Reproducibility studies on thin-film copper indium diselenide prepared from copper indium oxide

M. E. BECK, M. COCIVERA*
Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Thin-film copper indium diselenide was prepared by selenization of copper indium oxide deposited by spray pyrolysis of an aqueous solution containing copper and indium salts. The degree of reproducibility in thickness, composition and electrical parameters was found to be good. The electrical parameters could be controlled and tuned for photovoltaic applications reproducibly by means of this cost-efficient fabrication technique.

1. Introduction

Among the various absorber compounds employed in high-efficiency thin-film solar cells, polycrystalline copper indium diselenide (CIS) has proved to be a leading candidate [1–6]. Thin-film, p-type CIS has been prepared by various deposition techniques [1, 7]. Parameters that are thought to be essential for high-efficiency photovoltaic devices such as resistivity, carrier concentration and composition have been reported for CIS prepared by various techniques [3, 8–18]; however, few studies have addressed the question of the reproducibility of these properties for the deposition techniques employed.

Earlier publications [19, 20] reported a new, potentially low-cost procedure for preparation of CIS that had electrical and optical parameters suitable for photovoltaic device applications. The intent of the present work was to assess the degree of reproducibility in thickness, composition and electrical parameters of CIS prepared by this two-stage process developed in our laboratory.

2. Experimental procedure
2.1. Film preparation

Thin-film (CIS) was prepared by a process developed in our laboratory as previously described [19, 20]. This process involved two steps: (a) the formation of copper indium oxide (CIO) films by spray pyrolysis of an aqueous solution containing copper and indium nitrate salts at 28.6 mM and 46.6 mM, respectively ($Cu(NO_3)_2 \cdot 6H_2O$, Johnson Matthey 99.999%, $In(NO_3)_3 \cdot 5H_2O$ Aldrich 99.99%); (b) subsequent reaction of the CIO in a stainless steel reaction chamber containing selenium pellets (Aldrich 99.999 + %) and sealed with nitrogen at atmospheric pressure. Deposition of CIO on to Corning 7059 glass substrates was carried out at 150 °C, and selenization of CIO was carried out at a temperature of 400 °C for 240 min quantitatively to form CIS. The efficiency of the spray pyrolysis process was found to be between 13% and 35% [20], which is substantially higher than previously reported efficiencies except for an electrostatically assisted process [21].

2.2. Characterization

The techniques applied to characterize the materials have been described in a previous publication [20]. In this work, emphasis was placed on the thickness profile measurements, compositional analysis by means of energy-dispersive X-ray spectroscopy (EDS), and carrier density and mobility as determined by constant current resistivity and Hall voltage measurements.

3. Results and discussion

In order to examine the degree of reproducibility of the two-stage fabrication technique, CIS samples were prepared in 26 separate selenization reactions. From these reactions, 20 resulted in films of good visual appearance and suitable morphology. The typical scanning electron micrograph for these samples was identical to earlier ones [20], which exhibited fairly large grains and a smooth surface. Likewise, the X-ray diffraction pattern (XRD) for these samples was the same as the earlier ones [20], which indicated a chalcopyrite phase with a preference for the (1 1 2) orientation. A few other conversions provided poorer quality samples because of poor seals in the reaction chamber. As was shown earlier [20], the CIO precursor films consist of a mixture of secondary and ternary Cu–In oxides. Previous analysis by atomic absorption spectroscopy (AAS) showed that the efficiency of the spray pyrolysis deposition and the composition of CIO could be reproduced. Furthermore, thickness as

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well as morphology and structure determinations of CIO obtained in the present study are consistent with the results from our earlier studies. In the present work we assessed the reliability of the selenization step.

3.1. Film thickness

Fig. 1 shows the thickness for the precursor CIO and the corresponding CIS for all 20 samples prepared under the same conditions. Each data point represents an average of four measurements across the length of each sample and the vertical line indicates the standard deviation, 1σ. It can be seen that all CIS samples are grouped close to the average of $2.53 \pm 0.24\,\mu m$ with a maximum of $2.87 \pm 0.03\,\mu m$ and a minimum of $1.96 \pm 0.07\,\mu m$, suggesting reasonable reproducibility. As was reported earlier [20], the thickness increase upon selenization is below the factor of 2–3 that was observed in the selenization of metal layers [4], and for the current series, an average CIS/CIO thickness ratio was only 1.36 ± 0.11. This small increase may account for the good adhesion of the CIS films.

3.2. Film composition

Because CIS is a ternary chalcopyrite semiconductor compound, the atomic ratios of the elements have a major influence on the characteristics of the films. Sample composition was obtained by means of standardized EDS analysis, which is commonly accepted to give relative errors of $\pm 3\%$–5% of the measured weight per cent for each element analysed [22, 23]. Prior to sample investigations, the calibration of the EDS system was checked by use of two CIS standards (analysed by WDS at the National Renewable Energy Laboratories, Golden, CO). Fig. 2 shows the averaged selenium, copper and indium composition measured for the 20 successful conversions. Each data point is an average of four to six measurements across the film surface, and the standard deviations are indicated by the vertical lines. As can be seen, the selenium content is rather uniform. The average of these data points is
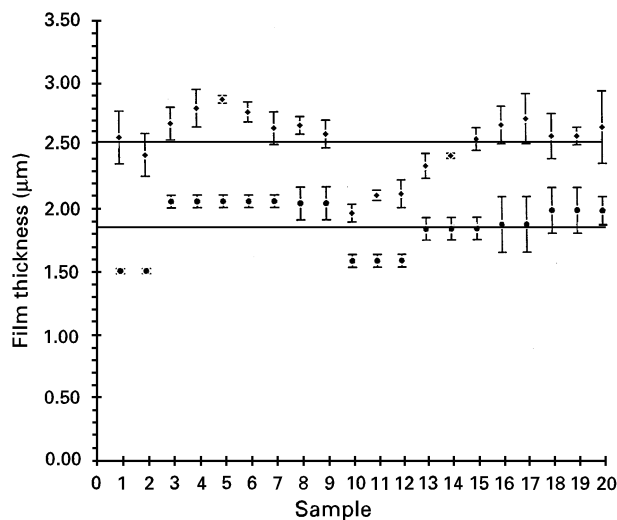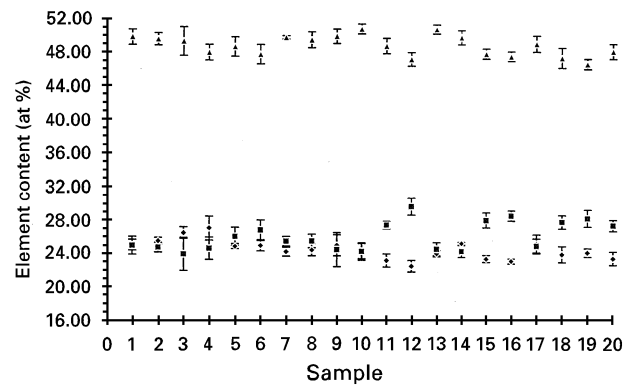

Figure 2 Average (♦) copper, (■) indium and (▲) selenium content in CIS by EDS for the 20 samples in Fig. 1.

49.0 ± 1.17 at % with all but six samples in the 48–50 at % range. In the case of copper, the average of the data points is 24.7 ± 1.07 at %, and for indium the average concentration is 26.3 ± 1.79 at %. This shows the degree of reproducibility for our technique in independent runs. In order to assess the accuracy of the individual results, the standard deviation of the average (four to six measurements per portion) was compared to the accepted relative error in EDS analysis of $\pm 3\%$–5% of the measured wt % for each element. It was found that in the case of selenium, all values of σ were smaller than the relative error of $\pm 3\%$ of the weight per cent, while in the case of copper and indium all the samples had σ values within the upper limit of EDS error. Correlating this information with the compositional data in atomic per cent shows a fluctuation across the sample area of $5\,mm \times 5\,mm$ to $10\,mm \times 5\,mm$ well below 1 at % with only two samples ranging up to 2 at %. Thus the accuracy of the EDS determination can be taken as less than ± 1 at % for each element. This is in accordance with the value reported in the review by Rockett and Birkmire [6].

It is difficult to compare the reproducibility of our preparation procedure with those of many of the other techniques, because most publications on CIS report compositional ranges rather than specific values for a large number of samples [9, 10, 13–18]. Furthermore, the compositions quoted in most cases do not indicate the degree of accuracy. However, there are a few reports. For CIS prepared by physical vapour deposition, McCandless and Birkmire [16] estimate the relative error on their standardized EDS results to be $\pm 3\%$; Schmid *et al.* [24] quote an absolute accuracy better than 0.5 at % for their EDS analysis. Yang and Rockett and co-workers [25, 26] mention the accuracy of their EDS measurements for CIS prepared by hybrid sputtering and evaporation to be limited by a random error due to system noise of ± 0.5 at % to give standardized results better than ± 1 at %. They also report a compositional uniformity of ± 2 at % for copper and indium over a $2.5\,cm \times 2.5\,cm$ substrate area.

Figure 1 (●) Precursor CIO and (♦) corresponding CIS film thickness for 20 samples prepared under identical conditions. (——) Averages.

3.3. Electrical parameters

For the 20 samples described above, room-temperature resistivity measurements were carried out. The

values of the room-temperature resistivities varied between 0.57 and 64.60 Ωcm with all but three samples in the 0.6–21 Ωcm range. These values fall well within the optimum range of 10^{-1}–$10^2 \Omega$cm required for solar-cell quality CIS [8]. On the other hand, Hall voltage could be determined for only 15 samples, all of which exhibited p-type conductivity. This indicates that using solutions of identical compositions consistently results in p-type CIS. Majority (hole) carrier concentrations, p, at room temperature were determined to lie in a range from 6.7×10^{15}–1.7×10^{18} cm^{-3}. Subsequent determination of the carrier mobility, μ, by the use of $\mu = (\rho p q)^{-1}$, with q being the electronic charge, resulted in values of 1.14–14.4 cm^2 V^{-1} s^{-1}, and this corresponds well to the values given in the literature [27–29]. Thus this two-stage preparation technique can be used to prepare reproducibly p-type CIS of suitable electrical parameters for solar cell applications. In our previous study [20], we observed that linking the electrical parameters at room temperature to the composition corresponded well to the models proposed by Noufi *et al.* [11] and Yamaguchi *et al.* [30] if the cross-over from n-type to p-type material is at 47 at % Se and Cu/In 0.80 rather than 50 at % and 1.0, respectively. The current results demonstrate an improvement because conditions could be found which reproducibly result in p-type material of good electrical properties.

4. Conclusion

It has been shown that the two-stage fabrication technique for CIS provides films having reproducible thickness and composition. Furthermore, these films exhibit electrical parameters suitable for photovoltaic applications. Film thicknesses showed an average of $2.53 \pm 0.24 \mu$m and, therefore, fall within the 2–3 μm range normally employed for photovoltaic devices based on CIS. Compositional analysis showed an accuracy of < 1 at % for all elements and revealed a rather uniform selenium content on average of 49.0 ± 1.17 at % and copper and indium contents in the ranges 22.8–27.2 and 24.0–29.9 at %, respectively. These results correspond well to the ranges quoted in the literature for the optimum concentration for solar-cell applications of CIS. As for the compositional fluctuations across the sample area of 5 mm × 5 mm to 10 mm × 5 mm, they were found to be well below 1 at % for most films, and only two ranged up to 2 at %. Room temperature resistivity of these samples varied within the 10^{-1}–$10^2 \Omega$cm range while the majority carrier concentration was mainly in the 10^{16}–10^{17} cm^{-3} range suitable for PV devices. The next step is to prepare and investigate solar cells based on CIS prepared by the two-stage fabrication technique.

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