

Optimization of the CZTSe thin film composition obtained by a sequential electrodeposition process

Ramazan Katirci*^a,

E-mail: ramazan@asrelektrokimya.com.tr;

John Michael Walls^b,

E-mail: j.m.walls@lboro.ac.uk

^a Istanbul Aydın University, Beşyol Mah.Inönü Cad.No: 38, Sefaköy-Küçükçekmece / İstanbul/Turkey

^bCentre for Renewable Energy Systems Technology, Wolfson School of Mechanical, Electrical and Manufacturing Engineering,
Loughborough University, Leicestershire, LE11 3TU, U.K.

Abstract

The influence of the elemental composition of CuZnSn coatings deposited by electrodeposition on the formation of the Cu₂ZnSnSe₄ crystal structure following a selenization process was investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy. This study showed that the optimum alloy ratio to achieve the Cu₂ZnSnSe₄ crystal without impurity phases was in the range of 0.37-0.50 for Cu/(Zn+Sn) and 2.5-4 for Zn/Sn.

Keywords: Kesterite (Cu₂ZnSnSe₄) electroplating; Photovoltaic absorber; Thin film electrodeposition.

*Corresponding author: ramazan@asrelektrokimya.com.tr; Phone: +905353313748; Fax: +902122767966

Permanent address: Talatpasa Mah. Celebi Cad. Yanihan Sk: No:5; Okmeydani-Kagithane/Istanbul-TURKEY

1. Introduction

Copper indium diselenide (CIS), and copper indium gallium diselenide (CIGS) thin films are widely used as the p-type absorber in photovoltaic devices. Thin film CIGS is an attractive photovoltaic absorber due to its high stability. However, CIGS absorbers contain expensive and rare elements such as 'In' and 'Ga', which limit their long-term sustainability for use in photovoltaic (PV) devices. Therefore, current research has been focused on replacing these rare elements with low-toxic and earth-abundant materials [1-3].

$\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ contains earth-abundant and low-toxic elements and is one of the most promising materials for the p-type absorber layer of thin film solar cells [4-5]. A number of studies on the fabrication of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ thin film solar cells have been reported [6].

Many coating methods have been used to deposit $\text{Cu}_2\text{ZnSnS}_4$ thin films. These include radio frequency (RF) magnetron sputtering [7], hybrid sputtering [8], thermal evaporation [9], photo-chemical coating [10], electroplating [11] spray pyrolysis [12], pulsed laser deposition [13], DC magnetron sputtering, etc. [14]. DC and RF magnetron sputtering deposition are the most common coating methods used for $\text{Cu}_2\text{ZnSnS}_4$ [15]. However, the high capital expenditure required to install a vacuum-based cell production line is a serious barrier to implementation. An atmospheric fabrication process would be much more financially attractive. Therefore, we use the electrodeposition method in this study. Previous studies of the electrodeposition of $\text{Cu}_2\text{ZnSnS}_4$ have examined the effects of process temperature, time, and medium during annealing after precursor deposition. [15-17].

Electroplating is comparatively cost-effective compared with other deposition methods due to its easy industrial implementation and low capital cost. Therefore, many $\text{Cu}_2\text{ZnSnSe}_4$ studies have been conducted using electrodeposition in recent years. This technique does not require high pressure, temperature or a vacuum environment and has a wide range of applications, including semi-conductor technology. $\text{Cu}_2\text{ZnSnSe}_4$ thin film has been electrodeposited using two approaches, sequential and co-deposition of metal layers [16,18]. Sequential metal

deposition in separate electrochemical baths offers a convenient way to deposit each of the elements step by step. It also has the potential for precise control of the stoichiometry of the $\text{Cu}_2\text{ZnSnSe}_4$ film.

Changing composition systematically and studying its influence on the lattice of $\text{Cu}_2\text{ZnSnSe}_4$ solar cells has been carried out by Márquez et al. [19]. They obtained the $\text{Cu}_2\text{ZnSnSe}_4$ thin films using the sputtering method. Schurr et al. [17] investigated the effects of the crystal phases obtained before annealing on the structure of $\text{Cu}_2\text{ZnSnS}_4$. They showed that the phases formed prior to annealing, significantly affect the formation of $\text{Cu}_2\text{ZnSnS}_4$. The effects of elemental compositional changes on the $\text{Cu}_2\text{ZnSnSe}_4$ films obtained using the electroplating method and the formation of secondary phases have not been previously investigated.

In this study, the effect of the composition changes systematically in the CuZnSn precursor films on the coating morphology and the crystal structure of the $\text{Cu}_2\text{ZnSnSe}_4$ was investigated. The changes in the composition of the $\text{Cu}_2\text{ZnSnSe}_4$ after annealing were monitored. In particular, the amount of Sn and Zn due to evaporation was observed.

2. Experimental

Mo deposited thin film on Soda-lime glass was used as the substrate. Prior to the electrodeposition, the substrates were cleaned with the cathodic electro-cleaning process for 5 minutes in the room temperature in alkaline solution ($\text{pH} > 10$) using a current of 6 A/dm^2 and then rinsed under flowing deionised water. Cu, Zn and Sn layers were sequentially electrodeposited on $5 \times 5 \text{ cm}$ substrates. Cu was electroplated in a bath containing 10 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 100 g/L pyrophosphate. Zn was electroplated in a bath consisting of 80 g/L ZnCl_2 and 150 g/L NH_4OH . Tin was electroplated in a bath including 10 g/L SnSO_4 and 100 g/L pyrophosphate. All platings were performed at room temperature using a current of 0.4 A/dm^2 and the pH's of the baths were adjusted to 8.5, 8.5 and 4.5 respectively. The coating thickness before and after annealing was about 2 and $6 \mu\text{m}$. Four samples with different composition were prepared and labelled from S1 to S4 (Table 2-4). The duration of

electrodeposition of each sample was presented in Table 1. Sn electroplating for all samples was carried out for 5 minutes. In the next step, the annealing process was performed at 540 °C for 1 hour in a quartz tube in the presence of 0.6 g Se, under a nitrogen atmosphere whose pressure was 0.39 atm. The annealing and the other processes were performed in the same way for all samples.

Table 1. The electrodeposition duration of Cu and Zn elements.

Samples	Cu (min.)	Zn (min.)
S1	6	12
S2	12	6
S3	12	12
S4	6	6

Table 2. Elemental percentage of CZT (CuZnSn) coating before annealing.

Samples	Cu /(Cu+Zn+Sn) %	Zn /(Cu+Zn+Sn) %	Sn /(Cu+Zn+Sn) %	Cu/(Zn+Sn)	Zn/Sn
S1	23	45	32	0.29	1.43
S2	43	24	33	0.75	0.71
S3	35	38	27	0.53	1.43
S4	29	29	41	0.42	0.71

Cu, Sn and Zn multilayer precursor films were electrodeposited using a Thurlby 30V-1A model direct-current generator. The annealing process was performed in the quartz furnace tube combined with a heater (Lenton). The structural properties of the annealed films were studied using XRD, Raman spectroscopy and SEM-EDS. XRD measurements were carried out at room temperature using a Bruker D2 Phaser model instrument, scanning between 30° and 70°. The step width was set to 0.02 with 2 steps per second. Raman spectroscopy measurements (LabRam HR model) were performed using the 633 nm line of a HeNe laser

(50 mW) as an excitation source. Scanning electron microscopy was carried out on a JEOL JSM-7800F High-resolution Analytical Field Emission Scanning Electron Microscope (FEG-SEM). Energy dispersive X-ray spectroscopy (EDS) microanalysis was obtained using an Oxford Instruments X-max 80 mm² detector, combined with Aztec software allowing standardless quantitative elemental analysis to be carried out.

3. Results and discussion

Table 2 and Table 3 show the elemental composition of the CuZnSn and Cu₂ZnSnSe₄ thin films before and after annealing respectively. The percentage of Se in the Cu₂ZnSnSe₄ films is presented in Table 4. When comparing Table 2 and 3, Sn losses have been observed [8] due to evaporation during annealing. This causes the ratios of Cu/(Zn + Sn) and Zn/Sn to increase. Previous studies have concluded that the ideal ratios of Cu/(Zn+Sn) and Zn/Sn are ~0.9 and ~1.25 respectively [20-21]. In this study, we have changed the elemental composition in the CuZnSn films systematically (Table 3). The surface map was drawn to define the quality of the Cu₂ZnSnSe₄ and secondary phase formations.

Table 3. Elemental ratios of CZTSe (CuZnSnSe) coating after annealing.

Samples	Cu /(Cu+Zn+Sn) %	Zn /(Cu+Zn+Sn) %	Sn /(Cu+Zn+Sn) %	Cu/(Zn+Sn)	Zn/Sn
S1	33	58	9	0.50	6.72
S2	64	20	16	1.78	1.23
S3	50	38	12	1.00	3.22
S4	27	56	17	0.37	3.29

Table 4. The alloy ratio of Se.

Samples	Se (wt. %)
S1	37.2
S2	41.7
S3	43.2
S4	53.7

Fig. 1 shows the surface morphology of $\text{Cu}_2\text{ZnSnSe}_4$ thin films. It was observed that the zinc-rich films, S1 and S4, have a smoother surface than the copper-rich films, S2 and S3. As seen in Fig 1, some defects are present on the surface of S3. These defects probably arise due to the hydrogen gas trapped while electroplating and is released after annealing. Copper-rich films have more secondary phases, which is probably caused by a high copper content because it forms the CuSe impurity phase. Consequently, S4 has the purest $\text{Cu}_2\text{ZnSnSe}_4$ structure, probably due to the high percentage of Zn and Sn in the film. Actually, the concentration of Zn in S4 is the same as S1, but S4 has much less impurity phases. Accordingly, the higher Sn concentration contained in S4 may be responsible for the decreased impurity phases.

Fig 1.

Fig 2 shows the XRD patterns and Raman scattering spectra of the $\text{Cu}_2\text{ZnSnSe}_4$ films. According to the XRD data, all samples exhibit CZTSe crystallinity. But the XRD data alone does not prove the existence of the $\text{Cu}_2\text{ZnSnSe}_4$ phase because the peaks of ZnSe and Cu_2SnSe_3 are very close to the peak of $\text{Cu}_2\text{ZnSnSe}_4$ [18]. Therefore, Raman spectra of these samples has been used to distinguish them. In the Raman spectra, the peaks at 172-173, 194-197, 231-235 and 239-254 cm^{-1} confirm the presence of the $\text{Cu}_2\text{ZnSnSe}_4$ structure [22]. In our study, XRD patterns indicate that S1 and S4 have the purest $\text{Cu}_2\text{ZnSnSe}_4$ crystals, but the Raman spectrums show that there are impurity phases in the S1 sample. It is difficult to distinguish the peaks of the ZnSe and CZTSe crystals via XRD spectrum because the appearance of the ZnSe and CZTSe peaks are very similar. Raman spectrum proves that the peaks at $\sim 250 \text{ cm}^{-1}$ in the S1 sample result from a ZnSe structure in the film [22]. S4 has the best $\text{Cu}_2\text{ZnSnSe}_4$ crystallinity, as deduced from the Raman and XRD spectra. Impurity phases were not detected in this film. Peaks at about 26, 31 and 55° originate from a MoSe_2 compound and were detected in all the samples. As seen in Table 3, the $\text{Cu}/(\text{Cu}+\text{Zn}+\text{Sn})$ and $\text{Zn}/(\text{Cu}+\text{Zn}+\text{Sn})$ ratios of the S1 and S4 samples are similar, but the Sn in S4 is higher than

S1. This provides evidence that Sn enhances the crystallinity of the $\text{Cu}_2\text{ZnSnSe}_4$ and prevents the formation of secondary phases. Also, many impurity phases were observed in the XRD spectra from the S2 and S3 samples, in which the concentration of Cu is high, but the Zn is low. It is likely that the high Cu concentration increases the secondary phase concentration when the Zn concentration in the film is low.

Fig. 2.

Fig. 3 and Fig. 4 show the effect of the ratios of Zn/Sn and Cu/(Zn+Sn) to the intensity of $\text{Cu}_2\text{ZnSnSe}_4$ and impurity phase peaks. The intensities in Fig 3 give the total of the peak heights (193, 171, 237) of the $\text{Cu}_2\text{ZnSnSe}_4$ and Fig 4 shows the total of the peak heights (140, 250) corresponding to impurity phases collected from Raman Scattering Spectra.

Fig. 3.

Fig. 4.

The maximum intensity in Fig. 3a corresponds to the area of the best $\text{Cu}_2\text{ZnSnSe}_4$. This region is the dark green area in the contour plot (Fig. 3b). According to these plots, the ratios of Cu/(Zn+Sn) and Zn/Sn should be maintained in the range of 0.37-0.50 and 2.5-4 respectively. The formation of impurity phases in the $\text{Cu}_2\text{ZnSnSe}_4$ film affects the quality of the $\text{Cu}_2\text{ZnSnSe}_4$ crystal. Impurity phase formation should be restricted. In our work, the elemental ratios required to keep the impurity phases at a minimum level are presented in Fig. 4. It indicates that the ratio of Cu/(Zn+Sn) should be below 0.5 and that the Zn/Sn ratio should be in the range of 1.9-4.4. These ratio intervals are wider than the elemental ratios required to form the structure of $\text{Cu}_2\text{ZnSnSe}_4$ crystal. Hence, the elemental ratios used to obtain the maximum intensity of the $\text{Cu}_2\text{ZnSnSe}_4$ structure can also be used to restrict the formation of impurity phases. The dark green region in the contour plot in Fig. 4b shows the elemental ratios where the impurity phase density is the highest. It is important to ensure that the elemental ratios are outside these values. The elemental ratios in the coatings before and after annealing are different due to the evaporation of Sn at the annealing temperature. This

makes the elemental ratios difficult to control. The evaporation amount of Sn depends on the elemental ratios and the structure as well as the annealing temperature [17].

4. Conclusions

In this study, the effect of the elemental ratios, prior to annealing, on the elemental ratios following annealing and the formation of the $\text{Cu}_2\text{ZnSnSe}_4$ crystal structure were investigated. Impurity phases formed during annealing were also investigated. The crystal purity of $\text{Cu}_2\text{ZnSnSe}_4$ in the S4 sample is maximum when the concentration of Cu in the coating is low, and Zn is high. When comparing S1 and S4, although the ratios of $\text{Cu}/(\text{Cu}+\text{Zn}+\text{Sn})$ and $\text{Zn}/(\text{Cu}+\text{Zn}+\text{Sn})$ are similar, it was observed that impurity phases were higher in the S1 sample. However, the concentration of Sn in S4 sample was higher than S1. Thus, Sn has a significant effect in preventing the formation of impurity phases. However, when S4 and S2 were examined together, the impurity phases in the S2 sample were too high, although the ratios of $\text{Sn}/(\text{Cu}+\text{Zn}+\text{Sn})$ in S2 and S4 samples were similar. This shows that Sn is not sufficiently efficient by itself to prevent impurity phases. The concentrations of Cu and Zn are also very important.

In conclusion, in this study, the optimum elemental ratio to obtain the highest intensity of the $\text{Cu}_2\text{ZnSnSe}_4$ without impurity phases was determined to be in the range of 0.37-0.50 for $\text{Cu}/(\text{Zn}+\text{Sn})$ and 2.5-4 for Zn/Sn respectively, if the other conditions are maintained constant (such as annealing, etc.). At these ratio values, the formation of secondary phases was minimised.

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Table Captions

Table 1. The electrodeposition duration of Cu and Zn elements.

Table 2. Elemental alloys ratio of CZT (CuZnSn) coating before annealing.

Table 3. Elemental alloy ratios of CZTSe (CuZnSnSe) coating after annealing.

Table 4. The alloy ratio of Se.

Figure Captions

Fig. 1. SEM images of the surfaces of CZTSe films presented in Table 2

Fig. 2. XRD and Raman scattering spectra of the CZTSe film samples listed in Table 2.

Fig. 3. Surface (a) and contour plot (b) of the total intensity of CZTSe crystal structure peaks vs $\text{Cu}/(\text{Zn}+\text{Sn})$, Sn/Sn .

Fig. 4. Surface (a) and contour plot (b) of the total intensity of secondary (impurity) phase peaks vs $\text{Cu}/(\text{Zn}+\text{Sn})$, Sn/Sn .