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Crystallographic properties and elemental migration in two-stage prepared $CuIn_{1-x}Al_xSe_2$ thin films for photovoltaic applications

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ABSTRACT

Two-stage fabrication of $CuIn_{1-x}Al_xSe_2$ thin films for photovoltaic absorbers using sputtered Cu–In–Al metallic precursors has been investigated. Precursors containing different relative amounts of Al were selenised and their structural and chemical properties characterised. X-ray diffraction (XRD) analyses revealed that the Al was only incorporated into the chalcopyrite structure for precursor composition ratios $x = [Al]/([Al] + [In]) \geqslant 0.38$, while chemical analysis of the cross-section indicated partial segregation of Al near the back of the film. Precursor films in the range of compositions that yielded no Al incorporation were then selenised at four different temperatures. Glow discharge optical emission spectroscopy, plasma profiling time-of-flight mass spectrometry and XRD analyses provided an insight into the diffusion processes and reactions taking place during the selenisation stage. The effect of post-selenisation annealing without additional Se was also investigated, and led to partial incorporation of the Al into the $CuInSe_2$ lattice but no rediffusion.

1. Introduction

The most efficient thin-film solar cells to date, with a record efficiency of 20.3 ± 0.6% [1], are based on a $CuIn_{1-x}Ga_xSe_2$ (CIGS) absorber layer. $CuIn_{1-x}Ga_xSe_2$, like $CuInSe_2$ (CIS), is chalcopyrite, with Ga substituting In in the ratio $x = [Ga]/([Ga] + [In])$. This ratio can be altered to tune the band gap between that of $CuInSe_2$ (CIS), 1.0 eV, and that of $CuGaSe_2$ (CGS), 1.7 eV [2,3]. In an ideal device, a band gap increase yields, in terms of current–voltage (I–V) characteristics, an increase of the open-circuit voltage (V_{OC}) and a parallel decrease of the short-circuit current (I_{SC}). As a result there exists an optimal band gap for single junction devices, representing the best trade-off between V_{OC} and I_{SC}. According to detailed balance calculations, and because of the specific bands of absorption of the solar spectrum in the atmosphere, two band gaps actually yield almost equal optimal efficiencies under air mass 1.5 illumination: 1.15 eV, with 32.8% efficiency, and 1.35 eV, with 33.0% efficiency [4]. In CIGS devices, the V_{OC} increase with band gap becomes less pronounced for $x > 0.3$, due to increasing defect concentrations [5]. This $x = 0.3$ ratio corresponds, if the Ga distribution is uniform, to a band gap of ≈1.2 eV [3]. For this reason, the best performing solar devices are made with the nearest optimal (effective) band gap $E_G \approx 1.15$ eV [6,7]. However, being able to reach the higher band gap optimum without V_{OC} degradation would help to reduce resistive losses in solar cells, and even more so in modules, where the current has to be transported over greater distances and where cell interconnects are present [2]. An alternative to CIGS is $CuIn_{1-x}Al_xSe_2$ (CIAS), obtained by replacing Ga by Al. The CIAS band gap is tunable over a much wider range than CIGS: from 1.0 eV for CIS to 2.7 eV for $CuAlSe_2$ (CAS). CIAS devices of efficiencies up to 16.9% have been obtained by Marsillac et al. by co-evaporation [8]. This latter device performed 0.4% better than an equivalent CIGS device of identical band gap (1.15 eV) built along with it, which suggests reduced losses in CIAS. Several specificities of CIAS might explain this result. Among them, the fact that less Al is required in CIAS to reach a given band gap than the amount of Ga necessary to reach the same band gap in CIGS. Furthermore, since both $CuAlSe_2$ and $CuGaSe_2$ have similar lattice parameters [9,10] then, according to Vegard's law, CIAS films with identical band gap to CIGS can be fabricated with less lattice strain, compared to the lattice of $CuInSe_2$. By reducing the lattice strain, less crystal defects (e.g. dislocations) are likely to form.

CIAS could therefore find applications in single junction solar devices (i.e. to reach 1.35 eV with reduced losses) as well as in tandem or multi-junction devices, where the different combinations of band gaps identified as optimum can be reached. For this work, the so-called two-stage process was chosen over co-evaporation because it is easier to scale-up and yields equivalent or higher efficiencies for CIGS devices at the module scale [11]. In this article, we

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present the crystallographic properties of CIAS thin films produced by selenisation of sputtered metallic precursors as a function of metallic precursor composition and selenisation conditions.

2. Experimental

Cu–In–Al metallic precursors were sputter-deposited on a soda lime glass (SLG) substrate coated with an 850 nm thick Mo back contact layer. A Nordiko 2000 radio frequency (RF) magnetron sputtering system with elemental targets was used for depositing the back contact and the metallic precursors. The system geometry was set up for sequential deposition. The substrates were continuously rotated (5 rpm) underneath the targets so as to deposit a succession of very thin (≈1 nm thick) elemental layers.

The metallic precursor thicknesses, as measured by stylus profilometry, were in the range 1100 ± 200 nm for the samples of Section 3.1 and ≈650 ± 60 nm for those of Section 3.2. An additional 100 nm thick Cu capping layer was deposited on top of the precursors of Section 3.2 because it has been reported to limit the oxidation of the Al [12]. After selenisation, the thicknesses for the samples grown in both Sections 3.1 and 3.2 were in the range 2.4–2.6 μm and 2.0–2.3 μm, respectively. Note that the error on the thickness measurements was due to a high surface roughness on as-deposited precursors. This phenomenon is due to In “islands” protruding from the surface (see Ref. [13] for more details). These islands were already reported to form in Cu–In precursors for [In]/[Cu] > 2 by Chung et al. [14]. They were systematically observed in the precursors produced in our setup when both In and Al were present.

Elemental Se was thermally evaporated on the metallic precursors in a K.J. Lesker Nano38 system, and the films were subsequently annealed in a 3-zone large bore Carbolite GHC 12/450 tube furnace. Samples were loaded in a quartz tube and pumped down to ≈0.1 Pa before injecting a pure atmosphere of Ar or H_2/N_2 prior to the annealing process. The thickness of the selenium was varied between 2.2 μm and 3.0 μm, depending on the precursor thickness, to allow full conversion of the precursor into CIAS. Imaging of the cross-section was performed in a FEI Quanta 200 secondary electron microscope (SEM). The chemical properties of the bulk were characterised by energy dispersive (EDS) or wavelength dispersive (WDS) X-ray spectroscopy with Oxford Instruments INCA ENERGY or INCA WAVE spectrometers, respectively. Note that EDS compositions were affected by partial overlapping of the Al K series and the Se L series when these two elements were present. Indeed, the energy difference between the two series is less than 90 eV, lower than the 133 eV limit of resolution of the instrument. The error resulting from this partial overlap was not precisely quantified, but must be bore in mind for the interpretation of the data from Table 3. WDS, on the other hand, offers a much higher resolution (typically 5 eV) and can resolve the Al K series and Se L series. This is the reason why it was used for the detection of these two elements in Section 3.1, in parallel with EDS for the remaining elements. However, quantitative analysis with WDS requires prior calibration, for which the appropriate calibration standards were not available to us. Therefore, the results of the WDS/EDS experiment on A3′ (Fig. 4) were only qualitative. For clarity, the ratios $x = [Al]/([Al] + [In])$ are noted x_p, x_s and x_{xrd} depending on whether they were measured on the as-deposited precursor, on the selenised sample or calculated from the X-ray diffraction (XRD) data, respectively.

The structural properties were analysed by XRD in a Brüker D5000 diffractometer. The chemical depth profiles were measured in two Horiba Scientific instruments using glow discharge-based techniques: a Plasma Profiling Time-of-Flight Mass Spectrometer (PP-TOFMS) and a GD-Profiler 2 Glow Discharge Optical Emission Spectrometer (GD-OES). These two techniques have low matrix effects and average the signal over large areas to reduce the effect of local features or inhomogeneities. Deposition and processing data for the samples of this article are summarised in Table 1.

3. Results and discussions

3.1. Impact of precursor composition on the level of alloying with Al

The effect of altering the $x_p = [Al]/([Al] + [In])$ ratio, as measured in the metallic precursors, was tested on four samples selenised in similar conditions. A1, A2 and A3 were selenised at 530 °C under 1000 Pa of H_2/N_2 and A4 at 540 °C under 1000 Pa of Ar. Note that selenisation trials under Ar and H_2/N_2 atmospheres have been compared and led to no obvious variation, so that the change from one to the other is considered as neutral. The difference in selenisation temperature between A1 and A3 (530 °C) and A4 (540 °C), on the other hand, could have induced some limited variation, so that A4 is included for qualitative comparison only. The XRD results for the selenised samples are reported in Fig. 1.

The composition ratios $x_p = 0.11$ (A1) and $x_p = 0.27$ (A2) did not yield any incorporation of the aluminium into the CIS (powder diffraction file PDF 01-078-2001) lattice, and the element was not present in any detectable crystalline form. For $x_p = 0.38$ (A3), however, Al-incorporation was observed. The pattern of this sample reveals several broad, overlapping peaks, which remained after potassium cyanide etching, indicating that they belong to multiple $CuIn_{1-x}Al_xSe_2$ phases (with different x values) and not to $Cu_{2-x}Se$ [15]. At $x_p = 0.51$ (A4), also, some CIAS was observed, although only as traces, and In-free CAS (PDF 00-044-1269) was detected. The presence of CAS is implied from the relative increase in the intensity and area of the peak normally assigned to CIS (1 0 3), in comparison to the CIS (1 1 2) peak. The level of incorporation of aluminium observed in A3 was shown to vary from sample to sample. A3′, consisting of the same metallic precursor and selenised together with A3, also showed some incorporation of Al, but the XRD pattern suggests a different distribution of this incorporation (Fig. 2). In particular, some Al seems to have segregated completely from the In, causing the formation of a $CuAlSe_2$ phase (PDF 00-044-1269).

GD-OES was performed on sample A3 and the depth profiles are presented in Fig. 3. A certain depth of film is removed at each sputtering cycle, so that the *x*-axis (“sputtering time”) can be associated with the depth into the sample. $t = 0$ s therefore corresponds to the film upper surface, while the drop of all but Mo signal for $t > 250$ s indicates that the interface of the film with the back contact has been reached. The Al signal has a maximum in region *a* and then a dip and a gradual increase towards the back (region *b*). Indium is depleted in region *a* and follows a reverse trend to Al in region *b*, with a decreasing gradient towards the back contact. Cu and Se are maximum at the surface and evenly distributed throughout the bulk. Oxygen (not shown) also increases at the surface and is almost absent from region *b*. The interface with the back contact ($180\ s < t < 250\ s$) is believed to be relatively rough, so that

Table 1

Deposition and processing data for the samples presented. EDS compositions for samples B1–B4 are overall compositions including the Cu capping layer. They were extrapolated from the precursor composition and mass before capping, and the thickness of the Cu cap.

ID	Layout	Comp. (at%)			Se	Gas	Pressure (Pa)	Dwell Temperature	Dwell duration (min.)	Ramp duration (min.)
		Cu	In	Al						
A1	Cu–In–Al	46.0	48.0	6.0	Yes	H_2/N_2	1000	530	30	≈30
A2	Cu–In–Al	48.0	38.0	14.0	Yes	H_2/N_2	1000	530	30	≈30
A3	Cu–In–Al	49.0	31.5	19.5	Yes	H_2/N_2	1000	530	30	≈30
A4	Cu–In–Al	48.0	25.0	27.0	Yes	Ar	1000	540	30	≈30
A3′	Cu–In–Al	49.0	31.5	19.5	Yes	H_2/N_2	1000	530	30	≈30
B1	Cu–In–Al/Cu	62.0	33.8	4.2	Yes	Ar	600	130–250	30 (x2)	≈13
B2	Cu–In–Al/Cu	62.0	33.8	4.2	Yes	Ar	600	130–250–350	30 (x3)	≈20
B3	Cu–In–Al/Cu	62.0	33.8	4.2	Yes	Ar	600	130–250–450	30 (x3)	≈25
B4	Cu–In–Al/Cu	62.0	33.8	4.2	Yes	Ar	600	130–250–530	30 (x3)	≈30
					No[a]	Ar	1000	573	60	≈30

[a] Post-selenisation anneal.