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Research

PREPARATION OF CZTS THIN FILM EMPLOYING RAPID THERMAL PROCESSING METHOD

Mehmet Ali OLĞAR[1,*], Yavuz ATASOY[2]

[1]*Niğde Ömer Halisdemir University, Department of Physics, 51240, Niğde*
[2]*Niğde Ömer Halisdemir University, Niğde Zübeyde Hanım Health Services Vocational High School, 51240 Niğde*
[1,2] *Niğde Ömer Halisdemir University, Nanotechnology Application and Research Center, 51240 Niğde*

ABSTRACT

CZTS thin film was fabricated by sulfurization process of deposited thin films on Mo coated glass substrates. Cu, Zn, and Sn thin film layers were deposited sequentially to form Glass/Mo/CuSn/Zn/Cu. The CuSn layer in the stacked structure was formed by annealing process in the sputtering chamber after sequential deposition of Cu and Sn, respectively. The sulfurization process was performed by rapid thermal processing method (RTP) so as to obtain kesterite CZTS structure. The obtained CZTS thin film was analyzed using several characterization methods such as EDX, XRD, Raman spectroscopy, SEM and PL measurements. The EDX measurements showed that elemental loss was not observed after the annealing process in sulfur atmosphere. The fabricated CZTS thin film showed Cu stoichiometric and Zn rich composition. The XRD pattern of annealed sample revealed formation of kesterite CZTS structure. The Raman spectra of the sample proved formation of kesterite CZTS structure. In addition, some CTS phases were detected in the structure by Raman spectroscopy. Polycrystalline surface microstructure was seen in SEM surface measurement. The room temperature PL measurement exhibited a transition around at 1.39 eV that is very close to band gap of kesterite CZTS structure. Overall, with this study, it has been shown that the CZTS thin film structure can be easily produced using the RTP method with very high heating rate.

Keywords: CZTS, RTP, Sputtering, Kesterite, Thin film

1. INTRODUCTION

Cu_2ZnSnS_4 (CZTS) thin film semiconducting materials gained huge interest in thin film photovoltaic (PV) industry recently. Although the CdTe and Cu (In, Ga)Se_2 (CIGS) based thin films are the most common materials studied in this area due to their high conversion efficiencies, the scarce nature of In and Ga, and toxic nature of Cd cause a reduction in further improvement of such kind of solar materials [1, 2]. Therefore, the CZTS is emerged as an alternative material thanks to the fact that it contains plentiful raw materials, 1.4-1.5 eV direct optical band gap, convenient absorption coefficient, and p-type conductivity [3]. Such optical and electrical characteristics of CZTS thin film make this material favorable for photovoltaic applications.

The CZTS samples commonly fabricated by two stage process [4]. In this first stage, deposition of precursor layers (Cu, Sn, and Zn) are performed using either vacuum-based or solution-based techniques. The most common used vacuum and solution-based techniques are DC and RF magnetron sputtering [5, 6], thermal and e-beam evaporation [7, 8], pulsed laser deposition [9], spin coating [10], electrodeposition [11], spray pyrolysis etc. [12]. The sputtering method is the more preferable technique in preparation of CZTS thin films because it ensures pure, uniform, more controllable film thickness, and more suitable for large scale production.

The CZTS solar cell has a theoretical limit above the 30% conversion efficiency [13]. However, the record conversion efficiency is 13.0 % [14]. Many different approaches are being tried to increase the cell efficiency and converge to highest CZTS based solar cell efficiency. Foremost among these approaches is optimizing the growth parameters of the CZTS films. For example, employing various stacking order of precursor layers [15], preparing the CZTS compound in different chemical composition [16], and optimizing the sulfurization parameters [17, 18].

The sulfurization process is generally carried out by two different procedures that are conventional thermal processing (CTP) and rapid thermal processing (RTP) methods [19, 20]. The latter method ensures that reaching to reaction temperature is more quickly (up to 50 °C/s), minimizing the decomposition processes, and reducing production time and cost.

In this work, CZTS semiconductor compound was prepared by annealing of Glass/Mo/CuSn/Zn/Cu stacked film prepared by sputtering system using RTP method in sulfur atmosphere. The Glass/Mo/CuSn/Zn/Cu stack was selected for preparation of CZTS thin films since more promising films were obtained using this stack by our research group [21]. Furthermore, the CuSn structure was formed intentionally in the sputtering chamber so as to prevent Sn-loss in the sample. It is well known that SnS is

* Corresponding author, e-mail: mehmetaliolgar@ohu.edu.tr (M. A. Olğar)
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a volatile phase due to its high vapor pressure. The CuSn alloy may limit formation of SnS phase and thus prevents the formation of decomposition reactions.
The prepared CZTS sample was characterized using several techniques, such as energy dispersive X-ray spectroscopy (EDX), X-ray diffractometer (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and photoluminescence (PL).

2. MATERIAL AND METHOD

The Glass/Mo/CuSn/Zn/Cu stacked film was produced by sputtering method. High purity Mo (4N), Cu (5N), Zn (4N) and Sn (4N) targets were used for the fabrication of stacked precursor film. Prior to deposition process, the glass substrates were cleaned using the standard cleaning procedure. It was cleaned first in acetone, then isopropanol, and finally in distilled water solutions in ultrasonic cleaner. The cleaned glass sheets were dried with nitrogen gas and placed in the sputtering system for the deposition process. The Mo layer (250 nm) and Cu layers were deposited using DC power source, Zn and Sn layers were coated using RF power supply. After the glass substrate was coated with Cu and then Sn, the temperature of sample holder was set to 200 °C, and CuSn alloy was obtained by annealing this structure for 5 minutes in the sputtering chamber. Just above this structure, the Zn and approximately 30% of the total thickness of Cu were deposited sequentially to obtain complete Glass/Mo/CuSn/Zn/Cu stacked film. The thickness of Cu (175 nm), Zn (165 nm) and Sn (230 nm) was measured by profilometer.

After the precursor layer pulled out from the sputtering system, it was placed in the graphite box with 50 mg of high purity sulfur pieces and it was placed in the RTP system. The sulfurization process was carried out at 550 °C temperature using the highest heating rate (5 °C/s) allowed by our system, using a dwell time of 1 minute. The sulfurization temperature and time were selected subject to our previous reported studies [15, 22].

The chemical composition of the produced CZTS sample was analyzed by EDX, the structural properties were characterized by XRD and Raman spectroscopy (633 nm), the surface morphology was investigated by SEM, and the optical properties were determined by room temperature PL measurements.

3. RESULTS AND DISCUSSION

The chemical composition of precursor and CZTS thin films was characterized by EDX measurement. The EDX spectrum of CZTS thin film was given in Fig. 1.

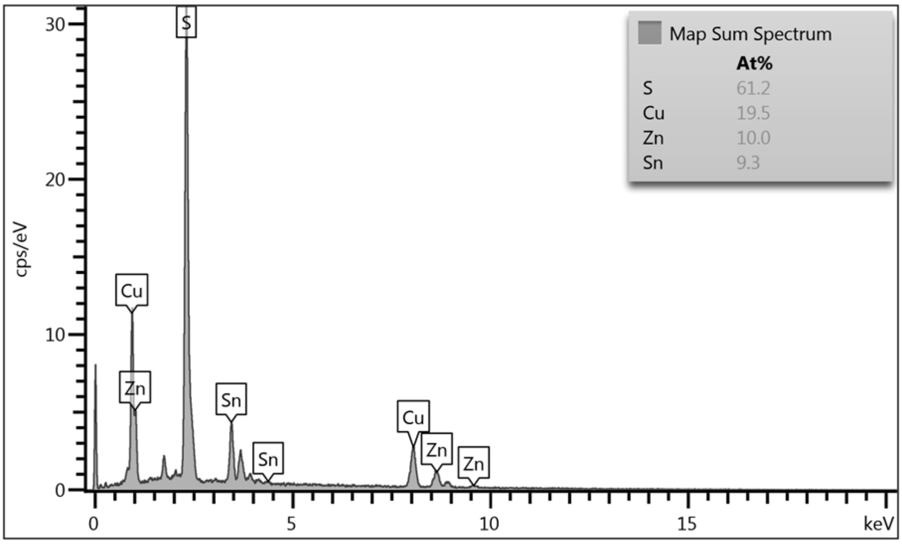

Figure 1. EDX spectrum of CZTS thin film.

The EDX analyses performed by map measurement (~150 µm x 150 µm) since a point measurement may not reflect actual composition of the films due to inhomogeneous elemental distribution. The chemical composition of precursor and CZTS thin film were presented in Table 1. As displayed in the table, Cu/(Zn+Sn) and Zn/Sn ratio of the samples showed similar values. The Cu/(Zn+Sn) and Zn/Sn atomic ratios are ~1.01 and 1.08, respectively. These results showed that the sulfurization process did not cause any elemental loss in the sample. The SnS phase is a volatile phase since it has high vapor pressure and it causes

Sn-loss in the samples when unsuitable sulfurization conditions are applied to the precursor films [23]. According to our EDX results, it can be easily said that the sulfurization process was carried out successfully.

Table 1. Chemical composition of precursor and CZTS thin film.

Sample	Atomic percentage %)				Atomic Ratio		
	Cu	Zn	Sn	S	Cu/(Zn+Sn)	Zn/Sn	S/Metal
Precursor	50.5	25.7	23.8	-	1.02	1.08	-
CZTS	19.5	10.0	9.3	61.2	1.01	1.08	1.58

The crystal structure of CZTS thin film was characterized by XRD measurement. XRD plot of CZTS film was presented in Fig. 2.

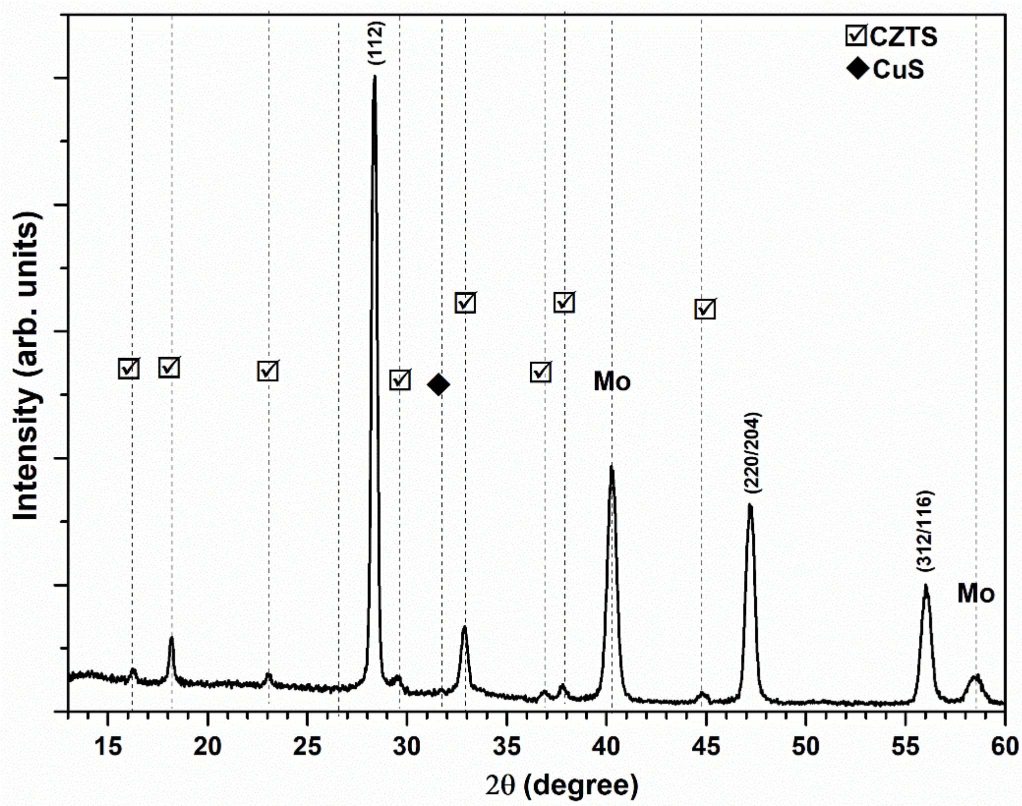

Figure 2. XRD pattern of CZTS sample prepared in this study.

As seen in the figure, the XRD pattern is dominated by (112), (220/204), and (312/116) diffraction planes of the kesterite CZTS phase (JCPDS 26-0575). The other peaks of the same phase are shown in the figure. The diffraction peaks from Mo back contact layer are also shown in the figure (JCPDS 42-1120). A very low intensity peak at around $2\theta=31.70°$ was detected. This peak can be attributed to occurrence of CuS phase (JCPDS 03-065-3556). This phase can be removed from the surface of the sample by KCN etching process [24]. Therefore, it is possible to obtain almost pure kesterite CZTS sample by this simple etching process. Overall, except for minor peak of CuS, XRD pattern of CZTS sample revealed almost pure kesterite CZTS.

The Raman spectroscopy technique was used to prove occurrence of kesterite CZTS phase because Cu_2SnS_3 (CTS) and ZnS phases have resembling XRD patterns compared to CZTS structure [16].

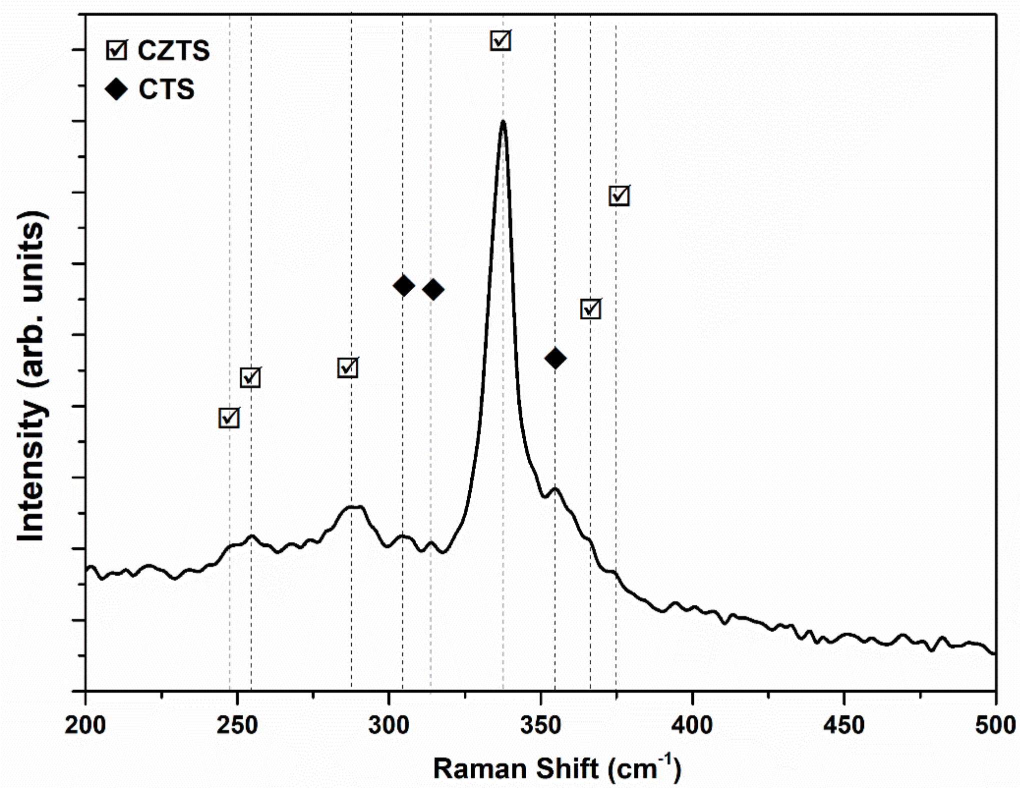

Figure 3. Raman spectrum of CZTS thin film.

As we can see from the figure that a strong peak at around 338 cm^{-1} was detected. It is attributed to vibration mode of kesterite CZTS phase [25]. The other CZTS peaks were marked in the figure. In addition to kesterite CZTS phase, some minor peaks at around 303, 314 and 355 cm^{-1} were detected [26]. These peaks can be ascribed to constitution of CTS phase that is not distinguished by XRD technique. Formation of this phase can be explained by short sulfurization time that may be not enough for obtaining complete CZTS structure [27].

The morphology of precursor and CZTS sample was investigated by SEM technique. The SEM microstructure of the films was displayed in Figure 4. As displayed in the figure, precursor film showed homogenous and dense surface microstructure. After the sulfurization process, the CZTS sample revealed dense and large-grained polycrystalline surface microstructure that is desired situation for solar cell application since small grains gives rise to formation of more grain boundaries and such formation act as recombination centers in the cell [28]. The grain size was found to be on the order of 1 μm.

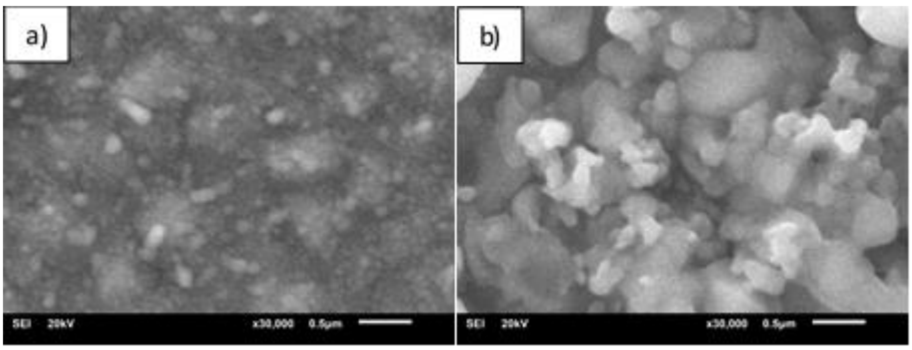

Figure 4. SEM surface image of a) precursor, and b) CZTS thin films.

The photoluminescence (PL) measurement was performed at room temperature and it was presented in Figure 5. As can be seen in the figure, a broad band peaked at around 1.39 eV. It was seen that the obtained value is in good agreement with the reported literature [22, 29]. Considering that the forbidden band gap energy of the kesterite CZTS phase is around 1.4-1.5 eV, it can be seen that the obtained value is very close to this range [30].

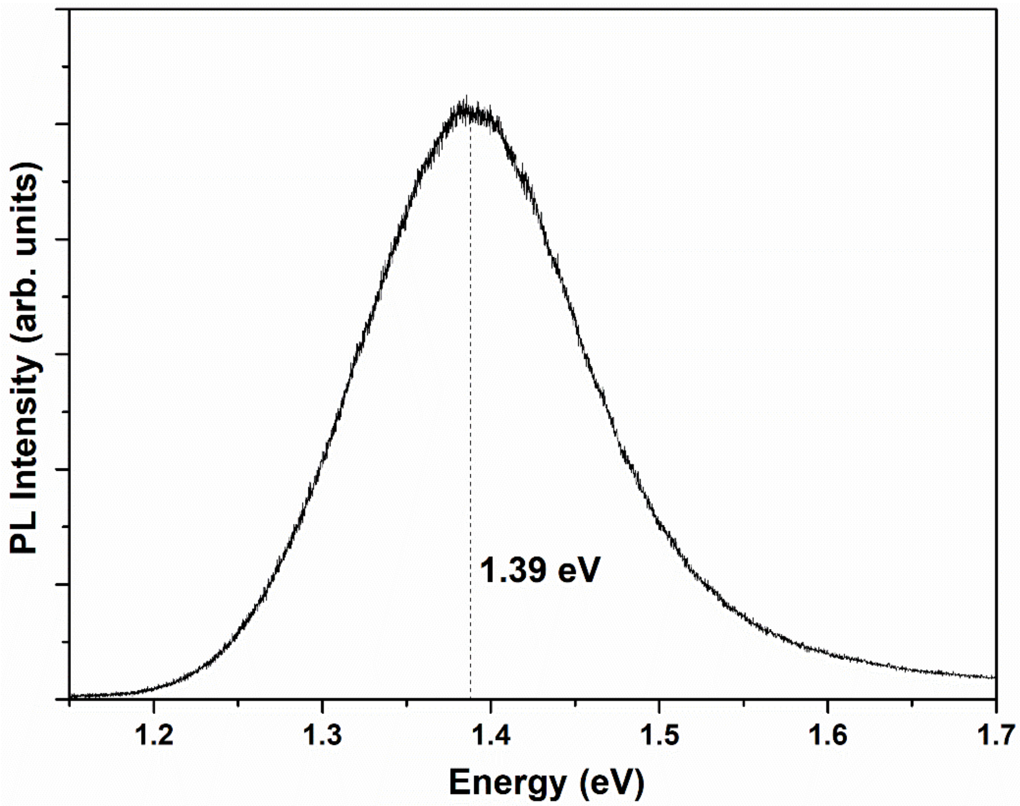

Figure 5. Photoluminescence spectrum of CZTS sample

4. CONCLUSION

In the present work, the CZTS sample was successfully produced using a two-stage method. In the first step, Cu, Sn and Zn layers were sputtered on Mo-coated glass to form Glass/Mo/CuSn/Zn/Cu. In the second stage, the precursor film annealed in sulfur atmosphere using the RTP method to convert it into kesterite CZTS structure. The CZTS sample was analyzed by different methods. As a result of EDX measurements, it was observed that there were no elemental losses as a result of the sulfurization process. The Cu stoichiometric and Zn rich composition was obtained in the prepared CZTS film. The diffraction planes of kesterite CZTS phase and trace of CuS were detected in the XRD pattern. As a result of Raman spectroscopy measurement, occurrence of kesterite CZTS phase was proved. In addition, presence of the CTS phase was also distinguished. The SEM image of CZTS sample exhibited polycrystalline surface structure. It was noted that the PL measurement show a transition around 1.39 eV and this is closed to the forbidden energy gap belonging to the CZTS phase. In summary, in this study, it has been shown that CZTS thin film structure can be formed without elemental loss with the RTP method employing very high heating rate.

SIMILARTY RATE: 22%

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