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Preparation and characterization of $CuInSe_2$ particles via the hydrothermal route for thin-film solar cells

Chung-Hsien Wu, Fu-Shan Chen, Shin-Hom Lin, Chung-Hsin Lu*

Department of Chemical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei 106, Taiwan, ROC

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ABSTRACT

$CuInSe_2$ powders with a chalcopyrite structure used in thin-film solar cells were successfully prepared via a hydrothermal method at low temperatures within short durations. Well-crystallized $CuInSe_2$ particles were formed via the hydrothermal reaction at 180 °C for 1 h. The concentrations of stabilizer, triethanolamine (TEA), significantly affected the purity, morphology and particle sizes of the prepared powders. Increasing the reaction duration and temperatures led to decrease the amount of second phase $In(OH)_3$ and resulted in the formation of pure $CuInSe_2$. Densified $CuInSe_2$ thin films were prepared from ink printing with the addition of the flux. Increasing the selenization temperatures increased the grain size and improved the crystallinity of $CuInSe_2$ films.

1. Introduction

Chalcopyrite $CuInSe_2$ (CIS) is one of the potential materials as the absorber layer for thin-film solar cells. Because of its high absorption coefficient, the thickness of the absorption layers can be reduced to several micrometers. The band gap of $CuInSe_2$ can be tuned from 1 eV to 1.68 eV by substituting part of In^{3+} by Ga^{3+}. High efficiency $CuInSe_2$ solar cells are commonly prepared via the physical vapor deposition method [1–3]. This kind of process requires a complicated facility, thereby leading to the high fabrication cost. To avoid these drawbacks, new deposition methods are required to be developed.

To simplify the solar cell production process, non-vacuum processes have been extensively investigated in recent years. Different kinds of processes such as the spray pyrolysis method [4], the electrodeposition process [5,6] and the ink printing method [7] have been studied. Among them, the ink printing method using particles is considered a promising process because of its low cost, efficiency of resource material usage and simplified scaling up potential [8]. In this process, the ratios of metal ion can be easily controlled and the uniform films can be prepared over a large area [9,10]. Furthermore, this method also can be applied to continuous roll-to-roll processes for the large scale fabrication. Thus the preparation of $CuInSe_2$-based particles becomes an important subject for $Cu(In,Ga)Se_2$ solar cells [11–15].

In previous reports, $CuInSe_2$ particles were synthesized via the solvothermal route [16,17]. However, the required synthesis time was long, and the required ethylenediamine solvent was costly and easily evaporated. To improve these disadvantages, the hydrothermal route was utilized to synthesize $CuInSe_2$ particles in this study. H_2O was used as the solvent in the hydrothermal process, and it was more environmental friendly than ethylenediamine. In the developed process, varying the concentration of the stabilizer-triethanolamine, $CuInSe_2$ particles were prepared at low temperatures within a short reaction period. The effects of hydrothermal temperatures and time on the structure and morphology of the synthesized powders were studied. $CuInSe_2$ thin films were coated onto Mo/glass substrates via the doctor blade process. The influence of selenization temperatures on the crystallinity and morphology of $CuInSe_2$ thin films was also investigated.

2. Experimental

$CuInSe_2$ powders were prepared via the hydrothermal process by employing triethanolamine (TEA) as the stabilizer. Copper (II) chloride and indium (III) chloride were dissolved in deionized water with the addition of triethanolamine. The concentrations of triethanolamine were varied from 0 to 2 M. Selenium was dissolved in 5 M sodium hydroxide (NaOH) solution. The copper, indium, and selenium ion concentrations in the solutions were fixed at 0.1, 0.1 and 0.5 M, respectively. The prepared solutions were mixed in accordance to the molar ratio of $Cu^{2+}:In^{3+}:Se^{2-} = 1:1:3$. The mixed solutions were transferred into a Teflon container and hydrothermally treated ranging from 160 to 200 °C for 1 to 9 h. The prepared powders were filtered and washed with deionized water and ethanol several times to remove the residues presented in the powders. The obtained powders were dried at 70 °C in a vacuum oven for 24 h. $CuInSe_2$ thin films were also coated via the doctor blade method. Copper and indium ion precipitates were used as the flux. The paste comprised 30 wt% of $CuInSe_2$ powders prepared at 180 °C for 3 h, 5 wt% of flux, 1 wt% of

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

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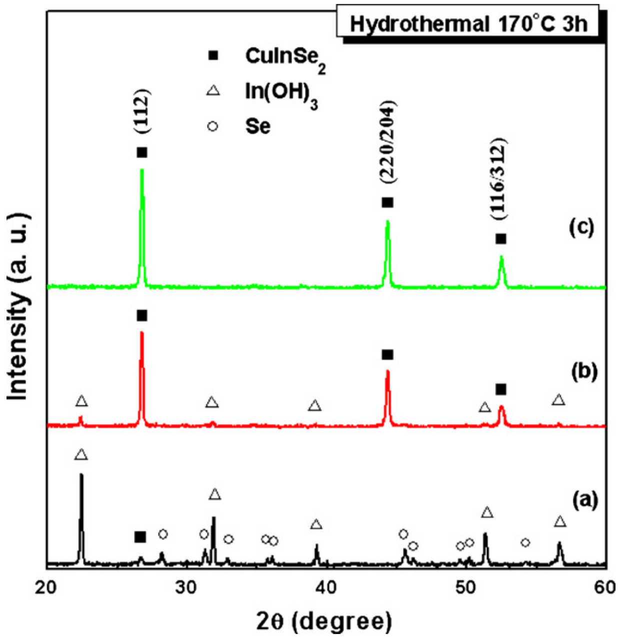

Fig. 1. X-ray diffraction patterns of the hydrothermal derived $CuInSe_2$ powders prepared at 170 °C for 3 h with (a) 0.5 M, (b) 1 M and (c) 2 M TEA in the hydrothermal process.

sorbitan monooleate and 64 wt% of ethanol. The prepared pastes were coated onto Mo/glass substrates and then dried at 250 °C for 10 min on a hot plate, followed by heating at 350 °C in air for 10 min to evaporate the residual organics. The as-prepared films were selenized from 450 to 550 °C for 30 min under an inert atmosphere with selenium vapor.

The X-ray diffraction (XRD) analysis and the Raman spectra analysis were carried out to determine the crystal structures and phase purity of the prepared powders and films. The phases of the prepared films at the different depths were investigated via grazing incident X-ray diffraction (GIXD). The microstructures and the chemical composition of the obtained powders and films were analyzed using a scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDX). The optical properties of the prepared $CuInSe_2$ powders were investigated using a UV–Vis–NIR spectrophotometer in the wavelength range of 500–1500 nm at room temperature.

3. Results and discussion

3.1. Effects of the reaction conditions on the microstructures of $CuInSe_2$ powders in hydrothermal process

NaOH solution was used to dissolve selenium in water in this study. The presence of NaOH will result in the precipitation of copper and indium ions. To avoid the precipitation of copper and indium ions, triethanolamine ($N(C_2H_4OH)_3$, TEA) was used as the stabilizer to react with cations to form $[Cu(N(C_2H_4O)_3)_2]^{4-}$ and $[In(N(C_2H_4O)_3)_2]^{3-}$ complexes in the solution as shown in reactions (1) and (2).

$$In^{3+} + 2(N(C_2H_4OH)_3) + 6OH^- \rightarrow [In(N(C_2H_4O)_3)_2]^{3-} + 6H_2O \tag{1}$$

$$Cu^{2+} + 2(N(C_2H_4OH)_3) + 6OH^- \rightarrow [Cu(N(C_2H_4O)_3)_2]^{4-} + 6H_2O \tag{2}$$

Fig. 1 illustrates the X-ray diffraction patterns of $CuInSe_2$ powders prepared at 170 °C for 3 h employing TEA with various concentrations ranging from 0.5 to 2 M. As shown in Fig. 1(a), when the TEA concentration was set to be 0.5 M, $CuInSe_2$ started to form with the major impurity $In(OH)_3$ and small amounts of Se. As the TEA concentration increased to 1 M (Fig. 1(b)), the intensity of $CuInSe_2$ diffraction peaks were also increased, and only a small amount of $In(OH)_3$ remained. After increasing the TEA concentration to 2 M, single-phased $CuInSe_2$ was obtained. The diffraction peaks of the particles prepared with 2 M TEA were in good agreement with the data reported in ICDD File No. 89-5647. This result indicated that tetragonal $CuInSe_2$ with chalcopyrite structure was formed. This reveals that TEA could prevent the production of $In(OH)_3$, thereby facilitating the formation of single-phased $CuInSe_2$.

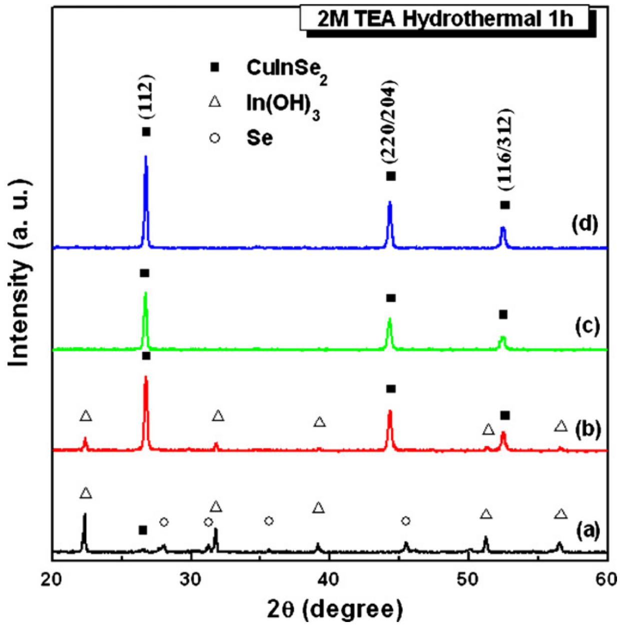

Fig. 2. X-ray diffraction patterns of the hydrothermal derived $CuInSe_2$ powders prepared at (a) 160 °C, (b) 170 °C, (c) 180 °C and (d) 200 °C for 1 h with 2 M TEA.

To investigate the reaction temperature effects on the structure and morphology of $CuInSe_2$ particles, the hydrothermal reaction was carried out from 160 °C to 200 °C for 1 h with 2 M TEA. The XRD patterns of the $CuInSe_2$ powders prepared at different temperatures are shown in Fig. 2. After heating at 160 °C, a small amount of $CuInSe_2$ was found to coexist with the impurities of $In(OH)_3$ and Se (Fig. 2(a)). When the heating temperature was increased to 170 °C, the intensity of $CuInSe_2$ diffraction peaks increased significantly. When the hydrothermal temperature reached 180 °C, single-phased $CuInSe_2$ was obtained. As the hydrothermal temperature was further increased to 200 °C, the crystallinity of $CuInSe_2$ was further enhanced. In previous reports, single-phased $CuInSe_2$ powders were synthesized at 180 °C via the solvothermal process for a least 15 h [18]. In_2Se_3 and Se are the major intermediates in the solvothermal process. High temperature and long duration are required to convert these intermediates to form single-phased $CuInSe_2$ [19]. In this study, selenium was easily dissolved in NaOH solution with no In_2Se_3 formed. Hence the reaction temperature and time for preparing pure $CuInSe_2$ powders were significantly reduced. In addition, the band gap of the prepared $CuInSe_2$ powders was calculated about 1.02 eV using a UV–Vis–NIR spectrophotometer in the wavelength range of 500–1500 nm at room temperature. The band gap of the prepared powders is consistent with the previous report [20].

The microstructures of the hydrothermal-derived $CuInSe_2$ particles prepared at various temperatures for 1 h with 2 M TEA are shown in Fig. 3. When the reaction temperature was 160 °C, the synthesized powders exhibited a cubic shape and few spherical particles with a diameter around 50 nm were also observed (Fig. 3(a)). As the temperature was increased to 170 °C, the amount of particles with a cubic shape decreased significantly (Fig. 3(b)). As shown in

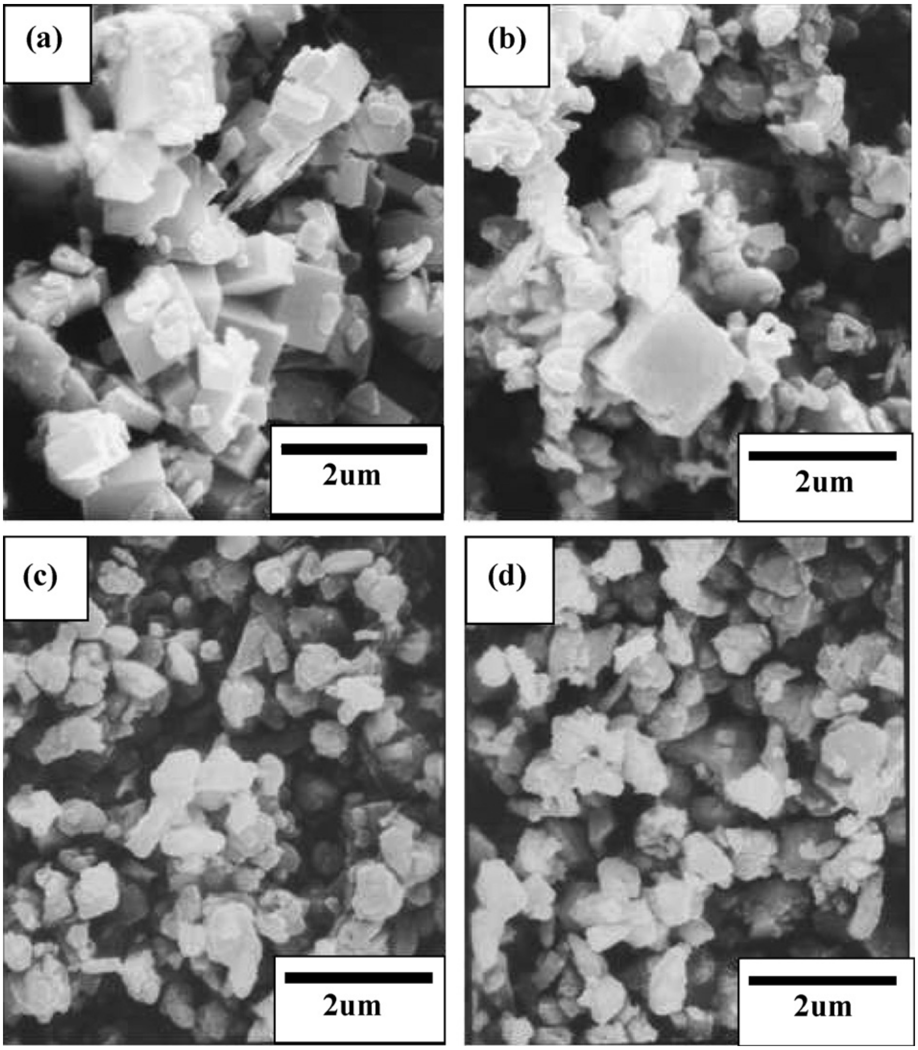

Fig. 3. Scanning electron micrographs of the $CuInSe_2$ powders prepared at (a) 160 °C, (b) 170 °C, (c) 180 °C and (d) 200 °C for 1 h in the hydrothermal process.

Fig. 3(c), the particle size of the prepared powders was about 0.5 μm and no cubic shape of particles was observed at 180 °C. Upon further increasing the reaction temperature to 200 °C, the shape and particle size of the prepared powders remained similar. The chemical composition of the powders prepared at 160 °C and 170 °C for 1 h were analyzed using EDX. It was found that the chemical compositions of the particles with a cubic shape were indium and oxygen, and no other elements were detected. According to the XRD results, it is suggested that the particles with a cubic shape are deduced to be $In(OH)_3$.

Fig. 4 illustrates the XRD patterns of $CuInSe_2$ synthesized via the hydrothermal route at 170 °C for various durations. As the reaction time was 1 h, $In(OH)_3$ was still observed as shown in Fig. 4(a). When the heating time reached 3 h, single-phased $CuInSe_2$ was obtained (Fig. 4(b)). Further increasing the reaction duration to 6 and 9 h led to an increase in the crystallinity of the obtained $CuInSe_2$ powders. These results reveal that an increase in hydrothermal duration can help the formation of single-phased of $CuInSe_2$. As compared with the results in Fig. 2(c) and Fig. 4(b), the intensity of the diffraction peak of $CuInSe_2$ powders prepared at 170 °C for 3 h was higher than that prepared at 180 °C for 1 h. This implies that the soaking treatment can increase the crystallinity of the prepared powders.

Fig. 5 depicts the Raman spectra of $CuInSe_2$ particles prepared at 170 °C for various duration. After heating at 170 °C for 1 h (Fig. 5(a)), three peaks were observed at 173, 215 and 309 cm^{-1}. The peaks at 173 and 215 cm^{-1} were assigned to the A1 and E mode of $CuInSe_2$, respectively [21]. In addition, the peak at 309 cm^{-1} was attributed to $In(OH)_3$ [22]. After prolonging the reaction duration to be longer than 3 h, only the Raman spectra belonging to $CuInSe_2$ were observed, and no other peaks were detected in the powders. The observation indicated that single-phased of $CuInSe_2$ particles were obtained via the hydrothermal route at 170 °C for 3 h.

3.2. Formation mechanism of $CuInSe_2$ powders in hydrothermal process

The resulting compounds of the powders prepared at various conditions with 2 M TEA are summarized in Fig. 6. It can be seen that the phases of the prepared samples can be separated into three parts. Within zone A $CuInSe_2$ coexists with $In(OH)_3$ and Se. Increasing the reaction temperature or prolonging the reaction duration, all Se was reacted, and only $In(OH)_3$ coexisted with $CuInSe_2$ (zone B). Further increasing the reaction temperature than 170 °C and prolonging the reaction duration then 1 h, single-phased $CuInSe_2$ was formed in zone C. According to the above results, $CuInSe_2$, $In(OH)_3$ and Se compounds were produced first. When the reaction time and temperature were increased, the $In(OH)_3$ and Se impurities diminished and helped the formation of pure $CuInSe_2$.

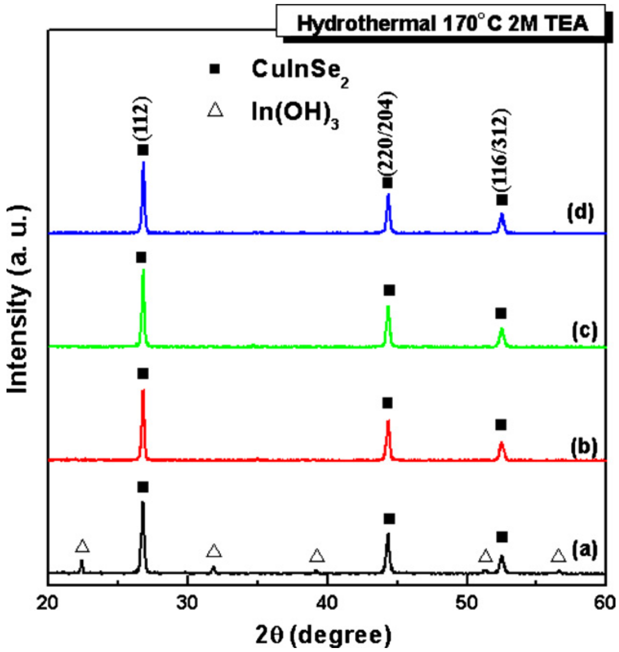

Fig. 4. X-ray diffraction patterns of the hydrothermal derived CuInSe$_2$ powders prepared at 170 °C for (a) 1 h, (b) 3 h, (c) 6 h and (d) 9 h with 2 M TEA.

3.3. *Preparation of CuInSe$_2$ films*

CuInSe$_2$ films were prepared via particle pastes coated onto Mo/glass substrates. The as-prepared films were heated in air at 350 °C to evaporate the residual organics and selenized under an inert with Se vapor for 30 min. X-ray diffraction patterns of the prepared films with the flux selenized at various temperatures are shown in Fig. 7(a). After selenizing at 450 °C, CuInSe$_2$ was found to coexist with In$_2$O$_3$. The appearance of In$_2$O$_3$ is due to the oxidation of the flux when the organic species were removed at low temperature in air. With an increase in the selenization temperature to 550 °C, well crystallized and single-phased CuInSe$_2$ was obtained.

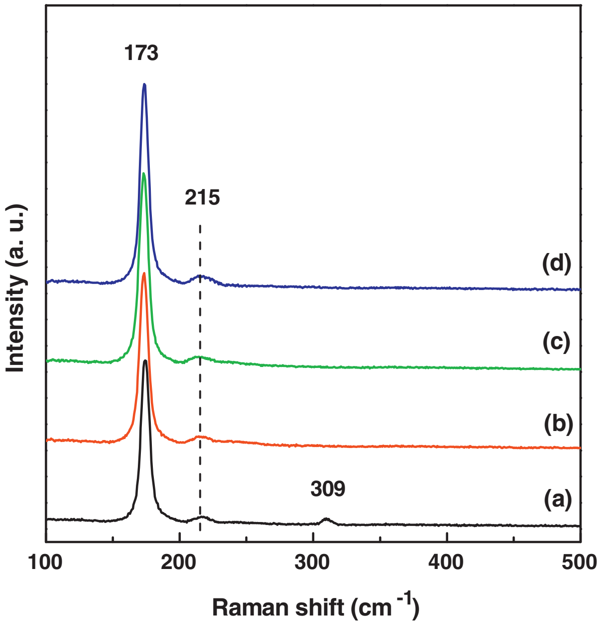

Fig. 5. Raman spectra of the hydrothermal derived CuInSe$_2$ powders prepared at 170 °C for (a) 1 h, (b) 3 h, (c) 6 h and (d) 9 h with 2 M TEA.

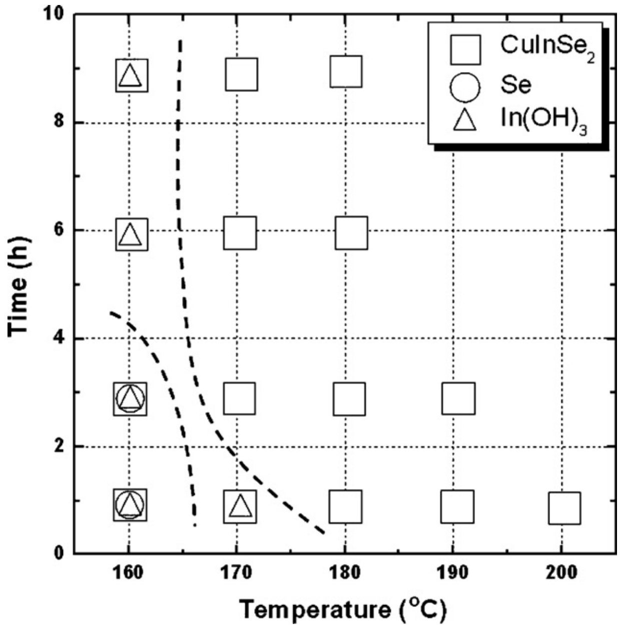

Fig. 6. Resultant compounds of the samples prepared with different reaction conditions in the hydrothermal process.

Grazing incident X-ray diffraction (GIXD) was employed to investigate the prepared CuInSe$_2$ films. The relation between the resultant compounds and the incident angle (ω) of the X-ray beam is illustrated in Fig. 7(b). The penetration depths of the X-ray into the thin films became deeper with increasing X-ray beam incident angles. Similar intensities for the diffraction peaks of In$_2$O$_3$ were observed in Fig. 7(b). This implies that In$_2$O$_3$ in the film was not selenized at this temperature. However, the intensity of CuInSe$_2$ decreased as the ω increased, indicating that the reaction took place from the surface to the interior. This is because that the selenium

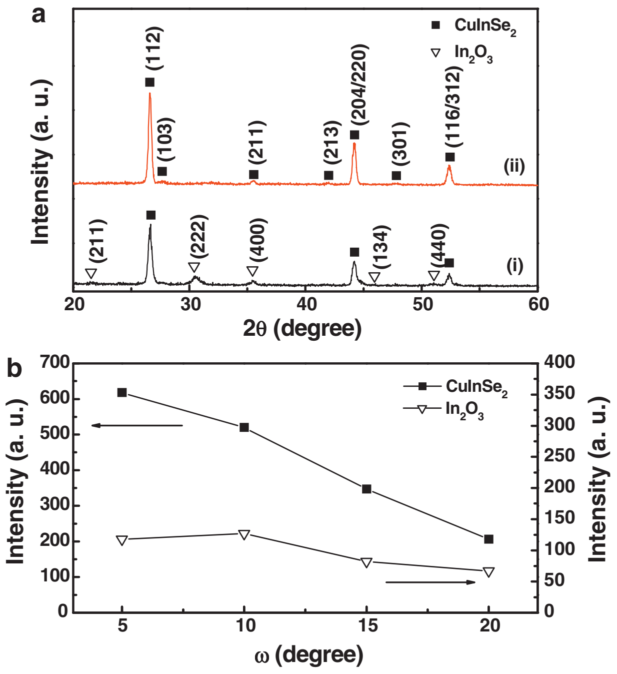

Fig. 7. (a) X-ray diffraction patterns of CuInSe$_2$ film with the flux selenized at (i) 450 °C and (ii) 550 °C for 30 min. (b) The relation between the resultant compounds of CuInSe$_2$ film selenized at 450 °C for 30 min with the flux and the incident angle (ω) of the X-ray beam.

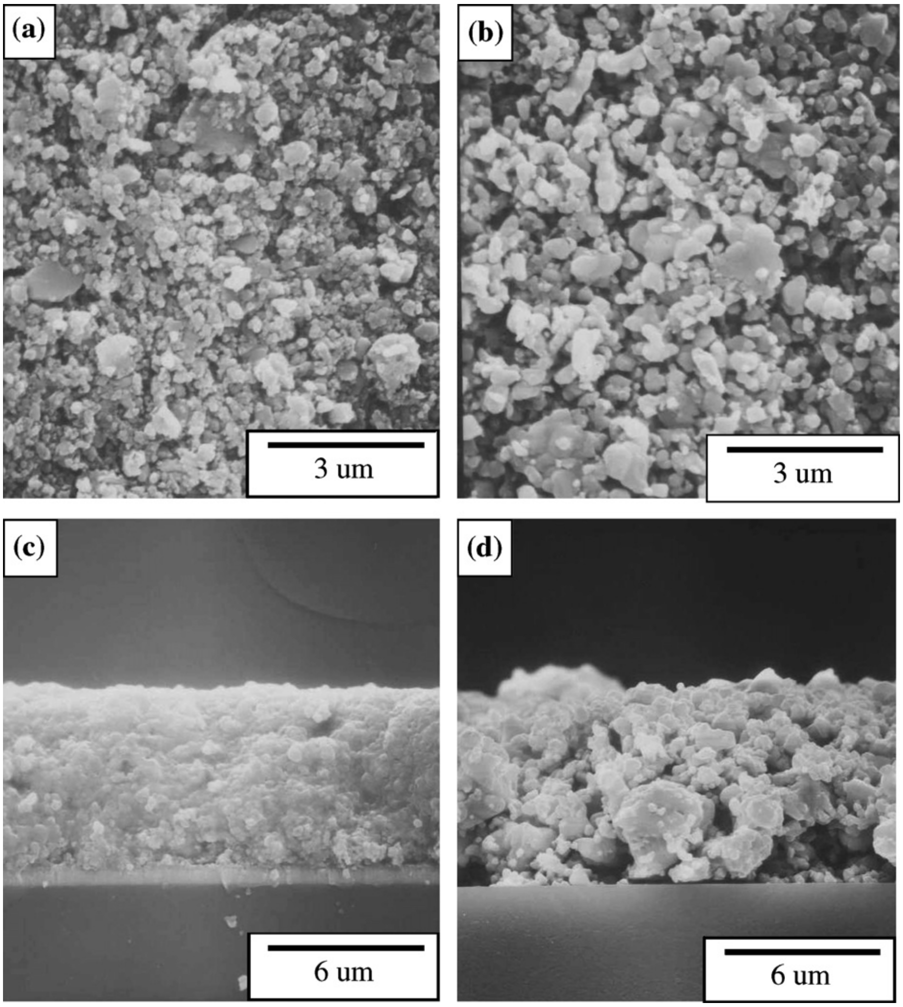

Fig. 8. Planar scanning electron micrographs of $CuInSe_2$ films with the addition of the flux selenized at (a) 450 °C and (b) 550 °C for 30 min. Cross-sectional scanning electron micrographs of $CuInSe_2$ films selenized at 550 °C for 30 min (c) with the flux and (d) without the flux.

vapor reacts with the surface particles first, then diffuses into the inner region.

Planar views of $CuInSe_2$ thin films with the addition of the flux selenized at 450 °C and 550 °C for 30 min are shown in Fig. 8(a) and (b), respectively. As the selenization temperature was increased, the grain size also increased. The copper species used in the flux is considered to react with the selenium vapor to form Cu_xSe compounds during the selenization process. The solid–liquid phase transition of Cu_xSe in the selenization process can promote the densification and enlarge the grain size of the films because of the low melting point of Cu_xSe [23]. In addition, in order to correspond with the stoichiometry of $CuInSe_2$, indium ions were needed to be added. The cross-sectional scanning electron micrographs of $CuInSe_2$ thin film selenized at 550 °C with the flux are shown in Fig. 8(c). The prepared film exhibited a smooth and densified microstructure. The flat surface and absence of porous microstructure is believed to reduce the number of defects at the junction and prevent the shunt path, resulting in enhanced solar cell efficiency [24,25]. To compare the effects of the flux addition on the film morphology, the cross-sectional scanning electron micrographs of $CuInSe_2$ thin film without the flux are illustrated in Fig. 8(d). A non-uniform film was observed with a large number of pores existing inside the film. It was found that the addition of the flux promotes particle growth. This reveals that smooth and dense $CuInSe_2$ films can be successfully obtained via the addition of the flux.

4. Conclusions

Well-crystallized $CuInSe_2$ has been successfully prepared via the hydrothermal route at 180 °C for 1 h. The TEA concentrations significantly affected the purity of the obtained powders. As the TEA concentration was increased to 2 M, the impurity $In(OH)_3$ diminished and the pure phase of $CuInSe_2$ was formed. Increasing the reaction temperature and reaction time facilitated the reaction to form single-phased $CuInSe_2$. $CuInSe_2$ thin films were prepared from particle paste printing with the addition of the flux. As the selenization temperature was increased to 550 °C, well-crystallized and densified films were obtained. The addition of the flux into the process led to enlarge the grain size and the formation of dense and smooth $CuInSe_2$ films.

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