

Article

Effect of Sulfurization Temperature on Properties of Cu₂ZnSnS₄ Thin Films and Diffusion of Ti Substrate Elements

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Abstract: The addition of flexible Cu₂ZnSnS₄ (CZTS) thin film solar cells to titanium (Ti) substrates is an attractive way to achieve the low-cost manufacturing of photovoltaics. Prior research has indicated that the appropriate diffusion of Ti elements can enhance the crystalline growth of CZTS films. However, the excessive diffusion of Ti has been shown to adversely affect the photovoltaic performance of CZTS photovoltaic devices. Therefore, it is essential to regulate the diffusion of Ti elements within CZTS thin films to optimize their photovoltaic properties. The tendency for Ti substrate elements to diffuse into CZTS films is also influenced by the activation energy associated with these Ti elements. The sulfurization temperature is posited to be a critical factor in modulating the diffusion and activation energy of Ti elements within CZTS thin films. Consequently, this research investigates the alteration of the sulfurization temperature of CZTS thin films in order to enhance the properties of these thin films and to examine the diffusion behavior of titanium elements. The results reveal that as the sulfurization temperature increases, the diffusion of Ti elements within the CZTS thin films initially increases, then decreases, and subsequently increases again. This pattern suggests that the diffusion of Ti elements is affected not only by the activation energy of the Ti elements but also by the defect hopping distance within the CZTS thin films. Notably, at a sulfurization temperature of 550 °C, the grains at the base of the CZTS thin film demonstrate an increased density, which is associated with a reduced defect hopping distance, thereby hindering the diffusion of Ti elements within the CZTS thin films. Furthermore, at this specific sulfurization temperature, the slope of the current–voltage (I–V) curve for the CZTS/Ti structure reaches its maximum, indicating optimal ohmic contact characteristics.

Keywords: sulfurization; CZTS films; titanium; diffusion



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1. Introduction

The kesterite-structured copper–zinc–tin–sulfide (CZTS) thin films have attracted widespread attention due to their favorable bandgap, high absorption coefficient, and p-type conductivity [1–3]. In contrast to the elemental components of Cu(In,Ga)Se₂ (CIGS) thin films, CZTS thin films are characterized by their nontoxicity, abundance, and cost-effectiveness [4,5]. Consequently, CZTS absorber layers can serve as a potential replacement for traditional copper-based absorber layer materials (CIGS) [6]. Presently, there are a paucity of studies in the literature that address the impact of titanium (Ti) elements (or substrates/layers) on CZTS thin films [7–11]. Research has demonstrated that Ti substrates or Ti elements facilitate the crystal growth of CZTS thin films. The Ti foils are suitable for the application of photovoltaic devices. An optimal thickness of the Ti layer within CZTS thin films can enhance the crystalline growth of CZTS thin films and lower the work function of these thin films when utilized in photovoltaic devices [10]. Guo et al. indicated that the power conversion efficiency (PCE) of CZTS photovoltaic devices increases from

2.52% to 3.98%. The highest PCE observed in CZTS photovoltaic devices is attributed to an optimal diffusion of Ti elements within the CZTS absorber. However, when CZTS photovoltaic devices are fabricated on excessively thick Ti layers, the PCE can decline significantly, dropping from 3.98% to 2.7%. Wei et al. reported on the performance of CZTS solar cells prepared with varying thicknesses of Ti layers, noting that the PCE increased from 2.25% to 2.88%, but subsequently decreased to as low as 1.56%. Furthermore, it was observed that the lower PCE of 1.56% corresponded with a reduced diffusion of Ti elements in the CZTS thin films [11]. Therefore, it is advantageous to enhance the photovoltaic properties of CZTS thin film devices by regulating the extent of Ti element diffusion through effective methods.

The diffusion coefficient of elements is significantly affected by both temperature and activation energy [12,13]. Higher temperatures lead to increased diffusion coefficients, thereby enhancing the likelihood of diffusion for these elements. Furthermore, the tendency of elements to diffuse into thin films is influenced by their associated activation energy. Specifically, a lower activation energy is associated with a higher diffusion coefficient, which facilitates the diffusion process. Additionally, the diffusion of elements within thin films is determined not only by the diffusion coefficients of the elements themselves but also by the defect hopping distance present in the thin films [14]. A reduced defect hopping distance within thin films can hinder the diffusion of impurity elements. In this context, the defects in CZTS thin films and the diffusion of Ti elements are directly influenced by the sulfurization temperature, which can be employed as a process parameter to regulate the diffusion coefficient of Ti elements from the substrate into the CZTS thin films.

The addition of flexible $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin film solar cells to titanium (Ti) substrates is an attractive way to achieve the low-cost manufacturing of photovoltaic devices. Prior research has indicated that the appropriate diffusion of Ti elements can enhance the crystalline growth of CZTS thin films [7–11]. However, the excessive diffusion of Ti has been shown to adversely affect the performance of CZTS photovoltaic devices. Therefore, the diffusion of Ti elements within the CZTS thin films was considered in this work. In this study, the influence of sulfurization temperature on the crystal phases of CZTS thin films, the surface and cross-sectional morphology of CZTS/Ti structures, Ti diffusion in CZTS thin films, and the electrical properties of CZTS/Ti structures were investigated. The constructed CZTS/Ti metal–semiconductor junction enabled the exploration of the interconnections between Ti diffusion, the properties of CZTS thin films, and the electrical contact within the CZTS/Ti junction. This work optimizes the best sulfurization temperatures and diffusion of Ti elements. The findings of this work have the potential to refine the design and fabrication of CZTS thin film solar cells on Ti metal substrates, contributing to the advancement of low-cost, high-efficiency photovoltaic technologies.

2. Experiments

2.1. Materials

The chemicals used in this work are commercially available and were used directly, without further purification. The copper target, zinc target, tin target, and titanium target were purchased from Nanchang Guocai Technology Co., Ltd., Nanchang, China, with purities of 99.99%, 99.99%, 99.99%, and 99.95%, respectively. The sulfur powder, with a purity of 99.98%, was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China, and acetone and anhydrous ethanol were obtained from Tianjin Zhiyuan Chemical Reagent Co., Ltd., Tianjin, China.

2.2. Preparation of CZTS/Ti Metal–Semiconductor Junction

In this work, flexible Ti metal foils were selected as substrates for preparing CZTS thin films, with dimensions of $2\text{ cm} \times 2\text{ cm} \times 0.05\text{ mm}$. Prior to magnetron sputtering, to prepare the Cu–Zn–Sn (CZT) precursor thin films, the flexible Ti metal substrates were ultrasonically and sequentially cleaned in deionized water, acetone, anhydrous ethanol, and deionized water, and finally dried using N_2 gas. Following the cleaning procedure of

Ti foils, the FJL560 high-vacuum magnetron sputtering equipment was used to prepare CZT thin films on Ti foils. The principle of magnetron sputtering involves the introduction of argon (Ar) gas as the sputtering medium within the sputtering chamber, alongside the application of either DC or RF voltage between the substrate and the target holder. Under the influence of the electric field, Ar gas becomes ionized into Ar ions and electrons. The electrons generated by plasma glow discharge are subsequently accelerated towards the substrate due to this electric field, while Ar ions are also propelled by the electric field, continuously bombarding the targets and resulting in the ejection of a significant number of target atoms. Simultaneously, when electrons and neutral Ar atoms interact within the magnetic field at the cathode surface of the target, collisions between these particles occur under Lorentz force effects. This interaction leads to an increased generation of Ar ions that bombard the target surface extensively. The entire sputtering equipment mainly consists of a vacuum sputtering chamber, power control cabinet, gas mixing room, temperature control system, and vacuum pumping system (mechanical pump and molecular pump). In the vacuum sputtering chamber, there are two DC sputtering targets positions, and an RF sputtering target position. The Cu and Zn targets were placed on the DC sputtering target positions, and the Sn targets were placed on the AC sputtering target position. The metal targets for Cu, Zn, and Sn were used to fabricate the Cu, Zn, and Sn layers. Each target had a diameter of 60 mm and a thickness of 3 mm, with an Ar gas flow rate maintained at 20 mL/min. The base pressure within the sputtering chamber was established at 5×10^{-4} Pa, while the sputtering pressure for the CZT precursors was set to 0.5 Pa. The sputtering times for the Zn and Cu layers were determined to be 92 s and 540 s, respectively, with both layers being sputtered at a power of 50 W. For the Sn layers, radio frequency sputtering was utilized, with a power of 50 W and a time of 1560 s. The composition of the Cu-Zn-Sn metallic precursor thin film was controlled by the sputtering times and sputtering powers of Cu, Zn, and Sn layers.

Subsequently, the CZT thin film precursors underwent a post-sulfurization process. The sulfurization of CZT thin film precursors was performed using an NBD-O1200 programmable quartz tube furnace manufactured by Henan Nuobadi Materials Co., Ltd., Zhengzhou, China. During sulfurization, the CZT layers were positioned in a quartz boat centrally located within a quartz tube, with 1 g of sulfur powder placed at each end of the tube. To facilitate the sulfurization heat treatment of the CZT precursors, N_2 gas was introduced as a protective atmosphere to eliminate air from the tube. In this work, the sulfurization temperature for the CZT precursors was varied between 400 °C and 600 °C, with an annealing time of 60 min for all samples. The cooling rate of the CZTS thin films was maintained at 20 °C/min. After completing the set sulfurization curve process, the samples were cooled down along with the furnace. Once the temperature of the tube furnace dropped to room temperature, the samples were removed. Upon completion of the CZTS/Ti structure, a Mo front electrode was sputtered onto the surface of the CZTS thin films. The working pressure during this process was maintained at 0.5 Pa, and the sputtering power for the Mo layer was set at 50 W, with a sputtering time of 10 min. The Ti/CZTS/Mo structures were used to test the current–voltage curve. A schematic representation of the fabrication of the Mo/CZTS/Ti structure is illustrated in Figure 1.

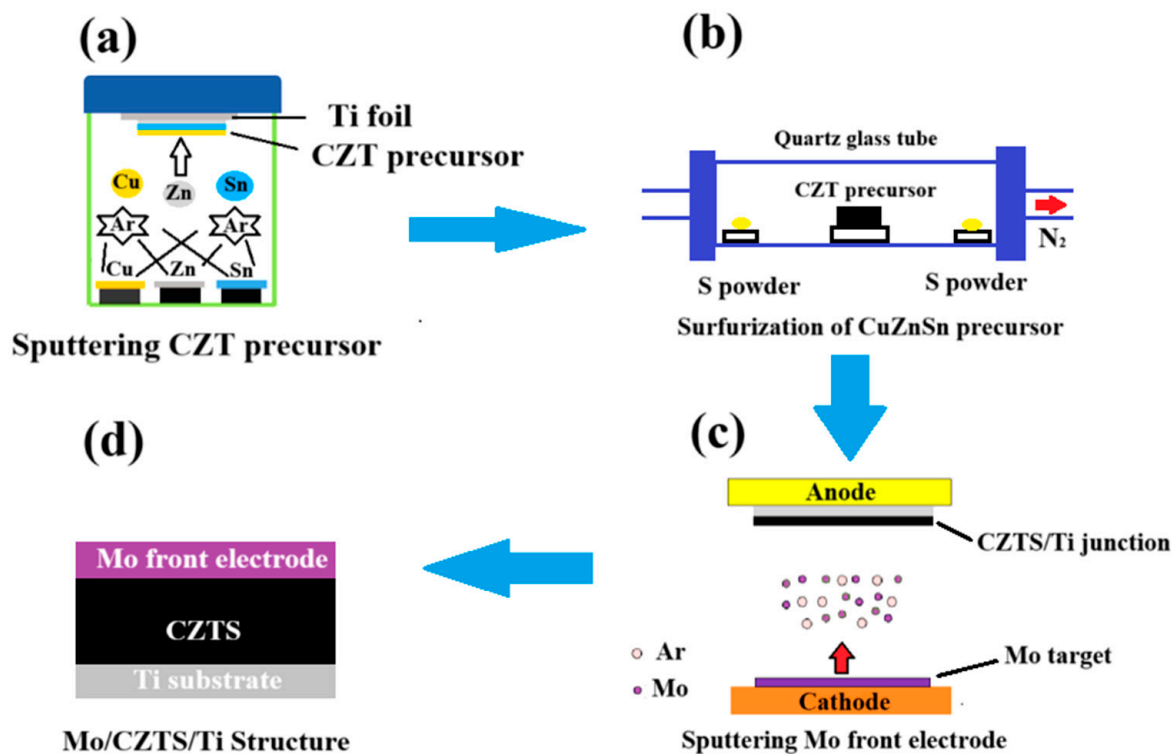


Figure 1. The preparation process of Mo/CZTS/Ti structure: (a) sputtering CZT thin films, (b) sulfurization of CuZnSn thin films, (c) sputtering Mo front electrode, and (d) Mo/CZTS/Ti structure.

2.3. Characterization

The crystal phase of CZTS thin films was measured using X-ray diffraction (XRD, Rigaku D/MAX-Ultima IV, Shanghai, China) and Raman spectroscopy (Finder Vista, Guangzhou, China) with a 532 nm laser. The surface morphologies of CZTS thin films and the cross-sectional morphologies of CZTS/Ti junction were characterized by scanning electron microscopy (SEM, Hitachi SU8010, Qingdao, China). In order to study the diffusion of Ti elements in CZTS thin films, a glass was attached to the surface of CZTS thin films using epoxy. The CZTS thin films and Ti foil were separated by mechanical exfoliation when the epoxy was dried. Then, the back surface of CZTS thin films was measured using energy-dispersive X-ray spectroscopy (EDS, IXRF Systems, SDD3030). The current–voltage (I–V) curves of the Mo/CZTS/Ti structures were measured using the source meter (Keithley 2450).

3. Results and Discussion

3.1. Influence of Sulfurization Temperature on the Microstructure of CZTS Thin Films

During the sulfurization of the CZTS thin films, the sulfurization temperature of the thin films has an impact on the diffusion of Ti elements within the CZTS thin films. Therefore, the impact of sulfurization temperature on the crystal phases, morphology, Ti diffusion, and electrical contact of CZTS/Ti structures was studied in this work. The XRD patterns and Raman spectra of samples subjected to various sulfurization temperatures are presented in Figure 2. The CZTS thin film samples grown on Ti substrates exhibit crystalline diffraction peaks at 28.5°, 47.6°, and 56.5°, which correspond to the standard PDF card for the kesterite structure of CZTS. Notably, the XRD peak intensity of CZTS prepared at 500 °C is the highest, indicating that this temperature yields the best crystallinity for the CZTS thin films. The peaks of the Sn₂S₃ phase are observed in all samples, which agree with the reported peak of Sn₂S₃ [15]. The samples with sulfurization temperatures of 400 °C, 450 °C, 550 °C, and 600 °C contain Cu₉S₅ and SnS phases, which agree with the reported peaks

of the Cu_3S_5 and SnS phases [16,17]. Compared with CZTS thin films with other sulfurization temperatures, the CZTS thin films with a sulfurization temperature of 500 °C had fewer secondary phases. In this study, the lattice parameters of the CZTS thin films at different temperatures were calculated using Jade software 6.5 version, and the results are shown in Table 1. When the temperature increased from 400 °C to 450 °C, the lattice constant of CZTS thin films decreased to 0.53936 nm. With further increases in temperature, the lattice parameters of the CZTS thin films rose to 0.55124 nm. When the sulfurization temperature reached 600 °C, the lattice parameters of CZTS thin films decreased to 0.53869 nm. To further explore the crystal phases of CZTS thin films treated at different sulfurization temperatures, Raman spectroscopy was used for testing. Figure 2b shows the Raman peaks of all the CZTS thin films, which correspond to the reported results in the literature [18,19]. The vibration peaks of the CZTS thin films with a temperature of 400 °C were observed at 336 cm^{-1} . In addition, the vibration peaks of SnS were found at 164 cm^{-1} , which agree with the reported results in the literature [20]. As the sulfurization temperature increased to 550 °C, the peak for the CZTS thin film was observed at 330 cm^{-1} . This shift in the vibrational peak may be attributed to lattice deformation of the CZTS thin films induced by the increased sulfurization temperature. For the CZTS thin films sulfurized at 600 °C, Raman peaks were observed at 144, 254, 338, 388, and 440 cm^{-1} . The emergence of multiple Raman peaks within the CZTS thin films may be attributed to lattice deformation caused by significant diffusion of Ti elements and the elevated sulfurization temperature.

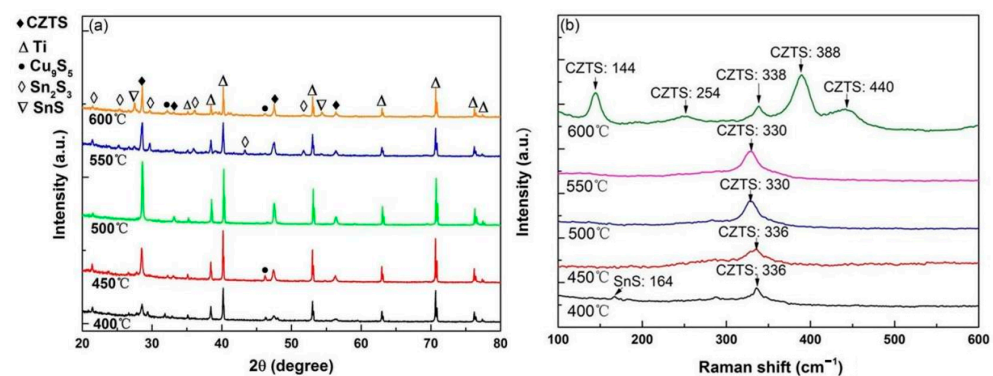


Figure 2. (a) XRD patterns and (b) Raman spectra of CZTS thin films treated at different sulfurization temperatures.

Table 1. Lattice parameters (a and c) of kesterite CZTS thin films with various sulfurization temperatures.

Samples	a (nm)	c (nm)
400 °C	0.55206	1.084
450 °C	0.53936	1.0774
500 °C	0.54892	1.0795
550 °C	0.55124	1.081
600 °C	0.53896	1.0772

3.2. Effect of Sulfurization Temperature on the Morphology of CZTS Thin Films and CZTS/Ti Interface

Figure 3 shows the SEM images of the surfaces of the CZTS thin films treated at different temperatures. The surface morphology of the CZTS films prepared at a sulfurization temperature of 400 °C was characterized by a rough texture with compact grains, although some voids were still present. When the sulfurization temperature was increased to 500 °C, the grains of the CZTS thin films became more uniformly distributed. This uniformity was reflected in the particle size distribution of the CZTS thin films. However, when the sulfurization temperature of the sample exceeded 500 °C, particles of varying sizes reemerged on the surface of the CZTS thin films. This may be attributed to high

sulfurization temperatures causing decomposition reactions within the CZTS thin films, resulting in an uneven morphology characterized by particle sizes.

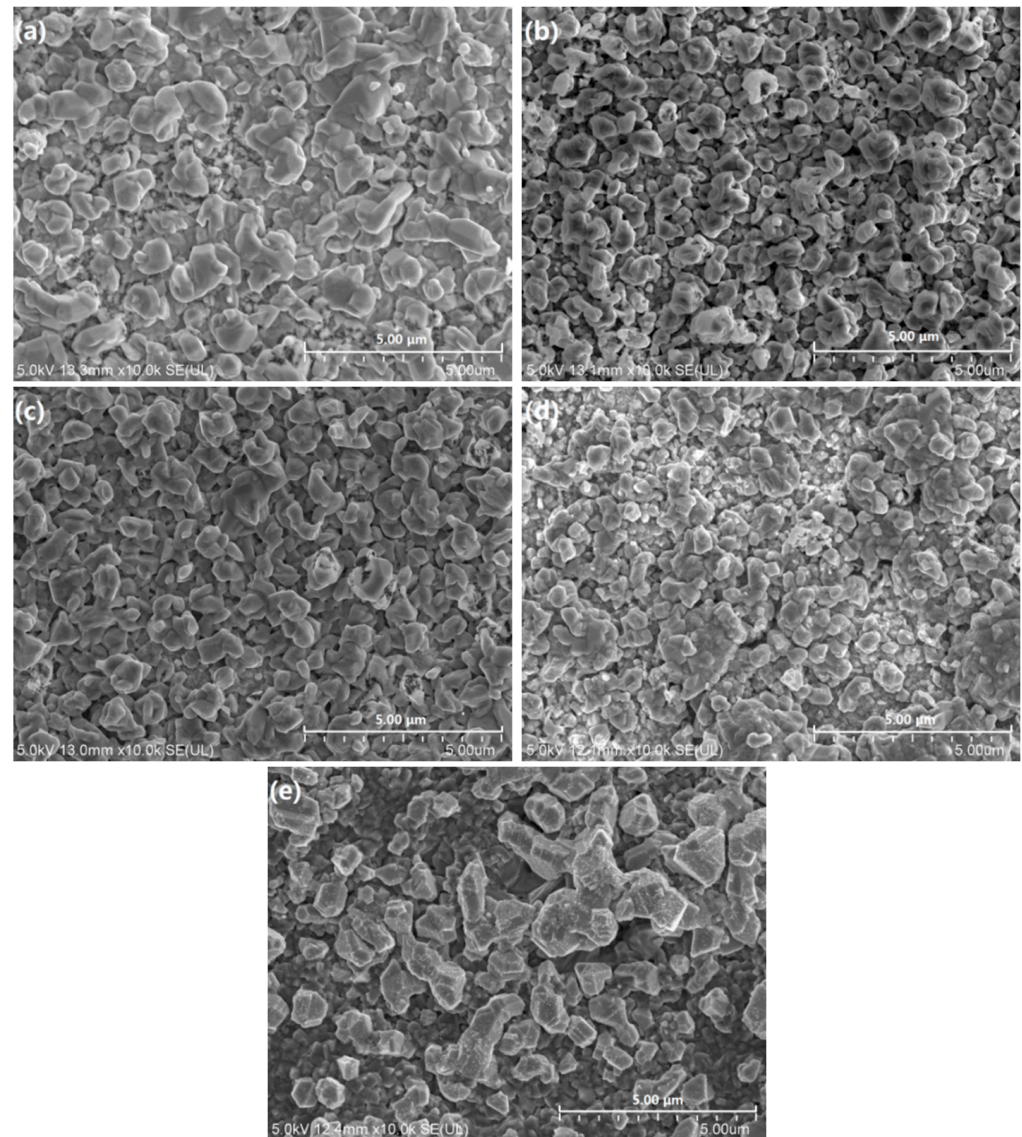


Figure 3. The surface SEM images of CZTS thin films with various sulfurization temperatures: (a) 400 °C, (b) 450 °C, (c) 500 °C, (d) 550 °C, and (e) 600 °C.

Figure 4 shows the cross-sectional SEM images of CZTS thin films treated at different sulfurization temperatures. From top to bottom for all samples, there are the CZTS thin films and the Ti foil. When the sulfurization temperature of the sample was 400 °C, a layered structure appeared in the CZTS thin films. Larger particles of CZTS thin films grew at the top, and finer particles grew at the bottom. When the sulfurization temperature of the sample continued to rise to 450 °C, the grain morphology of the CZTS thin films resembled structures with two distinct sublayers. When the sulfurization temperature of the sample reached 500 °C, the finer particles at the bottom of the CZTS thin films disappeared. This was due to the enhanced sulfurization of the Cu-Zn-Sn thin films caused by the increased sulfurization temperature. As the sulfurization temperature further increased to 550 °C, the grain sizes at the bottom of the CZTS thin films increased. However, voids were observed in the CZTS thin films, which can affect photogenerated carrier transport and collection. When the sulfurization temperature of the sample increased to 600 °C, the grains of the CZTS thin films became compact and dense, but cracks appeared. These cracks may have

originated from external stresses applied during sample preparation, or they may have been due to the high sulfurization temperature, which caused stress in the CZTS thin films.

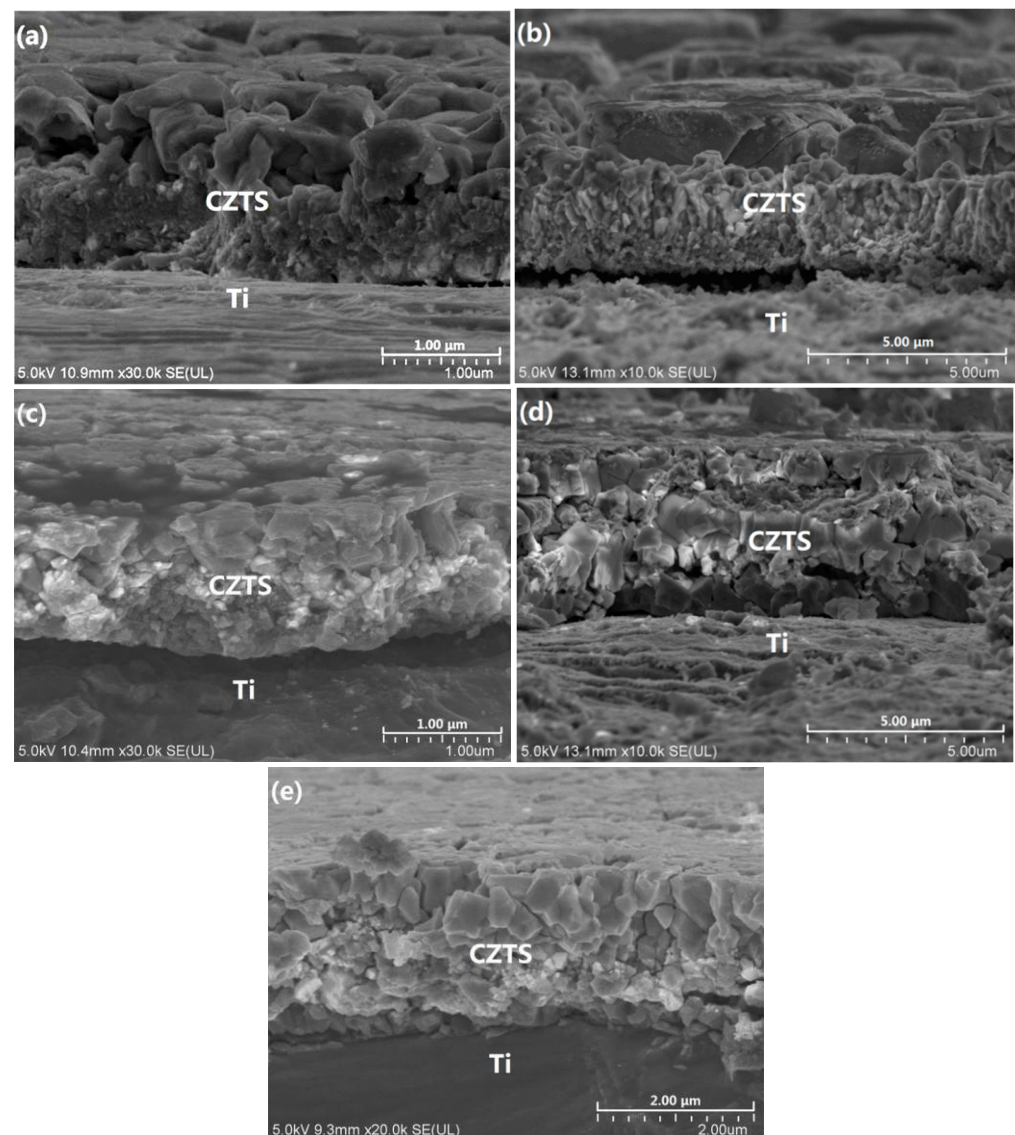


Figure 4. The cross-sectional SEM images of CZTS thin films heat-treated at different sulfurization temperatures: (a) 400 °C, (b) 450 °C, (c) 500 °C, (d) 550 °C, and (e) 600 °C.

3.3. Effect of Sulfurization Temperature on the Composition of CZTS Thin Film Samples

To analyze the effect of sulfurization temperature on the diffusion of Ti elements in the CZTS thin films, the CZTS thin films and Ti foils were separated using a mechanical stripping method. Then, EDS was used to analyze the elemental composition on the backside of CZTS thin films at different sulfurization temperatures, as shown in Table 2. The extent of Ti element diffusion in CZTS thin films varied with changes in sulfurization temperature. Firstly, when the sulfurization temperature of the sample was 400 °C, the diffusion of Ti elements in CZTS thin films was relatively low. Due to the lower temperature, the diffusion coefficient of Ti elements was small, making it difficult for Ti elements to diffuse into CZTS thin films. When the sulfurization temperature of the sample increased to 450 °C, the diffusion coefficient of Ti elements increased, enhancing the diffusion of Ti elements in the CZTS thin films. Notably, when the sulfurization temperature of the sample further increased to 550 °C, the diffusion of Ti elements in the CZTS thin films actually decreased. The diffusion of Ti elements in the CZTS thin films not only depends on the

diffusion coefficient of Ti elements themselves but also on the defect hopping distance within the CZTS films. In Figure 3c,d, it can be seen that when the sulfurization temperature of the sample increased to 550 °C, the grain size at the bottom of the CZTS thin films grew larger and became denser and more compact. At this point, the defect hopping distance in the CZTS thin films was smaller, inhibiting the diffusion of Ti elements in the CZTS thin films. When the sulfurization temperature of the sample increased to 600 °C, the diffusion of Ti elements in the CZTS thin films was enhanced. In Figure 4d,e, it can be observed that the grains at the bottom of the CZTS thin films prepared at a sulfurization temperature of 600 °C grew irregularly and were not as neatly compact as those prepared at a sulfurization temperature of 550 °C. This suggests that the defect hopping distance in the CZTS thin films prepared at a sulfurization temperature of 600 °C may have been larger, further promoting the diffusion of Ti elements in the CZTS thin films. The alteration of Ti elements in the CZTS thin films exhibited a comparable trend with that of the lattice constant of the CZTS thin films. Therefore, the variation in the lattice constant of the CZTS thin films observed with XRD also indicates that Ti elements may have diffused into the CZTS thin films and may have been incorporated within the crystal structure.

Table 2. EDS results of back of CZTS thin films heat-treated at different sulfurization temperatures.

CZTS	400 °C	450 °C	500 °C	550 °C	600 °C
Cu (at.%)	23.38	15.07	23.54	20.83	13.07
Zn (at.%)	15.62	6.43	8.16	15.37	6.23
Sn (at.%)	17.76	5.26	9.02	13.62	5.62
S (at.%)	43.03	43.23	48.96	45.15	45.06
Ti (at.%)	0.21	30.01	10.32	5.03	30.02
Cu/(Zn + Sn)	0.70	1.29	1.37	0.72	1.10
Zn/Sn	0.88	1.22	0.90	1.13	1.11
S/(Cu + Zn + Sn)	0.76	1.61	1.20	0.91	1.81

3.4. Effect of Sulfurization Temperature on the I–V Characteristics of CZTS/Ti Structures

Figure 5 shows the I–V curves of the CZTS/Ti structures prepared at different sulfurization temperatures. It can be observed that the I–V curves of the five samples are linear, indicating that an ohmic contact was formed between the CZTS thin films and the Ti substrate. The slopes of the I–V curves for the CZTS/Ti structures prepared at sulfurization temperatures of 400 °C, 450 °C, 500 °C, 550 °C, and 600 °C are 0.37 S, 0.42 S, 0.46 S, 0.55 S, and 0.50 S, respectively. When the sulfurization temperature of the sample increased from 400 to 550 °C, the slope of the I–V curve of the CZTS/Ti structure increased, indicating better ohmic contact characteristics between the CZTS thin films and Ti foils. When the sulfurization temperature of the sample increased from 550 °C to 600 °C, the slope of the I–V curve of the CZTS/Ti structure decreased. Therefore, it can be seen that at a sulfurization temperature of 550 °C, the CZTS/Ti structure exhibited the best I–V characteristic curve with the lowest resistance, which is beneficial for the transport of carriers between the CZTS thin films and the Ti substrate. The formation of the best ohmic contact between the CZTS thin films and Ti foil may be attributed to the appropriate diffusion of Ti elements within the CZTS thin films.

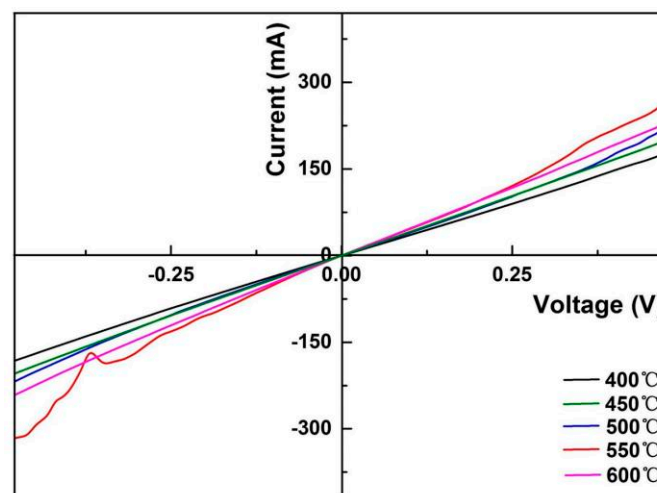


Figure 5. *I*–*V* curves of CZTS/Ti structures heat-treated at different sulfurization temperatures.

4. Conclusions

In summary, we investigated the influence of sulfurization temperature on the composition of CZTS thin films, the diffusion of Ti elements, and the microstructure, cross-sectional morphology, and *I*–*V* characteristics of CZTS/Ti structures. An analysis of the XRD results revealed that the lattice parameters of CZTS thin films initially increased, followed by a decrease, and then an increase again. This indicates that Ti elements may diffuse into the CZTS thin films and become incorporated within their crystal structure. As the sulfurization temperature rose, the degree of Ti element diffusion in the CZTS thin films first increased, subsequently decreased, and then increased once more. This behavior suggests that Ti element diffusion is influenced not only by its activation energy but also by defect hopping distances within the CZTS thin films. At a sulfurization temperature of 550 °C, denser grain growth occurred at the bottom layer of the CZTS thin film; this corresponds to a reduced defect hopping distance, which inhibits the further diffusion of Ti elements. Moreover, it was observed that the CZTS/Ti structure prepared at this specific sulfurization temperature exhibited an *I*–*V* curve with the steepest slope, indicating optimal ohmic contact characteristics. The results of this work have the potential to refine the design and fabrication of CZTS thin film solar cells on Ti metal substrates, contributing to the advancement of low-cost, high-efficiency photovoltaic technologies.

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Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

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References

1. He, M.R.; Sun, K.W.; Suryawanshi, M.P.; Li, J.J.; Hao, X.J. Interface engineering of p-n heterojunction for kesterite photovoltaics: A progress review. *J. Energy Chem.* **2021**, *60*, 1–8. [\[CrossRef\]](#)
2. Kondrotas, R.; Chen, C.; Sb, J. Sb₂S₃ solar cells. *Joule* **2018**, *2*, 857–878. [\[CrossRef\]](#)

3. Allen, T.G.; Bullock, J.; Jeangros, Q.; Samundsett, C.; Wan, Y.M.; Cui, J.; Hessler-Wyser, A.; Dewolf, S.; Javey, A.; Cuevas, A. A low resistance calcium/reduced titania passivated contact for high efficiency crystalline silicon solar cells. *Adv. Energy Mater.* **2017**, *7*, 1602606. [[CrossRef](#)]
4. Freitag, M.; Teuscher, J.; Saygili, Y.; Zhang, X.; Giordano, F.; Liska, P.; Hua, J.; Zakeeruddin, S.M.; Moser, J.E.; Gratzel, M.; et al. Dye-sensitized solar cells for efficient power generation under ambient lighting. *Nat. Photonics* **2017**, *11*, 372–379. [[CrossRef](#)]
5. Freitag, M.; Giordano, F.; Yang, W.X.; Pazoki, M.; Hao, Y.; Zietz, B.; Gratzel, M.; Hagfeldt, A.; Boschloo, G. Copper Phenanthroline as a Fast and high-performance redox mediator for dye-sensitized solar cells. *J. Phys. Chem. C* **2016**, *120*, 9595–9603. [[CrossRef](#)]
6. Chen, H.L.; Kou, D.X.; Chang, Z.X.; Zhou, W.H.; Zhou, Z.J.; Wu, S.X. Effect of crystallization of $\text{Cu}_2\text{ZnSnS}_4$ counter electrode on the performance for efficient dye-sensitized solar cells. *ACS Appl. Mater. Interfaces* **2014**, *6*, 20664–20669. [[CrossRef](#)] [[PubMed](#)]
7. Lin, J.H.; Xu, J.X.; Yang, Y.Z. Study of interface properties between $\text{Cu}_2\text{ZnSnS}_4$ thin films and metal substrates. *Ceram. Int.* **2019**, *46*, 218–226. [[CrossRef](#)]
8. Buldu, D.G.; Cantas, A.; Turkoglu, F.; Akca, F.G.; Meric, E.; Ozdemir, M.; Tarhan, E.; Ozyuzer, L.; Aygun, G. Influence of sulfurization temperature on $\text{Cu}_2\text{ZnSnS}_4$ absorber layer on flexible titanium substrates for thin film solar cells. *Phys. Scr.* **2018**, *93*, 024002. [[CrossRef](#)]
9. Yazici, S.; Olgar, M.A.; Akca, F.G.; Cantas, A.; Kurt, M.; Aygun, G.; Tarhan, E.; Yanmaz, E.; Ozyuzer, L. Growth of $\text{Cu}_2\text{ZnSnS}_4$ absorber layer on flexible metallic substrates for thin film solar cell applications. *Thin Solid Films* **2015**, *589*, 563–573. [[CrossRef](#)]
10. Guo, H.F.; Ma, C.H.; Zhang, K.Z.; Jia, X.G.; Wang, X.Q.; Yuan, N.Y.; Ding, J.N. Dual function of ultrathin Ti intermediate layers in CZTS solar cells: Sulfur blocking and charge enhancement. *Sol. Energy Mater. Sol. Cells* **2018**, *175*, 20–28. [[CrossRef](#)]
11. Wei, Z.F.; Dunlop, T.O.; Heard, P.J.; Charbonneau, C.; Worsley, D.A.; Watson, T. Successes and challenges associated with solution processing of kesterite $\text{Cu}_2\text{ZnSnS}_4$ solar cells on Titanium substrates. *ACS Appl. Energy Mater.* **2020**, *3*, 3876–3883. [[CrossRef](#)]
12. Xu, W.; Shang, S.; Zhou, B.; Wang, Y.; Chen, L.; Wang, C.; Liu, X.; Liu, Z. A first-principles study of the diffusion coefficients of alloying elements in dilute α -Ti alloys. *Phys. Chem. Chem. Phys.* **2016**, *18*, 16870–16881. [[CrossRef](#)] [[PubMed](#)]
13. Jensen, F. Activation energies and the arrhenius equation. *Qual. Reliab. Eng. Int.* **1985**, *1*, 13–17. [[CrossRef](#)]
14. Bialon, A.F.; Hammerschmidt, T.; Drautz, R. Ab initio study of boron in α -iron: Migration barriers and interaction with point defects. *Phys. Rev. B* **2013**, *87*, 104109. [[CrossRef](#)]
15. Lin, J.H.; Wu, X.S.; Xu, J.X.; Yang, Y.Z. Inhibiting the formation of MoS_2 between $\text{Cu}_2\text{ZnSnS}_4$ thin film and Mo (211) foil substrate by inserting a Mo (110) intermediate layer. *Opt. Mater.* **2022**, *124*, 111996. [[CrossRef](#)]
16. Khatter, J.; Chauhan, R.P. Visible light-motivated photo-catalytic activity of $\text{CdS-Cu}_9\text{S}_5$ heterostructure for degradation of methylene blue. *Appl. Nanosci.* **2022**, *12*, 1683–1696. [[CrossRef](#)]
17. Rana, T.R.; Kim, S.; Kim, J. Existence of multiple phases and defect states of SnS absorber and its detrimental effect on efficiency of SnS solar cell. *Curr. Appl. Phys.* **2018**, *18*, 663–666. [[CrossRef](#)]
18. Chen, G.L.; Wang, W.H.; Zhang, J.; Chen, S.Y.; Huang, Z.G. Formation mechanism of secondary phases in $\text{Cu}_2\text{ZnSnS}_4$ growth under different copper content. *Mater. Lett.* **2017**, *186*, 98–101. [[CrossRef](#)]
19. Awadallah, O.; Cheng, Z. Study of the fundamental phase formation mechanism of sol-gel sulfurized $\text{Cu}_2\text{ZnSnS}_4$ thin films using in situ Raman spectroscopy. *Sol. Energy Mater. Sol. Cells* **2018**, *176*, 222–229. [[CrossRef](#)]
20. Cao, M.; Yao, K.F.; Wu, C.S.; Huang, J.; Yang, W.G.; Zhang, L.; Lei, F.; Sun, Y.; Wang, L.J.; Shen, Y. Facile synthesis of SnS and SnS_2 nanosheets for FTO/SnS/ SnS_2 /Pt photocathode. *ACS Appl. Energy Mater.* **2019**, *1*, 6497–6504. [[CrossRef](#)]

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