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INFLUENCE OF SULFURIZATION ON THE PROPERTIES OF Cu_2ZnSnS_4 (CZTS) THIN FILMS PREPARED BY A TWO-STAGE PROCESS

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ABSTRACT

In this study, CZTS thin films were grown by a two-stage method involved sputter deposition of metallic Cu, Zn, and Sn layers to form Cu/Sn/Zn/Cu metallic stacks on glass and sulfurization of the metallic stacks at 540 and 580 °C for 1 and 5 min in sulfur vapor atmosphere. The reacted samples at two different sulfurization temperatures and sulfurization times were characterized employing XRD, SEM, EDX, Raman spectroscopy, optical spectroscopy, and Van der Pauw methods. The metallic stacks and CZTS thin films showed Cu-rich and Zn-poor composition. XRD patterns of the reacted films showed almost pure kesterite CZTS phase except for presence of very small amount of $Cu_{2-x}S$ phase. Raman spectra of the films verified formation of kesterite phase in the films. SEM images showed that the CZTS540-1 sample had more compact, denser and uniform structure. Optical band gap values were found to be in good agreement with the literature. The CZTS540-1 thin film showed the highest carrier concentration and lowest resistivity values amongst the other samples.

Keywords: CZTS, sputtering, sulfurization time, sulfurization temperature, two-stage method

İKİ AŞAMALI YÖNTEM İLE HAZIRLANAN Cu_2ZnSnS_4 (CZTS) İNCE FİLMLERİN ÖZELLİKLERİNDE SÜLFÜRLEMENİN ETKİSİ

ÖZET

Bu çalışmada CZTS ince filmler; Cu, Zn ve Sn metalik katmanların saçtırma yöntemi ile Cu/Sn/Zn/Cu yapılarının cam üzerine kaplanması ve bu yapıların 540 ve 580 °C sıcaklıkta 1 ve 5 dakika sürelerince sulfur atmosferinde sülfürlenmesi şeklinde iki-aşamalı metot kullanılarak büyütülmüştür. Değişik sıcaklık ve sürelerde sülfürlenen örnekler XRD, SEM, EDX, Raman spektroskopisi, Optik spektroskopi ve Van der Pauw yöntemleri kullanılarak karakterize edilmiştir. Tabakalı metalik yapı (Cu/Sn/Zn/Cu) ve CZTS örneklerinin Cu-zengini ve Zn-fakiri kompozisyona sahip olduğu gözlemlendi. Üretilen CZTS ince filmlerin XRD verileri incelediğinde, çok az $Cu_{2-x}S$ fazı dışında neredeyse saf CZTS yapısına sahip kırınım deseni gösterdiği görülmüştür. Raman spektroskopisi kullanılarak CZTS fazının oluştuğu teyit edilmiştir. SEM görüntüleri incelendiğinde, CZTS540-1 örneğinin daha kompakt, yoğun ve homojen bir yapıya sahip olduğu gözlemlenmiştir. Elde edilen optik yasak enerji aralıklarının literatür ile uyum içinde olduğu görülmüştür. Elektriksel ölçümler, CZTS540-1 ince filminin en yüksek taşıyıcı yoğunluğuna ve en düşük özdirenç değerlerine sahip olduğunu göstermiştir.

Keywords: CZTS, saçtırma, sülfürleme süresi, sülfürleme sıcaklığı, iki-aşamalı metot

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1. INTRODUCTION

Thin film solar cells have attracted increasing interest due to the fact that they have low cost fabrication process and high power conversion efficiency which has approached to comparable level with silicon (Si) based solar cells. $Cu(In,Ga)Se_2$ (CIGS) based thin film solar cells have already reached over 20% conversion efficiency [1]. However, scarcity of In and Ga may restrict very large scale development of CIGS-based thin film solar cell technology. Therefore, Cu_2ZnSn_4 (CZTS) thin film has been recently studied intensively since it comprises earth-abundant and more environmental-friendly raw materials. The CZTS absorber layer has a direct band gap energy of 1.4-1.5 eV and high absorption coefficients ($\geq 10^4$ cm^{-1}) [2]. Promising semiconductor properties of CZTS makes it a good alternative to CIGS and a promising compound for photovoltaic (PV) applications. Although the theoretical Shockley-Queisser limit for CZTS(e)-based thin film solar cell is over 30 % [3], the reported record conversion efficiency is still 12.6 % [4], which is still far from the theoretical limit. Therefore, studies on this material are still being carried out to improve its conversion efficiency.

Growth of CZTS thin films is usually carried out by two-stage processes that include deposition of metallic Cu, Zn, and Sn layers either by vacuum methods such as sputtering [5, 6], thermal evaporation [7], pulsed-laser deposition (PLD) [8], or by non-vacuum methods such as spin coating [9], sol-gel [10], and electrodeposition [11]. This step is then followed by a sulfurization process performed at high reaction temperatures in sulfur vapor atmosphere. The sulfurization process can be performed using Conventional Thermal Processing (CTP) method or Rapid Thermal Processing (RTP) that allows high temperature ramp rates (up to 50 °C/s), higher throughput, and lower energy consumption.

Recent studies on CZTS layers have mostly focused on the optimization of the film growth parameters such as the stacking order of the elements (Cu, Zn, and Sn) in the metallic stack [12, 13], sulfurization temperature and time [14, 15], soft annealing/pre-annealing of metallic layers before the sulfurization/selenization process and sulfurization pressure [5, 16-18], and variation of film composition [19, 20]. Some of the past studies related to sulfurization time concluded that the sulfurization process may be carried out for sulfurization times varied from 1 min to 120 min at 500 - 600 °C sulfurization temperatures. The common result of the past studies revealed that the sulfurization time should be at least greater than 10 min in order to obtain fully completed CZTS structure with good crystallinity and free-secondary phase structure [21-23]. Each research group uses different sulfurization parameters according to own sulfurization equipment. Unlike the reported studies in the literature, in this study short dwell time (1 and 5 min) of the reaction was selected for two different sulfurization temperatures that one of them is the most used one (540 °C) and the other one is higher temperature (580 °C) respectively employing RTP approach. By this way, CZTS solar cell can be fabricated with lower energy consumption and can be adjusted for industrial applications.

In the present study, optimization of the sulfurization process for short sulfurization periods at two different sulfurization temperature using the RTP approach was studied. In the first part of the growth process Cu, Zn, and Sn were sequentially deposited on soda lime glass (SLG) substrates to form SLG/Cu/Sn/Zn/Cu stacks. In the latter part, reaction temperatures (540 and 580 °C) and short sulfurization periods (1 and 5 min) were employed to optimize growth of CZTS thin films in a high throughput process.

2. EXPERIMENTAL

Metallic Cu, Zn, and Sn layers were sequentially deposited on soda lime glass using DC magnetron sputtering method. Cu/Sn/Zn/Cu metallic stacks were sputtered employing high purity Cu (5N), Sn (5N) and Zn (4N) targets. The base pressure of the sputtering chamber was 10^{-6} mbar before the deposition process. The operating pressure was 10^{-3} mbar during the deposition process. The thicknesses of Cu, Zn, and Sn layers were calibrated to 175, 165, and 230 nm, respectively. About 70% portion of the Cu layer was deposited over the glass substrate, the remaining portion (30%) was deposited on top of the Zn layer. The thicknesses of the films were calibrated through many calibration runs using DektakXT surface profilometer measurements.

After deposition of the metallic Cu/Sn/Zn/Cu stacks, these stacks were annealed in an enclosed graphite box to form CZTS layers. Elemental sulfur (50 mg) with high purity (99.98%) was placed to the area near the samples through each annealing process to create a sulfur atmosphere in the graphite box. After loading the samples in the graphite box, the box was pushed to the heating zone of a tubular furnace. The annealing furnace was pumped and purged by inert gas mixture (95% Ar + 5% H_2) several times before initializing the heating at a rate of 4 °C/s employing quartz lamps. Sulfurization process was performed at 540 and 580 °C for 1 and 5 min dwell time for each reaction temperature. Then, the quartz lamps were turned off and the graphite box was drawn back to the cool zone of the annealing furnace under flowing inert gas mixture. The reacted samples were labeled according to their reaction temperature and the reaction time of the sulfurization. For example, CZTS540-1

represents the sample sulfurized at 540 °C for 1 min and CZTS580-5 represents the sample sulfurized at 580 °C for 5 min. Table 1 summarizes the sulfurization temperature and dwell time of the reaction for each sample.

The crystalline structure of the films were investigated by X-ray diffraction (XRD) measurements using Rigaku SmartLab diffractometer with a CuKα radiation source (λ=1.5405 Å). Renishaw inVia Spectrometer was employed for Raman spectroscopy of the films using an excitation wavelength of 532 nm. Microstructure and chemical composition of the films were characterized using scanning electron microscope (SEM) Jeol JSM 6610 and an Oxford Instruments Inca X-act energy dispersive X-ray spectroscopy (EDX) system. Optical band gap of the films was characterized employing Dongwoo Optron spectrophotometer in the wavelength range of 550-1400 nm. The Van der Pauw method at room temperature was used for electrical characterization of the samples. Ag paste dots of about 1 mm diameter were formed for electrical contacts of Van der Pauw samples. The four electrical contacts were placed at the four corners of the 1cmx1cm square samples.

Table 1. Growth parameters of CZTS thin films

Sample	Stacking Order	Sulfurization Temperature (°C)	Dwell Time (min)
CZTS540-1	Cu/Sn/Zn/Cu	540	1
CZTS540-5	Cu/Sn/Zn/Cu	540	5
CZTS580-1	Cu/Sn/Zn/Cu	580	1
CZTS580-5	Cu/Sn/Zn/Cu	580	5

3. RESULTS AND DISCUSSION

3.1. EDX Analysis

The atomic percentages and atomic ratios of the as-deposited metallic stack and CZTS thin films obtained by reaction at different sulfurization temperatures (540 and 580 °C) and dwell times (1 and 5 min) were presented in Table 2. As shown in the table, both as-deposited metallic stack and the CZTS thin films had Cu-rich (Cu/(Zn+Sn)>1) and Zn-poor (Zn/Sn<1) composition. While the CZTS540-1, CZTS580-1, and CZTS580-5 samples show some Sn-loss compared to the metallic stack, the CZTS540-5 sample shows some Zn-loss according to Zn/Sn atomic ratio. The Zn and Sn losses from the samples may be attributed to high vapor pressure of Zn and SnS [24, 25]. All the data shows that there was enough S for full reaction of the films as indicated by the S/Metal ratio of around 1.

Table 2. Atomic percentages and atomic ratios of as-deposited metallic stack and CZTS thin films

	Atomic (%)				**Atomic ratio**		
Sample	% Cu	% Zn	% Sn	% S	Cu/(Zn+Sn)	Zn/Sn	S/Metal
SLG/Cu/Sn/Zn/Cu	52.00	22.00	26.00	-	1.08	0.85	-
CZTS540-1	25.40	10.70	11.70	52.20	1.13	0.91	1.09
CZTS540-5	24.92	10.12	12.71	52.25	1.09	0.80	1.09
CZTS580-1	25.52	10.82	11.91	51.75	1.12	0.91	1.07
CZTS580-5	25.50	11.20	11.90	51.40	1.10	0.94	1.06

3.2. XRD Structural Analysis

The XRD patterns of CZTS thin films obtained using different sulfurization temperatures (540 and 580 °C) and dwell times (1 and 5 min) were shown in Figure 1. As can be seen from this figure, regardless of the reaction temperature and dwell time, all of the CZTS films exhibit diffraction peaks at the expected positions of CZTS (112) (2θ=28.44°), (220/204) (2θ=47.31°), and (312/116) (2θ=56.17°) (JCPDS 26-0575) planes. Other characteristic peaks related to the CZTS phase were also seen as shown in the figure. Most of the films showed pure kesterite CZTS phase in their XRD patterns except for the very small peak which is attributed to formation of $Cu_{2-x}S$ (JCPDS 02-1290) secondary phase which is more pronounced for CZTS580-1 thin film.

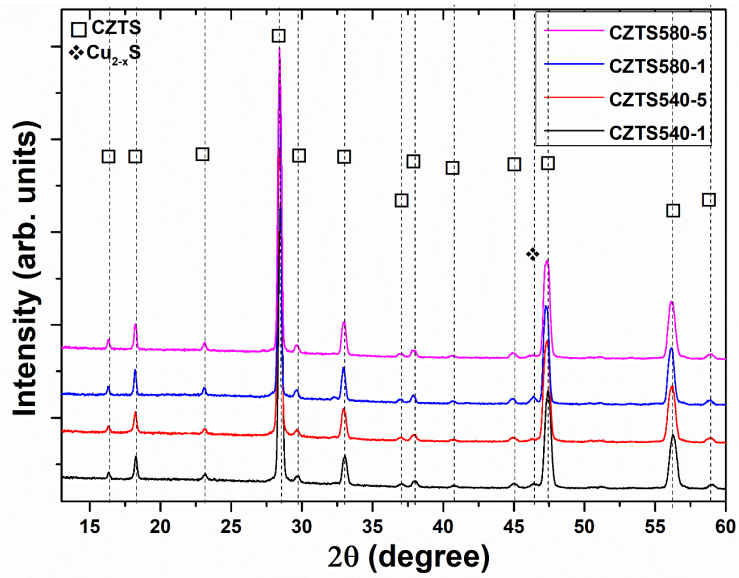

Figure 1. XRD patterns of CZTS thin films

Table 3 presents the full-width-at-half-maximum (FWHM) values for the CZTS thin films, extracted from the (112) diffraction peaks of Figure 1. As can be seen in the table, as the sulfurization time of the reaction increased the FWHM value got to higher values for each reaction temperature. And it should be noted that CZTS580 films revealed smaller FWHM values with respect to CZTS540 thin films. The difference in FWHM values may be attributed to crystalline quality of the films. According to Scherrer's formula there is an inverse linear relationship between the crystalline quality and the FWHM value [26]. It should be noted that the reacted samples for lower sulfurization time show better crystalline quality according to Table 3. The better crystalline quality of a film which is achieved using shorter sulfurization time in this study is a desired property for CZTS-based solar cell applications since the better crystalline quality or larger grain size may enhance photovoltaic performance of solar device.

Table 3. Full-at-half-maximum (FWHM) of the (112) XRD peaks of CZTS thin films

	Sample			
	CZTS540-1	**CZTS540-5**	**CZTS580-1**	**CZTS580-5**
Peak width (cm^{-1})	0.24	0.28	0.19	0.21

3.3. Raman Spectroscopy Analysis

Raman spectroscopy was used in order to confirm presence of CZTS phase in the films and distinguish this phase from others that share similar XRD patterns with CZTS phase. It should be noted that the CZTS (JCPDS 26-0575), ZnS (JCPDS 05-0566) and Cu_2SnS_3 (CTS) (JCPDS 027-0198) phases have very similar XRD patterns. Raman spectra of the CZTS thin films were shown in Figure 2. As can be seen from this figure, irrespective of the sulfurization temperature and time, all of the Raman spectra of the films are dominated by a

strong peak placed around at 336-337 cm^{-1} that is attributed to A symmetry derived from vibration of S atoms belonging to kesterite CZTS phase [27].The other characteristic Raman peak of CZTS is also marked in the figure. Apart from the CZTS peaks, secondary phases were not detected in the Raman spectra of the films. From the Raman spectra of the films can be concluded that the kesterite structure of CZTS may be obtained even at shorter sulfurization time (1 min). Although the Raman spectra of the films do not show presence of ZnS phase, we could not exclude presence of this phase since low Raman cross-section of the wavelength of the used laser light [18].

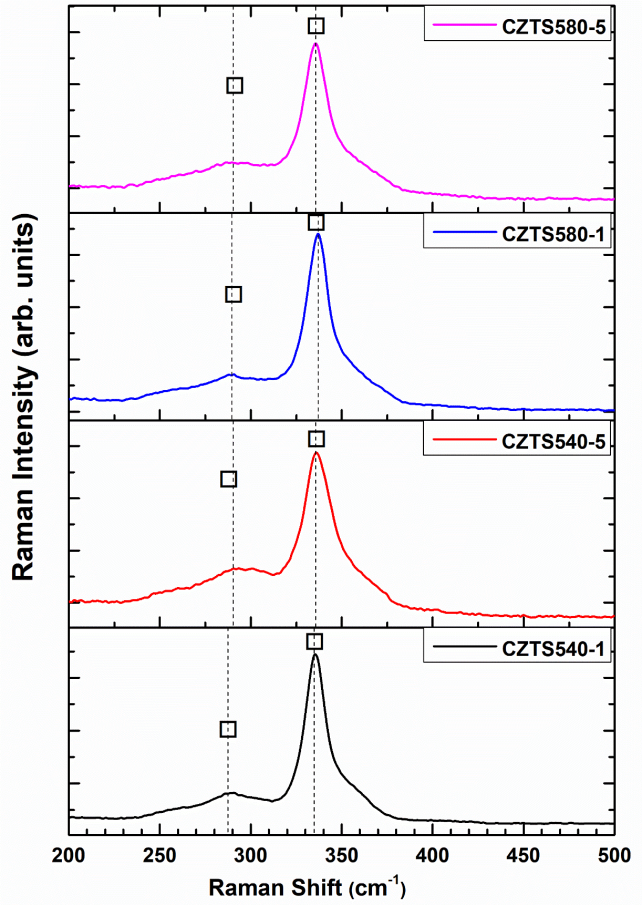

Figure 2. Raman spectra of the CZTS thin films

3.4. Morphological Analysis

Figure 3 displays the SEM top and cross-sectional images of the CZTS thin films. As illustrated in the Figure 3 (a-d), regardless of the sulfurization temperature and dwell time of the reactions, all of the CZTS thin films exhibit dense and granular surface structures. Although the samples had different growth parameters, notable differences were not observed in the surface structure of the films. On the other hand, cross-sectional structures of the films showed some variability. Unlike the other films, CZTS540-1 sample showed more compact, denser, and uniform structure (see Figure 3 (e-h)). Although the CZTS580-1 sample has some large grains, it has a structure of coalescence of large and small grains. The CZTS540-5 and CZTS580-5 samples display dense and non-uniform grain distribution.

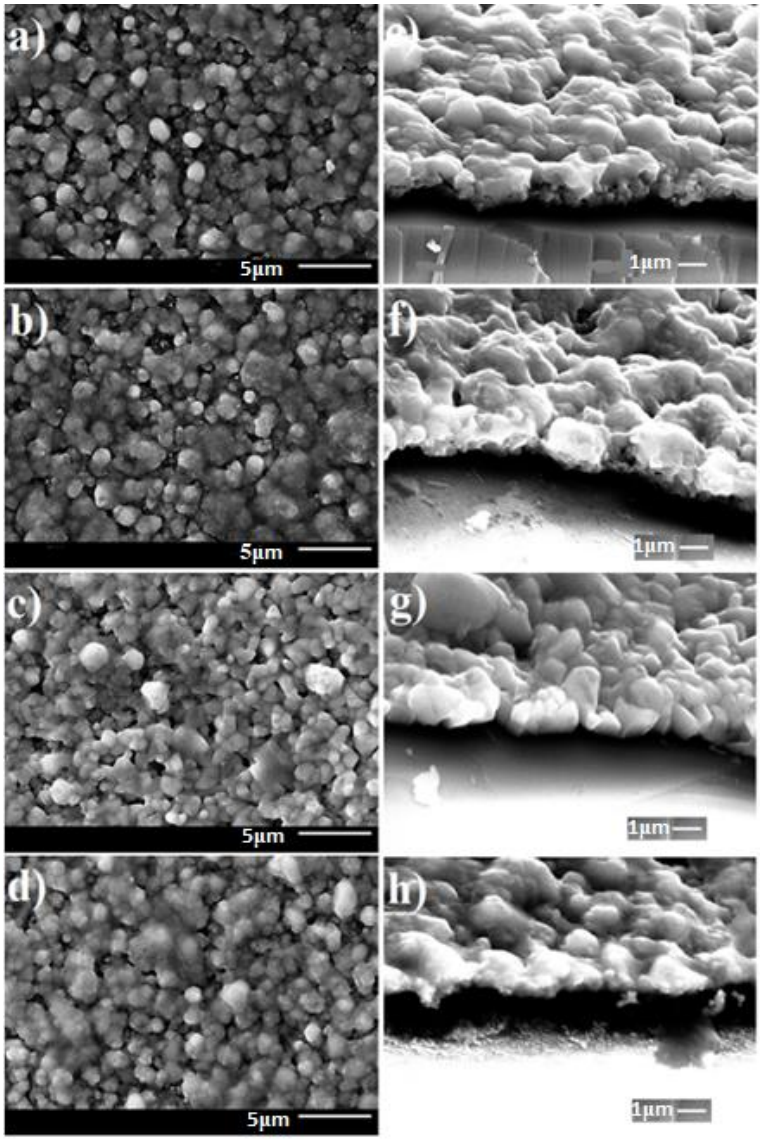

Figure 3. SEM top and cross-section images of CZTS540-1 (a, e), CZTS540-5 (b, f), CZTS580-1 (c, g), and CZTS580-5 (d, h) thin films

3.5. Optical and Electrical Properties

The optical band gap of the CZTS films were calculated from the equation (1) [28]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^{1/2} \quad (1)$$

where α is the optical absorption coefficient, A is a constant, and E_g is the optical band gap. The band gap values were obtained by extrapolating the $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) plots to intercept the horizontal photon energy axis as shown in Figure 4. The optical band gap values obtained are in a good agreement with prior works reported in the literature for CZTS thin films [10]. Although CZTS540-1, CZTS540-5, and CZTS580-5 thin films have an optical band gap of around 1.42 eV, CZTS580-1 thin film has a relatively higher bandgap (1.46 eV) compared to others. The respectively higher band gap value may be attributed to interference by the bandgap of $Cu_{2-x}S$ secondary phase since the direct optical band gap may change from 1.4 eV to 1.55 eV for this phase depending on the "x" value [29].

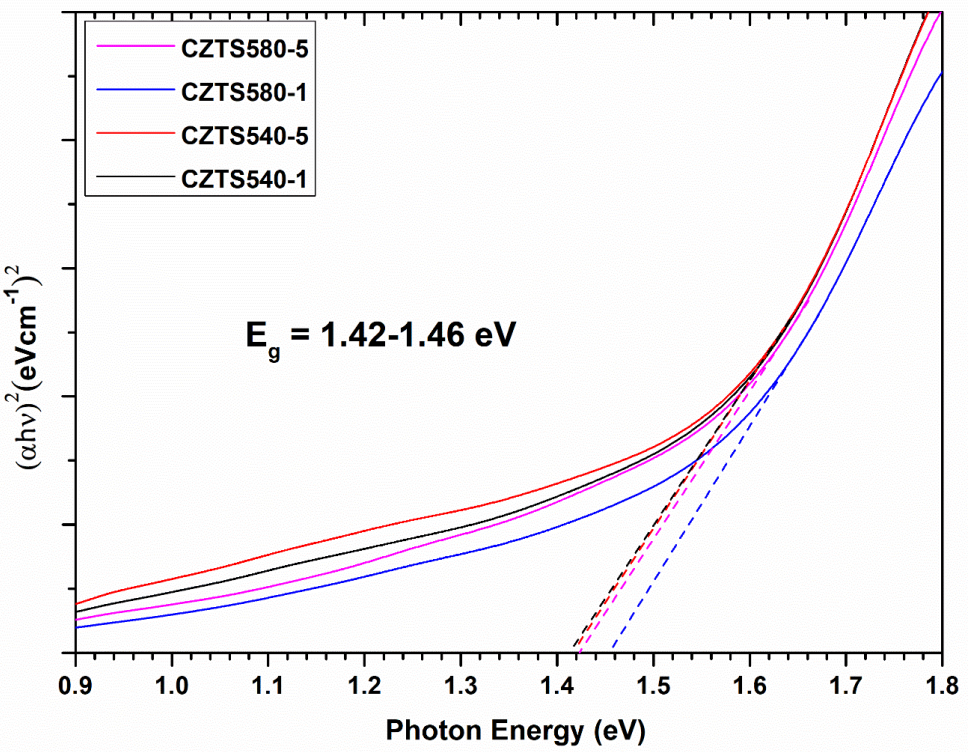

Figure 4. Plot of $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) for the estimation of optical band gap energy for the CZTS540-1, CZTS540-5, CZTS580-1, and CZTS580-5 thin films

The electrical characterization of the CZTS thin films showed that regardless of the sulfurization temperature and dwell time, all of the films exhibited p-type conductivity. Results of the Van der Pauw measurements carried out on the films are summarized in Table 4. As can be seen from this table, the electrical properties of the films showed variability. The carrier concentration of the films changed from 1.9×10^{15} to 3.1×10^{16} cm^{-3}, and the resistivity values changed from 2.9×10^{-1} to 3.4×10^{-2} Ω-cm. The CZTS540 thin films exhibited higher carrier concentration and lower resistivity values than the CZTS580 thin film. Such electrical properties of CZTS absorber layer (resistivity and carrier concentration) are in a good agreement with the values reported in the literature [30].

From Table 4 data can be concluded that as the sulfurization temperature and dwell time of reactions increased, the carrier concentration of charge carriers decreased and the resistivity of the films increased. It means that lower-resistive and higher carrier concentrated of CZTS thin film was obtained using short dwell time of reaction that are more preferable properties for solar cell applications.

Table 4. Electrical properties of CZTS540-1, CZTS540-5, CZTS580-1, and CZTS580-5 thin films

Sample	Resistivity (Ω-cm)	Carrier Concentration (cm^{-3})
CZTS540-1	3.4×10^{-2}	3.1×10^{16}
CZTS540-5	6.2×10^{-2}	1.8×10^{16}
CZTS580-1	1.7×10^{-1}	4.8×10^{15}
CZTS580-5	2.9×10^{-1}	1.9×10^{15}

4. CONCLUSION

In the present study, growth of the CZTS thin films was performed by two-stage method comprising sputter deposition of metallic Cu, Zn, and Sn layers to form Cu/Sn/Zn/Cu metallic stacks then it was followed by annealing treatment at 540 and 580 °C for 1 and 5 min in sulfur vapor atmosphere. The obtained CZTS thin films by reaction of the metallic stacks at different temperatures and sulfurization times were characterized using XRD, SEM, EDX, Raman spectroscopy, optical spectroscopy, and Van der Pauw methods. The metallic stack and CZTS thin films showed Cu-rich and Zn-poor composition. XRD pattern of the films showed almost pure diffraction peaks of kesterite CZTS phase except for presence of $Cu_{2-x}S$ phase. The Full-at-half-maximum (FWHM) of the (112) XRD peaks of CZTS thin films revealed that the sulfurization process for shorter dwell time yields better crystalline quality. Raman spectra of the films confirmed formation of kesterite phase in all films. Although all of the films displayed dense surface morphologies, CZTS540-1 thin film revealed more compact and uniform cross-sectional structure. Optical band gap values are in a good agreement with the literature. CZTS540-1 thin film presented the highest charge carrier concentration and lowest resistivity values amongst the other samples. Overall, it was shown that preparation of promising CZTS thin films for solar cell applications is possible even for short dwell time of sulfurization process.

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