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Growth of Cu_2ZnSnS_4 Thin Films Using Moderate Annealing Temperature and Short Dwell Time

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Abstract. In this study CZTS thin films were fabricated by a two-stage process that sputter deposition of metallic Cu, Zn, and Sn on Mo coated glass substrates and annealing process at 500 °C using various short dwell times (4, 8, and 12 min) using Rapid Thermal Processing (RTP) approach. The X-ray diffraction (XRD), Raman spectroscopy, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX), and photoluminescence were employed to characterize the CZTS samples synthesized employing different sulfurization times. It was observed that all CZTS thin films showed Cu-poor and Zn-rich composition according to EDX results. XRD patterns displayed formation of kesterite CZTS and CuS secondary phases. Raman spectra of the films justified formation of kesterite CZTS phase for all CZTS thin films and formation of CTS phase, which is difficult to distinguish by XRD pattern of the films for CZTS-8 and CZTS-12 samples. SEM images of the films displayed dense, void-free, and inhomogeneous surface structure regardless of the sulfurization time. The optical band gap of the films as determined by photoluminescence was found to be about 1.36-1.37 eV.

***Keywords*:** Cu_2ZnSnS_4, Sputtering, Annealing Time, Annealing Temperature, RTP

Yüksek Olmayan Tavlama Sıcaklığı ve Kısa Bekleme Süresi Kullanılarak Cu_2ZnSnS_4 İnce Filmlerin Üretimi

Özet. Bu çalışmada CZTS ince filmler iki-aşamalı yöntem kullanılarak üretildi; Mo kaplı cam üzerine saçtırma yöntemiyle metalik Cu, Zn ve Sn katmanlarının kaplanması ve sonrasında bu katmanlı yapının 500 °C sıcaklık ve farklı kısa sürelerde (4, 8 ve 12 dakika) hızlı ısıl işlem (RTP) yaklaşımı ile tavlanması. Farklı tavlama süreleri ile üretilen CZTS örnekler X-ışını kırınımı (XRD), Raman spektroskopisi, Taramalı Elektron Mikroskobu (SEM), Enerji Dağılımlı X-ışını Spektroskopisi (EDX) ve fotoluminesans teknikleri kullanılarak karakterize edilmiştir. Üretilen bütün CZTS örneklerin Cu-fakiri ve Zn-zengini kimyasal kompozisyona sahip olduğu ve XRD desenlerinde CZTS fazı oluşumun yanında CuS fazının da oluştuğu görülmüştür. Raman spektroskopisi ile hem CZTS fazının oluştuğu doğrulanmış olup hem de XRD ile ayırt edilemeyen CTS fazının oluştuğu tespit edilmiştir. SEM ile elde edilen film yüzey görüntülerinin sülfürleme süresinden bağımsız olarak yoğun, deliksiz ve homojen olmayan bir yapıya sahip oldukları tespit edilmiştir. Fotolüminesans spektrumları ile optik yasak enerji aralığının 1.36-137 civarında olduğu belirlenmiştir.

***Anahtar Kelimeler*:** Cu_2ZnSnS_4, saçtırma, tavlama süresi; tavlama sıcaklığı, RTP

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1. INTRODUCTION

Thin film solar cells have attracted increasing interest due to the usage of fewer materials and high conversion efficiency. The current record conversion efficiency of CIGS-based thin film solar cells have already reached 22.9 % [1]. Despite its high conversion efficiency, scarcity of In and Ga has been shown as a major issue for further developments of CIGS-based thin film solar cells. Thin film solar cells can be further developed by exploring new materials which includes both earth-abundant and environmental-friendly raw materials. Based on the research in the literature, kesterite Cu_2ZnSnS_4 (CZTS) thin film compound has been considered as a promising material in place of CIGS in the last decade since it contains more abundant elements (Zn and Sn instead of Ga and In) and shows superior optical properties for thin film solar cell applications such as p-type conductivity, at around of 1.4-1.5 eV optical band gap energy and over 10^4 cm^{-1} absorption coefficient [2]. Although Shockley–Queisser limit demonstrated that the theoretical limit is over %30 [3] for CZTS-based thin film solar cell, so far the record conversion efficiency is still 12.6% obtained by $Cu_2ZnSn(S, Se)_4$ thin film compound fabricated using hydrazine-based solution method [4]. The difference between theoretical limit and reported record conversion efficiency value may be attributed to several reasons. Therefore, further investigations should be performed to decrease the gap between the theoretical limit and reported efficiencies.

CZTS thin films can be synthesized using different methods. For example, thermal evaporation [5], e-beam evaporation [6], sputtering [7], and pulse laser deposition (PLD) [8] are vacuum-based methods, sol-gel deposition [9], electro-deposition [10], spin coating [11] and spray pyrolysis [12] methods non-vacuum methods. The vacuum-based preparation techniques are preferable rather than non-vacuum methods with respect to controlling thickness of metallic precursor layers and composition of the films, homogenous film structure and reproducibility of the fabrication process. Sputtering method is one of the vacuum-based technique and the most common method for fabrication of thin film precursor layers since it can easily be scaled up for large area film deposition. After deposition of the metallic precursor layers (Cu, Zn, and Sn) using sputteing method, they are annealed to obtain complete CZTS structure. The Rapid Thermal Processing (RTP) method is more suitable for industrial applications thanks to usage of less energy and higher throughput. In addition, the RTP is an attractive method since the shorter dwell time at high reaction temperature restricts decomposition of the reaction hence restricts loss of elements.

To obtain high conversion efficiency CZTS-based thin film solar cells, many different approaches have been used. Most of the reported studies have focused on the optimizing fabrication parameters of the CZTS absorber layer since solar cell efficiency is strongly-dependent on the quality of the absorber layer. These studies include optimization of the sulfurization temperature[13] , sulfurization time [14], variation order of the metallic stack [15], composition of film [16, 17], and the pressure of the sulfurization [18, 19] etc. The prior works have suggested that although high reaction temperatures (> 500 °C) may enhance the grain morphology, it also gives rise to loss of Sn and Zn thanks to the high vapor pressure of SnS and Zn [20]. Many different approaches were used to prevent Sn-loss from films. For example, employing different sulfurization temperatures and time [7, 13], variation of the sulfurization pressure [18, 19] and stacking order of the metallic Cu, Zn, and Sn layers [15], alloying of Sn with Cu or heating of the metallic constitutes prior sulfurization process [21, 22], and using single target in replace of metallic layers [23], etc.

In this study, it was targeted to grow Sn loss-free CZTS thin films by employing moderate sulfurization temperatures. Therefore, the Mo/Cu/Sn/Zn/Cu metallic stack which was firstly suggested by our research group was utilized [15] and presents promising results for solar cell performance [24] . Then, the metallic stacks were annealed at 500 °C for short dwell times (4, 8, and 12 min) using RTP approach.

2. MATERIAL AND METHOD

The metallic layers (Cu, Zn, and Sn) were sequentially deposited on molybdenum (Mo) coated glass employing DC magnetron sputtering to obtain Cu/Sn/Zn/Cu metallic stacks. High purity Cu (%99.99), Sn (%99.999), and Zn (%99.99) were utilized for sputtering process. The base pressure of the sputter chamber before the deposition process was 10^{-6} torr and operation pressure through the

deposition process was 10^{-3} torr. The thickness of the metallic films was calibrated to 175, 165, and 230 nm for Cu, Zn, and Sn layers, respectively. 120 nm of Cu layer was deposited on Mo and 55 nm of Cu was deposited on top of Zn. DektakXT profilometer was utilized for thickness calibration of the films. For example, one of the thickness calibration measurement taking from profilometer was given in Figure 1. In the present figure, calibration measurement of Zn layer was displayed. As can be seen in the figure, the thickness of the Zn layer was found around 165 nm. It is worth noting that this measurement is one of the several calibration measurement. The real value was obtained by taking average of several measurements from different points.

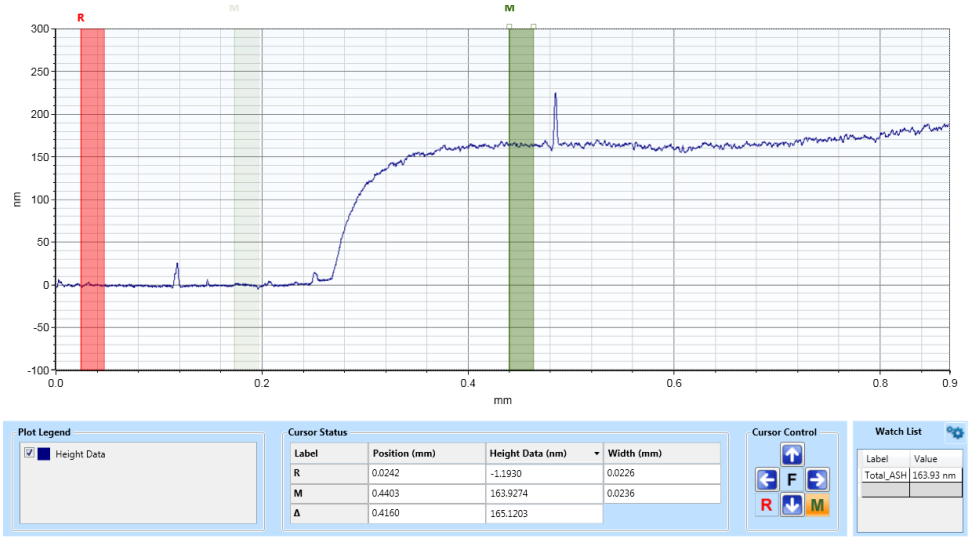

Figure 1. Thickness calibration measurement of Zn layer taken from profilometer.

After loading of the metallic stacks into a graphite box with elemental sulfur, the sulfurization process was carried out at 500 °C using quartz lamps at a rate of 3 °C/s in a 95% Ar + 5%H_2 gas mixture for dwell times of 4, 8, and 12 min at the reaction temperature. Further details about the annealing process have been reported elsewhere [7]. The CZTS samples obtained after sulfurization process were encoded according to their sulfurization time. For example, CZTS-4 stands for the sample sulfurized at 500 °C for dwell time of 4 min, and CZTS-8 represents the sample sulfurized for dwell time of 8 min (see Table 1).

PANalytical Empyrean diffractometer (λ=1.5405 Å) was employed to characterize crystalline quality of the films. Raman analysis was carried out using Renishaw inVia Spectrometer (λ=633 nm). The microstructure and concentration of the films were examined by Scanning electron microscope (SEM) Zeiss Evo 40 and an EDAX energy dispersive X-ray spectroscopy (EDX) system. Optical properties of the films were characterized by photoluminescence spectra (Renishaw inVia Spectrometer, λ= 532 nm) obtained at ambient temperature.

Table 1. Fabrication parameters of CZTS thin films.

Specimen	Layer Order	Annealing Temperature (°C)	Annealing Time (min)
CZTS-4	Cu/Sn/Zn/Cu	500	4
CZTS-8	Cu/Sn/Zn/Cu	500	8
CZTS-12	Cu/Sn/Zn/Cu	500	12

3. RESULTS AND DISCUSSION

3.1. EDX

The atomic percentage of the metallic precursor (Cu/Sn/Zn/Cu) and CZTS thin films taken by EDX was displayed in their EDX spectrum of the samples (Figure 2).

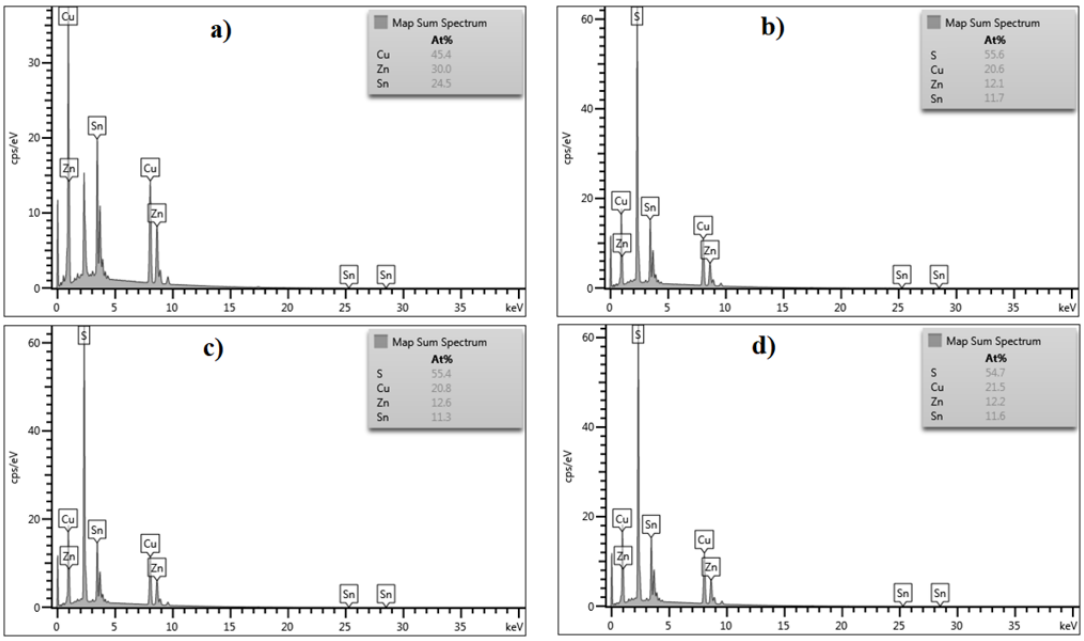

Figure 2. EDX spectrum of metallic precursor (a), CZTS-4 (b), CZTS-8 (c), and CZTS-12 (d) films.

In order to show how composition of the films change with variation of the sulfurization time more clearly, atomic ratio of the metallic precursor and CZTS thin films was also summarized in Table 2. As shown in Table 2, the metallic precursor film showed compositionally Zn-rich (Zn/Sn>1) and Cu-poor (Cu/(Zn+Sn)<1) chemical composition which desired property for solar cell applications [4]. The atomic ratio of the films, on the other hand, revealed variability according to their atomic ratios. The Cu/(Zn+Sn) atomic ratio showed variation from 0.83 to 0.90, Zn/Sn ratio from 1.03 to 1.22, and S/Metal ratio from 1.20 to 1.25.

Table 2. Chemical composition of metallic and CZTS samples.

Specimen	Atomic Ratio		
	Cu/(Zn+Sn)	Zn/Sn	S/Metal
Cu/Sn/Zn/Cu	0.83	1.22	-
CZTS-4	0.86	1.03	1.25
CZTS-8	0.87	1.12	1.24
CZTS-12	0.90	1.05	1.20

Regardless of the dwell time of the samples at reaction temperature, all CZTS thin films showed Cu-poor composition (Cu/Zn+Sn<1) that all films share similar Cu content. However, alteration of sulfurization time caused variability in Zn composition of the films. Although the CZTS-4 and CZTS-12 thin films shared similar Zn composition, the CZTS-8 film had more Zn-composition, respectively. It can be said that all of the CZTS thin films showed Zn-loss but CZTS-4 and CZTS-12 samples showed more Zn deficiency. The Zn-loss for all samples can be explained with high vapor pressure of elemental Zn. It means that some elemental Zn had exist in CZTS-4 and CZTS-12 thin films due to probable decomposition process or incomplete reaction and evaporated during sulfurization process. All CZTS samples exhibited amount of sulfur more than necessary for complete Cu_2ZnSnS_4 structure. Excess amount of sulfur may stem from the fact that the graphite box was pulled to cool zone of the furnace with cap over it. Some residual sulfur could have precipitated on the surfaces of the films. It can be concluded that although some compositional variations were observed in the films, all reacted samples displayed compositionally Cu poor and Zn rich chemical composition, as targeted.

3.2. XRD

The XRD patterns of metallic Cu/Sn/Cu/Zn precursor and CZTS thin films were presented in Figure 3. The intended diffraction peaks for elemental Cu, Sn and Zn were labeled in the figure. Although diffraction peaks of Sn (JCPDS 03-065-7657) were separated clearly and shown in the figure, the diffraction peaks of Cu (JCPDS 00-003-1015) and Zn (JCPDS 00-004-0831) around at 2θ= 43.25° were not separated since diffraction peak positions of Cu, Zn, CuZn (JCPDS 03-065-9061) , and Cu_6Sn_5 (JCPDS 00-045-1488) phases are very close to each other. Additionally, Cu_6Sn_5 at 2θ=30.20 ° binary phase was detected even though not any annealing treatment was applied. It means that Cu and Sn elements can form alloy phase even at room temperature. Diffraction peak of Mo (JCPDS 01-089-4896) at 2θ=40.55 due to substrate was also detected in the films.

As can be seen in the Figure 3, regardless of the sulfurization time all CZTS thin films displayed diffraction peaks at 2θ=28.44°, 2θ=47.31°, and 2θ=56.17° that corresponds (112), (220/204) and (312/116) diffraction planes of kesterite CZTS phase (JCPDS 26-0575). Other characteristic peaks associated with the CZTS are also shown in the figure. Apart from CZTS phase, formation of CuS (JCPDS 01-078-0877) at around 2θ=31.80° was traced for CZTS-4 and CZTS-12 samples as distinct from CZTS-8 thin film. It is well known that CuS secondary phase can be easily removed from the surface of the films by employing KCN etching process [15]. Additionally, as the sulfurization time increased above 4 min, the CZTS samples showed formation of MoS_2 (JCPDS 00-009-0312) phase as a result of reaction of the sulfur vapor with the substrate. It means that extending the sulfurization time above 4 min may contribute to the penetration of sulfur vapor to the lower part of the film. Overall, it was shown that the CuS-free films was successfully obtained using sulfurization time above 4 min for CZTS-8 thin film. However, extending the sulfurization time above 4 min may cause formation of MoS_2 phase. Therefore, pure CZTS phase can be obtained by calibrating the sulfurization time between 4 and 8 min.

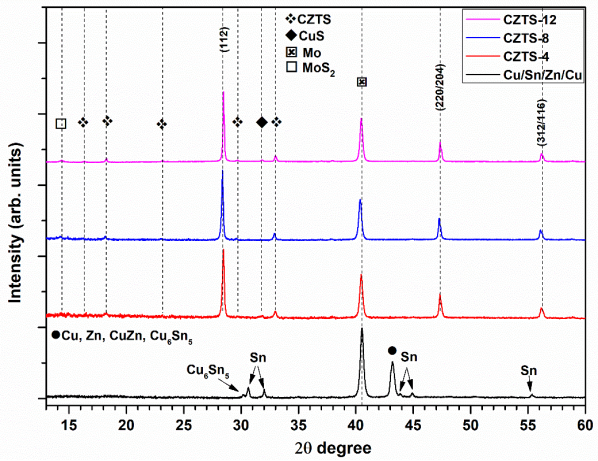

Figure 3. X-ray diffraction patterns of metallic precursor and CZTS thin films.

3.3. Raman Spectroscopy Analysis

Due to the fact that the CZTS, ZnS and Cu_2SnS_3 (CTS) phases share similar XRD patterns, Raman spectroscopy was utilized to prove formation of CZTS phase by distinguishing such phases. Raman spectra of the films which were prepared at different sulfurization times were presented in Figure 4. As can be seen in the figure, Raman spectra of the all films has a dominant peak at around 336-337 cm^{-1} that is ascribed to CZTS phase. The lower intense Raman peaks associated with CZTS phase are displayed in the figure. Except for formation of CZTS phase, the $Cu_{2-x}S$ and Cu_2SnS_3 (CTS) peaks were observed for CZTS-4, CZTS-8, and CZTS-12 respectively [18, 25]. Detection of $Cu_{2-x}S$ phase for CZTS-4 in its Raman spectra supports the XRD pattern of this film. Formation of CTS phase was determined for CZTS-8 and CZTS-12 samples. Such a phase could not be distinguished in their XRD patterns since CZTS and CTS phases have similar XRD patterns. Formation of CTS phase can be explained with the fact that longer sulfurization time may cause decomposition reaction for CZTS-8 and CZTS-12 thin films.

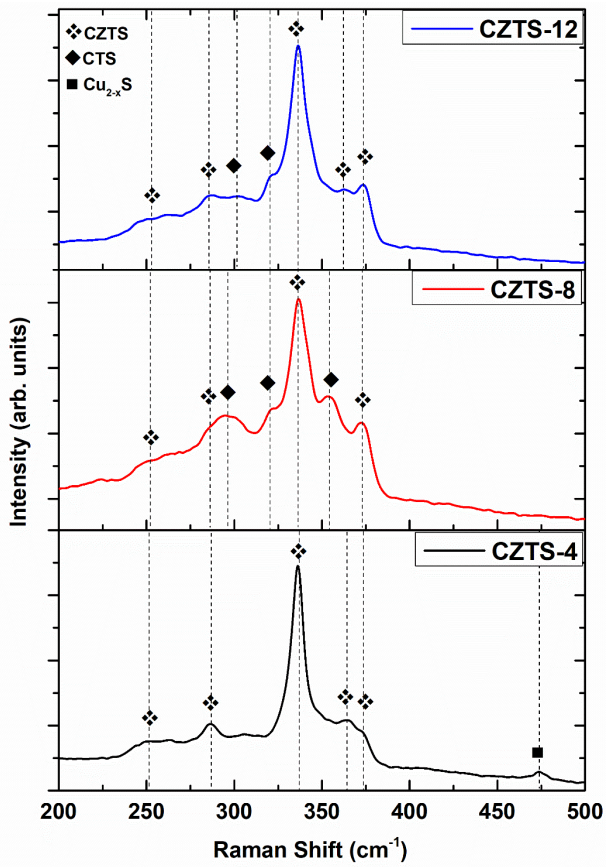

Figure 4. Raman spectra of CZTS-4, CZTS-8, and CZTS-12 thin films.

3.4. SEM

The surface morphology of the films was demonstrated by SEM images in Figure 5 with a broader image (5.00 KX) and their insets (20.00 KX) to show surface of the films more clearly. As shown in the figure, metallic film showed dense and homogenous surface structure (Figure 5 (a)). Regardless of the different sulfurization time, all reacted samples demonstrated dense, void-free, and inhomogeneous surface structure. As the sulfurization time increased, the granular- shaped microstructures decreased and more homogenous surface morphologies were obtained. The EDX results revealed that the micro segregations formed on top of the films (especially for CZTS-8 and CZTS-12) have deficiency of Zn and abundance of Cu-Sn-S elements which may point out probable formation of Cu_2SnS_3 phase. Such result is in good accordance with the Raman spectra of CZTS-8 and CZTS-12 thin films. It means that extending sulfurization time above 4 min may initialize the decomposition process and give rise to formation of CTS phase.

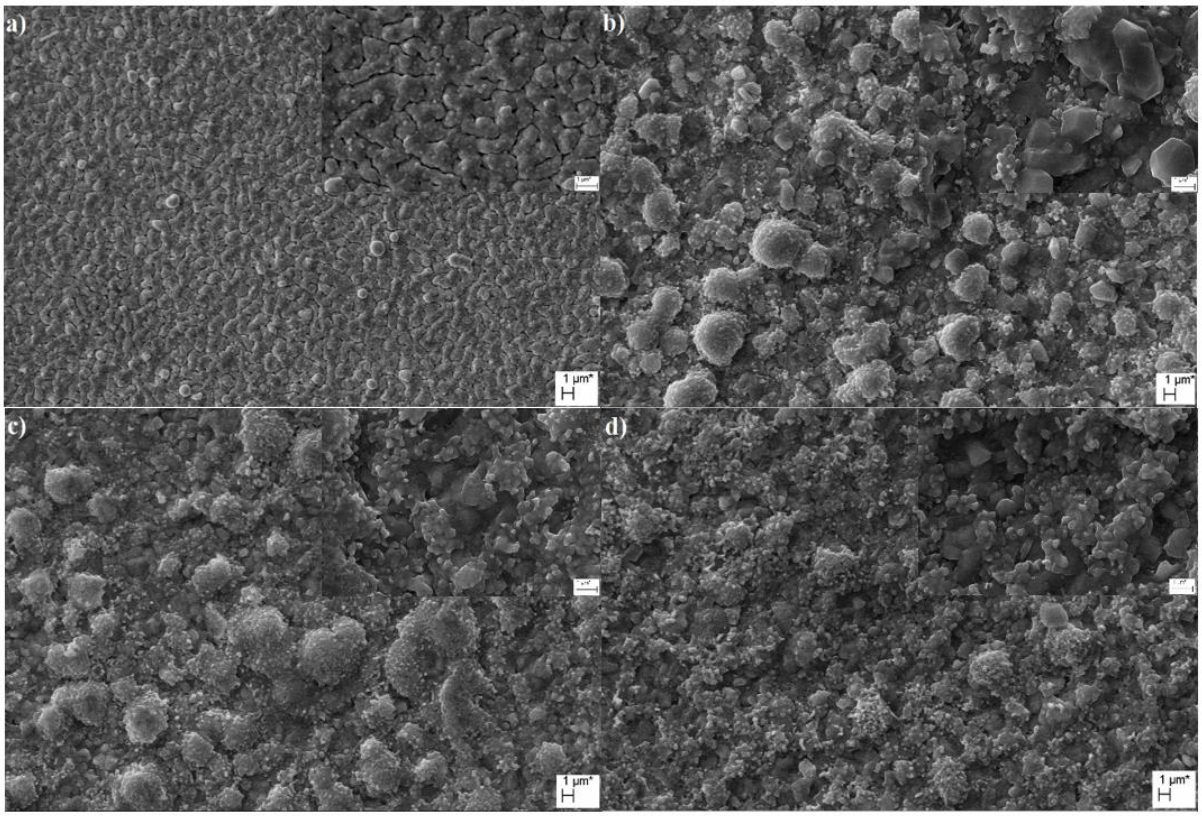

Figure 5. SEM images of metallic (a), CZTS-4 (b), CZTS-8 (c), and CZTS-12 (d) thin films.

3.5. Photoluminescence Analysis

Photoluminescence (PL) spectra obtained at room temperature of the films were displayed in Figure 6. As can be shown in the figure, one broad band at around 1.36-1.37 eV was peaked for all PL spectra of the films. The obtained PL results are compatible with the reported results in the literature [26]. The 1.36-1.37 eV value can be ascribed to conduction band to acceptor transition and involved recombination paths in the CZTS samples [24]. It can also be concluded that the sulfurization time does not affect PL emission results of the CZTS thin films remarkably.

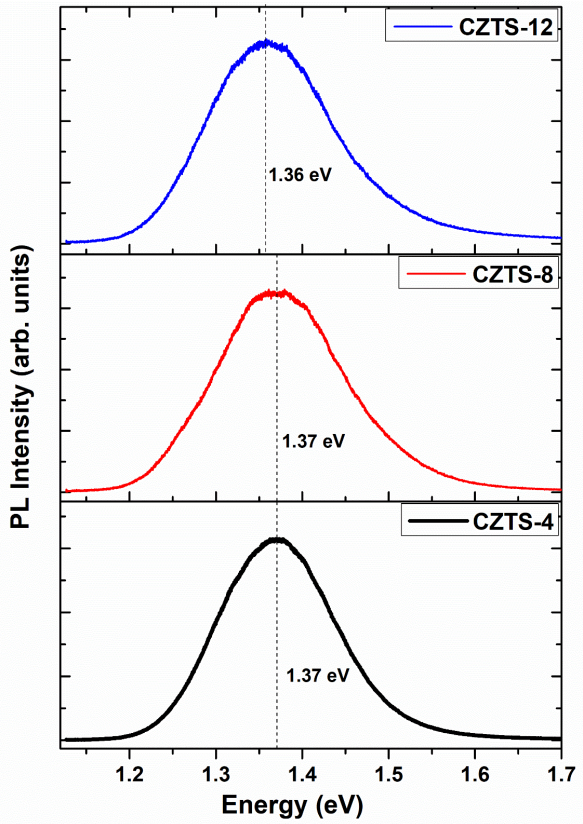

Figure 6. Photoluminescence properties of the CZTS samples.

4. CONSCLUSION

In the present study, CZTS samples were prepared by sequential sputter deposition of Cu, Zn, and Sn on Mo coated glass followed by sulfurization of metallic stacks at 500 °C reaction temperature for various sulfurization times (4, 8, and 12 minutes). The EDX results showed that although some Zn deficiency was observed for the samples, all CZTS thin films had compositionally Cu-poor and Zn-rich atomic ratio. In addition to CZTS phase, formation of some secondary phases such as CuS and MoS_2 was observed in their XRD patterns. Raman spectra of the films were dominated by a strong peak that attributes to kesterite CZTS phase for all samples and distinguished formation of CTS phase for CZTS-8 and CZTS-12 samples. Surface morphology of the films displayed dense and inhomogeneous morphology regardless of the sulfurization temperature. Band gap of the CZTS samples obtained using different sulfurization time was determined at around 1.36-1.37 eV, which exhibits dwell time of the reaction does not influence the band gap of the films remarkably. Overall, it was shown that the pure CZTS thin film can be obtained at moderate sulfurization temperature either by fine-tuning the short dwell time of sulfurization process or employing proper etching process.

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