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Selenisation of sequentially electrodeposited Cu–Zn and Sn precursor layers

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ABSTRACT

$Cu_2ZnSnSe_4$ (CZTSe) thin films were produced through the selenisation of sequentially electrodeposited Cu–Zn and Sn stacked films. The micro-structural and compositional properties of the precursor stacked and selenised films were characterised using scanning electron microscopy/energy dispersive spectroscopy, X-ray diffraction and Raman spectroscopy. The electrodeposited Cu–Zn layers had a high concentration of zinc to compensate for the loss of zinc that occurred during the following deposition of the tin layer. It was observed that a Cu/Zn ratio equal to 1.1 in the electrodeposited Cu–Zn layers is optimal and provides the desired ratio of all the metallic components in selenised CZTSe films. Selenisation for 60 min resulted in highly crystalline CZTSe films with a grain size of 1.5–4 μm. In addition, the influence of the Cu–Zn ratio in the electrodeposited stacked layers on the morphology and the elemental and phase compositions of the CZTSe films was investigated.

1. Introduction

Within the photovoltaic (PV) sector, material concepts based on abundant and less costly elements has attracted increasing attention. Compounds that can possibly replace the indium-containing $CuInSe_2$ absorbers have been introduced in a variety of reports. These compounds include $CuSbS(Se)_2$ [1], Cu_2CoSnS_4 [2] and SnS [3–5]. However, the absorber material that has attracted the greatest attention is $Cu_2ZnSnSe(S)_4$ (CZTSe(S)) due to its tolerable band gap from 1 eV [6,7] to 1.5 eV [8,9] and its high absorbance coefficient that is greater than 10^4 cm^{-1}. The best PV device produced to date, with an efficiency of 10.1%, was produced from materials using a hybrid solution-particle slurry method [10]. However, in this approach, highly toxic and unstable hydrazine is used as a solvent, which could lead to limitations for this method. The development of the electrodeposition-annealing route for producing CZTSe absorbers is one of the most promising steps towards obtaining inexpensive solar cells. The current best efficiency value for solar cells was obtained using electroplated Cu_2ZnSnS_4, and this value is 7.3% [11]. In this study, metal precursor layers were sequentially electrodeposited and the influence of the composition of the electrodeposited Cu–Zn layer on the microstructure, morphology and composition of the CZTSe absorber layers was investigated. Additionally, the study seeks to investigate the peculiarities of crystal growth during the selenisation process.

2. Experimental details

The Cu–Zn alloy and Sn precursor layers were prepared by sequential electrodeposition under potentiostatic conditions. The experimental setup consisted of a conventional three-electrode cell configuration with Ag/AgCl as a reference-electrode and platinum gauze as a counter-electrode. A rotating disc electrode (Radiometer Analytical) with Mo-coated soda lime glass with dimension of 15×15 mm was used as a substrate and working electrode. Before the electrodeposition process, the substrates were cleaned in ethanol and rinsed with distilled water. The deposition was performed at room temperature using a Gamry 3000 potentiostat. Two series of precursor layers, named Sol A and Sol B, were prepared and used for selenisation. For both series, the Cu/Zn ratio was varied: in Sol A, the Cu/Zn ratio was equal to 1.7; and in Sol B, the Cu/Zn ratio was equal to 1.1. The precursors for Sol A were prepared from an electrolyte that contained 0.1 M $Na_3C_6H_5O_7$, 0.02 M $CuSO_4 \cdot 5H_2O$ and 0.015 M $ZnSO_4 \cdot 7H_2O$ with an electrodeposition potential of −1.23 V. In the electrolyte for the preparation of the Sol B precursors, an increased concentration of $ZnSO_4 \cdot 7H_2O$ (0.02 M) was used while the concentrations of copper and sodium citrate were unchanged. The electrodeposition potential for the preparation of the Sol B precursors was increased to −1.24 V. Tin was deposited for the same duration and at the same potential −1.3 V vs Ag/AgCl electrode on both series of the initial CuZn layers. The tin electrolyte was composed of a saturated sodium pyrophosphate solution and 0.02 M $SnCl_2 \cdot 2H_2O$. In this investigation, we used a rotating disc electrode, which allowed us to improve the uniformity of the electrodeposited precursor layers in contrast to our previous experiments [12]. A 300 rpm rotation speed was used for the electrodeposition. The total thickness of precursor films was around 650 nm. The metallic precursor layers were applied in the same sequence as in [12] for the Mo/Cu–Zn alloy/Sn. The reverse deposition sequence of layers leads to poor adhesion of Sn to the Mo surface.

The stacked precursors were placed in evacuated quartz ampoules (1.3 Pa) and subsequently heated isothermally at 470 °C for 20, 40 and 60 min. A piece of selenium (30 mg) was inserted into the ampoule before it was sealed.

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Table 1
Compositions of the precursors and selenised films of Sol A and Sol B.

Type	Cu (at.%)	Zn (at.%)	Sn (at.%)	Se (at.%)	Cu/Zn
Metallic precursors					
Sol A-1	62.6	37.4	–	–	1.7
Sol B-1	53.1	46.9	–	–	1.1
Sol A-2	51.4	21.9	27.2	–	2.3
Sol B-2	43.1	23.9	33	–	1.8
Selenized films					
Experiment 1					
Sol A	24.7	10.7	13.3	51.4	2.3
Sol B	21.3	12.3	14.9	51.4	1.7
Experiment 2					
470 °C/20 min	20	11.6	15.6	52.8	1.7
470 °C/40 min	21.3	11.5	15.4	51.7	1.8
470 °C/60 min	22.4	12.7	12.6	52.4	1.8

The precursor and selenised films were analysed using high resolution-scanning electron microscopy (HR-SEM Zeiss ULTRA 55). Measurements were made at operating voltage 2.5 kV and the chemical composition of films as well as the distribution of their components was determined via energy dispersive X-ray analysis (EDS), equipped with Röntec EDX-XFlash detector, at 20 kV. Room temperature micro-Raman spectra were recorded on a Horiba LabRam 800 high-resolution spectrometer equipped with a multichannel CCD detection system in the backscattering regime, which provided a spectral resolution of 0.5 cm^{-1}. The light source for the micro-Raman measurements was a green laser with a 532 nm wavelength focused on a spot that was at least 10 μm in diameter. X-ray diffraction (XRD) measurements were performed using a Bruker D5005 diffractometer (Bragg–Brentano geometry) and Cu $K\alpha_1$ radiation with $\lambda = 1.5406$ Å at 40 kV, 40 mA.

3. Results and discussion

3.1. Dependence of the composition and morphology of the selenised films on the composition of the electrodeposited CuZn layer

Based on the composition of $Cu_2ZnSnSe_4$, the ratio of metals in the electrodeposited Cu/Zn alloy must be approximately two to obtain a stoichiometric atomic ratio of metals in the final $Cu_2ZnSnSe_4$ films. According to the literature, changes in the concentrations of the metals (except tin) before and after thermal treatment do not occur. However, many groups have reported a significant loss of tin during annealing due to its high volatility [13,14]. Therefore, we electrodeposited Sn with a greater concentration than that required by stoichiometry (see Table 1).

CuZn layers with a 1.7 ratio were electrodeposited for 5 min from the Sol A electrolyte. The EDS analysis indicated that after the electrodeposition of tin, there was a loss of zinc from the precursors and the ratio of Cu/Zn changed from the initial 1.7 to 2.3. The results are presented in Table 1. The possible explanation for this loss of Zn in final precursor films can be attributed to the dissolution of Zn in the $SnCl_2$ electrolyte before and during the electrodeposition of Sn. Zinc, which is a more active metal than Sn or Cu, reacts with the $SnCl_2$ electrolyte and a displacement reaction consequently occurs.

The initial CuZn layer with a 1.1 ratio was obtained by increasing both the zinc concentration in the electrolyte to 0.02 M and the deposition potential to −1.24 V. For convenience, this type of precursor was called Sol B. After the electrodeposition of tin, the Cu/Zn ratio increased to 1.8 (see Table 1).

For the first experiment, the Sol A and Sol B precursors were used. The stacks of precursors were selenised at 470 °C for 40 min in sealed quartz ampoules in a selenium atmosphere. The compositions of the resulting CZTSe films are presented in Table 1. Films from both series are tin rich; however, in the Sol B-type CZTSe films, the content of zinc is higher and the composition of Zn is closer to that required by stoichiometry. A decrease in the copper concentration is also observed (see Table 1). SEM images of the surfaces of the selenised precursor films (Fig. 1) indicate that the use of the Sol B-type precursors results in a uniform and smooth CZTSe layer with small-sized crystals, which have different shapes with round edges. However, the use of the Sol A-type precursors resulted in non-homogenous and non-uniform CZTSe films. Large formations with a hexagonal shape of approximately 4 μm were detected on the surfaces of these films. The EDS analyses allowed to determine that these formations are separate CuSe crystals ([Cu] = 49%, [Se] = 51%). The formed CZTSe layer exhibits a "wrinkled"

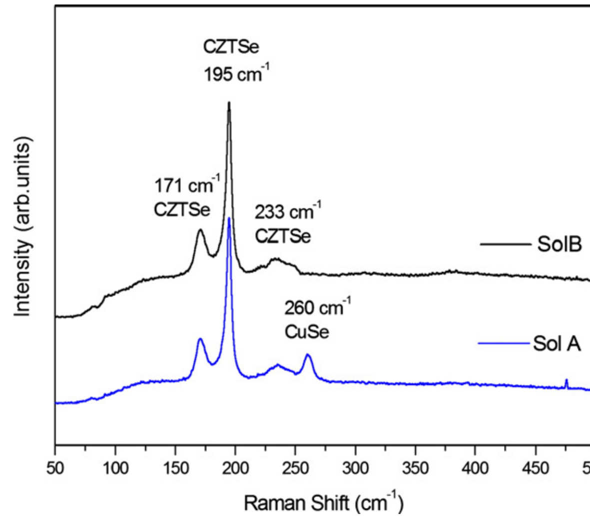

Fig. 2. Raman spectra of $Cu_2ZnSnSe_4$ thin layers selenised at 470 °C for 40 min.

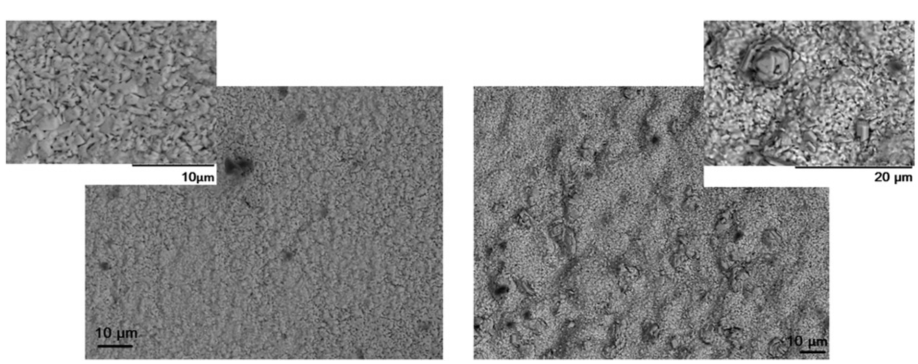

Fig. 1. SEM surface images of the films selenised at 470 °C for 40 min.