

## A low-temperature X-ray diffraction study of the $\text{Cu}_2\text{ZnSnSe}_4$ thin films

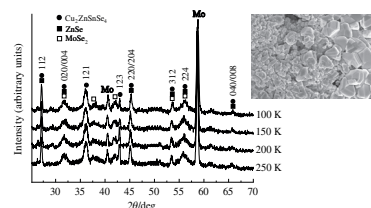
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**Low-temperature XRD measurements were performed to confirm the phase composition and structural parameters of the electrochemically deposited  $\text{Cu}_2\text{ZnSnSe}_4$  thin films on flexible metal substrates.**



**Keywords:** electrochemical deposition, flexible metal substrates, thin films,  $\text{Cu}_2\text{ZnSnSe}_4$ , low-temperature X-ray studies.

Flexible solar cells offer several advantages for their manufacturing and applications compared to traditional solar cells on glass substrates. At present, the most efficient flexible solar cells are based on  $\text{Cu}(\text{In,Ga})\text{Se}_2$  (CIGS) thin films (17.9%).<sup>1</sup> However, they contain expensive rare and toxic components in CIGS films. The  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) thin films have attracted considerable interest for applications in flexible solar cells due to their optical properties, abundant and non-toxic components.<sup>2</sup> Flexible solar cells with efficiencies of 6.48% were prepared using the CZTSe films.<sup>3</sup> It is important for the crystal structure of light-absorbing materials to be stable at working temperature changes for sustainable efficiency of solar cell. It was shown that the transition from the ordered to disordered kesterite structure of CZTSe occurs at the temperature of 200 °C.<sup>4</sup> The partial disordering of Cu and Zn atoms in the (disordered) kesterite structure is responsible for band gap fluctuations,<sup>5</sup> which are the reason for the low open-circuit voltage and, consequently, the efficiency of solar cells. Therefore, it is important to study the CZTSe films under various temperature conditions. To date, the CZTSe thin films have been explored at high temperatures compared to low temperatures. The aim of this work was to study the crystal structure of the CZTSe thin films deposited on a Mo foil in a temperature range from 100 to 250 K by XRD analysis.

The CZTSe thin films<sup>†</sup> were produced by the selenization of Cu/Sn/Zn precursors deposited on a Mo foil substrate in galvanostatic mode.<sup>6,7</sup> The electrodeposited precursors were annealed in a tube furnace in an atmosphere of 95% Ar + 5% H<sub>2</sub> at 350 °C for 30 min. Then, the precursors were selenized in a

**Table 1** Elemental composition and atomic ratios of the CZTSe thin films.

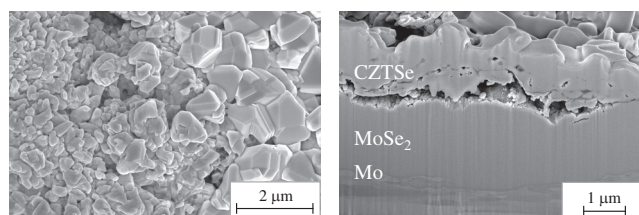
Elemental composition (at%)				Ratio	
Cu	Zn	Sn	Se	Cu/(Zn + Sn)	Zn/Sn
25.07	15.39	10.14	49.40	0.98	1.51

quartz container (volume, ~13 cm<sup>3</sup>) with 5 mg of Se powder at an Ar gas pressure of 1 bar at 580 °C for 30 min.

Table 1 summarizes the elemental composition of the CZTSe films. The Cu/(Zn + Sn) and Zn/Sn ratios indicate a deficiency of copper and an excess of zinc in the films. Note that the elemental composition of the obtained films on Mo foil corresponds to the criterion of high-efficiency solar cells based on the CZTSe thin films.<sup>2</sup>

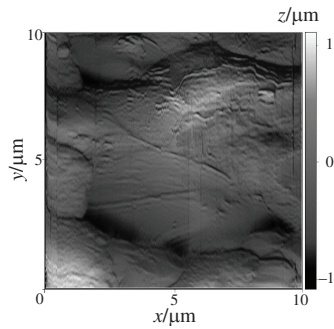
Figure 1 shows the micrographs of the CZTSe films with two types of crystals with sizes of about 27 nm and >1 μm. The CZTSe layer thickness was about 2 μm. The micrograph of a cross section of the film displays a MoSe<sub>2</sub> layer at the interface between the Mo substrate and the CZTSe layer. The MoSe<sub>2</sub> layer, which is important for device performance,<sup>8</sup> was formed as a consequence of a high Se vapor pressure in the chamber during the annealing of films. We observed voids at the film/substrate interface (see Figure 1). The presence of such voids at the interface between a substrate (glass/Mo) and a light-absorbing CZTSe layer was detected previously;<sup>9–12</sup> however, the reason for the appearance of such voids is unclear.

Figure 2 shows the AFM images of the CZTSe films deposited on a Mo foil. The film surface exhibited grains of 6 × 7.2 and 1 × 1.1 μm and 280 nm in height with deep gaps between them.



**Figure 1** Micrographs of the CZTSe thin film on a Mo foil substrate.

<sup>†</sup> The SEM and EDS analysis of the CZTSe thin films was carried out in a dual beam system FE-SEM-FIB Helios Nanolab 650 (FEI Company) equipped with an X-Max X-ray spectrometer (Oxford Instruments). The topography of the CZTSe films was investigated using a Microtestmachines NT 206 atomic-force microscope operating in the contact mode. The structural behavior of the CZTSe films was studied using a TUR-62M X-ray diffractometer with a Rigaku low-temperature camera. The XRD patterns were recorded at 100–250 K in a vacuum. The phase composition was analyzed with the Crystallography Open Database (COD) using the Match software package. The Rietveld analysis implemented in the MAUD software package was used for the determination of lattice parameters.



**Figure 2** AFM image of the CZTSe thin film on a Mo foil substrate.

The root mean square and arithmetic roughnesses of the surface of CZTSe films were 112 and 144 nm, respectively.

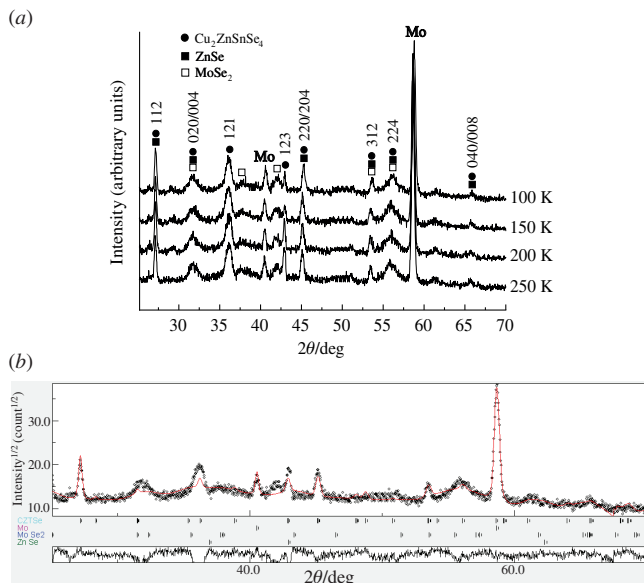
Figure 3 depicts the XRD patterns of CZTSe thin films obtained at 100–250 K. The peaks at  $2\theta$  of 27.1, 31.7, 36.2, 43.0, 45.3, 53.7, 56.2, and 65.9° belong to the reflections of the (112), (020)/(004), (121), (123), (220)/(204), (312), (224), and (040)/(008) planes, respectively, of the tetragonal structure of CZTSe (COD card no. 96-722-0527). The XRD patterns also have reflections from a Mo substrate (COD card no. 96-900-8544) and a MoSe<sub>2</sub> layer (COD card no. 00-077-1715). These results agree well with the XRD analysis data for the thin films of CZTSe at room temperature.<sup>13</sup> However, ZnSe as a secondary phase probably existed in CZTSe films since the peaks of ZnSe (COD card no. 00-037-1463) coincided with or were very close to the peaks of CZTSe. The existence of a ZnSe phase in films was confirmed earlier by Raman spectroscopy.<sup>13</sup>

Figure 3 indicates that the peaks were shifted towards lower angles with a change in the temperature from 100 to 250 K. The lattice parameters linearly decreased as the temperature of the X-ray measurements was decreased from room temperature to 100 K (Figure 4). The structural behavior of the CZTSe films deposited on a Mo foil substrate was similar to the structural behavior of CZTSe single crystals at a low temperature.<sup>14</sup>

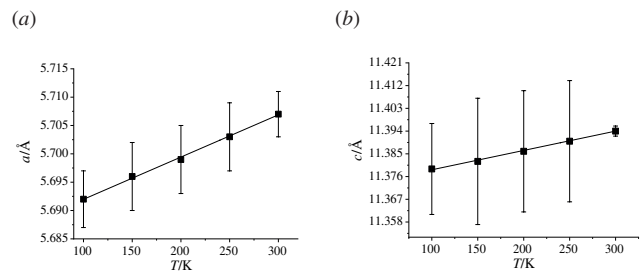
The coefficients of linear thermal expansion of the CZTSe films were calculated from the lattice parameters at five temperatures in a range of 100–300 K using the equations:

$$\alpha_a = (a_T - a_{300})/a_{300}(T - 300), \quad (1)$$

$$\alpha_c = (c_T - c_{300})/c_{300}(T - 300), \quad (2)$$



**Figure 3** (a) XRD patterns of the CZTSe films at 100–250 K and (b) a typical Rietveld refined XRD pattern of the CZTSe films at 250 K.



**Figure 4** Temperature dependences of the lattice parameters (a)  $a$  and (b)  $c$  of the CZTSe thin films.

where  $a_T$  and  $c_T$  are the lattice parameters at 100 K, and  $a_{300}$  and  $c_{300}$  are the lattice parameters at 300 K.<sup>13</sup>

The thermal expansion coefficients  $\alpha_a$  and  $\alpha_c$  are  $13.2 \times 10^{-6}$  and  $6.59 \times 10^{-6} \text{ K}^{-1}$ , respectively. The calculated thermal expansion coefficient  $\alpha_a$  was higher by a factor of  $>2$  than a published value for CZTSe single crystals ( $5.4 \times 10^{-6} \text{ K}^{-1}$ ).<sup>14</sup>

Thus, we produced the thin films of CZTSe on a flexible Mo foil by a three-step process. The presence of a Cu<sub>2</sub>ZnSnSe<sub>4</sub> basic phase and a ZnSe secondary phase in the films was detected. From the XRD analysis data, the lattice parameters of CZTSe were determined. The crystal structure of the deposited CZTSe thin films was stable at low temperatures (100–250 K). This fact indicates the possibility of using solar cells based on the synthesized CZTSe films on a Mo foil at low temperatures.

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