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Chemical Incorporation of Copper into Indium Selenide Thin Films

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Abstract

Indium selenide thin-films have been treated in a copper-containing chemical bath with the goal of forming a precursor layer capable of being converted into copper indium diselenide. The conversion process was carried out by annealing the layers in a tube furnace in the presence of selenium vapour. The phase content of the layers as a function of composition and annealing temperature has been investigated by Raman spectroscopy. It is concluded that copper selenide is formed during the chemical bath treatment and that during annealing the copper selenide reacts first with elemental selenium vapour and then with the indium selenide to form chalcopyrite CuInSe_2 . Secondary phases of CuIn_3Se_5 and Cu-Au ordered CuInSe_2 have been detected in annealed copper-poor layers.

Introduction

Polycrystalline thin-films of copper indium diselenide (CIS) and their alloys with gallium and sulphur have been successfully used as absorber layers in high efficiency photovoltaic devices [1]. The absorbers in the current record efficiency devices were produced by co-evaporation at high temperature, however, high efficiency CIS solar cells and modules have been produced by alternative, two step processes that could potentially be easier to scale up to large area production [2, 3]. In these processes, a precursor layer is formed first and then converted into CIS by annealing. Since the annealing stage is often performed in the presence of a source of selenium it is sometimes referred to as selenization. The highest efficiency devices processed from absorbers formed by a two step process were created from vacuum deposited precursor layers. Since the capital cost of semiconductor deposition equipment has a strong impact on the cost of the resulting photovoltaic product [4], a range of potentially lower cost non-vacuum methods has been investigated for depositing the precursor layers [5].

In this work we have investigated the use of a chemical method to form a precursor suitable for conversion into CIS. Whilst the exact

mechanism of this process has not been confirmed, it has many similarities to ion exchange techniques such as were used to produce $\text{Cu}_2\text{S}/\text{CdS}$ solar cells [6] and have more recently found application in the preparation of CuInS_2 and In_2S_3 thin films [7, 8]. Ion exchange reactions are attractive from a technical point of view since they occur at relatively low temperatures, require only low-cost equipment and the solutions involved may be re-used extensively. It is shown in this work that copper may be incorporated into indium selenide layers from a chemical bath with no increase in thickness and that the resulting layers may be converted into CIS by annealing in the presence of selenium vapour.

Experimental

Indium selenide layers were prepared on molybdenum coated soda lime glass substrates by vacuum coevaporation of elemental indium and selenium. Coevaporation was employed to provide a reproducible precursor for the investigation of the copper incorporation process, a long-term goal would be to replace co-evaporation with a low-cost, non-vacuum technique. The copper incorporation process was performed in boiling aqueous solution containing CuSO_4 (0.1M) and acetic acid (0.2M). The copper content of the precursor layers was controlled by varying the duration of their immersion in this chemical bath. After immersion, precursor layers were rinsed thoroughly in deionised water and dried with nitrogen before being selenized in a two-temperature-zone quartz tube-furnace under flowing nitrogen. One of the zones was used to heat the substrate, whilst the other was used to heat a quartz crucible of elemental selenium. Typically, the substrate temperature was ramped up in stages to 575°C whilst the selenium source was heated to around 400°C .

A Jobin Yvon LabRam HR micro-Raman system was used to investigate the phase content of the layers produced during this work. The system was fitted with a He-Ne laser ($\lambda=632.817\text{ nm}$) and a x10 objective lens. The composition and thickness of the layers were measured by energy dispersive X-ray

analysis (EDX) and stylus profilometry, respectively.

Results and Discussion

Indium selenide layers were immersed in the copper chemical bath for a range of durations and subsequent EDX measurements revealed that the copper content of these layers increased with immersion duration. Further EDX measurements, after these layers were selenized, indicated a decrease in the measured Cu/In ratio. This is interpreted as the result of non-uniform copper composition through the depth of the precursor after immersion in the chemical bath making the quantization of EDX measurements unreliable.

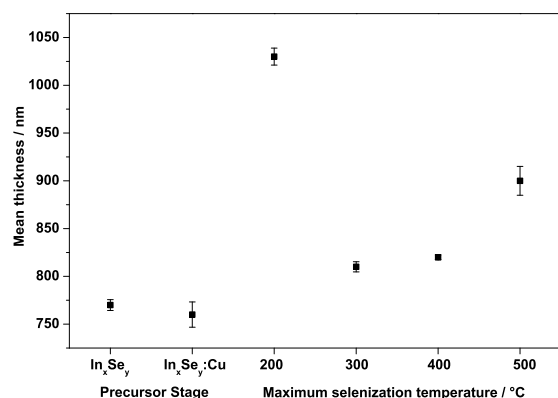


Figure 1: Stylus profilometer thickness measurements made on precursor and selenized samples. The selenized samples were annealed for equal durations but at different maximum temperatures. Each point is the mean of 8 measurements.

Figure 1 displays mean thickness measurements for a precursor layer before and after immersion in the copper solution for a duration suitable to incorporate the desired amount of copper (approximately 1 hour for this layer thickness). It is observed that no significant change in thickness occurs during immersion. The lack of any significant change in thickness is consistent with an ion-exchange mechanism of copper incorporation, however further investigation is required to confirm this. Figure 1 also shows the measured thickness of four pieces of the same sample that were selenized for equal durations but at different maximum temperatures. A large increase in thickness was observed for the sample heated to 200 °C that was not observed for samples heated to 300 °C and 400 °C. A smaller increase in thickness was measured for the sample selenized at 500 °C.

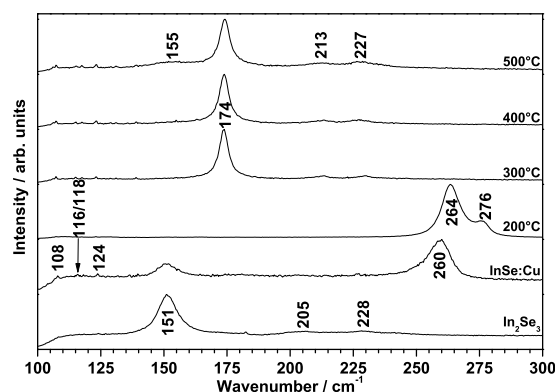


Figure 2: Normalised Raman spectra measured from precursor and selenized layers. The selenized samples were annealed for equal durations but at different maximum temperatures.

Figure 2 shows Raman scattering measurements made on the same samples described in relation to Figure 1. The peaks in the spectrum measured from the indium selenide layer correspond well to the values reported for $\gamma\text{-In}_2\text{Se}_3$ [9]. The spectrum recorded from a sample that was immersed in the chemical bath exhibits the same indium selenide peak at 151 cm^{-1} and an additional peak at 260 cm^{-1} that is characteristic of binary copper selenides [10]. The formation of copper-selenium bonds indicates that copper incorporation is not achieved simply by diffusion into vacancies in the indium selenide lattice. The spectrum recorded from the sample annealed at 200 °C in the presence of selenium vapour no longer exhibits the indium selenide peak at 151 cm^{-1} and the copper selenide peak at 260 cm^{-1} has been replaced by 2 peaks at 264 cm^{-1} and 276 cm^{-1} . A peak at 263-264 cm^{-1} has been reported for CuSe [11], however, no reports of a peak around 276 cm^{-1} could be found in the literature for any of the materials present in our layers. The peak at 264 cm^{-1} , the absence of any peaks associated with indium selenide compounds and the large increase in thickness measured for this sample are interpreted as evidence of a reaction between copper-rich copper selenides in the precursor layer with elemental selenium to form CuSe. A volume expansion would be expected from this reaction and this may be enough to 'mask' the indium selenide layer from the Raman measurements (the interaction depth of the measurement is on the order of a few hundred nano-metres). The Raman spectra measured from all of the samples selenized at higher temperatures exhibit a strong peak at 174 cm^{-1} and weaker peaks at 213 cm^{-1} and 227 cm^{-1} , in good agreement with the reported positions of the

A1 and B2/E modes of chalcopyrite CuInSe_2 [12]. Additionally, the spectrum recorded from the sample selenized at 500°C exhibits a broad peak around 155 cm^{-1} , an A1 mode peak has been reported around this position for the ordered defect compound CuIn_3Se_5 [13].

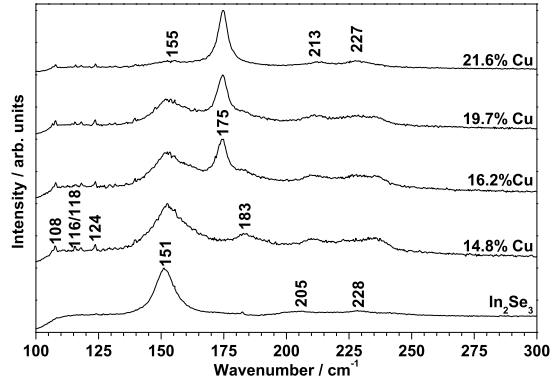


Figure 3: Normalised Raman spectra measured from samples with varying copper contents (indicated in atomic %) selenized at 575°C . The spectrum measured from and In_2Se_3 layer is given for comparison.

The Raman scattering spectra displayed in Figure 3 were recorded from samples selenized at 575°C (the indium selenide spectrum is repeated for comparison). The precursors were prepared with different copper-poor compositions, from very copper poor to device-relevant. The spectrum recorded from the most copper deficient selenized sample exhibits a broad peak around 151 cm^{-1} , consistent with the presence of un-reacted $\gamma\text{-In}_2\text{Se}_3$. However, a contribution from the A1 peak of CuIn_3Se_5 cannot be ruled out due to overlap in the position of these two broad peaks. Whilst no peak is observed in the position expected for the A1 mode of chalcopyrite CuInSe_2 , the peak at 183 cm^{-1} has been associated with Cu-Au ordered CuInSe_2 [14, 15]. As the copper content of the layers is increased, the chalcopyrite CuInSe_2 peaks at 175 cm^{-1} , 213 cm^{-1} and 227 cm^{-1} are recorded and the intensity of the peaks at 151 cm^{-1} and 183 cm^{-1} decrease relative to these peaks.

With the exception of the spectrum recorded on as-deposited In_2Se_3 layers, all of the Raman spectra presented in this work exhibit sharp, low intensity peaks at or near 108 cm^{-1} , 116 cm^{-1} , 118 cm^{-1} and 124 cm^{-1} . These peaks indicate that the layers may contain secondary phases and whilst they have not been positively identified they are close in position to peaks associated with $\alpha\text{-In}_2\text{Se}_3$ [16] and InSe [17]. A peak at 124 cm^{-1} has been

associated with Cu-Au ordered CuInSe_2 , however the presence of this peak in the spectrum measured before selenization seems to preclude this interpretation of our data [15]. Further measurements to detect peaks below 100 cm^{-1} are required to positively identify which secondary phases are present in our films; however such measurements were not possible with the holographic notch filter that was used during this work.

Conclusions

A chemical method of incorporating copper into indium selenide layers has been developed that is notable for the simplicity of the equipment required. Raman spectroscopy measurements of the precursor films after immersion in the copper chemical bath indicate that they consist of mixed copper and indium selenides. Raman spectroscopy measurements on films annealed in the presence of elemental selenium indicate that the precursors have been successfully converted into chalcopyrite CuInSe_2 , however the presence of small unknown peaks in the spectra mean that the presence of secondary phases cannot be ruled out.

References

- [1] Repins I, Contreras M,A., Egass B, DeHart C, Scharf J, Perkins C,L., To B and Noufi R. 19.9%-efficient $\text{ZnO/CdS/CuInGaSe}_2$ Solar Cell with 81.2% Fill Factor. *Progress in Photovoltaics Research and Applications* 2008;
- [2] Nishiwaki S, Satoh T, Hayashi S, Hashimoto Y, Shimakawa S, Negami T and Wada T. Preparation of Cu(In,Ga)Se_2 thin films from Cu-Se/In-Ga-Se precursors for high-efficiency solar cells. *Solar Energy Materials & Solar Cells* 2001; **67** : 217-223.
- [3] Probst V, Palm J, Visbeck S, Niesen T, Tolle R, Lerchenberger A, Wendl M, Vogt H, Calwer H, Stetter W and Karg F. New developments in $\text{Cu(In,Ga)(S, Se)}_2$ thin film modules formed by rapid thermal processing of stacked elemental layers. *Solar Energy Mater. Solar Cells* 2006; **90** : 3115.
- [4] Zweibel K. Issues in thin film PV manufacturing cost reduction. *Solar Energy Materials & Solar Cells* 1999; **59** : 1-18.
- [5] Kaelin M, Rudmann D and Tiwari A, N. Low cost processing of CIGS thin film solar cells. *Solar Energy* 2004; **77** : 749-756.
- [6] Pfisterer F. The wet-topotaxial process of junction formation and surface treatments of $\text{Cu}_2\text{S-CdS}$ thin-film solar cells. *Thin Solid Films* 2003; **431-432** : 470-476.
- [7] Moller J, Fischer C-, Muffler H-, Konenkamp R, Kaiser I, Kelch C and Lux-

- Steiner MC. A novel deposition technique for compound semiconductors on highly porous substrates: ILGAR. *Thin Solid Films* 2000; **361-362** : 113-117.
- [8] Dloczik L, Lux-Steiner MC and Koenenkamp R. Study on the preparation of structured CuInS_2 films by ion exchange processes. *Thin Solid Films* 2003; **431-432** : 131-134.
- [9] Emziane M and Le Ny R. Crystallization of In_2Se_3 semiconductor thin films by post-deposition heat treatment. Thickness and substrate effects. *Journal of Physics D: Applied Physics* 1999; **32** : 1319-1328.
- [10] Izquierdo-Roca V, Perez-Rodriguez A, Romano-Rodriguez A, Morante J,R., Alvarez-Garcia J and Calvo-Barrio L. Raman microprobe characterization of electrodeposited S-rich $\text{CuIn}(\text{S,Se})_2$ for photovoltaic applications: Microstructural analysis. *Journal of Applied Physics* 2007; **101** : 103517-1-103517-8.
- [11] Ishi M, Shibata K and Nozaki H. Anion distributions and phase transitions in $\text{CuS}_{1-x}\text{Se}_x(x=0-1)$ studied by Raman spectroscopy. *Journal of Solid State Chemistry* 1993; **105** : 504-511.
- [12] Neumann H. Lattice vibrational, thermal and mechanical properties of CuInSe_2 . *Solar Cells* 1986; **16** : 399-418.
- [13] Tiwari A, N. and Blunier S. Characterisation of heteroepitaxial CuIn_3Se_5 and CuInSe_2 layers on Si Substrates. *Applied Physics Letters* 1994; **65** : 3347-3349.
- [14] Lazewski J, Neumann H, Parlinski K, Lippold G and Stanbery B. J. Lattice dynamics of CuAu-ordered CuInSe_2 . *Physical Review B* 2003; **68** : 144108.
- [15] Stanbery B,J., Kincal S, Kim. S and Chang C,H. Epitaxial growth and characterization of CuInSe_2 crystallographic polytypes. *Journal of Applied Physics* 2002; **91** : 3598-3604.
- [16] Kambas K, Julien C, Jouanne M, Likforman A and Guittard M. Raman spectra of alpha- and gamma- In_2Se_3 . *Physica Status Solidi B* 1984; **124** : K105-K108.
- [17] Emery J, Y., Brahim-Otsmane M, Jouanne M, Julien C and Balkanski M. Growth Conditions of In_2Se_3 Films by Molecular Beam Deposition. *Materials Science and Engineering* 1989; **B3** : 13-17.