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INCORPORATION OF COPPER INTO INDIUM GALLIUM SELENIDE LAYERS FROM SOLUTION

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ABSTRACT

A chemical method for the incorporation of copper into indium gallium selenide (IGS) layers has been developed. The resulting copper-containing precursor layers have been annealed in the presence of selenium vapour with the goal of forming Cu(In, Ga)Se₂ (CIGS) layers. It is found that copper ions in solution are incorporated into IGS layers during immersion, resulting in the formation of a precursor layer containing both copper selenides and IGS. When aqueous solutions are used for this process, corrosion of the molybdenum back contact occurs by reduction of copper ions in the solution. Use of an ethylene glycol solution prevents corrosion of the Mo and allows higher process temperatures, corresponding to higher reaction rates. During annealing, the precursor layers are converted into CIGS and the morphology of these layers is strongly affected by the availability of selenium whilst the substrate temperature is ramped up.

INTRODUCTION

The highest efficiencies reported to date for thin-film solar cells have been for devices based on Cu(In, Ga)Se₂ (CIGS) absorber layers [1, 2]. These CIGS layers are deposited using expensive, high-vacuum equipment and it is expected that reductions in the cost of CIGS-based photovoltaics (PV) could be achieved by moving to simpler, non-vacuum based deposition techniques. Many such techniques have been investigated [3] and we have previously reported the use of an ion-exchange reaction as a step in the formation of a precursor layer suitable for conversion into CuInSe₂ (CIS) [4]. Similar reactions have been applied to other thin-film PV applications, including formation of Cu₂S-CdS structures, In₂S₃ and CuInS₂ [5-7]. Ion-exchange reactions are attractive from an industrial point of view as they require only simple, low-cost equipment, require relatively low temperatures compared

to vacuum deposition, proceed at high rates and, unlike chemical bath deposition, allow extensive re-use of the reaction solutions.

In this work we report the advantages of using organic solutions over aqueous solutions for incorporating copper into IGS layers on molybdenum coated glass substrates and present the results of investigation into the chemical-phase and morphological transformations these layers undergo during conversion into CIGS.

EXPERIMENTAL

The copper incorporation process was performed on 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. 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 IGS layers was performed in both aqueous and organic baths. The aqueous bath typically contained 0.1M CuSO₄ and 0.2M acetic acid (to prevent hydrolysis of the Cu²⁺) whilst the organic bath typically contained 0.6M CuCl and 1M NaCl as complexant.

The precursor layers were annealed in a two temperature-zone quartz tube furnace under flowing N₂ in order to investigate their conversion to CIGS, similar furnaces with both open and closed designs have been reported by previous authors [8, 9]. Se was supplied from a removable quartz crucible that was heated separately from the substrates to allow control of the Se supply during annealing. The heating rate of this system was limited to ≈50°C / min.

Secondary electron images were recorded on a field-emission gun Scanning Electron Microscope (SEM) at 5keV acceleration voltage whilst EDX measurements were performed on a tungsten filament SEM at 20keV. Unpolarised micro-Raman spectroscopy measurements were performed using a He-Ne laser ($\lambda = 632.817 \text{ nm}$) with x10 objective lens. Electrochemical open-circuit potential measurements were recorded in an unstirred cell with a Ag/AgCl reference electrode (+0.222 V vs NHE) in a side arm connected to the cell by a Luggin probe.

RESULTS AND DISCUSSION

Chemical incorporation of Cu

When In_2Se_3 layers were immersed in hot, aqueous, acidic copper sulphate solution it was found that copper was incorporated into the layers as Cu_2Se [4]. The composition of a set of such layers as measured by EDX before and after annealing with Se vapour is shown in Fig. 1A. The composition measurements of the precursor layers before annealing are provided for comparison only. Due to the compositional gradient present in the layers exact quantification is not possible with EDX. The measured compositions lie close to the In_2Se_3 - Cu_2Se pseudo-binary tie-line, though offset to the Se-poor side. The selenium deficiency is more pronounced for very copper poor layers.

All of the layers represented in Fig. 1A were 700-800 nms thick. To incorporate $\approx 21 \text{ at.}\%$ Cu into a layer of this thickness requires ≈ 60 minutes in boiling aqueous solution. When converted to CIS by annealing in Se vapour, such layers were found to increase in thickness by $\approx 10\%$. Such layers are still thinner than desired for use as absorbers in solar cells, however attempts to increase the thickness of the layers were hampered by the corrosion of the Mo back contact when exposed to the solution, which led to undercutting of the In_2Se_3 layer.

To investigate the cause of the Mo corrosion, open circuit potential measurements were made on Mo films in solutions of acetic acid and in solutions of acetic acid with CuSO_4 . The evolution of the open circuit potential of these films with time is shown in Fig. 2. The potential in the copper-free solution indicates that the Mo layer is inert in dilute acetic acid whilst the open circuit potential in the copper solution indicates that Cu^{2+} is being reduced, most likely according to Equation 1, with the expected counterpart anodic reaction being the oxidation of Mo (Equation 2).

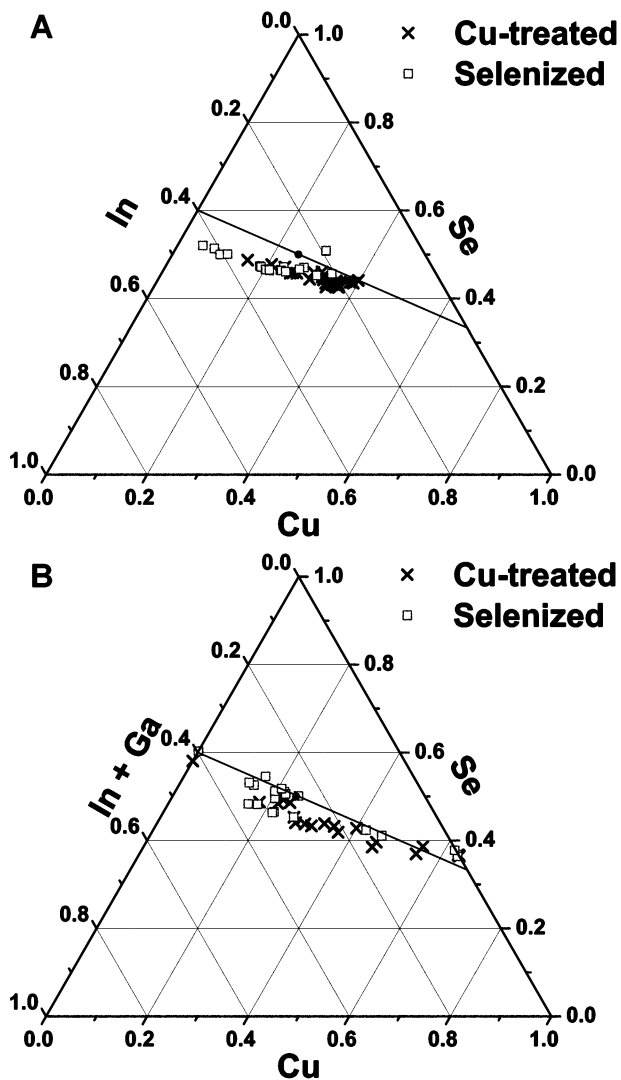
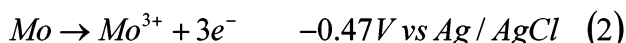
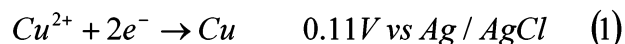


Fig. 1. Ternary composition diagrams for indium selenide layers treated in aqueous CuSO_4 solution (A); and indium gallium selenide layers treated in organic CuCl solution (B). All samples represented here in the Cu-treated data sets are also represented in the selenized data sets.

The destruction of Mo layers has previously been reported to occur in acidic $\text{NaSO}_4/\text{CuSO}_4$ solution by the same mechanism during investigation of electrochemical reactions involving Cu, In and Se [10]. Replacement of the Mo layer with other contact materials (FTO, ITO) resulted in no incorporation of Cu into the layers, which indicates that the reduction of Cu^{2+} by Mo is required to produce a source of Cu^+ ions for incorporation into the In_2Se_3 film.

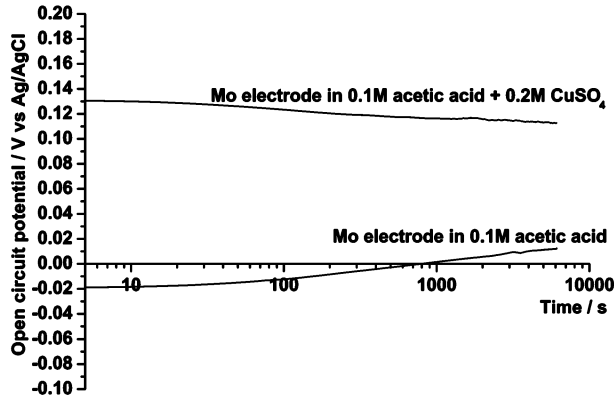


Fig. 2. Open circuit potential (E^0) of Mo coated glass in 2 different electrolytes. That E^0 is close to zero in the acidic solution indicates that no corrosion is occurring. In CuSO_4 solution E^0 is close to the value expected for the reduction of Cu^{2+} ions to Cu.

Since Cu^+ salts are soluble in aqueous solutions only at very low pH, alternative solvents were investigated. Ethylene glycol was found to be a very good solvent in which to perform the reaction as it is inexpensive, non-toxic and has a high boiling point ($\approx 196^\circ\text{C}$). After processing in ethylene glycol solution, no damage to the Mo layers was observed. When the composition of IGS layers was measured by EDX after immersion in ethylene glycol solutions containing CuCl, it was found that Cu was incorporated into the IGS layers. The composition of a set of these layers before and after annealing is shown in Fig. 1B. Since the Mo back contact is stable in the ethylene glycol solution, thicker layers could be processed and the results presented in Fig. 1 are for 1.5-2 micron thick layers. Since the temperature and duration of the Cu treatment controls the quantity of Cu incorporated into the IGS layers, they can be processed in relatively very short times in the high-temperature solution, i.e. 40 minutes at 160°C for 21 at.% Cu in a 2 micron thick IGS layer. Samples prepared at the extremes of the Cu-treatment (i.e. no copper treatment and treatment for sufficient time to completely convert the IGS layer) reveal terminal compositions corresponding to the compounds $(\text{In}_{1-z}\text{Ga}_z)_2\text{Se}_3$ and Cu_{2-x}Se . The results presented in the following sections of this article are for IGS layers processed at 160°C in ethylene glycol solution containing 0.6M CuCl and 1M NaCl.

Fig. 3A and B display SEM micrographs of the morphology and cross-section of as-deposited IGS and a Cu-treated layer. The morphology of both layers is very similar, though the sharp edges visible on the surface of the IGS layer appear more rounded after Cu-treatment. In cross-section it is clear that no significant increase in layer thickness occurs during Cu-treatment, an observation that is supported by stylus profilometry measurements. The unchanged morphology and thickness are taken as strong evidence that the incorporation of Cu into the IGS layers occurs by an ion-exchange process. The change in contrast that is seen in the upper half of the Cu-treated

layer cross-section micrograph is due to an increase in the electrical conductivity of this portion of the layer due to replacement of IGS by Cu_{2-x}Se phases at the surface. Increases in electrical conductivity have been confirmed by four-point-probe measurements.

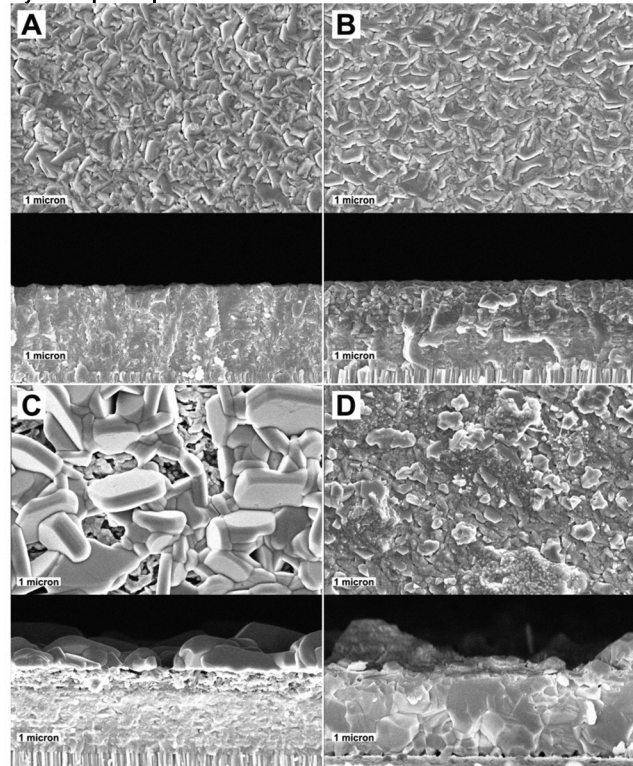


Fig. 3. Secondary electron images of as-deposited indium gallium selenide (A); Cu-treated indium gallium selenide (B); a precursor layer annealed at 250°C with Se vapour (C); and a precursor layer annealed at 575°C with Se vapour (D).

Selenization of precursor layers

Fig. 3C and D show SEM micrographs of CIGS layers formed by annealing precursor layers with the Se vapour source pre-heated before substrate heating commenced, ensuring a supply of Se vapour throughout the entire annealing process. The layer shown in C was annealed at 250°C whilst the layer shown in D was annealed at a maximum temperature of 575°C . It is clear that a large volume expansion relative to the precursor occurs at a temperature below 250°C , accompanied by a phase segregation at the surface of the layer. The segregated surface phase consists of copper selenides with the general formula CuSe_y ($1 \leq y \leq 2$), whilst the under layer contains the IGS. Similar surface grains have been observed by other groups and identified as $\gamma\text{-CuSe}$ [11, 12]. X-ray diffraction and Raman spectroscopy measurements (not shown) confirm that the layer selenized at 575°C has recrystallised as CIGS, but with a very rough morphology as observed by SEM.

CuSe_y compounds are only stable up to at most 377°C at which point they can undergo phase transitions by loss of Se, resulting in a reversal of the volume expansion observed at lower temperatures [13]. A decrease in volume would also be expected if the CuSe_y were to react with IGS to form CIGS. These large changes in volume are thought to be responsible for the rough surface morphology of the CIGS layers and possibly for the formation of voids within the layers. In order to investigate them further, precursor layers were annealed with Se vapour for 30 minutes at ≈280°C and ≈380°C, SEM micrographs of these samples are shown in Fig. 4A and B, respectively. At 280°C a distinct layer of CuSe_y can still be seen on the surface of the layer, though the boundary between the layers is less distinct than in Fig. 3C. By 380°C the distinct bi-layer structure is no longer apparent and the large CuSe_y grains have collapsed, leaving many small voids and high surface roughness.

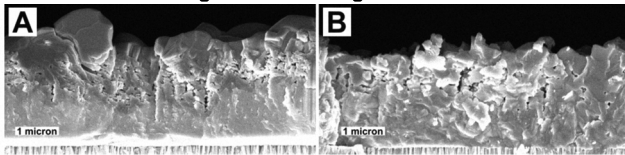


Fig. 4. SEM images of Cu-treated indium gallium selenide layers annealed with Se vapour at ≈280°C (A); and ≈380°C (B).

Raman spectroscopy measurements of these two films are displayed in Fig. 5. Due to the high absorption coefficients of copper selenides, the Raman signal is detected from just the top few hundred nanometres of the layers. As a result, only a peak corresponding to the CuSe_y compounds is detected for the sample annealed at ≈280°C, whilst the spectrum for the sample annealed at ≈380°C exhibits two strong peaks, one characteristic of copper selenide compounds and one characteristic of CIGS [14, 15]. This confirms that by 380°C the formation of CIGS has already begun and that the layer contains a mixture of binary and ternary/quaternary phases. During annealing these phases undergo structural and chemical phase transformations but the speed of these reactions is relatively slow at 380°C, since not all of the copper selenide has been consumed after 30 minutes of annealing. Formation of CIGS whilst the layer is still so rough from the CuSe_y grain formation and collapse indicates that the morphology of the CIGS layers is strongly influenced at low temperatures during annealing.

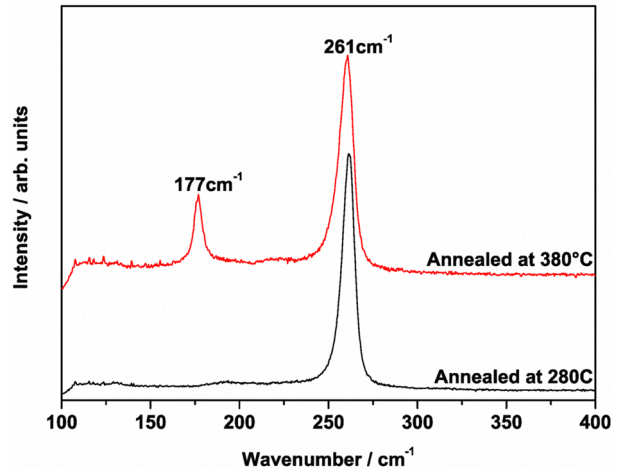


Fig. 5. Raman spectra for layers annealed at ≈280°C and ≈380°C. The peak around 261 cm⁻¹ is characteristic of copper selenide compounds and the peak at 177 cm⁻¹ is associated with the A₁ vibrational mode of CIGS.

A rough interface is considered to be undesirable for CIGS layers to be used as absorber layers in PV devices for two reasons. Firstly, shunts through either the absorber or buffer layer are expected to occur more frequently than for smooth, compact absorber layers and secondly, interface area, hence device dark current density, increases with absorber surface roughness. To improve the smoothness of the CIGS layers, precursor layers were annealed at 250°C in the absence of Se vapour. Fig. 6A shows a SEM micrograph of such a layer and comparison with Fig. 3B reveals no change in morphology with respect to the un-annealed Cu-treated layer. Fig. 6B shows a secondary electron micrograph of a layer after annealing at 575°C, in this case heating of the Se source did not begin until the substrate temperature reached ≈400°C. It is seen that the layer has recrystallised homogeneously throughout its depth and has a very smooth surface. Whilst a large difference in grain size is observed between Fig. 3D and Fig. 6B, no conclusions should be drawn from this as dissimilar grain sizes have been observed in other samples that exhibit the same surface roughness dependence on Se supply. Understanding of the cause of these grain size differences requires further investigation.

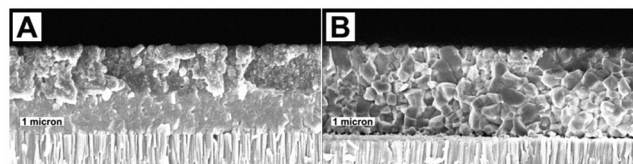


Fig. 6. Secondary electron images of layers annealed at 250°C in the absence of Se (A) and at 575°C with Se supplied once the substrate temperature was ≥400°C (B). The absence of Se at low temperatures prevents the formation of CuSe_y compounds and leads to smoother CIGS layers.

CONCLUSION

Cu ion-exchange into indium gallium selenide layers is a potential step in the creation of a precursor for CIGS absorber layer formation by simple, low cost, non-vacuum methods. An improved solution in which to carry out this process has been identified to replace the aqueous solution used in our earlier work. This ethylene glycol solution of CuCl has the advantages of avoiding the corrosion of the Mo back contact and allowing higher temperatures, hence faster reaction rates, to be accessed. The precursor layers may be converted to CIGS by annealing and the supply of Se during the annealing has been investigated. These investigations show that the details of the Se supply during annealing have a huge impact not just on the chemical-phase transformations undergone by the layers during annealing but also on the morphology of the layers and the crystallisation of the CIGS grains. Further work is required to optimise the annealing process to produce CIGS layers for use in high-efficiency solar cells.

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