Materials Research Bulletin 76 (2016) 85–93

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Fabrication of high quality copper indium disulphide absorbers by bell-like wave modulated electrodeposition

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ARTICLE INFO

Article history:
Received 23 June 2015
Received in revised form 23 November 2015
Accepted 6 December 2015
Available online 9 December 2015

Keywords:
A. Chalcogénide
A. Intermetallic compounds
B. Optical properties
C. Electron microscopy
C. Raman spectroscopy
D. Electrical properties

ABSTRACT

High-quality $CuInS_2$ (CIS) thin films have been fabricated by sulfurization of electrodeposited copper–indium bilayer. A novel bell-like wave modulated square wave (BWMSW) electrodeposition technique is employed for the deposition of copper thin film. Three independent parameters (current or potential, frequency, duty cycle) are available for the BWMSW electrodeposition, which is different from the traditional electrodeposition technique with only one adjustable parameter (current or potential). The influences of deposition parameters such as frequency, duty cycle and the concentration of complexing agent are investigated. Benefited from the high quality copper film obtained by the BWMSW technique, the indium film is electrodeposited successfully on the copper layer to form a compact copper–indium alloy bilayer. After sulfurized at 600 °C for 60 min, the phase pure CIS film is obtained with better crystallinity. The structures, morphologies and optoelectronic properties of the CIS film are also characterized.

1. Introduction

In recent years, thin-film solar cells have attracted the attention of researchers due to their low cost in raw materials [1,2]. Among them, chalcopyrite thin film solar cell has become one of the leaders in this field [3–6]. Many research groups have reported the fabrication of high-efficient copper–indium–gallium–diselenide (CIGS) solar cells by vacuum deposition processes [7,8], and a conversion efficiency of 20.8% has recently been achieved [9]. However, the toxicity of Se element limits its wide application. Compared with the CIGS, the sulfide analogue of copper–indium–sulphide (CIS) is less toxic. Although its record conversion efficiency (12.5%) is much lower than that of CIGS, direct band gap of 1.55 eV, high absorption coefficient ($\sim 10^5\ cm^{-1}$) and non-toxicity of the constituents make it a promising candidate for the absorber materials of thin film solar cells [10–13].

CIS absorber material can be prepared by several methods including vacuum and non-vacuum methods. The high production cost of traditional vacuum-based processes, i.e., multi stage co-evaporation and sputtering are considered to be a main obstacle for the widespread use of CIS thin film solar cells [14,15]. Many efforts have been devoted to develop alternative deposition techniques for thin film CIS solar cells. Among them, the most intensively investigated and striking strategy may be the electrodeposition. This method offers great advantages in terms of low cost, high rate, high efficient utilization of raw materials and feasibility in making large area films [16–18]. In 1983, Bhattacharya reported the electrodeposition of CIS film for the first time [19]. Since then, CIGS and $CuInSe_2$ (CISe) based solar cells prepared directly from the electrodeposition have been reported by many research groups [20–22]. Lincot et al. reported a record efficiency of 12.4% for the co-electrodeposited CIGS with a bandgap of 1.47 eV [23]. Calixto et al. reported the fabrication of CISe thin films by co-electrodeposition and the depth profile of them were investigated using the auger electron spectroscopy (AES) [24]. Bhattacharya et al. reported the highest efficiency of 15.4% for the CIGS-based photovoltaic devices from a three-stage electrodeposition in which the final film composition was adjusted using the physical vapor deposition (PVD) method [25].

Although there have been so many reports on direct deposition of CISe and CIGS absorber materials, few reports can be found for the co-electrodeposition of CIS due to the irreversibility of sulfur. On the other hand, the standard reduction potential values of Cu^{2+}-Cu and In^{3+}-In are +0.342 and −0.338 V vs SHE, respectively [26]. The significantly different potentials often cause the preferential

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http://dx.doi.org/10.1016/j.materresbull.2015.12.003
0025-5408/

deposition of Cu or In. The control of the stoichiometry of ternary CIS materials is a challenging task for the co-electrodeposition method. Therefore, a sequential route to electrodeposit a Cu/In precursor film followed by sulfurization has been developed. Recently, Ikeda et al. fabricated the polycrystalline CIS films by sulfurization of electrodeposited Cu/In bilayer under the constant potential mode [27]. Conversion efficiency less than 1.5% was obtained, which was mainly due to the poor adherence between the Cu film and substrate. The poor adherence originated from the less crystalline nature of the Cu layer as the authors pointed out. Due to the poor quality of Cu film, an island-like In film were obtained, which would cause pinholes inside the film after the sulfurization. When the Cu/In precursor film was pretreated at 110 °C in Ar, 5% efficiency was obtained due to the improvement of adherence and the elimination of pinholes. Obviously, the deposition quality of Cu film is one of the key factors to improve the performances of CIS thin film solar cells.

Aimed to improve the quality of Cu/In bilayer, a novel bell-like wave modulated square wave (BWMSW) in constant current mode (patent number: CN201087149) was employed for the deposition of Cu layer. Different from the traditional electrodeposition technique with only one adjustable parameter (current or potential), three independent parameters (current or potential, frequency, duty cycle) are available for the BWMSW electrodeposition. It may result in a smooth, compact film with better adherence to the substrate. The basic operating principle of the BWMSW deposition technique was shown in Fig. 1. The influences of deposition parameters such as frequency, duty cycle and the concentration of complexing agent were investigated in this research. Benefited from the high quality copper films fabricated by the BWMSW deposition technique, the indium film was electrodeposited successfully on the copper layer with smooth and compact surface. After sulfurized at 600 °C for 60 min, the phase pure CIS films were obtained with better crystallinity. The structures, morphologies, composition and optoelectronic properties of the CIS films were also characterized.

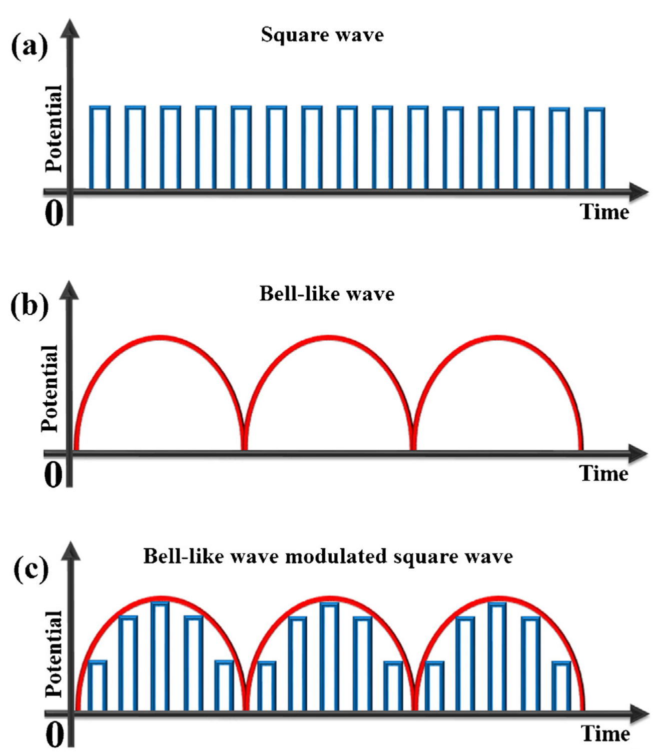

Fig. 1. Schematic diagram of the operation principle for the BWMSW technique.

2. Experimental

2.1. Electrodeposition of Cu/In bilayer film and the subsequent sulfurization procedure

Electrodeposition of Cu/In bilayer films were performed from an aqueous bath solutions at room temperature. The experimental setup consisted of a conventional three-electrode setup with platinum gauze as a counter electrode, Ag/AgCl as a reference electrode and fluorine-doped tin oxide (FTO) glass substrate as a working electrode. The Cu layer was electrodeposited from a 0.01 M copper sulfate ($CuSO_4{\cdot}5H_2O$) based solution using the BWMSW deposition technique in a constant current mode with a current density of 2 mA/cm^2 for 30 min. All the experiments were carried out with a 2 cm distance between the working electrode and counter electrode. Mechanical stirring at a speed of 120 r/min was adopted. After the Cu layer deposition, an In layer was deposited on the Cu-covered FTO substrate from a 0.01 M $InCl_3{\cdot}4H_2O$ based solution using the pulsed deposition in constant current mode. The current density of 4 mA/cm^2 was used. The composition ratio of Cu and In in the Cu/In bilayer film could be conveniently regulated by changing the deposition time of the In layer.

After deposition, the Cu/In bilayer samples were placed in a double-temperature-zone tube furnace together with sufficient sulfur powder. The Cu/In bilayer films were pretreated at 120 °C under vacuum condition before increasing the temperature to the target sulfurization temperature. The tube was heated at a rate of 10 °C/min and the argon was used as carrier gas. The temperature of sulfur powder region was kept at 350 °C. Meanwhile, the temperature of Cu/In bilayer film region was kept at 600 °C for 60 min. Finally, the samples were cooled down naturally to room temperature in the furnace.

2.2. Characterization techniques

The surface morphologies, cross-sectional morphologies and elemental composition of the samples were measured using a JEOL 5600 field emission scanning electron microscopy (FESEM) equipped with an energy dispersive X-ray spectroscopy (EDS). The structures of the sample were characterized by X-ray diffractometry (XRD) (X′Pert MRD-Philips) equipment with Cu kα radiation. The Raman spectrum was characterized by the confocal microscopic Raman spectrometer (RM$^-$1000). The ultraviolet–visible (UV–vis HEλIOSα) spectrophotometer was employed to characterize the optical properties of the samples. The optoelectronic properties of the CIS films were investigated by the surface photovoltage spectrum (Stanford, SR830).

3. Results and discussion

3.1. The influences of frequency, duty cycle and the concentration of complexing agent on the quality of Cu layer

The BWMSW deposition technique has several advantages over the traditional constant potential or constant current methods. Three independent deposition parameters provided the possibility to improve the film quality, such as the improvement of deposition distribution and the adherence. In this section, the influences of deposition parameters for copper film including frequency, duty cycle and the concentration of complexing agent were investigated. In order to explore the influence of the frequency on the quality of Cu layer during the BWMSW electrodeposition, the concentration of citric acid and duty cycle were fixed to 0.01 M and 50% respectively. Fig. 2 shows the FESEM images of Cu layers deposited on the FTO substrate using different deposition frequencies.