Structural properties of Cu(In,Ga)Se$_2$ thin films prepared from chemically processed precursor layers

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Abstract

We have developed a chemical process for incorporating copper into indium gallium selenide layers with the goal of creating a precursor structure for the formation of copper indium gallium diselenide (CIGS) photovoltaic absorbers. Stylus profilometry, EDX, Raman spectroscopy, XRD and SIMS measurements show that when indium gallium selenide layers are immersed in a hot copper chloride solution, copper is incorporated as copper selenide with no increase in the thickness of the layers. Further measurements show that annealing this precursor structure in the presence of selenium results in the formation of CIGS and that the supply of selenium during the annealing process has a strong effect on the morphology and preferred orientation of these layers. When the supply of Se during annealing begins only once the substrate temperature reaches ≈400°C, the resulting CIGS layers are smoother and have more pronounced preferred orientation than when Se is supplied throughout the entire annealing process.

Introduction

Vacuum-evaporated, polycrystalline copper indium gallium diselenide (CIGS) thin films are used as the absorber layers in the highest efficiency thin film photovoltaic (PV) cells reported to date [1, 2]. However, the high cost and low material utilisation of the equipment used to produce these layers may be a barrier to their commercialisation and will increase the cost of the electricity generated by CIGS-based systems [3]. Non-vacuum techniques for CIGS deposition offer potential reductions in capital cost and many such techniques have been investigated [4]. These techniques generally split CIGS formation into two stages, one in which a precursor is deposited and one in which the precursor is converted into CIGS.

One potential method for non-vacuum CIGS precursor formation is the simple, non-vacuum technique of ion-exchange, which involves the exchange of ions between a solid and either a liquid or gas. This technique has been applied to the processing of thin films and nano-structures for a variety of thin film PV applications [5-8]. Ion-exchange methods are attractive due to the simplicity and low cost of the equipment required and the low temperatures employed (relative to vacuum deposition techniques). We have shown previously that copper can be incorporated into In$_2$Se$_3$ layers from solution via such an ion-exchange process and that the resulting precursor structure can be converted into chalcopyrite CuInSe$_2$ (CIS) by annealing [9]. Solar cells based on CIS layers are not able to reach the same high efficiencies as those based on CIGS and so in this work we report the incorporation of Cu ions into indium gallium selenide (IGS) thin films and present characterisation of the precursor and annealed layers.

Experimental Details

The Cu incorporation process was performed with IGS layers deposited onto molybdenum-coated soda lime glass substrates. The Mo was deposited by DC sputtering and the IGS layers were deposited by co-evaporation of the elements. The In and Ga were evaporated from line sources and an excess of Se was provided from an effusion cell, substrate temperature was maintained at 400°C. Throughout deposition the substrates moved back and forth over the line sources, 15 passes were typically required to deposit the ≈2 micron thick layers used in this work. Vacuum deposition was used to provide a high degree of control over the IGS layers, however it would be desirable in future work to use a non-vacuum technique to deposit these layers.

The incorporation of Cu into the indium gallium selenide layers was performed in ethylene glycol containing 0.6M CuCl and 1M NaCl. The ethylene glycol bath was heated in a glycerol bath to improve the temperature stability throughout the process, typically to better than ±2°C. Temperatures from 140-190°C have been investigated but all layers reported here were processed at 160°C. At this temperature it takes around 40 minutes to achieve 21 at.% Cu content in a 2 micron thick layer, as measured by EDX after annealing.

The precursor layers were annealed in a two temperature-zone quartz tube furnace under flowing N$_2$, similar furnaces with both open and closed designs have been reported by previous authors [10, 11]. Se was supplied from a removable quartz crucible that was heated separately from the substrates to allow control of the Se supply during annealing.

Layers were analysed using POWDER x-ray diffraction (XRD) recorded in reflection mode using monochromated Cu K$_{\alpha 1}$ radiation over the 2-theta range 10-70° with a step size of 0.0147° over a period of 3 h using a position sensitive detector. The software package EVA was used to subtract the background and, using the Mo (100) reflection as an internal standard (JCPDS 42-1120), overcome the small (ca. 0.2°) offset resulting from the positioning of the glass slide in the sample holder. Unpolarised micro-Raman spectroscopy measurements were performed using a He-Ne laser ($\lambda = 632.817$ nm) with x10 objective lens. Secondary-ion mass spectrometry (SIMS) measurements were recorded in positive mode using O$_2$ ions.

Results and Discussion

EDX measurements performed on IGS layers after deposition indicated a composition corresponding to atomic ratios Ga/(Ga + In) = 0.23 and

Se/(Ga + In) = 1.14. EDX measurements following immersion in the Cu solution revealed that Cu is incorporated into the layers during immersion, however these measurements could not be quantified since the composition of the layers is not homogeneous throughout their depth at this stage of processing. Stylus profilometry measurements did not reveal any increase in the thickness of the Cu treated layers, consistent with an ion-exchange process rather than deposition of Cu from solution.

XRD diffractograms measured from precursor layers are displayed in Figure 1. Diffractogram A was recorded from an as-deposited IGS layer (A). Measurements of indium selenide layers deposited under the same conditions (not shown) identified single phase γ-In$_2$Se$_3$ (JCPDS 40-1407). An analogous solid solution has been reported with the composition $(In_{1-z}Ga_z)_2Se_3$ [12], however our data does not fit well to the diffraction pattern expected of these ternary compounds (JCPDS 77-1920 and 78-1745). Both the In-Se and Ga-Se systems crystallise into a number of different binary phases and this makes definite phase identification difficult, though an approximate fit to the data is obtained by the pattern expected of a mixture of α-In$_2$Se$_3$ (JCPDS 34-1279) and InSe (JCPDS 44-1007). GaSe (JCPDS 81-1971) provides the closest match to the data for a gallium selenide phase and accounts for some strong peaks in the data not present in the In-Se diffraction patterns. However, some strong reflections are missing from the expected GaSe pattern which is likely to be a result of preferred orientation of certain diffraction planes resulting from the layering of the sample. Clearly the deposition of the IGS is a non-equilibrium process, with the broad diffraction peaks indicating a low degree of crystallisation.

After Cu incorporation (B) there is some alteration in the relative intensities of the peaks associated with the IGS phases and an extra peak is detected around 25.3°. This peak is close to the position expected for strong peaks in the diffraction patterns of the slightly copper-rich selenide phases Cu$_3$Se$_2$ and Cu$_5$Se$_4$ (JCPDS 47-1745 and 21-1016) and appears in the diffraction pattern of some compounds with the general formula Cu$_{2-x}$Se ($0 \leq x \leq 0.2$) (JCPDS 65-2982 and 06-0680). Confirmation of Cu$_{2-x}$Se compounds by XRD is difficult for these layers as the main Cu$_{2-x}$Se diffraction peaks overlap with the main peaks from the IGS patterns. Since a definite phase composition could not be determined for the precursor layers, it is not possible to propose a detailed reaction mechanism for the incorporation of Cu as was possible for previous work with Ga-free precursor layers [9].

Many more diffraction peaks are observed after annealing at 250°C in the presence of Se (C), all of which can be associated with copper selenide phases with higher Se content and the general formula CuSe$_y$ ($1 \leq y \leq 2$) (JCPDS 49-1457, 83-1814 and 19-0400). This is consistent with the binary phase diagram for Cu and Se, which shows that such phases can be formed in selenium rich conditions [13]. Formation of CuSe$_y$ phases from Cu-rich selenide phases involves a volume increase of +20-140% based on room temperature unit cell dimensions from the JCPDS records. This volume increase will be reversed at temperatures above 377°C when even the most stable of these compounds undergo phases changes by loss of Se

[13]. This effect has been suggested as the cause of the very rough morphology of CIS layers formed by other two-stage processes [14]. To investigate this further, precursor layers were annealed at 250°C in the absence of Se (D), the CuSe$_y$ peaks are not present in the diffractogram measured from such samples. Instead, the IGS peaks are broadened relative to the as-deposited layer and the peaks at 27.1° and 44.6° are strengthened relative to the other IGS peaks. The increase in the intensity of these peaks is attributed to the improved crystallisation of Cu$_{2-x}$Se phases.
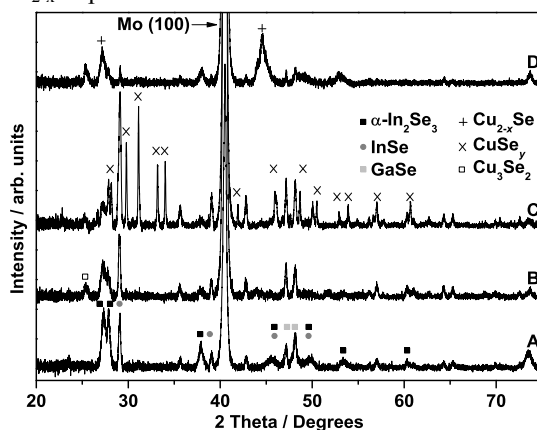

Figure 1: XRD diffractograms recorded from as-deposited IGS (A); Cu-treated IGS (B); and precursor layers annealed at 250°C with Se (C); and without Se (D). Supply of Se during annealing at this temperature promotes formation of CuSe$_y$ phases.
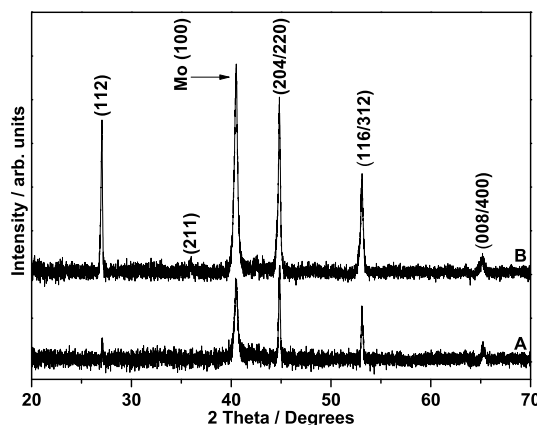

Figure 2: XRD diffractograms of layers annealed at 575°C with Se supplied only once substrate temperature reached ≈400°C (A); and throughout the entire annealing process (B). Miller indices indicate CIGS peaks. Delaying the supply of Se suppresses CuSe$_y$ formation and changes the orientation of the films.

Figure 2 displays XRD diffractograms recorded from samples annealed at 575°C with two different selenium supply patterns. For sample A the Se source was preheated before the substrate temperature was ramped up. In contrast, heating of the Se source did not begin for sample B until the substrate temperature reached ≈400°C, preventing the formation of CuSe$_y$. When Se supply was delayed an increase in the strength of the (204/220) and (116/312) peaks relative to the (112) peak is observed. The position of the (112) peak at 27° indicates a Ga/In+Ga ratio of around 0.5, greater than that in the as-deposited IGS films (0.23, calculated from EDX measurements).

The Raman spectra displayed in Figure 3 indicate that the as-deposited IGS layers (A) contain $(In_{1-z}Ga_z)_2Se_3$. Whilst the peak at 151cm^{-1} is at the position expected for $z = 0$,

the single shoulder on the low-wavenumber side has been observed for Ga-containing material whereas Ga-free material is reported to exhibit symmetrical shoulders on both sides [12, 15]. The peak at 259cm^{-1} in the spectrum from the Cu-treated sample (B) indicates the presence of copper selenides in the precursor layer following immersion in the Cu solution [16]. Since these phases are formed from the surface of the layer they absorb the signal from the underlying IGS to a large extent. Raman spectroscopy measurements of samples annealed at 250°C reveal a slight blue shift in the position of the Cu-Se peak, consistent with the formation of CuSe from Cu-rich selenides [17]. Due to the volume increase accompanying the formation of CuSe, no signal can be detected from the IGS layer in this spectrum. Raman spectra (D and E) from the samples analysed by XRD in Figure 2 both contain peaks characteristic of CIGS at 175cm^{-1} (A1 mode), 215cm^{-1} and 228cm^{-1} (B2/E modes) [18].
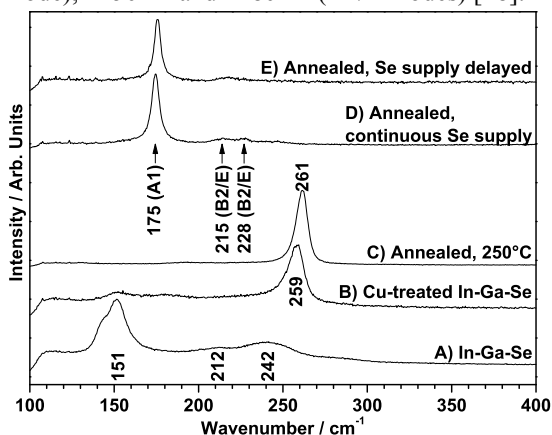

Figure 3: Raman spectra recorded from as-deposited IGS (A); Cu-treated IGS (B); a precursor layer heated to 250°C with Se (C); and layers annealed at 575°C with Se supplied throughout the entire annealing process (D); and only once substrate temperature reached ≈400°C (E). The peaks in spectra D and E are identified with CIGS vibrational modes.

The Scanning Electron Microscope (SEM) micrographs displayed in Figure 4 show the surface and cross-section of layers annealed at 575°C with Se supplied continuously throughout annealing (left) and only once the substrate temperature reached ≈400°C (right). In the latter case CuSe$_y$ formation and the accompanying expansion and contraction of the layer is avoided and it is clear that this results in a much smoother layer. Whilst a large affect on grain size is observed in these images, other layers that exhibit the same trend in surface roughness have shown different trends in grain growth and so conclusions cannot be drawn without further investigation.
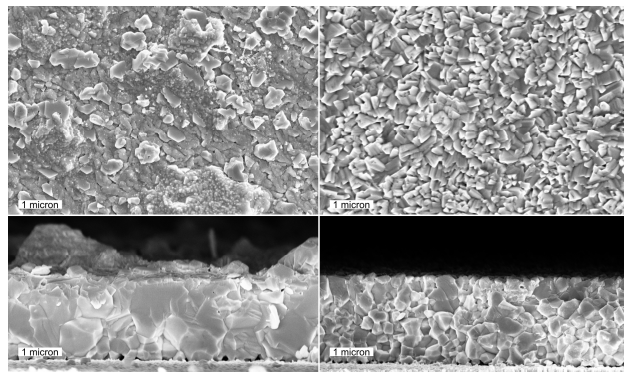

Figure 4: Surface (top) and cross-section (bottom) SEM micrographs of layers annealed at 575°C with Se supplied throughout the entire annealing process (left); and only once substrate temperature reached ≈400°C (right).

Figure 5 shows SIMS depth profiles of layers at various stages of processing. The IGS films used to make these samples were not quite of the same thickness, due to their positions in the deposition chamber, hence conclusions cannot be drawn from apparent changes in thickness. The composition of the as-deposited IGS layer (A) is homogeneous throughout its depth, however a regular oscillation in Ga/In signal strength ratio is observed. Since the number of oscillations corresponds to the number of passes that the substrates made back and forth across the sources, they are attributed to incomplete mixing of the In and Ga during deposition. The layer analyzed following Cu treatment (B) indicates that Cu is incorporated from the surface and that loss of In occurs in preference to loss of Ga, explaining the higher than expected Ga content in the annealed CIGS layers. That Ga-Se compounds have greater enthalpies of formation than their In-Se analogues is a possible explanation for Cu ions exchanging more rapidly for In ions than Ga ions [19]. Two other possible explanations for the different reaction rates are proposed, firstly, the atomic radii of Cu and In are similar, whilst the ionic radius of Ga is significantly smaller. As a result, the energy of a Cu ion occupying a Ga site in the IGS layer is likely to be higher than that of a Cu ion occupying an In site, again making the exchange reaction likely to occur more rapidly for In than for Ga. Secondly, solubility differences between In and Ga selenides may also explain the differing reaction rates [8], however to the best of the authors' knowledge data are not available for comparison. The Cu distribution data indicate that some grading of Cu into the underlying IGS layer occurs during immersion in the solution, however a component of the decaying Cu signal will have arisen from forward sputtering effects. The depth profiles measured from the annealed layers, both with preheated Se source (C) and delayed Se supply (D) indicate broadly homogenised depth profiles. However, in both cases there is a decrease in Ga signal towards the front of the layer which is slightly more pronounced for the layer annealed with delayed Se supply.

Conclusion

We have investigated a simple, low-cost method for incorporating Cu into indium gallium selenide layers. When these layers were immersed in a solution containing Cu, it was found that Cu was incorporated into the layers as Cu-Se compounds with no increase in the thickness of the layers. These observations are consistent with the

occurrence of an ion-exchange process. SIMS measurements revealed the preferential exchange of Cu for In rather than Ga, possibly due to differences in enthalpy of formation, ionic radii and solubility. Controlling the Se supply during the annealing treatment that was used to recrystallise the multi-phase precursor layers into single phase CIGS was shown to be key to controlling the morphology of the CIGS layers. Delaying the supply of Se until the substrate temperature reached ≈400°C led to smoother CIGS layers by preventing the formation of Se-rich copper selenides during substrate heating. Further optimisation of the recrystallisation process is required to produce CIGS layers suitable for use in high efficiency solar cells.
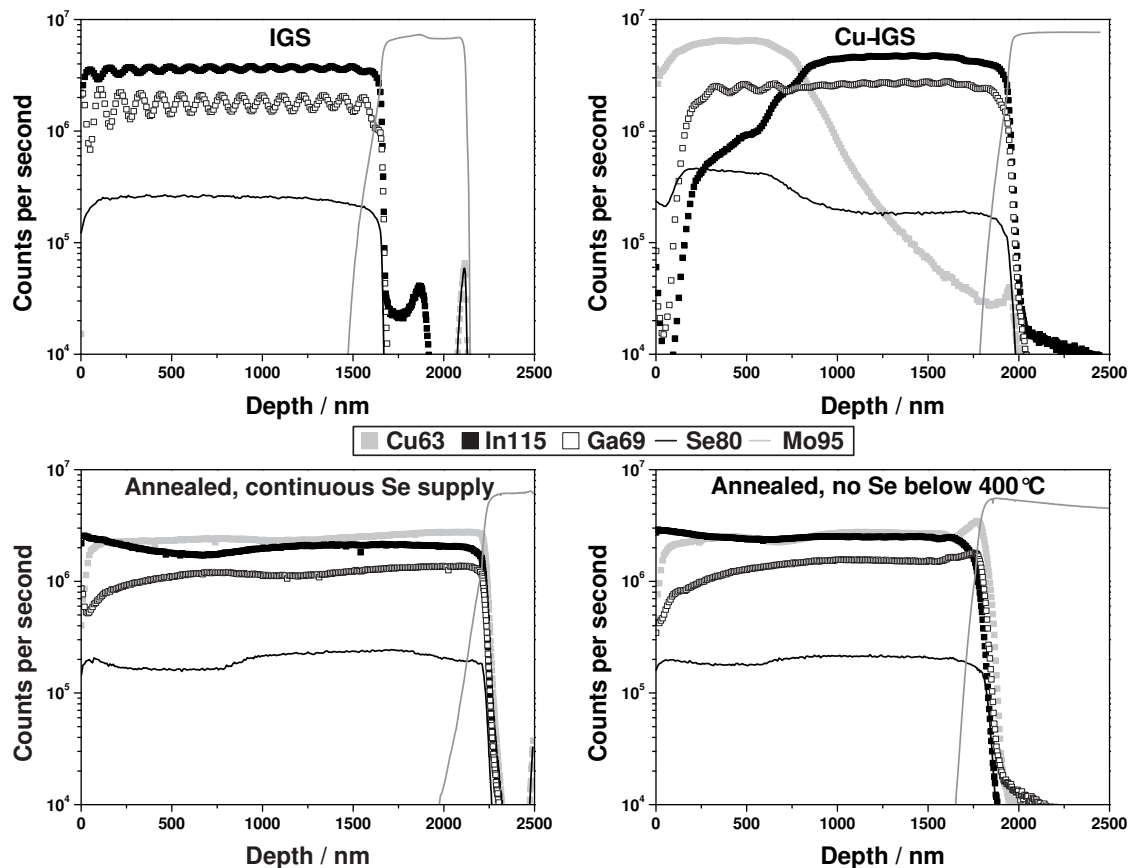

Figure 5: SIMS depth profiles of as-deposited IGS (A), Cu-treated IGS (B) and layers annealed at 575°C with Se supplied throughout the entire annealing process (C) and only once substrate temperature reached ≈400°C (D). Oscillation in the In and Ga signals in A and B result from substrate movement during deposition.

Acknowledgements

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