Thin Solid Films 517 (2009) 6853–6856

Contents lists available at ScienceDirect

Thin Solid Films

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

Letter

Low-temperature processing of a solution-deposited CuInSSe thin-film solar cell

William W. Hou [a], Brion Bob [b], Sheng-han Li [a], Yang Yang [a,*]

[a] Department of Materials Science and Engineering, University of California-Los Angeles, Los Angeles, CA 90095, USA
[b] Department of Physics, Harvard University, 17 Oxford Street, Cambridge, MA 02138, USA

ARTICLE INFO

Article history:
Received 14 May 2009
Received in revised form 16 June 2009
Accepted 17 June 2009
Available online 26 June 2009

Keywords:
Non-vacuum
Spin-coating
Solar cell
Photovoltaics
Hydrazine
CuInSSe

ABSTRACT

A low-temperature (~350 °C) solution-processed CuInSSe photovoltaic cell is reported. The CuInSSe film was solution-deposited via spin-coating from a precursor solution consisting of metal chalcogenides (Cu_2S and In_2Se_3) dissolved in hydrazine (N_2H_4). X-ray diffraction data indicated a full conversion from the hydrazine precursor to $CuInS_xSe_{2-x}$ structure at 350 °C with an average crystallite size of approximately 45 nm. Bandgap tuning of the $CuInS_xSe_{2-x}$ was achieved by varying the excess amount of sulfur in the precursor solution. Based on the (220) reflection of the XRD pattern, the bandgap of $CuInS_xSe_{2-x}$ ranged from 1.00 to 1.14 eV. Standard testing conditions at 1-sun intensity resulted in a power conversion efficiency of 7.43%.

Published by Elsevier B.V.

1. Introduction

The ability to fabricate light-weight and flexible photovoltaic cells with scalable processing has initiated numerous research activities in the solar community. Among the various materials, chalcopyrites, such as $CuInSe_2$ (CIS), $CuIn(S,Se)_2$ (CISS), and $Cu(In,Ga)Se_2$ (CIGS) have attracted considerable attention. These materials have an absorption coefficient on the order of 10^5 cm^{-1}, which translates to 90% absorption with 200-nm thickness [1]. This property renders the chalcopyrites advantageous for weight considerations. However, the standard thickness of the chalcopyrite layer in a solar cell is presently 1.5–2 μm [2], and a thinner absorber layer thickness is generally associated with an increase in shunt conductance. The shunting is a result of surface roughness on the same order as film thickness [3–4]. In addition to decreasing the chalcopyrite thickness, replacing soda-lime glass with polyimide substrates would provide further advantages in reducing the weight of the device and also the possibility of being flexible. Given that the glass-transition temperature of polyimide is approximately 400 °C, adopting the conventional deposition methods for CIS, such as coevaporation or electrodeposition, has been shown to be challenging [5].

Recently, a solution processing of CIGS method has been demonstrated using hydrazine as a solvent [6]. The chalcopyrite layer, processed at 470 °C, has been shown to have a photovoltaic efficiency of 10.2%. In the present work, we explore two facets of this hydrazine-processing method. First, the low-temperature regime of the transformation process is studied. After dissolving the metal chalcogenides in hydrazine, the solutions can be applied directly to a substrate to form smooth and dense films. Upon heating at 350 °C, the precursor film is converted to the chalcopyrite structure, and can then be subjected to further treatment. Second, the formation of CISS by incorporating sulfur (S) in the precursor solution is investigated. This method not only provides a low-temperature processing of chalcopyrite materials, but also demonstrates a simplified route of forming CISS by avoiding an additional chalcogenization step that is necessary in the traditional methods.

2. Experimental details

2.1. Solution preparation

Prior to forming the precursor solution, 1 mmol of copper sulfide (Cu_2S) and 2 mmol of sulfur (S) were combined with 4 mL of hydrazine. In a separate vessel, 1 mmol of indium selenide (In_2Se_3) and excess S or selenium (Se) were combined with 4 mL of hydrazine. A more detailed description of the precursor synthesis has been reported previously [7]. After several days of continuous stirring at room temperature, the suspensions of Cu_2S and In_2Se_3 formed clear

* Corresponding author. University of California-Los Angeles, Department of Materials Science and Engineering, Los Angeles, CA 90095, United States. Tel.: +1 310 825 4052; fax: +1 310 825 3665.
E-mail address: yangy@ucla.edu (Y. Yang).

0040-6090/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.tsf.2009.06.032

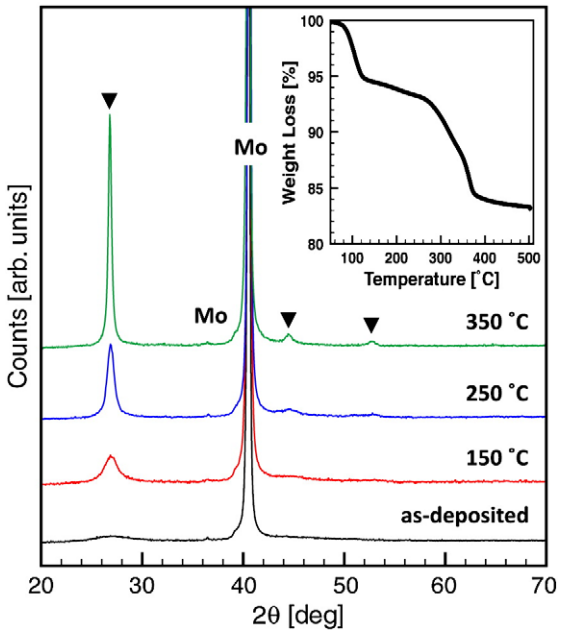

Fig. 1. X-ray diffraction of the precursor films deposited on the Mo substrate, which were subsequently thermally annealed at 150, 250, and 350 °C. Reflections of CuInSSe are marked with (▼). Inset: thermogravimetric analysis of the precursor material measured under a heating rate of 2 °C/min.

yellow and colorless solutions, respectively. It was noted that the dissolution of In_2Se_3 in the presence of excess chalcogen is accompanied by a noticeable increase in viscosity. Both solutions were filtered to remove any insoluble species, and were subsequently mixed to form the precursor solution. Figures that contain images of all three solutions can be found in a report by Hou et al. [8]. The amount excess chalcogen (S or Se) in the In_2Se_3 solution is varied depending on the desired chalcogen content in the resulting material.

2.2. Device fabrication

The fabrication of the photovoltaic cell began with the deposition of molybdenum (Mo, 1000 nm) onto a Corning 2947 glass slide by argon dc sputtering. The processing pressure was varied during deposition to achieve a bi-layer microstructure, as has been reported in the literature [9]. The $CuInS_xSe_{2-x}$ layer was deposited by spin-coating the precursor solution onto the Mo layer, followed by thermal annealing at 350 °C for 60 min. The deposition of the $CuInS_xSe_{2-x}$ layer was repeated several times, one layer on top of another, in order to achieve a film thickness of approximately 600 nm. The Cu:In concentrations were kept constant for all three depositions. Both deposition and annealing were carried out in a nitrogen-filled glove box. Next, the cadmium sulfide (CdS) layer was deposited by chemical bath deposition. Finally, 30 nm of intrinsic zinc oxide (ZnO) and 120 nm of indium tin oxide (ITO) were deposited by argon rf sputtering, and served as the top transparent electrode. The total area of the cell was 0.18 cm^2, as defined by the shadow mask used during sputtering.

2.3. Characterization

The photovoltaic performance was characterized in air without any encapsulation under an AM1.5G filter at 100 mW/cm^2 using a Newport Oriel 92192 Solar Simulator. The intensity of the light source was calibrated with an NREL-calibrated reference diode [10]. All X-ray diffraction samples (XRD) were prepared using the same deposition profile as that described for the photovoltaic cell fabrication. The XRD patterns were collected on a PANalytical X'Pert Pro X-ray Powder Diffractometer using Cu-Ka radiation (λ = 1.54050Å). The scanning electron microscope (SEM) images were taken on a Joel JSM-6700F that is equipped with an energy dispersive X-ray (EDX) analyzer based on an lithium drifted silicon detector (SiLi-204R2). Both the SEM images and EDX spectra were taken with an accelerating voltage of 10 kV.

3. Results and discussion

XRD patterns of the as-cast precursor film as well as films annealed at 150, 250, and 350 °C are shown in Fig. 1. The as-cast precursor film was prepared by placing the spin-coated precursor film in an antechamber overnight under vacuum. The XRD pattern of the as-cast film appeared to be amorphous, which is in good agreement with that reported previously [7]. As the temperature increased to 150 °C, the three reflections ((112), (220), and (312)) of the CuInSSe structure became apparent. The presence of these reflections suggested that a certain amount of CuInSSe crystallite is present even at 150 °C. At 250 °C, the patterns can be clearly indexed to be CuInSSe structure (JCPDS 36–1311). At 350 °C, the pattern essentially follows that of the pattern obtained at 250 °C, except with a decrease of full-width at half-maximum (FWHM), which indicates an increase in grain size. Based on FWHM of the (112) reflection, the estimated grain size is increased from 21.5 nm for the film annealed at 250 °C to 45.5 nm for the film annealed at 350 °C. Annealing at temperatures above 350 °C have resulted in ~100 nm grain size due to coarsening. However, given the formation of CISS crystallites at relatively low temperature, it is not possible to reach ~μm grain size by coarsening alone. Based on the observations in the XRD patterns at various temperatures, it is suggested that the reaction pathway of this hydrazine-derived CISS is different from that of reacting metal chalcogenides at elevated temperature. Perhaps this is the reason why CISS reflections are present at temperatures as low as 150 °C. This lower annealing temperature can be beneficial to achieve uniform distribution of Cu and In over a large area, which is critical to improving the overall efficiency of a solar module.

In an attempt to increase the bandgap by substituting S in the Se sites of the CISS structure, the amount of excess S in the precursor solution was varied to achieve S/[S + Se] mole ratios of 0.4, 0.5, and 0.6. Fig. 2 shows the XRD of CISS films spin-coated using precursor solutions with different sulfur content, which were subsequently thermally annealed at 350 °C. The position of the (220) reflection shifts to higher 2θ value as the sulfur content increases. This is

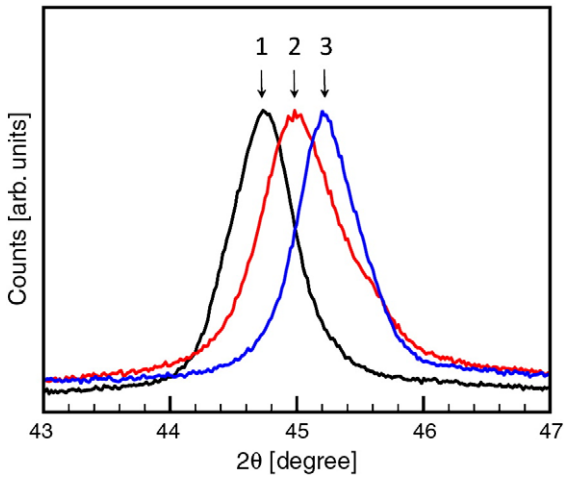

Fig. 2. The (220)/(204) reflection of $CuInS_xSe_{2-x}$ (annealed at 350 °C) using powder X-ray diffraction. The peak intensities are normalized to assist in comparison of peak positions. Different sulfur content for samples 1, 2, and 3 were prepared by varying the S/Se ratio in the precursor solution using mole fractions of sulfur of 0.4, 0.5, and 0.6, respectively.