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Characterization of $\text{Cu}_2\text{ZnSnSe}_4$ solar cells prepared from electrochemically co-deposited Cu–Zn–Sn alloy



R. Kondrotas^{a,*}, R. Juškėnas^a, A. Naujokaitis^{a,b}, A. Selskis^a, R. Giraitis^a, Z. Mockus^a, S. Kanapeckaitė^a, G. Niaura^a, H. Xie^c, Y. Sánchez^c, E. Saucedo^c

^a State Research Institute Centre for Physical Sciences and Technology, Savanoriu ave. 231, Vilnius, Lithuania

^b Vilnius university, Faculty of Physics, Sauletekio 9, LT-10222 Vilnius, Lithuania

^c IREC, Catalonia Institute for Energy Research, C. Jardis de les Dones De Negre 1, 08930 Sant Adria Del Besos, Barcelona, Spain

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ABSTRACT

Cu–Zn–Sn (CZT) precursors for $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) solar cell were prepared by electrochemical co-deposition method with different metals composition. CZT precursors were preliminary annealed in three different atmospheres in order to obtain homogenous, without pores Cu–Zn–Sn layers. A high crystalline quality CZTSe absorber was synthesised as has been determined by X-ray diffraction and Raman spectroscopy methods. CZTSe based solar cells were fabricated and champion cell demonstrated 2.7% efficiency and reached as high as 70% of external quantum efficiency. Scanning electron microscope investigations of CZTSe solar cells cross-section revealed that Mo/CZTSe interface exhibits large voids and local delamination from Mo layer. The back contact issues are detrimental to solar cell performance reducing shunt resistance and open circuit voltage.

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1. Introduction

$\text{Cu}_2\text{ZnSnS}(\text{Se})_4$ (CZTS(Se)) also referred as kesterite (their structure) is one of the most promising materials in thin film photovoltaic (PV) technologies. The main reasons are: (i) it consists of earth abundant, non-toxic and inexpensive chemical elements and (ii) exhibits similar optoelectronic properties to those reported for conventional CIGS solar cells. Naturally it is a p-type semiconductor with direct band-gap in the range of 1.0–1.5 eV depending on the S and Se content, and has a high optical absorption coefficient in visible spectrum range ($\alpha > 10^4 \text{ cm}^{-1}$). In recent years groups of scientists reported CZTS(Se) based solar cells close to or even exceeding 10% efficiency [1–4]. Alongside conventional vacuum based growth methods for kesterite materials [3,4] a non-vacuum based chemical routes are getting more favourable [1,2]. Non-vacuum based growth methods usually are less expensive and enable to reduce the cost of solar cells and modules production. Electrochemical deposition as technique for the synthesis of CZT precursors is one of the most attractive non-vacuum growth methods due to rather inexpensive equipment, it is easily exploited in industry on large area substrates and electrolytes are prepared from environmentally friendly and low cost precursors such as Cu, Zn and Sn salts. In addition there is no need for toxic

solvents, such as hydrazine used in other chemical preparation routes [1].

Electrochemically deposited CZT precursor layers for CZTS(Se) solar cells have been studied extensively since 2008 [5–12] and recently has drawn even more attention [13–38]. Till 2012 electrochemically deposited CZTS(Se) solar cells had a 3.2–3.4% power conversion efficiency [8,9,11,16], but recently Lin and et al. reported 5.6% efficiency for CZTS based solar cells [17]. IBM reported 7.3% and 7.0% efficiencies for CZTS and CZTSe solar cells respectively prepared from electrochemically deposited metallic stack Cu/Zn/Sn [25,26]. As far as CZTSe solar cells prepared from one-step electrochemically deposited CZT precursor are concerned to our knowledge highest efficiency achieved is 5.8% [27].

There are known various approaches for electrochemical deposition of CZT precursor: (i) consequential deposition of metallic stacks [5–7,12,16,17,25,26], (ii) consequential deposition of bi-layers CuZn and CuSn [18,22] or CuZn and Sn [33,35] (iii) consequential electrodeposition of metals and chalcogen [36] (iv) co-electrodeposition of Cu, Zn, Sn [8–11,13–15,19,23,24,27,31,37,38], (v) co-electrodeposition of CZT with following deposition of Se [28], (vi) co-electrodeposition of all constituents Cu, Zn, Sn, Se/S [21,29,30,32]. Co-electrodeposition is more favourable in the industry because it reduces production cost as well as chemical wastes: deposition takes place only in one bath and there is no need for intermediate sample cleaning and rinsing. Electrochemical deposition of Se is also advantageous since it utilises

* Corresponding author. Tel.: +370 61687912.

E-mail address: rokas.kondrotas@ftmc.lt (R. Kondrotas).

Se more effectively in comparison with vacuum-based growth methods.

Mostly studied electrolyte was citrate based [7,11,13,14,19,21,24,27,28,29,31,34,35,37,38], but other groups used pyrophosphate [9,10,18,22,35], alkaline with sorbitol [5,8,12,16], commercial electrolytes [25,26], ionic [15], cyanide [23], thiocyanate with lactic acid [30]. It should be noted that electrolyte stirring [5,8–10,25,26] or rotating disk electrode were rarely used [16,27,33].

Most publications about CZTS(Se) synthesised from electrochemically deposited precursors are limited to only the proof of the kesterite formation [5,7,10,12–15,18–23,28–30,32–38]. Some other reported papers include measurements of photovoltaic properties of full CZTS(Se) solar cells [6,8,9,11,16,24–26,31]. Notably there are much more publications about pure sulphur kesterites [6–16,21,23,25,30,32,34–38]. Concerning the structural characterization of kesterite solar cells, often cross section view of absorber or solar cell samples are prepared by breaking it which does not always give a very clear insight about interfaces. Samples prepared by focused ion beam (FIB) milling method allows to evaluate interface quality of back contact and kesterite in a better way, being very useful to estimate thickness of $\text{MoSe}_2/\text{MoS}_2$ and to detect secondary ZnSe phase and voids.

The goal of this work was to investigate how selenization process and initial composition affects CZTSe morphology, composition and Mo/CZTSe interface. In addition CZTSe based solar cells were fabricated from electrochemically co-deposited Cu–Zn–Sn precursors and optoelectronic parameters were measured. A promising 2.7% efficiency was achieved and remaining problems pointed-out.

2. Materials and methods

A Cu–Zn–Sn alloy was electrochemically deposited in a three-compartment glass electrolytic cell. Electrolyte solutions were prepared using deionized water and contained $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ –20 mM, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ –16 mM, SnSO_4 –10 mM and 100 mM of sodium citrate. Hydroquinone was used as an antioxidant in the electrolyte solution for co-deposition of CZT. The solutions' pH was adjusted with H_2SO_4 of spectroscopic purity.

A soda-lime glass coated with magnetron sputtered Mo bilayer was used as a working electrode. Prior to deposition, Mo substrates were immersed in 10% NH_4OH solution for 10 min. 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. The solution was kept at a constant temperature of $+20 \pm 1$ °C during electrodeposition of CZT. A stirring was provided with magnetic stirrer. Potentiostatic conditions were maintained using a programmable potentiostat PI-50-1.1. Other electrodeposition parameters were already reported by our authors elsewhere [28].

Annealing of the electrochemically deposited CZT was conducted in a tube furnace in Ar (purity 99.995%) atmosphere using elemental Se unless stated otherwise. The accuracy in the temperature stability was not worse than ± 1.0 °C. Temperature increase rate was 20 °C/min. After annealing process samples were left to cool-down naturally to room temperature. Prior CdS deposition all CZTSe absorber layers were chemically etched to remove ZnSe as previously described [43]. Solar cell devices were fabricated by depositing ~ 50 nm CdS layer by chemical bath deposition, then sputtering ~ 50 nm intrinsic ZnO layer and finalising front contact with deposition of 300–400 nm ITO layer (both oxides were deposited by DC-sputtering method, CT100 Alliance Concepts). Whole solar cell structure was as follows: Mo/CZTSe/CdS/i-ZnO/ITO.

XRD characterisation was performed using a diffractometer D8 Advance (Bruker AXS). $\text{Cu K}\alpha$ radiation (wavelength 0.154183 nm) was separated by a multilayer Ni/graphite monochromator, which also formed a parallel beam of X-rays. The XRD patterns were measured in grazing incidence (GID) step scan mode with a step size of 0.04° (in 2θ scale) and counting time of 5–10 s. An incidence angle of the primary beam was 0.5° . An appropriate adjustment of the diffractometer was controlled using the certified standard SRM 660b from NIST. Phase identification was performed using the powder diffraction data-base PDF-2 (2003 release).

Raman measurements were performed with 785 (diode laser) and 442 nm (He–Cd) excitations by using the Raman microscope inVia (Renishaw) equipped with a gratings containing 1200, 1800, and 2400 grooves/mm. Laser power at the sample was 1.8 and 0.8 mW for 785 and 442 nm excitation wavelengths, respectively. Raman spectra were taken using a $50\times$ objective lens. Integration time was 100 s. Parameters of the peaks were determined by fitting the experimental contour by Gaussian–Lorentzian components using Grams386 software.

Electron microscopy studies were carried out in FE-SEM-FIB HELIOS Nanolab 650 (FEI) arranged with an X-ray energy dispersive spectrometer (EDX) from Oxford Instruments. Cross-sections were performed using focused ion beam (FIB) in SEM chamber with 30 keV energy Ga ions.

The solar cells were scribed in 3×3 cm^2 using a micro-diamond scribe (MR200 OEG). The optoelectronic device characterization was performed using AAA class solar simulator (SUN 3000 Abet Technologies) with uniform illumination of 15×15 cm^2 equipped with an AM1.5 filter. External quantum efficiency was measured using a PVE300 Bentham system (wavelength range: 300–1600 nm).

3. Results and discussion

3.1. Morphology and composition of as-deposited and annealed CZT precursor layer

Electrochemically deposited Cu–Zn–Sn alloys are porous (Fig. 1a), so in order to homogenise and decrease porosity, CZT films were preliminary annealed under Ar, H_2 and $\text{Ar}+\text{H}_2$ atmospheres. Cross-section view of as-deposited CZT is shown in Fig. 1a and those after preliminary annealing in Ar, H_2 atmospheres at 200 °C for 1 h are presented in Fig. 1b and c respectively. Fig. 1d shows CZT film annealed at 350 °C in $\text{Ar}+\text{H}_2$ atmosphere.

As can be seen from cross-section view (Fig. 1b) after preliminary annealing in Ar atmosphere, homogenous and without pores CZT layer is obtained. However in the electrodeposited CZT precursor small amount of metal oxides is usually present. It is known that during annealing process in the presence of hydrogen gas, copper and partially tin oxides are reduced to their native metallic forms. For this purpose CZT precursor was annealed in H_2 atmosphere at 200 °C for 1 h. Cross-section view (Fig. 1c) shows that after annealing in H_2 density of pores of CZT layer was also reduced, nevertheless some voids are still observed. In the preliminary annealing in the presence of H_2 copper and partially tin oxide species are reduced to metallic form with a by-product of H_2O . At 200 °C water evaporation may cause formation of voids in the film. So, in order to obtain homogenous without pores and reduced quantity of metal oxides CZT precursor layers were annealed in $\text{Ar}+\text{H}_2$ atmosphere at 350 °C. Cross-section view is presented in Fig. 1d. It can be seen that film is homogenous and no pores are visible. From Fig. 1 CZT precursor layers thickness was evaluated and was in the range of 500–650 nm.

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