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Investigation of selenization process of electrodeposited Cu–Zn–Sn precursor for $Cu_2ZnSnSe_4$ thin-film solar cells

R. Kondrotas [a,*], R. Juškėnas [a], A. Naujokaitis [a], G. Niaura [a], Z. Mockus [a], S. Kanapeckaitė [a], B. Čechavičius [b], K. Juškevičius [c], E. Saucedo [d], Y. Sánchez [d]

[a] State Research Institute Centre for Physical Sciences and Technology, Chemistry Institute, Savanoriu ave. 231, Vilnius, Lithuania
[b] State Research Institute Centre for Physical Sciences and Technology, Semiconductor Physics Institute, Savanoriu ave. 231, Vilnius Lithuania
[c] State Research Institute Centre for Physical Sciences and Technology, Physics Institute, Savanoriu ave. 231, Vilnius, Lithuania
[d] Catalonia Institute for Energy Research (IREC), Jardins de les dones de negre 1, Sant Adrià de Besòs, Barcelona, Spain

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ABSTRACT

In this study we present the investigation of $Cu_2ZnSnSe_4$ (CZTSe) absorber layers formed using electrochemical co-deposition in the stirred citrate solution. Two different Mo back contacts were tested to evaluate the formation of $MoSe_2$ during selenization of electrodeposited Cu–Zn–Sn (CZT) precursor. Cleaved and focused ion beam made cross-sections of CZT/Mo and CZTSe/$MoSe_2$/Mo layers and surface morphology of CZTSe were studied by scanning microscopy. The chemical composition was determined by x-ray energy dispersive and fluorescence spectroscopy, whereas phase composition was examined by x-ray diffraction and Raman spectroscopy. The formation of $MoSe_2$ strongly depended on the microstructure of Mo and annealing conditions. Possible reasons for different selenization of Mo back contacts used were discussed. Photoluminescence (PL) measurements revealed that characteristics of CZTSe main PL peak were compositional dependent. The highest CZTSe solar cell efficiency obtained was 2.64%.

1. Introduction

Currently, $Cu_2ZnSnSe_4$ and Cu_2ZnSnS_4 (CZTSe and CZTS) are extensively studied materials for photovoltaic application. CZTSe(S) is a direct band gap semiconductor with band gap (E_g) ranging from 1.0 eV to 1.5 eV depending on Se to S ratio. It is composed of earth abundant, inexpensive and non toxic chemical elements and possesses a high absorption coefficient $\alpha > 10^4$ cm^{-1} which makes it an ideal absorber for the thin-film solar cells.

Traditionally, synthesis of CZTSe(S) layers includes two steps: i) the formation of metallic precursor and ii) the subsequent annealing under Se or S atmosphere at temperatures from 450 to 600 °C. To date numerous growth methods for fabrication of metallic precursor layers such as: evaporation [1], sputtering [2,3], laser beam deposition [4], spin-coating [5,6], and electrodeposition [7–11] were reported.

Electrochemical deposition is an attractive and promising approach for the formation of CZTSe(S) solar cells. However, using particular method specific demands have to be met for Mo back contact: it has to be very well-adherent to the glass and to have satisfactory conductivity. Unfortunately, sputtered Mo layers do not possess both characteristics simultaneously, therefore a multi-layered Mo films are used [12–14]. According to the literature Mo films sputtered at high Ar pressure are porous and well-adherent to the glass, but are relatively resistive, whereas sputtered at low Ar pressure films are compact, highly conductive, but under high compressive stress [15]. It was also noticed that compact Mo films are readily selenized, meanwhile selenization of porous ones is sluggish [16]. Thus the selenization of Mo/Cu–Zn–Sn (CZT) precursor will be dependent on the nature of Mo and microstructure of CZT precursor. In general electrochemically deposited CZT precursor differs from the ones deposited by vacuum-based methods. Because of the hydrogen evolution during electrodeposition CZT films are porous and less dense, therefore Se diffusion conditions can be different from the ones where CZT films were deposited by vacuum-based methods. For example, Shin et al. showed that the formation of $MoSe_2$ is limited by Se diffusion through CZTSe layer under saturated Se atmosphere [17].

So the purpose of this work is firstly to investigate the selenization of different Mo substrates, then to evaluate the influence of different Mo substrates on selenization process of electrochemically co-deposited CZT precursor, on the CZTSe morphology, crystal structure and photoelectrical properties.

2. Experimental details

A Cu–Zn–Sn alloy was electrochemically deposited in a three-compartment glass electrolytic cell. Electrolyte solution was prepared using deionized water and contained $CuSO_4 \cdot 5H_2O$ – 20 mM, $ZnSO_4 \cdot 7H_2O$ – 16 mM, $SnSO_4$ – 10 mM and 100 mM of sodium

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[*] Corresponding author. Tel.: +370 61687912.
E-mail address: rokas.kondrotas@ftmc.lt (R. Kondrotas).

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citrate. Hydroquinone was used as an antioxidant in the electrolyte solution for co-deposition of CZT. The pH of the solution was adjusted to 5.75 with H_2SO_4 of spectroscopic purity.

As a working electrode Mo coated soda-lime glass was used. Two types of Mo substrates were tested in this work that is commercial Mo ~600 nm thick, which further in this study will be referred as 'Mo1' and home-made Mo substrate, will be referred as 'Mo2'. The sheet resistance of Mo1 and Mo2 was 0.4 and 0.25 Ω/sq, respectively. The Mo2 film was formed by sputtering 500–600 nm and 200 nm Mo layers at 1.7 and 0.2 Pa Ar pressure, respectively. During sputtering the glass substrate was kept at room temperature although some heating from the plasma may occur. Before deposition working Mo electrodes were immersed in 10% NH_4–OH solution for 10–15 min to remove thin oxide layer. A platinum (purity 99.999%) plate of much larger dimensions than that of the working electrode was used as an anode. The reference electrode Ag/AgCl/KCl (saturated) was placed in vicinity of the working electrode through a Lugin capillary. During electrodeposition the solution was kept at a constant temperature of $+20 \pm 1$ °C. A stirring was provided with magnetic stirrer. Potentiostatic conditions were maintained using a programmable potentiostat PI-50-1.1.

Before annealing in the Se atmosphere Cu–Zn–Sn precursors were pre-heated under Ar atmosphere at 350 °C for 10 min. Annealing of the electrochemically deposited CZT was conducted in a tubular furnace under static 10^5 Pa Ar (purity 99.995%) atmosphere and using Se powder. Temperature increase rate was 20 °C/min. After annealing samples were left to cool-down naturally to the room temperature. Prior CdS deposition, all CZTSe absorber layers were chemically etched to remove ZnSe as previously described [18].

Solar cell devices were fabricated by depositing ~50 nm CdS layer by chemical bath deposition, then sputtering ~50 nm thick intrinsic ZnO layer and finalizing front contact with deposition of 300–400 nm indium-tin oxide (ITO) layer (both oxides were deposited by DC-sputtering method, CT100 Alliance Concepts). Then the whole solar cell structure was as follows: Mo/CZTSe/CdS/i-ZnO/ITO.

Electron microscopy studies were carried out in field emission scanning electron microscope (FE-SEM) HELIOS Nanolab 650 (FEI Company) arranged with an X-ray energy dispersive spectrometer (EDX) from Oxford Instruments. All composition measurements were performed at fixed operating parameters: 20 kV accelerating voltage, 5 mm distance between EDX detector and sample and integration time of 45 s. SEM images were recorded using at 5 kV accelerating voltage and secondary electron mode. Cross-sections were made using focused ion beam (FIB) located in SEM chamber with 30 keV energy Ga ions. The composition measurements were also performed by X-ray fluorescence spectrometer (Fisherscope XVD) which is routinely calibrated with inductively coupled plasma optical emission spectrometer, Perkin Elmer Optima 3200RL. The accelerating voltage of XRF was 50 kV and integration time at each point – 45 s.

XRD characterization was performed using an x-ray diffractometer SmartLab (Rigaku) with 9 kW rotating Cu anode x-ray tube. A conventional Bragg-Brentano optics with a graphite monochromator on the diffracted beam was used.

Raman measurements were performed with 632.8 nm (He–Ne laser) and 442 nm (He–Cd laser) excitations by using the Raman spectrometer inVia (Renishaw) equipped with a gratings containing 1800 and 2400 grooves/mm for 632.8 and 442 nm excitation wavelengths, respectively. Laser power at the sample was 0.2 mW (632.8 nm) and 0.8 mW (442 nm). Raman spectra were taken using a 50×/0.75 NA objective lens. The integration time was 100 s. The Raman frequencies were calibrated with the 520.7 cm^{-1} peak of a silicon standard, yielding a 1 cm^{-1} absolute wavenumber accuracy for sharp bands. For quantitative analysis of Raman bands the experimental contour was fitted by Lorentzian–Gaussian or Gaussian form components using GRAMS A1 software and assuming linear baseline.

Room temperature photoluminescence (PL) measurements were carried out using diode-pumped solid-state laser (532 nm) as an excitation source. Laser power varied from 3 mW to 190 mW, and beam was focused into ~0.4 mm^2 spot. PL was dispersed through 0.4 m monochromator, and detected by liquid-nitrogen- and thermoelectrically-cooled InGaAs detectors.

The solar cells were scribed in 3 × 3 mm^2 using a micro-diamond scriber (MR200 OEG). The optoelectronic device characterization was performed using an AAA class solar simulator (SUN 3000 Abet Technologies) with uniform illumination over 15 × 15 cm^2 area, equipped with an AM1.5 filter.

3. Results and discussion

3.1. Structure of Mo back contact

Two different Mo substrates were tested in this work. FIB prepared cross-sections of both Mo substrates are depicted in Fig. 1. For commercial Mo substrate (Mo1) typical thickness is ~550 nm, whereas the thickness of home-made Mo (Mo2) is around 920 nm. Mo1 layer is compact and neither pores, nor voids are visible (Fig. 1a). From cross-section SEM micrograph of Mo1 it is not obvious (for clear view see Fig. 3a) that commercial Mo substrate is composed of two layers of the same thickness, likely deposited under the same Ar pressure. Mo2 is composed of two clearly distinguishable layers, as can be seen in Fig. 1b. Bottom layer sputtered at relatively high Ar pressure (1.7 Pa) has a columnar structure with micropores and is around 600 nm in thickness. The top layer is sputtered at the lowest possible Ar pressure at the given power (for the used instrument), which was roughly about 0.2 Pa and is 320 nm thick. The latter sputtering conditions results in the formation of compact Mo layer without voids and pores. The layers are smooth and well-adherent; no gaps were detected at their interface. Such home-made bi-layer Mo structure is well-adherent to the soda-lime glass. Specific resistance is in a range of 1–3 · 10^{-5} Ω cm which is a satisfactory conductivity for back contact.

3.2. Selenization of Mo layers

In this study all thermal treatments under the certain conditions were done in pairs composed of one CZT precursor deposited on Mo1 and another one on Mo2. Therefore, this study allowed comparing samples deposited on two different Mo substrates, but annealed under exactly the same conditions. Four different annealing conditions were chosen to selenize Cu-poor and Zn-rich CZT metallic precursors. Annealing conditions were varied in order to determine under which the lowest quantity of $MoSe_2$ is formed. The amount of $MoSe_2$ was evaluated by XRF. The annealing conditions and Se quantity in atomic percentage (at %) are summarized in Table 1.

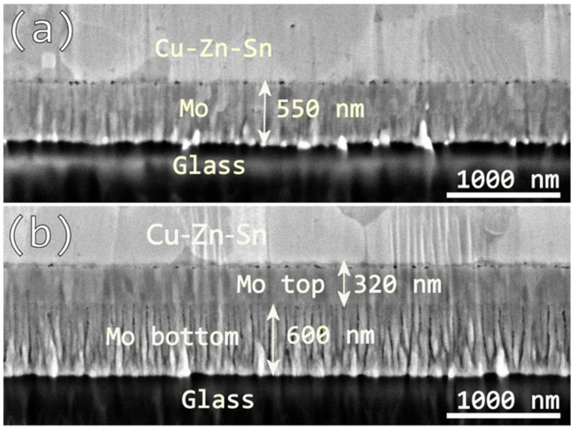

Fig. 1. SEM micrographs of glass/Mo/CZT cross-sections: (a) CZT deposited on Mo1 and (b) CZT deposited on Mo2, after preliminary annealing.