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# CuIn<sub>1-x</sub>Al<sub>x</sub>Se<sub>2</sub> thin film solar cells with depth gradient composition prepared by selenization of evaporated metallic precursors



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## ABSTRACT

Polycrystalline CuIn<sub>1-x</sub>Al<sub>x</sub>Se<sub>2</sub> (CIASe) thin films have been prepared on bare and Mo-coated substrates by selenization of evaporated Cu–In–Al precursors layers with  $0 \leq x \leq 0.3$  and thicknesses below 1.4 μm. X-ray diffraction measurements show several peaks around the (112) reflection corresponding to CIASe phases with different Al contents. This has been attributed to the existence of a depth compositional gradient in the layers with higher Al contents due to a diffusion of Al towards the back contact region. Raman scattering measurements directly performed with the excitation laser spot on both the front and back surfaces from absorbers that were previously mechanically removed from the Mo coated substrates confirm the existence of complex CIASe absorbers with graded Al content, which leads to a corresponding grading of the absorber bandgap. Enrichment of Al content at the back contact region is also accompanied by a decrease of the grain size as shown by cross-sectional Scanning Electron Microscopy (SEM). The best CIASe based solar cells have  $J_{sc}$ ,  $V_{oc}$ , FF and efficiencies of **29.3 mA/cm<sup>2</sup>**, **430 mV**, **51.1%** and 6.5%, respectively, for an overall Al/(In+Al) relative content  $x \sim 0.2$ . Comparison of these values with those from equivalent devices made without Al show a significant increase of the device efficiency. These data confirm the existence of a significant improvement of the device performance because of the increased absorber bandgap in the CIASe quaternary alloys.

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## 1. Introduction

CuInSe<sub>2</sub> (CISe) thin film solar cells have been widely studied for a long time and currently have reached notable importance in the photovoltaic (PV) market. In order to increase the CISe band gap energy for an optimal match with the solar spectrum, alloys with Ga or S are usually employed. Efficiencies above 20% at laboratory scale have been reported for CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> (CIGSe) with a Ga/(In+Ga) content around 0.3 [1,2]. However, increase of the Ga content further than 0.3 degrades the electronic properties of CIGSe thin film based junctions [3]. In order to seek new and cheaper semiconductors for PV applications, CuIn<sub>1-x</sub>Al<sub>x</sub>Se<sub>2</sub> (CIASe) has been considered as a promising alternative since it requires a smaller relative Al content than Ga in CIGSe to obtain similar band gap energy and Al is cheaper and more abundant in the earth crust than Ga. The band gap energy ( $E_g$ ) of CIASe can be tuned in a wide

range from 1.0 eV (CISe) to 2.7 eV [4] (CuAlSe<sub>2</sub>) by partial substitution of In by Al. CIASe thin films have been prepared by several techniques that includes co-evaporation from elemental sources [5–9], Molecular Beam Epitaxy (MBE) [10], sputtering deposition/thermal evaporation [11–15], electrodeposition [16,17], flash evaporation [18] and non-vacuum coating techniques based on oxides nanoparticles [19]. However, since the development of the first CIASe thin films solar cells in 2002, very few works have been reported on devices, most of them based on co-evaporation methods [5–10,14,20–24]. Reported efficiencies of devices based on a CIASe thin film absorber have been illustrated in Fig. 1 as a function of the Al/(In+Al) relative content,  $x$ . In 2002, CIASe devices prepared by a multisource evaporation method from elemental Cu, In, Al, and Se sources with absorber thicknesses around 2–2.5 μm and antireflecting coating (ARC) exhibited a conversion efficiency of 16.9% [21], 0.4% better than equivalent CIGS devices with similar bandgaps built along with them. One important issue to be face is the poor adherence of the CIASe thin films to Mo-coated substrates, usually attributed to high Al contents or high selenization temperatures [5,8] but it can be also due to film stress in thicker layers [14]. Some authors have included a Ga thin layer to increase the adherence to the Mo substrates [21]. The typical absorber thickness of the

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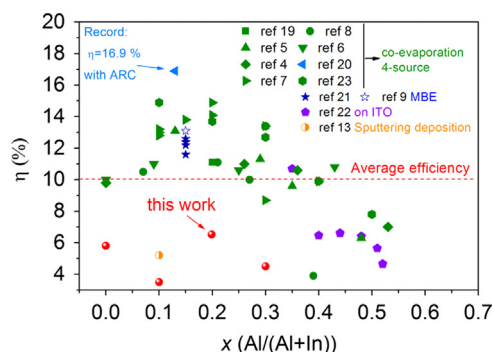


Fig. 1. CIASE solar cells efficiencies reported as a function of the Al/(In + Al) relative content.

reported devices ranged from 2 to 3  $\mu\text{m}$ , except in the case of sputtering deposition, where thicknesses below 1.7  $\mu\text{m}$  are typically used. It is observed that the highest efficiencies have been obtained for a relative Al/(In + Al) content  $\leq 0.2$ , lower than the equivalent relative Ga/(In + Ga) content of 0.3 that is typically required for CIGS solar cells [1]. In comparison with Ga in CIGSe and according to the reported efficiencies, system CuInAlSe<sub>2</sub> seems to allow a wider range of variation in the Al composition to achieve high efficiencies.

On the other hand, it is known that in the 2-stage processes Ga tends to segregate taking place an in-depth Ga distribution resulting in a band gap grading through the thickness of the layers. A V-shape profile Ga distribution is normally obtained with a 3-stage process. Similar composition gradient due to Al diffusion has also been observed for CIASE thin films with higher Al contents [14,15].

In this paper, we report the detailed structural and compositional analysis of CIASE thin films that were synthesized by a two stage process involving the sequential e-beam evaporation of the metallic precursors followed by a recrystallization step under selenization conditions. Layers were synthesized with different overall nominal compositions – corresponding to relative Al/(In + Al) relative contents between 0% and 30% – and with thicknesses in the range 1.3–1.4  $\mu\text{m}$ , to avoid adherence problems on the Mo coated substrates. Optimization of these processes requires for a deeper knowledge of their impact on the structural and compositional characteristics of the processed layers which, in turn, are determining for the optoelectronic characteristics of the corresponding devices. Analysis of the characteristics of the solar cells fabricated with these layers has allowed determining the main mechanisms likely limiting the device efficiency. Comparison of these data with those from equivalent devices fabricated without Al – using CuInSe<sub>2</sub> absorbers – and with equivalent Cu(In,Ga)Se<sub>2</sub> alloys corroborate the viability of the proposed Al based alloys for the development of high efficiency solar cells.

## 2. Material and methods

### 2.1. CuIn<sub>1-x</sub>Al<sub>x</sub>Se<sub>2</sub> (CIASE) thin films formation

Cu, In and Al precursor layers were sequentially deposited onto bare and DC sputtered 1  $\mu\text{m}$ -Mo-coated soda lime glass (SLG) substrates by e-beam evaporation of Cu and In and thermal evaporation of Al from a tungsten crucible in a vacuum chamber with a base pressure of  $10^{-5}$  Pa. The Al and In thicknesses were adjusted in order to vary the  $x = \text{Al}/(\text{Al} + \text{In})$  composition ratio between  $x = 0$  and  $x = 0.3$ . In order to improve the film homogeneity, the substrates were rotated during the precursor deposition. Furthermore, an oscillatory quartz crystal microbalance monitored the growth rates and thicknesses of the individual

layers inside the vacuum chamber. In order to ensure the natural Al diffusion towards the back contact and avoid the Al oxidation on the surface, the metallic layers were sequentially evaporated following the sequence SLG/Mo/In/Cu/Al/In. Thickness of the precursor layers was selected to obtain a thickness of the absorbers in the range 1.3–1.4  $\mu\text{m}$  after the selenization step. This allowed avoiding adherence problems in the layers and most of them survived to the device manufacture.

The metallic precursor layers were annealed under inert Ar atmosphere in the presence of reactive elemental selenium within a partially closed graphite box that was placed inside a quartz tube furnace. A small hole in the center of the box lid ensured an energetic over-pressure of Se during the selenization process. Excess Se leaked through the hole to balance the over pressure. The Se amount was varied over a wide range from 120 to 240 mg for  $2 \times 6 \text{ cm}^2$  precursor areas. The selenization process was performed in three steps based on the well known temperature–time profile reported for the crystallization of CuInSe<sub>2</sub> [25] increasing the temperature up to 773 K because the formation of the quaternary compound starts at a higher temperature (above 763 K) [26]. CIASE thin films with thickness of about  $1.3 \pm 0.1 \mu\text{m}$  were achieved after selenization. In order to remove potential Cu–Se secondary phases, a KCN treatment of the CIASE films in aqueous solution 0.5 M for 2 min at 40 °C was carried out.

Solar cells were fabricated without Al-grids and ARC by chemical bath deposition (CBD) of 50 nm-thick CdS and DC sputtering deposition of 50 nm-ZnO:i and 450 nm-ZnO:Al (AZO) layers. The active cell area was 0.09  $\text{cm}^2$  which was defined by mechanical scribing.

### 2.2. Characterization of the films

The structural characterization of the CIASE samples was carried out by means of X-ray diffraction (XRD) using a PHILIPS X'PERT diffractometer with  $\text{CuK}\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ ) radiation at room temperature. Morphology and composition were analyzed by a ZEISS series Auriga Field Emission Scanning Electron Microscopy (SEM) and by Energy Dispersive X-rays (EDX), respectively. Samples were characterized structurally by Raman scattering using a HR-320 Horiba Jobin-Yvon spectrometer with a solid state 532 nm laser as the excitation source, and aT64000 Horiba Jobin-Yvon spectrometer with the 514 nm line from an Ar<sup>+</sup> laser as the excitation source. For the used excitation wavelengths, the penetration depth of scattered light in CuInSe<sub>2</sub> related compounds is estimated around 100 nm. In both cases, the first-order Raman peak of monocrystalline silicon was measured as a reference before and after acquisition of each Raman spectrum, and the spectra were corrected with respect to the silicon peak position at  $520 \text{ cm}^{-1}$ . The film thickness and arithmetic average roughness were measured by a DEKTAK profilometer. For the optoelectronic characterization of the CIASE solar cells, illuminated current density–voltage, *J*–*V* curves were obtained using an ABET Technologies Sun 3000 Class AAA solar simulator under 100  $\text{mW}/\text{cm}^2$  air mass AM1.5 illumination conditions at 25 °C. The external quantum efficiency (EQE) of the devices was also measured and compared with the absorber composition and the device optoelectronic properties using a Bentham PVE300 equipment in the wavelength region between 300 nm and 1600 nm.

## 3. Results and discussion

The overall composition of the CIASE samples has been measured by EDX. Samples have been grown stoichiometrically and are slightly Se-poor as shown in Table 1.

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