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Synthesis of $CuInSe_2$ thin films on flexible Ti foils via the hydrothermally-assisted chemical bath deposition process at low temperatures

Chung-Hsien Wu, Jeng-Shin Ma, Shin-Hom Lin, Chung-Hsin Lu*

Department of Chemical Engineering, National Taiwan University Taipei, Taiwan, ROC

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ABSTRACT

Single phased copper indium diselenide ($CuInSe_2$) films have been successfully prepared on titanium substrates directly by adopting a hydrothermally-assisted chemical bath deposition technique. $CuInSe_2$ films belong to the chalcopyrite structure were uniformly prepared at various penetration depths. The synthesis temperature of the monophasic $CuInSe_2$ films was decreased to 180 °C without the selenization process. The required temperature for preparing single phased $CuInSe_2$ films was remarkably lower than the temperatures used in conventional vacuum and non-vacuum processes. During the hydrothermal reaction, highly reactive selenium ions reacted with copper and indium ions directly to produce $CuInSe_2$ films on the substrates without any high-temperature treatment, leading to the decrease in reaction temperatures appreciably. The increase in the hydrothermal temperatures significantly improved the crystallinity and enlarged the particle sizes of $CuInSe_2$ films. This developed process can be effectively applied for the preparation of $CuInSe_2$ films on flexible substrates at low temperatures.

1. Introduction

Copper indium diselenide ($CuInSe_2$), a promising material for thin-film solar cell applications, has been extensively investigated due to its high absorption coefficient, long-term stability, and high efficiency [1–3]. Recently, $CuInSe_2$ thin films have been deposited not only on rigid substrates but also on flexible substrates [4–6]. There are certain advantages of flexible $CuInSe_2$ thin-film solar cells over the solar cells fabricated on conventional substrates. Flexible solar cells can be used on irregular surfaces and soft materials. Because of the thin thickness of flexible substrates, the developed solar cells are lightweight and have a wide range of potential applications [7–9].

$CuInSe_2$ absorber layers are typically deposited on flexible substrates via the expensive high-vacuum processes, such as the co-evaporation and the sputtering methods [10–14]. But the high production-costs restrict the application of $CuInSe_2$-based solar cells developed via high-vacuum processes mentioned above. In order to reduce the required production costs, various kinds of non-vacuum processes, such as ink printing, solution coating, and electrodeposition methods have been developed to synthesize $CuInSe_2$-based solar cells [15–19]. Nevertheless, the precursor films formed via the above mentioned non-vacuum methods need to heat at 300–500 °C temperatures for crystallizing $CuInSe_2$ films. The high reaction-temperatures caused the melting of the substrates and the inter-diffusion of the species between the deposited films and the substrates. Such unfavorable reactions occurring in the film–substrate interface, which may degrade the electrical properties of $CuInSe_2$ films appreciably.

In this study, a new hydrothermally-assisted chemical bath deposition (HCBD) process was designed and developed to deposit $CuInSe_2$ films on titanium foils. The effects of the hydrothermal temperatures and the reaction duration on the prepared films were studied in detail. The microstructures of the prepared films and the formation process of $CuInSe_2$ films synthesized via the HCBD route were investigated and interpreted thoroughly. The conversion efficiency of the fabricated CIS solar cells was also examined.

2. Experimental

Highly crystalline $CuInSe_2$ films were prepared on titanium foils via the hydrothermally-assisted chemical bath deposition process. In the first step, Copper (II) chloride, indium (III) chloride, and triethanolamine were dissolved in deionized water. The concentration of triethanolamine was set at 1 M. Simultaneously, selenium was dissolved in 5 M sodium hydroxide (NaOH) solution and added to the as-prepared solution. The corresponding concentrations of copper, indium, and selenium ions in the solutions were fixed at 0.1, 0.1, and 0.5 M, respectively. The molar ratio of copper ions to indium ions to selenium ions was fixed to 1:1:3.

* Corresponding author. Tel.: +886 2 23651428; fax: +886 2 23623040.
E-mail address: chlu@ntu.edu.tw (C.-H. Lu).

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After that the mixed solutions and titanium foils were transferred into a Teflon container and hydrothermally treated at temperatures ranging from 160 to 200 °C for 0.5–9.0 h. After this hydrothermal treatment, the prepared films were washed with deionized water to remove the residues. The obtained films were dried at 70 °C in a vacuum oven for 24 h.

The X-ray diffraction (XRD, Philips X'Per/PMD) analysis has been carried out to determine the crystalline structures and the phase purity of the prepared films. The phase formation of the as-prepared films with different depths was investigated by using grazing incident X-ray diffraction (GIXD, Philips X'Per/PMD). The microstructures of the as-obtained films were analyzed using a scanning electron microscope (SEM, Hitachi S-800). The UV–vis–NIR spectrophotometer (Jasco V-570) was effectively used to analyze the optical properties of the prepared films. Raman spectra were measured using a micro-Raman spectrometer (Raman, Jobin Yvon T64000) using an Ar ion laser (λ=514.5 nm) as an excitation source.

To analyze the conversion efficiency of the prepared films, solar $CuInSe_2$-based cell devices were fabricated via using Ti foils as the substrates. CdS films, with the thickness of 50 nm, were coated on the prepared $CuInSe_2$ films via the chemical bath deposition route, and ZnO/ITO films, having the thickness of 400 nm, were then sputtered onto CdS films via RF sputtering process. The current density–voltage (J–V) characteristics of the devices were measured under AM 1.5G (100 mW/cm^2) illumination at 25 °C.

3. Results and discussion

3.1. Effects of hydrothermal temperature on the formation of $CuInSe_2$ films

$CuInSe_2$ films were prepared via the hydrothermally-assisted chemical bath deposition process. The X-ray diffraction patterns of the as synthesized $CuInSe_2$ films, deposited on Ti foils at various temperatures with a reaction time of 3 h, are represented in Fig. 1. After being heated at 160 °C, the $CuInSe_2$ phase was found to be coexisted with an impurity phase of $In(OH)_3$ (Fig. 1(a)). The diffraction peaks belonging to Ti substrates corresponding to the hexagonal structure were also observed. Upon heating at 180 °C, single phased $CuInSe_2$ was obtained. As shown in Fig. 1(b), the obtained diffraction pattern was well consistent with the ICDD Card no. 89-5649. With the further increment of the heating temperature to 200 °C and 220 °C, the crystallinity of $CuInSe_2$ was also enhanced, and no other secondary phase was observed, as can be seen in Fig. 1(c and d), respectively. The above results indicated that monophasic $CuInSe_2$ films were successfully prepared at 180 °C after only 3 h of heating. The synthesis temperature for the preparation of single phase $CuInSe_2$ films in this study was much lower than the temperature required for the preparation of $CuInSe_2$ films via the co-evaporation method or sputtering method (about 500 °C) [20–22]. It is suggested that the reactivity of selenium ions in the solution is higher than that of selenium molecules. High-reactivity selenium ions could react with copper and indium ions at low temperature in hydrothermal process. Therefore, monophasic $CuInSe_2$ films formed directly on the substrates via the HCBD process without further selenization. Hence, the synthesis temperatures were significantly decreased.

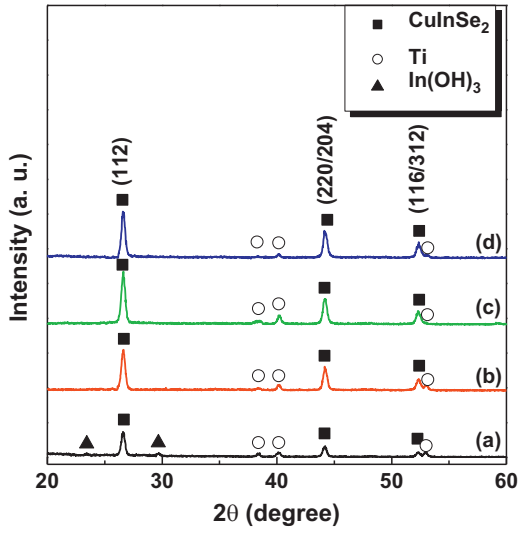

Fig. 1. XRD patterns of $CuInSe_2$ films prepared at (a) 160 °C, (b) 180 °C, (c) 200 °C, and (d) 220 °C for 3 h on Ti foils via the hydrothermally-assisted chemical bath deposition process.

The scanning electron micrographs of the prepared $CuInSe_2$ films are shown in Fig. 2. As shown in Fig. 2(a), after being heated at 160 °C, Ti foils were covered with small particles, and a small amount of particles with sizes of about 1–2 μm were also observed. When the hydrothermal temperature was raised, the particles were enlarged and the amount of particles increased as well (Fig. 2(b–d)).

3.2. Effects of the hydrothermal duration on the formation of $CuInSe_2$ films

Fig. 3 illustrates the X-ray diffraction patterns of $CuInSe_2$ films prepared at 180 °C temperatures for different time durations. After heating for 0.5 h, $CuInSe_2$ was found to coexist with $In(OH)_3$, indicating that the reaction was not complete (Fig. 3(a)). When the duration was prolonged to 3 h, single phased $CuInSe_2$ films were obtained (Fig. 3(b)). When the heating time was further increased, no impurity phase was observed (Fig. 3(c and d)). The diffraction intensity of $CuInSe_2$ films was enhanced as the reaction duration was increased (as shown in the inset of Fig. 3). This reveals that the crystallinity of the prepared films was enhanced with an increase in the reaction time.

In order to investigate the formation phases within the prepared films, the grazing-incidence X-Ray diffraction analysis was employed. The GIXD patterns of $CuInSe_2$ films prepared at 180 °C for 6 h are shown in Fig. 4. The X-ray penetration depths were calculated according to the following equation [23]:

$$D = \sin(\omega)/\mu \quad (2)$$

where D is the penetration depth, ω is the incident angle of the X-ray beam, and μ is the linear absorption coefficient. The penetration depths of the X-ray beam into the analyzed films were calculated to be 0.2 μm, 0.41 μm, 0.62 μm, 0.82 μm, 1 μm, and 1.24 μm for the ω values of 1°, 2°, 3°, 4°, 5° and 6°, respectively. Single phased $CuInSe_2$ film with a (112) orientation was observed at all incident angles. This implies that $CuInSe_2$ films were uniformly prepared at various penetration depths during the hydrothermally-assisted chemical bath deposition process. The inset of Fig. 4 represented the variation in the ratio of the intensity of (112) plane ($I_{(112)}$) to the intensity of (220/204) plane ($I_{(220/204)}$) as a function of the incident angle. As can be seen from this figure, the ratios of $I_{(112)}/I_{(220/204)}$ decreased as the incident angle was increased. It was reported that the orientation of Mo layers affected the preferred orientation of $CuInSe_2$ films in the literature [24]. Hence, it can be interpreted that the ratios of $I_{(112)}/I_{(220/204)}$ was also affected by Ti foils in this study.

A detailed discussion on the formation mechanism of $CuInSe_2$ films prepared on Ti foils via the hydrothermally-assisted chemical bath deposition process is given as follows. In hydrothermal system, well-distributed selenium ions react with copper and indium ions while the hydrothermal temperature and duration