

Effect of bath temperature on the properties of $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ thin films grown by the electrodeposition technique

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Abstract: Electrodeposition is a promising and low cost method to synthesize $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGS) thin films as an absorber layer for solar cells. The effect of bath temperature on the properties of CIGS thin films was investigated in this paper. CIGS films of 1 μm thickness were electrodeposited potentiostatically from aqueous solution, containing trisodium citrate as a complexing agent, on Mo/glass substrate under a voltage of -0.75 V , and bath temperatures were varied from 20 to 60 $^\circ\text{C}$. The effects of bath temperature on the properties of CIGS thin films were characterized by X-ray diffraction (XRD) and scanning electron microscopy. XRD revealed the presence of the $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ phase, the optimal phase for application in solar cells. The grain dimensions and crystallizability increase along with the increase of the bath temperature, and the films become stacked and homogeneous. There were few changes in surface morphology and the composition of the films.

Key words: CuInGaSe_2 ; thin films; solar cells; electrodeposition

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1. Introduction

The high absorption coefficient of CuInGaSe_2 ($\sim 10^5\text{ cm}^{-1}$) allows thin films thinner than 2 μm to be applied to PV devices^[1]. Polycrystalline $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ has exhibited very promising performance for thin film photovoltaic (PV) application, approaching 20% conversion efficiencies at the laboratory scale (19.9% NRSL^[2]), using high vacuum based techniques. The preparation of such high-efficiency CIGS material involves a process (specifically, physical vapor deposition) that is difficult to scale up. Electrodeposition deserves special attention as it is inexpensive, low-temperature and non-polluting, and offers good control of film thickness and potentially high utilization of bath species. Electrodeposition requires only off-the-shelf, low cost equipment and allows deposition over large areas under low-temperature conditions.

Although several groups have reported work on electrodeposited CIGS thin films, only a few of them used one-step electrodeposition to obtain stoichiometric CIGS thin films^[3–6]. Those who get good electrical characterization of films often use multistep deposition approaches, sometimes with vacuum techniques. Numerous groups have reported electrodeposition-based processing of CuInSe_2 and $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$ films, employing a number of approaches: sequential deposition of individual metal films, deposition of various precursors^[4, 5], and single-step deposition^[6], where all elements are deposited simultaneously. Single-step deposition processes are appealing in order to simplify device manufacture^[6–13]. The successful deposition of CuInSe_2 from a single electrochemical bath onto a range of different substrate types has been previously reported, and a few groups have attempted to describe the bath chemistry and mechanisms of film growth^[7, 8]. As-deposited films are generally of low crystallinity and a post-deposited anneal, often in a selenium-containing atmosphere^[10–15]. This

is required to drive formation reactions and film recrystallization^[9–13] while maintaining or controlling the film chemistry^[16, 17].

Electrodeposition offers the prospect of achieving stoichiometric, device-quality CIGS precursor thin films with Ga content as high as 30% ($\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$)^[8], which is almost the same as the vacuum techniques^[2]. It is very difficult to increase the proportion of In to fabricate stoichiometric thin films. During the present work, the optimization of the deposition condition using a warm solution could help to increase the In and Ga concentrations in the precursor films. Electrodeposition of CIGS thin films, with bath temperatures of electrolyte varying from 20 to 60 $^\circ\text{C}$, should offer proximal stoichiometric thin films synthesized by a simpler and industrially significant process. The effect of bath temperature on the thickness, microstructure and optical properties of the thin films has been investigated. The purpose of our work is to modulate the properties of CIGS by varying the bath temperature.

2. Experimental procedures

The electrodeposition was carried out in a conventional three electrode electrochemical cell, containing 50 mL solution, using an electrochemical setup (CHI660D) to deposit the films under a potentiostatic regime. A Pt plate was used as the counter electrode and a saturated calomel electrode (SCE) as a reference electrode, with 0.7- μm -thick Mo film on a glass substrate (total area, $1.5 \times 1.5\text{ cm}^2$) as the working electrode. The substrates were cleaned with ethanol, acetone and deionized water and then dried in flowing N_2 . The electrolyte was prepared by dissolving adequate quantities of the chemicals to give 5 mM CuCl_2 , 20 mM InCl_3 , 20 mM GaCl_3 and 10 mM H_2SeO_3 ^[18]. The concentration of trisodium citrate used as a complexing agent was as high as 0.1M to form strong com-

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plexes^[19]. The pH of the solution was fixed at 2.0 adjusted by HCl^[20]. Before each experiment, substrates were cleaned in suitable solution and rinsed with bi-distilled water. The cathodic deposition of the films was carried out in an unstirred bath at temperatures of 20, 40, 60 °C for 30 min.

The surface morphologies of the deposited films were investigated by scanning electron microscopy (SEM) using a JSM 7401 microscope and the current–time curves were recorded by the electrochemical setup (CHI660D). The crystallographic phase was monitored by X-ray diffraction (XRD), which was accomplished by a Philips PZ 3710 X-ray diffractometer using monochromatic CuK α 1 radiation ($\lambda = 1.5406 \text{ \AA}$) in a scanning angle range of 10°–90°. The operation voltage and current used were respectively 40 kV and 200 mA. The samples were scanned with a step width of 0.02° and pre-set time of 2 s. Spectral absorption was recorded using a U-3310 spectrophotometer. The measurements were carried out in wavelengths within the range of 200–800 nm with 1 nm steps.

The thickness (t) of the film was estimated theoretically using the following formula^[5,21]:

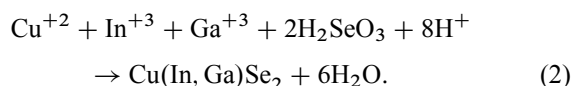
$$t = \frac{1}{nFA} \frac{isM}{\rho} \quad (1)$$

Here, n is the number of electrons transferred and is taken as 16, $F = 96500 \text{ C}$ is Faraday's number, A is the electrode area, i is the applied current, s is the deposition time, $M = 252.755 \text{ g/mol}$ is the CuInGaSe₂ molecular weight, and $\rho = 5.77 \text{ g/cm}^3$ is the density of the CuInGaSe₂ material^[22].

3. Results and discussion

3.1. pH buffer solution

During CIGS film formation, the general reaction occurring at the working electrode surfaces is as follows^[19]:



This reaction is a combination of electrochemical and chemical reactions that occur at certain pH values. The use of the pH buffer solution, which is a mixture of sulphamic acid and potassium biphthalate, permits the absorption of the free OH⁻ and H⁺ ions that exist in the deposition bath and also controls the pH of the solution bath^[6]. Control of the pH in the solution can help in the incorporation of Cu, In, and Ga into the film and, consequently, in the ratios of [Cu]/[In + Ga] and [Ga]/[In + Ga] in the film. The use of pH buffers also reduces the occurrence of oxide or hydroxide precipitates that interfere with the formation of Cu–Ga–In–Se precursor thin films.

3.2. Current–time curve of CIGS films

In the Current-time curve of deposition (Fig. 1), it was found that when the bath temperature was below 40 °C, the current density was basically fixed at a certain value, and decreased slowly, while when the temperature was above 40 °C, the curve was acutely fluctuant, and the current density was bigger than that at the lower temperature. The reasons for this phenomenon can be explained easily. The thermal motion of the molecular water was very intense when the electrolyte was

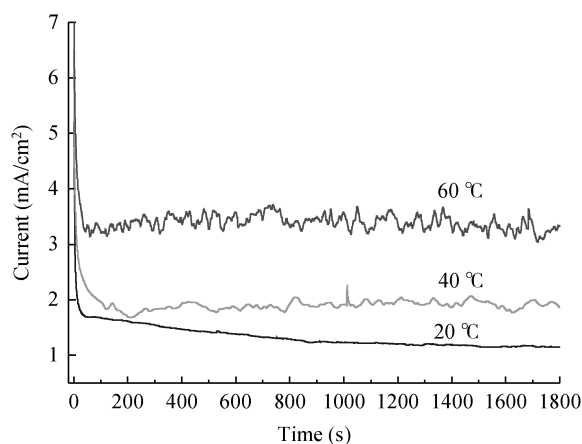


Fig. 1. Current–time curve of deposition at temperatures of 20, 40, 60 °C.

Table 1. Thickness of CIGS thin film deposited at different temperatures for different times.

Bath temperature (°C)	20	40	60
s (s)	1.5	2	3.5
t (μm)	0.9	1.5	2.2

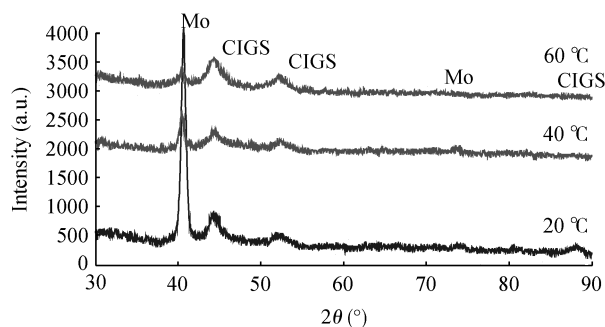


Fig. 2. XRD patterns of CuInGaSe₂ as deposited on Mo-coated glass substrate by the electrodeposition technique at 20, 40, 60 °C compared to CuIn_{0.7}Ga_{0.3}Se₂.

heated to a higher temperature. Atoms of Cu–In–Ga–Se precursor were disturbed by the impact of molecular H₂O when they adhered to the surface of the substrate. The current changes show that when the bath temperatures increase, the motions of atoms become intense, and make the deposition process rapid.

According to Eq. (1), the thickness (t) of the film was calculated. It can be observed that the films become thicker with higher bath temperature. The current density increases when films are deposited in a warmer bath, so the films became thicker.

4. XRD analysis of CIGS thin films

In the XRD patterns (Fig. 2) of the Cu–Ga–In–Se precursor thin films, there are three main diffraction peaks due to (112), (220) and (312) planes corresponding to CIGS.

This result shows that the films have a single chalcopyrite structure as the major phase and no secondary phase. The samples exhibit a strong preferential orientation (Fig. 2), and the

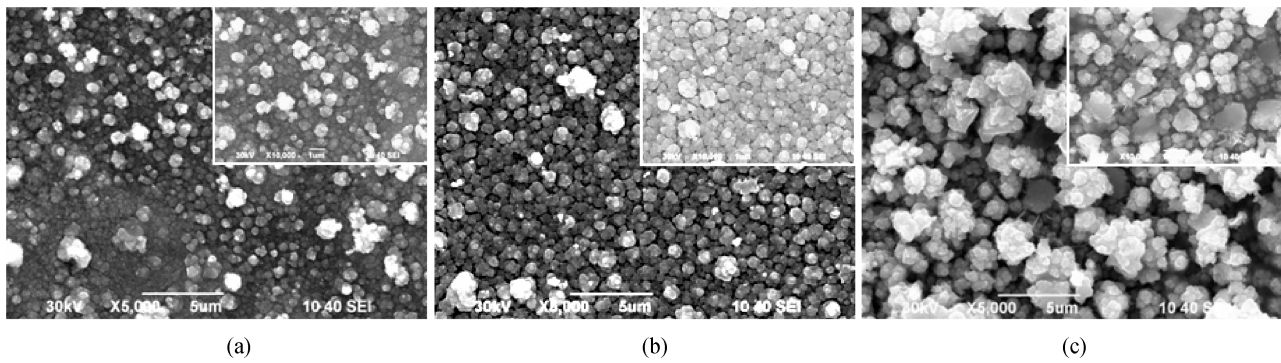


Fig. 3. Top-view SEM micrographs of CIGS layers in bath temperatures of (a) 20, (b) 40, and (c) 60 °C.

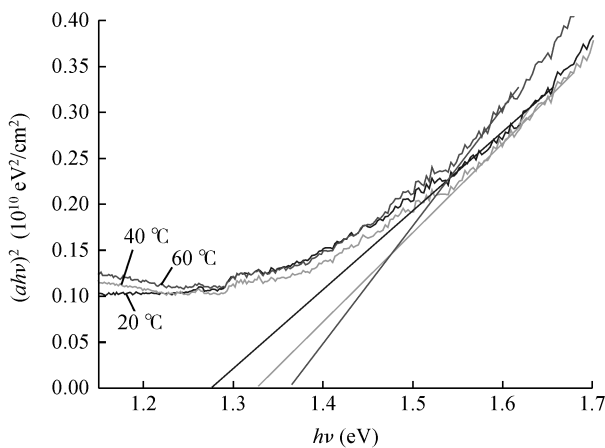


Fig. 4. Variation of $(\alpha hv)^2$ as a function of radiation energy hv of thin films fabricated at 20, 40, 60 °C.

most intense peak is situated at approximately 44.25°. However, the sample at 60 °C exhibits better crystallinity as is evident from the sharp XRD peaks. The effect of different bath temperatures on the crystallinity of the CIGS films can be observed in Fig. 2. Increasing the bath temperature is propitious to improving the crystallinity and uniformity of the layer, and makes them thicker, which is good for fabricating high quality solar cells.

5. SEM micrographs of CIGS films

Figure 3 shows surface micrographs of the $CuGa_x-In_{1-x}Se_2$ precursor thin films. It can be observed that there are many small crystallites with grain sizes of approximately 1 μm, a thin and non-dense distribution of which is visible on the surface of the CIGS film. It is indicated that the morphology is more compact and homogeneous when the bath temperature was 60 °C.

6. Optical characterization

It is well known that $CuInGaSe_2$ is a direct gap semiconductor, so the absorption coefficient in the region of strong absorption obeys the following equation^[23]:

$$\alpha = \frac{C}{hv} (hv - E_g)^{1/2}, \tag{3}$$

where h is the Planck constant, v is the radiation frequency, E_g is the band gap energy and C is a constant. The E_g values of the different thin films were evaluated from the plot of squares of optical absorption coefficient $(\alpha hv)^2$ as a function of the photon energy (hv) . The obtained results are displayed in Fig. 4.

The values of the band gap of the films annealed at 20, 40, 60 °C are estimated to be 1.27, 1.33, 1.38 eV, which are lower than that of the optimum value (1.45–1.7 eV) of the terrestrial solar spectrum^[1]. The percentage of Ga^{3+} determines the band gap of $CuIn_{1-x}Ga_xSe_2$ thin films^[13]. The band gap of the film deposited at 60 °C is bigger, and is much closer to the optimum value of CIGS thin film solar cells. So it is useful to elevate the bath temperature to get better CIGS films, which is in good agreement with the results published in Refs. [18, 24]. The study of the electrical properties of these films is in progress. The film characterization suggests that the film annealed for 45 min is the optimal one for $CuInGaSe_2$ production and used may be as an absorber layer in the fabrication of thin film solar cells.

7. Conclusion

In the co-electrodeposition process, the effect of variation of bath composition on film properties was studied. $Cu(In,Ga)Se_2$ thin films for solar cells were successfully prepared by electrodeposition on Mo-coated glass substrate. The results indicate that CIGS thin films deviate little from the ideal stoichiometric one and a single chalcopyrite structure. The SEM pictures show that CIGS thin films have uniform grain sizes and are compact. It may be suggested that the electrodeposition technique is an important technique for growing CIGS thin films for solar cells on a large area at low cost. A detailed study on the optical and electrical properties of the CIGS films is in progress.

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