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IMPACT OF DC-SPUTTERED Mo INTERLAYER ON THE STRUCTURAL AND COMPOSITIONAL PROPERTIES OF Cu_2ZnSnS_4 (CZTS) THIN FILMS ON FLEXIBLE Mo SUBSTRATES

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In this paper, a comprehensive study on the structural and compositional properties of sulfurized Cu_2ZnSnS_4 (CZTS) thin film is presented to elucidate technological challenges of fabrication on flexible Mo substrates. At first, CZTS thin films were deposited by RF sputtering technique on bare flexible molybdenum foil (Mo-foil) as well as on the Mo-foil with DC-sputtered Mo thin film layer (Mo thin film/Mo-foil). Then, samples were annealed in the presence of sulfur (S) and tin (Sn) powder from 550°C to 580°C. The results from XRD showed advantages of Mo thin film/Mo-foil over its counterpart in terms of peak intensity and overall structural quality. The existence of dominant (112) peak, which confirms the polycrystalline structure for all CZTS samples was observed. Compositional analysis was carried out by EDX and it was found that the atomic ratio for CZTS thin films on the Mo thin film/Mo-foil is prone to be Cu-poor and Zn-rich with the average value of 0.84 and 1.12, respectively. Therefore, Mo thin film/Mo-foil bilayer structure has been identified as a more suitable substrate configuration compared to bare Mo-foil for CZTS thin films.

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1. Introduction

Each hour energy from sunlight on the earth's surface can provide a greater power for the consumption of the entire human civilization per year [1]. At the present moment, wafer-based silicon technology is leading the market. However, a considerable use of solar energy requires an additional reduction in the production costs. In compensation, researchers explore and develop thin-film materials to produce efficient solar cells. In this perspective, Cu_2ZnSnS_4 (CZTS) is emerging as a non-toxic and abundant alternative for CdTe or $CuIn_xGa_{1-x}Se_2$ solar cells for quite some time [2-4]. It has the band gap of ~1.45 eV, which is close to the optimum value for single junction solar cells and high absorption coefficient (>10^4 cm^{-1}) [3]. The current word record efficiency of 12.6% is based on CZTSSe containing approximately 90% Se and 10% S on a rigid glass substrate [6]. For pure sulfide CZTS solar cell, the value is 11% with V_{oc} of 762 mV [7] on a rigid glass and in fact, the most of CZTS solar cells is deposited on a rigid soda lime glass. Only a few CZTS devices are deposited on flexible substrates, and this issue offers new possibilities for the application of solar cells. However, the efficiency of CZTS thin films on flexible substrates is far away from the 15% benchmark [8]. Table 1 summarizes some selected pure sulfide CZTS solar cells on flexible substrates. As shown, the maximum reported efficiency for stainless steel, polyimide, flexible glass, aluminium foil, and molybdenum foil (Mo-foil) is reported 4.1%, 0.49%,

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3.08%, 1.94% and 3.82%, respectively. The choice of substrate in photovoltaic (PV) industry is greatly important to reduce manufacturing costs for the high throughput fabrication of thin film solar cells. Mo-foil is considered as one of the best choices since it can be used as the both substrate and the back contact, allowing to reduce the fabrication steps.

Table 1. Summary of some reported flexible CZTS thin films solar cells.

Ref.	**CZTS process**	**Substrate**	**Solar cell structure**	**Solar cell area (cm^2)**	**Voc (m V)**	**Jsc (mA/ cm^2)**	**FF (%)**	**η (%)**
[9]	Successive ionic layer adsorption and reaction (SILAR)	Mo foil	Mo foil/CZTS/ CdS/i-ZnO/ AZO/Ag	0.12	477	11.29	45	2.42
[10]	Sol-gel	Mo foil	Mo foil/CZTS/ CdS/i-ZnO/ AZO/Al	0.25	370	13.52	45	2.25
[11]	Electrodeposition	Mo foil	Mo foil/Mo film/ CZTS/CdS/ ZnO/ZnO:Al/Al	0.35	473	18.84	42.9	3.82
[12]	Screen printing	Polyimide	Polyimide/Mo/C ZTS/CdS/ZnO:A l/Al grid	0.15	386	4.76	27	0.49
[13]	Sputtering	flexible glass (FG)	FG/Mo/CZTS/Cd S/ZnO/ITO/Ag	0.45	491	10.60	59.2	3.08
[14]	Solvothermal route and roll-to-roll printing	Al foil	Al foil/Mo/CZTS/Z nS/i- ZnO/ITO/Al–Ni	-	484	8.91	45.1	1.94
[15]	Sputtering	Stainless steel coated with chromium	CZTS/CdS/i- ZnO/ ZnO:Al	6.25	302	24.7	47.1	3.5
[16]	sputtering	Stainless steel	CZTS/CdS/i- ZnO/ ZnO:Al	-	638	13.38	48.0 1	4.10

Moreover, Mo-foil has its own pros such as high temperature resistance, typical mechanical strength, and appropriate coefficient of linear thermal expansion. Based on the limited literature about CZTS solar cells on Mo-foils, one of the key issue is the interface between Mo-foil and CZTS layer and it is expected that an additional Mo thin film can improve the interface [9-11]. Recently, B. Long et al. [17] demonstrated the effects of Mo thin film intermediate layer empirically, and ~15% improvement was achieved in their efficiency. Our previous experimental investigation and numerical simulation have expounded the interdependence of Mo back contact thin film microstructural properties to the formation of MoS_x interfacial layer and its concomitant effects to the performance of CZTS thin film solar [18-22]. However, the relationship between the Mo-foil substrate and CZTS layer requires more understanding to develop CZTS flexible thin film solar cells.

In the present work, we fabricated CZTS thin films on Mo-foil and Mo thin film/Mo-foil substrates by RF-magnetron sputtering from a single quaternary target and post-sulfurization was conducted in various temperatures. Structural and compositional properties of CZTS layers on both types of substrates are investigated to accomplish a clear understanding about the influence of sulfurization conditions. This study explains the effect of Mo thin film in the interface of Mo-foil and CZTS layer.

2. Experimental details

The Mo-foils (≥ 99.5% pure) with the thickness ~1 mm were purchased from Sigma-Aldrich and they were cut by the metal cutting machine into a small square area pieces (1 cm^2). Prior to the deposition step, the Mo-foils were cleaned through ultrasonic bath in following sequences methanol 15 min/acetone 15 min/methanol 15 min/de-ionized water 30 min and they were dried by nitrogen gas jet stream. Then, the samples were immediately loaded into the sputtering chamber to minimize any possible contamination [23]. The Mo thin film was deposited by DC magnetron sputtering at 100 W on the Mo-foil following our previously established process parameters [24]. Subsequently, CZTS thin films were deposited from a single quaternary target on both Mo-foil and Mo thin film/Mo-foil at RF power of 50 W, working pressure of X mTorr, deposition temperature of 180 °C and the substrate-target distance was fixed at 12 cm, respectively [25]. In the second step, these samples were annealed statically in the quartz tube (OTF-1200x) in the presence of 31.25 mg and 23 mg of sulfur (S) and tin (Sn), respectively. The ramp rate was 5°C/ min and 60 min was the holding time for sulfurization in various temperatures of 550, 560, 570, and 580 °C as shown in Fig. 1. At the end the samples were allowed to cool by the forced rapid cooling using a stand fan.

The crystalline structure of CZTS thin films was examined by Bruker AXS-D8 Advance X-ray diffraction (XRD) and the diffraction angle was varied from 10° to 80° with using Cu Kα radiation wavelength, $\lambda = 1.5408$ Å. The morphology of all CZTS thin films was studied using a scanning electron microscope (SEM; Hitachi S3400-N) equipped with energy dispersive X-ray spectroscopic (EDX) to measure the composition. All along the EDX measurements, we only take into account the Cu, Zn, Sn, and S elements for the calculation of CZTS thin film composition and the rest of elements were extracted from all samples.

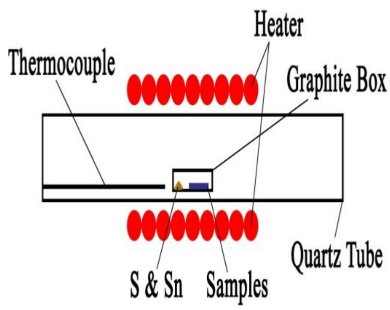
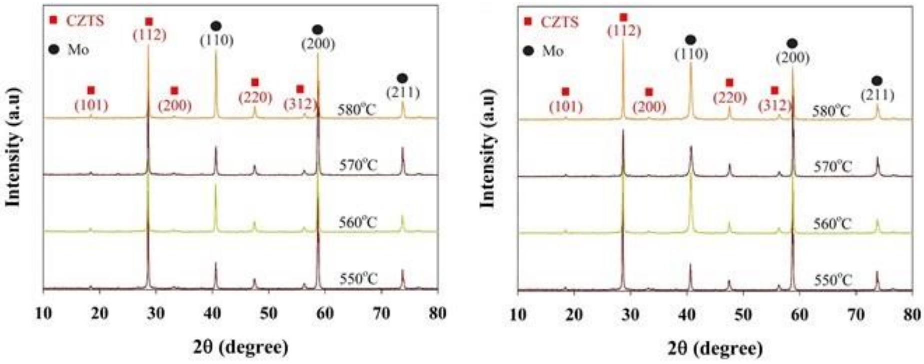


Fig .1. Schematic diagram for sulfurization setup.

3. Results and discussion

The X-ray patterns of both structures at various sulfurization temperatures (550°C, 560°C, 570°C, 580°C) during 60 min are shown in Fig. 2. Several phases are identified along with Mo ((110) for the sputtered Mo thin film (JCPDS# 42-1120), and (200) and (211) for the Mo-foil (JCPDS# 42-1120)). All obtained peaks (101), (112), (200), (220) and (312) match with the kesterite structure from the file JCPDS 26-0575. Linking the intensities of the kesterite CZTS thin films main peaks, denotes the preferential orientation in the (112) plane, similar to the reported results on a rigid glass and flexible substrates [15, 26-28] in all samples. The higher sulfurization temperature increases the polycrystalline feature of the thin films on both structures alongside the intensity of all CZTS peaks. However, the (112) plane due to the lowest surface energy [29] cannot show any linear pattern in its peak intensity as Fig. 2 depicts. The atoms are confined at the lowest energy position by the stable crystal structure. Increase in the sulfurization temperature can provide enough energy for further diffusion and migration of the atoms. Therefore, at 580°C, the diffusion of Cu, Zn, Sn, and S enhances and endorses random atomic arrangement, resulting the rise of the grain size from 68 to 77 nm and 56 to 81 nm for CZTS/Mo-foil and CZTS/Mo thin film/Mo-foil in the (112) preference, respectively. This phenomenon is also in agreement with the SEM images in Fig. 4 (a) and (b).



a) *b)*

Fig. 2. XRD patterns of CZTS films sulfurized at various temperatures 550-580°C on: (a) Mo-foil, (b) Mo thin film/Mo-foil.

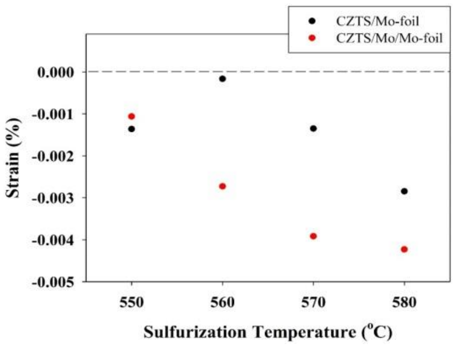


Fig. 3. Strain variations of (112) oriented crystal for CZTS films sulfurized at various temperatures 550-580°C on Mo-foil and Mo thin film/Mo-foil.

By comparing Fig. 2 (a) and (b), using Mo thin film/Mo foil can result in the higher crystallinity for CZTS at higher sulfurization temperature although it is significantly smaller than those CZTS thin films on a rigid glass [30]. Sun et al. [16] reported that the S incorporation in CZTS thin films can improve the grain size and also homogenize the metal element distribution. It was found that, there might be a link between the amount of SnS_2 phase present at the surface of the CZTS film and the sodium, knowing that a considerable amount of SnS_2 at the surface would degrade the cell performance. Other studies also have previously reported the influence of S to increase the grain size of CIGS and CZTS absorber layers [31, 32]. On the other hand, as shown in Fig. 3, Mo thin film/Mo-foil substrate mostly induces CZTS crystal with higher compressive strain (smaller lattice parameters) compared to bare Mo foil substrate for sulfurization temperature ranging from 560 to 580°C.

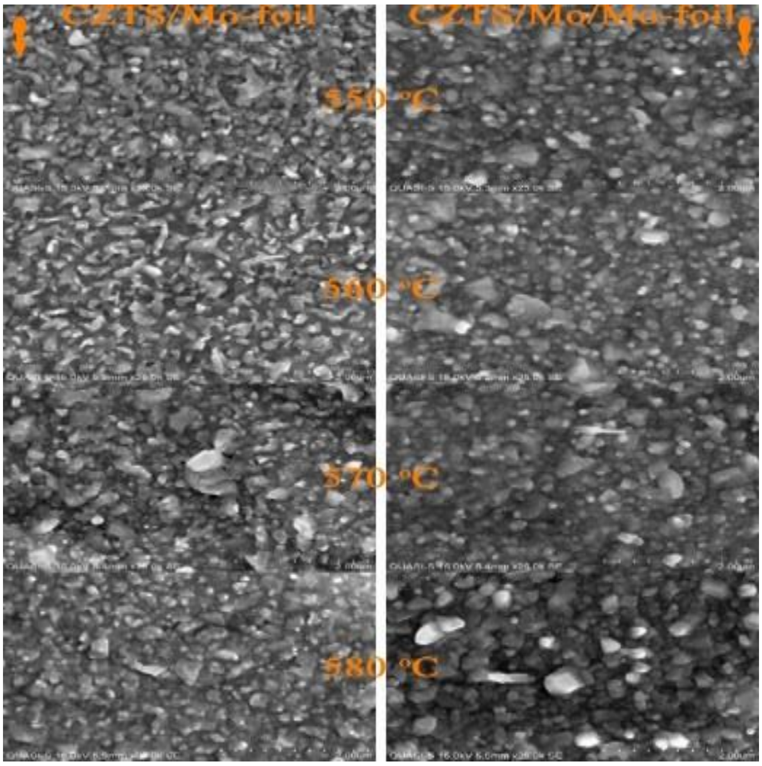


Fig. 4(a). Surface morphology of CZTS films sulfurized at 550°C and 580°C on Mo-foil and Mo thin film/Mo-foil.

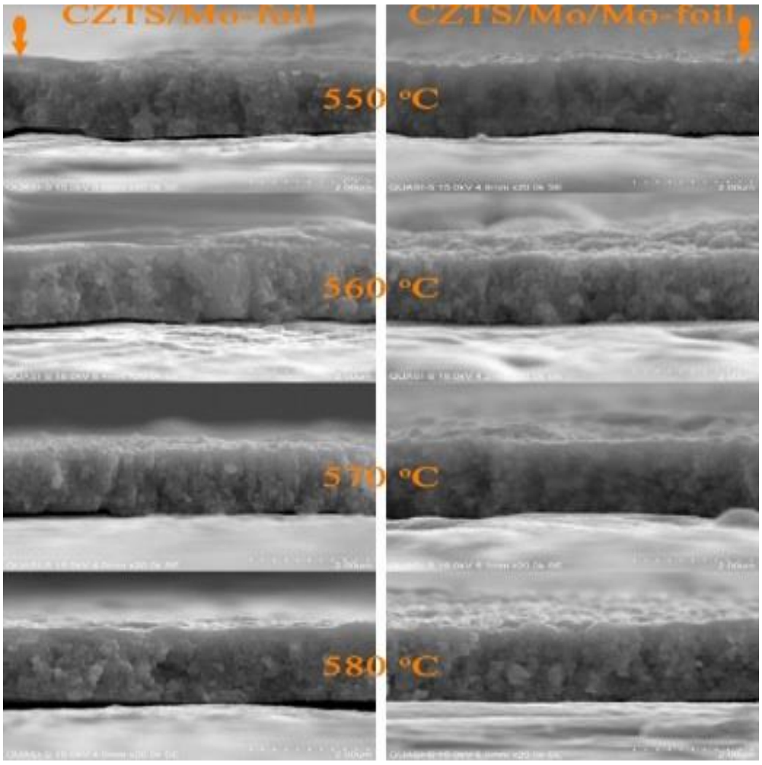


Fig. 4(b). Cross section of CZTS films sulfurized at 550°C and 580°C on Mo-foil and Mo thin film/Mo-foil.

Table 2 demonstrates the atomic concentration of Cu, Zn, Sn and S, and the atomic ratio of Cu/Sn, Cu/(Zn+Sn), Zn/Sn and S/(Cu+Zn+Sn) for the CZTS films sulfurized at various temperatures 550-580°C on the Mo-foil and the Mo thin film/Mo-foil. As shown, the increase of temperature does not have any significant effect on the S ratio on both individual structures and the average value for the CZTS/Mo-foil and the CZTS/Mo thin film/Mo-foil is measured ~0.88 and ~0.93, correspondingly. The Cu/(Zn+Sn) is increased by the rise of temperature up to 580°C on both structures and similar reverse trend is observed in the Zn/Sn from 550°C to 570°C. At 580°C, the Zn/Sn shows a slight increment compared to 570°C. The well-known decomposition reaction for the loss of S and then SnS [33] is controlled reasonably as illustrates in Fig.5 . Through the obtained results, we can easily observe the difference between the two structures. The composition is nearer to the stoichiometry in the CZTS/Mo thin film/Mo-foil than in the CZTS/Mo-foil. The average values of 0.84 in the Cu/(Zn+Sn) and 1.12 in the Zn/Sn are close to an optimal value, which are consistent with previous reports [34-37]. The reason is that a Cu-poor boosts the formation of Cu vacancies, which react as shallow acceptors in CZTS absorber layers, on the other hand a Zn-rich curbs the substitution of Cu in Zn sites, this results in relatively deep acceptors. Furthermore, this ratio is needed to minimize the amount of defect clusters [CuZn + SnZn] and [2CuZn + SnZn], which negatively affects the performance of kesterite thin film solar cells. Moreover, we can visualize that the concentration of Sn is higher in the CZTS/Mo thin film/Mo-foil structure. The presence of sputtered Mo layer suppresses the Sn loss, results in the decrease of voids formed at the interface between the CZTS and the Mo-foil [37].

Table 2. Elemental atomic% of CZTS films sulfurized at various temperatures 550-580°C on Mo-foil and Mo thin film/Mo-foil.

Sample		Composition (at%)			
		S	Cu	Zn	Sn
CZTS/ Mo-foil	550°C	46.82	25.65	16.79	10.74
	560°C	47.12	25.61	15.97	11.29
	570°C	46.80	25.25	16.10	11.86
	580°C	46.67	26.48	15.92	10.93
CZTS/Mo thin film/Mo-foil	550°C	47.84	23.93	15.04	13.20
	560°C	48.43	23.78	14.88	12.91
	570°C	48.51	23.08	14.67	13.74
	580°C	48.23	24.28	14.67	12.82

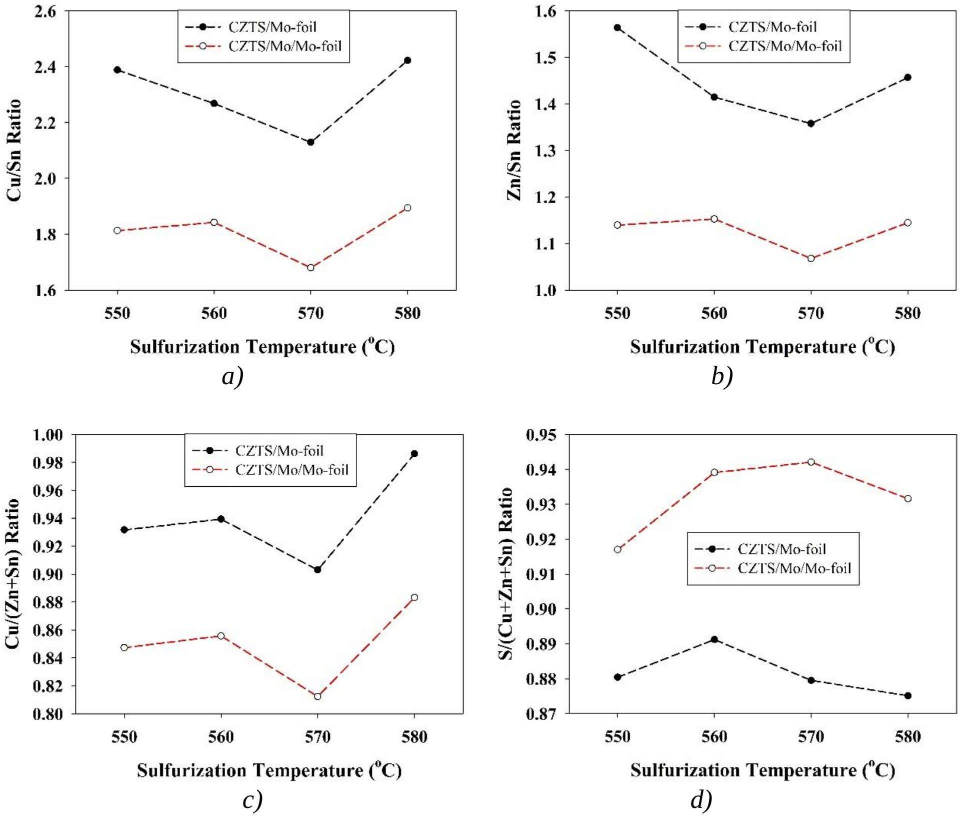


Fig. 5. Compositional ratio of CZTS films sulfurized at various temperatures 550-580°C on Mo-foil and Mo thin film/Mo-foil.

4. Conclusions

In this study, the effects of sulfurization temperatures on the properties of CZTS thin films on the Mo-foil and the Mo thin film/Mo-foil are investigated. The CZTS films were deposited by RF-magnetron sputtering from a single CZTS quaternary target, followed by static sulfurization. These samples were characterized by XRD, which gave an inconclusive determination of their phase purity. The maximum grain size for (112) CZTS peak was measured ~81 nm on the Mo thin film/Mo-foil, which also had the highest intensity. This results were confirmed by SEM images subsequently. The EDX analysis revealed that the composition for the CZTS/Mo thin film/Mo-foil was near to the stoichiometry. Therefore, the presence of Mo layer has positive effects in terms of the structure and composition on the CZTS thin films. This finding explains the efficiency difference between CZTS on the Mo thin film/Mo-foil and the Mo-foil in the literature. Our results support the proposal that the deposition of Mo thin film on the Mo-foil followed by sulfurization at 580°C might has a potential for solar cell applications.

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