Current Applied Physics 10 (2010) S383–S386

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Synthesis and characterization of $CuInSe_2$ thin films for photovoltaic cells by a solution-based deposition method

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ARTICLE INFO

Article history:
Received 2 November 2009
Accepted 19 January 2010
Available online 25 January 2010

Keywords:
Solar cell
Photovoltaic cell
$CuInSe_2$
Thin film
Absorber layer
Chalcopyrite

ABSTRACT

Polycrystalline $CuInSe_2$ thin films were deposited by a novel solution-based continuous flow microreactor (CFM) method at low temperature. In order to investigate the effect of the Cu to In mole ratio on the film formation, the concentrations of indium reagent were varied in the preparation of precursor solutions. The estimated optical band gaps were ~1.54 eV and ~1.25 eV for the as-deposited and the annealed $CuInSe_2$ thin films which could be a result of quantum size effect. A tetragonal chalcopyrite structure of $CuInSe_2$ was identified in XRD analysis. From the XRD analysis, it was found that the crystal growth of the as-deposited and the annealed films are affected by the molar concentration of indium reagents. The film deposited from a solution with 0.025 M of $InCl_3$ shows the best crystallinity. The film thickness reaches around 2.5 μm after only a 7 min of deposition time which will provide good throughput for thin film PV manufacturing.

1. Introduction

Polycrystalline $CuInSe_2$ thin films have received a great deal of attention for photovoltaic applications. $CuInSe_2$ is considered as one of the most important light absorbers in the family of I–III–VI_2 type ternary chalcopyrite materials for solar cells. It has a direct band gap around 1.04 eV and an absorption coefficient greater than 5×10^{-5} cm^{-1} in the terrestrial solar spectrum range, which are ideal for the fabrication of thin film photovoltaic devices. It was reported that energy conversion efficiency of $CuInSe_2$ solar cell could reach almost 20% [1,2]. A variety of methods including spray pyrolysis [3], electrodeposition [4], sputtering [5], thermal and flash evaporation [6], and chemical bath deposition (CBD) [7] have been reported for the formation of $CuInSe_2$ thin films. Many of these technologies require the use of expensive vacuum systems and high thermal budgets which contribute to higher production costs. Solution-based chemical deposition methods, however, do not require the vacuum systems and can be used to fabricate large area thin films on various substrates including glasses, semiconductors, metals, and plastics.

Recently, we have developed a novel solution-based deposition method to synthesize various semiconductor thin films. This approach uses a continuous flow microreactor (CFM), which is capable of decoupling the homogeneous particle formation from the heterogeneous thin film growth and is able to overcome the drawbacks associated with the conventional CBD process [8–13]. The $CuInSe_2$ thin films were deposited onto glass substrates by varying the indium reagent concentrations using the CFM process. We have demonstrated that the deposition of $CuInSe_2$ thin films by the CFM method is a viable process for the fabrication of $CuInSe_2$ thin film solar cells.

2. Experimental details

2.1. Preparations of substrates and precursor solutions

The commercial microscope glasses (Fisher Scientific) were used as substrates. The glasses were ultrasonically cleaned with a 1 M aqueous solution of sodium hydroxide (NaOH, Aldrich Inc.) and chemically cleaned using a standard acetone, methanol, and de-ionized (DI) water (AMD) process. In order to investigate the effect of the Cu to In mole ratio on the film formation, the indium reagent concentration was varied in the precursor solutions. Soluble sources of Cu and In were prepared by dissolving 0.1 M of copper chloride ($CuCl_2 \cdot 2H_2O$, Sigma–Aldrich Inc.) and 0.005–0.05 M indium chloride ($InCl_3 \cdot 2H_2O$, Sigma–Aldrich Inc.) in 200 ml DI water. Sodium selenosulfite (Na_2SeSO_3) as a source of selenium was prepared by mixing 0.05 M sodium sulphite (Na_2SO_3, Sigma–Aldrich Inc.) with selenium powder (Se, Sigma–Aldrich Inc.) into 200 ml DI water.

2.2. Depositions of $CuInSe_2$ thin films

In the CFM process, the precursor solutions A and B are initially introduced into a micro-mixing element and their individual

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doi:10.1016/j.cap.2010.01.006

streams are allowed to mix together in the element. The resulting mixture from the element is passed through a temperature-controlled channel, which was maintained at around 140 °C, before it is impinged on a temperature-controlled substrate. For the formation of thin films, the homogeneous particle formation process is highly undesirable since the adsorption of the particles on the substrate surface yields powdery and non-adherent films. The homogeneous chemistry of the impinging flux can be controlled precisely by the inlet concentrations, temperature, and most importantly the residence time. The reactant stream A consisted of the prepared aqueous precursor solution for the Cu and In sources. The stream B consisted of aqueous sodium selenosulfite solution. The flow rate of solution was fixed in 1 ml/s and the time of impinging was fixed at 7 min. The details of the CFM deposition procedure have been described in our previous papers [8–13]. In order to improve the crystallinity of the films, the as-deposited $CuInSe_2$ films were annealed at 400 °C under a nitrogen atmospheric condition.

2.3. Characterizations of $CuInSe_2$ thin films

The optical band gap, surface morphology, crystalline structure, and chemical binding information of the prepared $CuInSe_2$ thin films were analyzed using UV–visible spectrophotometer (Ocean Optics, USB-4000 optic spectrometer), scanning electron microscope (SEM, Hitachi S-4800), thin film X-ray diffraction spectrometer (XRD, Panalytical MPD for thin film), and X-ray photoelectron spectroscopy (XPS, ESCALAB, 250 XPS spectrometer).

3. Results and discussion

3.1. Structural characterization

The crystal structure and crystallographic orientation of the polycrystalline $CuInSe_2$ thin films deposited by the CFM method was determined by the analysis of XRD spectra in comparison with the JCPDS data and literatures. Fig. 1 shows X-ray diffraction patterns of the $CuInSe_2$ thin films deposited by varying the indium reagent concentration in the precursor solution. The spectrum (a) represents the XRD pattern of the as-deposited $CuInSe_2$ film prepared using a precursor solution containing 0.025 M aqueous $InCl_3$. The major characteristic diffraction lines (1 1 2), (2 1 1), and (2 0 4), which indicate the formation of $CuInSe_2$ ternary compound, are observed even in the as-deposited film although their intensity is very weak. The XRD spectra in Fig. 1b–d present the diffraction patterns of the thermally treated $CuInSe_2$ films, which were prepared from 0.005 M, 0.010 M, and 0.025 M $InCl_3$, respectively. More intensive peaks were observed after thermal annealing as shown in Fig. 1. This result indicates that more crystalline $CuInSe_2$ thin films were formed when the molar concentration of $InCl_3$ increases. The film deposited from a solution with 0.025 M of $InCl_3$ shows the best crystallinity. The diffraction peaks at $2\theta = 26.65°$, 35.54°, 44.184°, 52.433°, and 62.668° correspond to the (1 1 2), (2 1 1), (2 0 4), (3 1 2), and (3 2 3) crystallographic planes of the tetragonal $CuInSe_2$ structure, respectively. These X-ray diffraction peaks are in good agreement with the data of JCPDS 87-2265 for tetragonal chalcopyrite phase only except appearance of a CuIn metal alloy peak. A characteristic peak located at $2\theta = 41.93°$ was observed in the XRD pattern and it was identified as the CuIn metal alloy line belonging to Cu_4In and Cu_9In_4 systems [14]. The alloy line becomes more intensive as the $InCl_3$ content increases. The presence of microregions containing unreacted Cu and In elements could be the cause for the observed Cu_4In and Cu_9In_4 alloy diffraction lines [15]. If indium remains unreacted in the as-deposited films, the selenization of Cu can be interrupted by a reaction between In and Cu prior to the occurrence of selenization. It is inferred that the unreacted indium leads to the formation of the Cu_4In and Cu_9In_4 alloy during the thermal treatment process. From

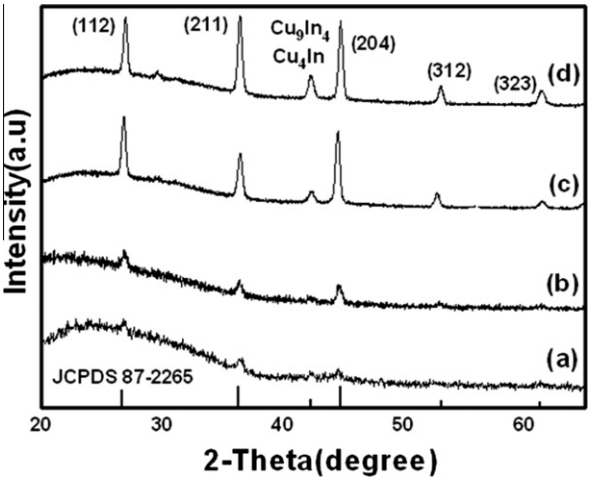

Fig. 1. X-ray diffraction patterns of the $CuInSe_2$ thin films annealed at 400 °C for 1 h: (a) the as-deposited, (b) 0.005 M of $InCl_3$, (c) 0.010 M of $InCl_3$ and (d) 0.025 M of $InCl_3$ in the precursor solution of In source.

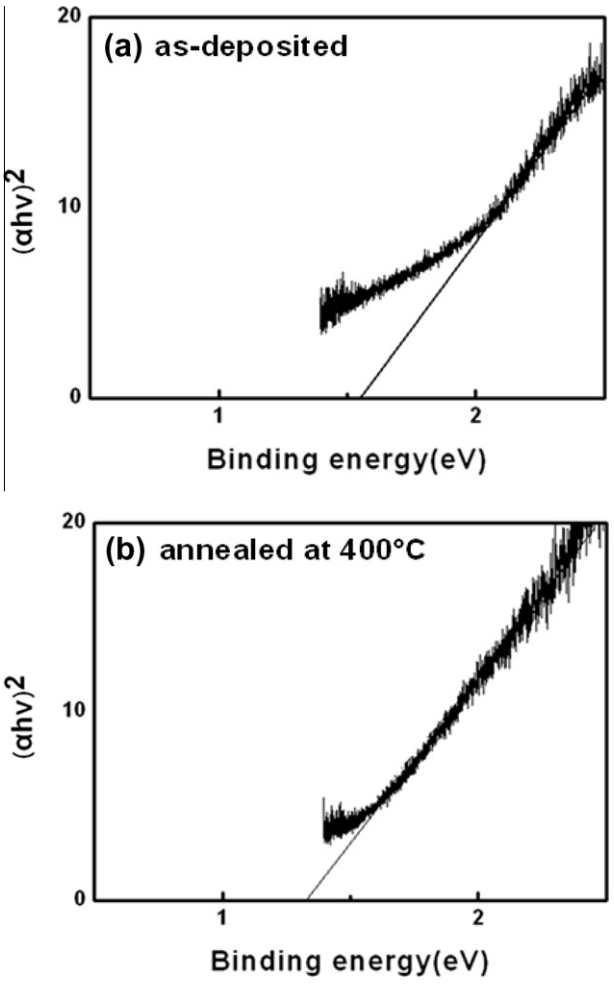

Fig. 2. UV–vis absorption spectra of the $CuInSe_2$ film deposited with the precursor solution containing 0.025 M of $InCl_3$ and its estimated optical band gap: (a) the as-deposited and (b) the annealed at 400 °C.