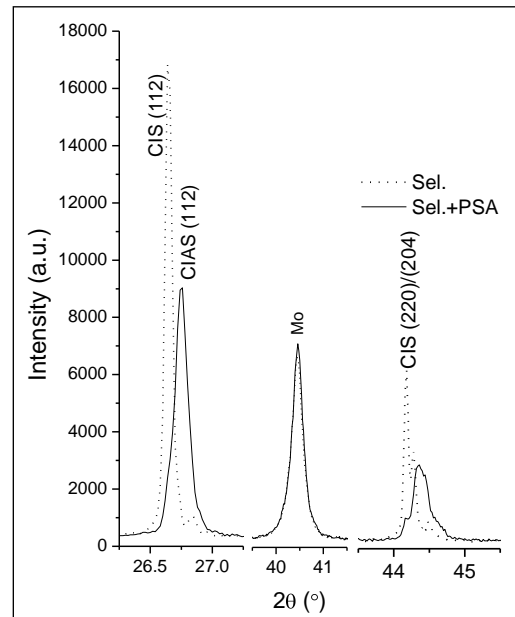
**Figure 5: GD-OES depth profile of sample D (130°C-250°C-540°C)**

In sample C (Figure 4) Cu, In and Se are distributed fairly evenly, whereas Al shows a somehow increased presence in the bulk compared to B. Finally, the depth profile of sample D (Figure 5) is very similar to that

of sample C for all the elements, with however an increased presence of Cu at the front, which likely indicates the segregation of the copper selenide phase.

#### Post-selenisation anneal (PSA)

In an attempt to obtain rediffusion of the Al in the bulk, an additional anneal of 1 hour was performed on sample D at 570°C in an Ar atmosphere of 10 mbar. This treatment, was reported by Marudachalam et al. [8] to yield rediffusion of segregated Ga in two-stage processed CIGS. The XRD spectrum of sample D after the treatment is displayed in (Figure 6).

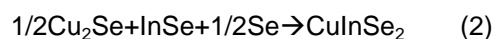


**Figure 6: XRD spectra of sample D before (dotted line) and after (solid line) post-selenisation anneal**

It clearly shows a modified CIS phase which peaks are shifted towards higher angles. This suggests the incorporation of Al into the CIS lattice, forming a CIAS phase. Indeed, Al atoms are smaller than In and lead to reduced lattice parameters, which in turn translates into a shift of the XRD reflections towards high angles. A small CIS reflection is however still present. The reflectance measurement was performed on PSA sample D, and showed no change in the cutting wavelength, corresponding to CIS band gap.

#### Discussion

First of all, let us discuss the known reaction pathways to form CIS. Two of the CIS formation paths reported in the literature [9] can apply to this work:



Reaction (1) starts at the melting point of Se, 221°C, with the formation of binary selenides, and is relatively slow. The required selenides can be formed via:



Reaction (2) starts at 380°C, and is faster than (1). It proceeds via the intermediary reaction:



These reaction pathways can be compared to the XRD spectra and the GD-OES depths profiles in order to understand the trends observed.

In sample A (250°C), the Se and the Cu cap have only partially diffused into the bulk, leading to a surface containing the elements Cu and Se, a bulk containing mostly Cu, In and a little amount of Se, and a back layer rich in Al. Most of the copper selenides  $\text{CuSe}_2$  and  $\text{Cu}_{2-x}\text{Se}$  observed by XRD are therefore likely to be located in the upper part of the absorber. Only reaction (1) could account for the possible presence of CIS in sample A. At the low crystallinity observed, CIS cannot be distinguished from  $\text{Cu}_2\text{Se}$ . The strong presence of the characteristic reflections of  $\text{In}_4\text{Se}_3$  and  $\text{CuSe}_2$  and the low presence of Se in the major part of the bulk seems to have prevented reactions (3) and (1) from occurring more than marginally. The notch observed in the Cu profile could arise from the presence of  $\text{In}_4\text{Se}_3$  in this region. It could have formed from In islands often observed in cap-free precursors, which aggregate at the bulk surface but could have been buried underneath the Cu cap.

In sample B (350°C), the CIS phase shows an important growth resulting from the total consumption of  $\text{CuSe}_2$  and  $\text{In}_4\text{Se}_3$ , to form CIS. This was most likely made possible by the peritectic decomposition of  $\text{CuSe}_2$  into CuSe and a Se melt at 340°C, to form CIS via (1). A better penetration of the Se from the front into the bulk is also a factor in this important growth.

In sample C (450°C), the maximum temperature was high enough to consume some of the  $\text{Cu}_{2-x}\text{Se}$  to form CIS via reaction (2). This is supported by the dampening of the (111)  $\text{Cu}_{2-x}\text{Se}$  reflections the most shifted towards high angles and

the slight growth of the CIS phase compared to B.

Sample D (540°C) is very similar to C, since all the selenides had already been consumed in C. The increased presence of Cu at the surface is indicative of an increased volume of the  $\text{Cu}_{2-x}\text{Se}$  phase.

The absence of Al from the XRD phases suggests that it must be found in an amorphous or too low crystallinity phase. A likely candidate is the oxide  $\text{Al}_2\text{O}_3$ , which is known to form very easily and fast.  $\text{Al}_2\text{O}_3$  was reported to be present at the back of CIAS films in [6], but was not detected here.

Depth profiles show that the segregation of Al at the back has already taken place at 250°C (sample A). This phenomenon is very similar to the observed segregation of Ga at the back of two-stage processed CIGS [8]. The most commonly advanced reason for this phenomenon is the relatively high temperature of formation of Ga selenides compared to In selenides [8, 10]. This hypothesis also applies for CIAS, since the only known selenide of aluminium is  $\text{Al}_2\text{Se}_3$ , which was reported to form at 480°C [11], against 221°C for the first In selenides. At the melting point of Se, In and Cu are driven towards the front by the formation of selenides with the liquid Se which started diffusing, while Al stays at the back since it cannot form any selenide. As the temperature increases, the binary selenides of In and Cu will then go onto forming CIS, and the Al will stay at the back until 480-490°C, when it will start forming CIAS and/or CAS [11]. At this stage, only interdiffusion between the CIS at the front and the CAS (or low In-content CIAS) at the back can yield a single phase CIAS bulk. This interdiffusion clearly did not occur in the selenised samples.

When sample D is re-annealed without Se, however, its XRD spectrum is interpreted as containing almost single phase CIAS. This means that Al has rediffused towards the bulk, and been incorporated into the CIS lattice. However, there is still a small reflection corresponding to pure CIS, which tends to indicate that the rediffusion is not complete, and some Al-free CIS is still present near the surface. This would also account for the fact that the reflectance spectrum remains virtually unchanged after PSA. Indeed, the reflected beam interacts only with a very shallow depth of the sample near its

surface (typically no more than a few tens of nanometers). The XRD suggests that the Al has not diffused so close to the surface, and therefore the band gap of the buried CIAS phase is not detected.

### Conclusion

CuInAl thin films were selenised at temperatures ranging 250-540°C. XRD and GD-OES analyses showed no formation of the quaternary CIAS compound due to excessive difference in formation temperature of the binary selenides. The Al migration towards the back of the film was found to occur for temperature as low as 250°C. A post selenisation anneal at high temperature indicated a partial re-diffusion of Al through the film and this could be a new route towards fabricating single phase CIAS.

### Acknowledgements

Part of this work was funded by the EPSRC SUPERGEN programme "Photovoltaics for the 21<sup>st</sup> Century".

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