Article Type | DOI:10.5281/zenodo.8007885
www.jnanosam.com

NANOSAM
Journal of NanoScience in Advanced Materials

Investigating Structural and Optical Properties of CZTS Thin Films through Ag/Ge Alloying

Mehmet Ali Olğar[1,2#], Recep Zan[1,2], Ali Çiriş[2] and Yavuz Atasoy[2,3#]

In this study, the effect of Ag and Ge doping on the structural and optical properties of CZTS thin films was investigated. Undoped, Ag-doped, and Ge-doped CZTS samples were fabricated by two-step process involving sputter deposition of precursor films on the Mo-coated glass substrates and the sulfurization process of these films by Rapid Thermal Annealing (RTA) method. Prepared samples were characterized through several methods. EDX measurements revealed that all samples had Cu-poor and Zn-rich chemical composition regardless of the dopant materials. Furthermore, Ag and Ge concentrations were found to be 4% and 13%, respectively. XRD spectra of CZTS samples revealed only diffraction peaks of the kesterite CZTS phase. It was observed in extended XRD graphs that there was a slight shift in the diffraction peaks of doped CZTS samples due to incorporating Ag and Ge in the host lattice, as expected. Raman spectra of the films confirmed the formation of kesterite CZTS phase. In addition, it was seen that the formation of CTS phase was prevented by doping of CZTS thin films through Ag and Ge dopant materials. The optical band gap of CZTS, Ge-CZTS, and Ag-CZTS thin films was found as 1.50, 1.52 and 1.55 eV, respectively. Overall, it was demonstrated that Ag and Ge doping was performed successfully and prevented the formation of a secondary phase, which has an adverse effect on potential solar cell performance.

1. Introduction

Thin film photovoltaic is one of the technologies that has attracted attention in the last few decades. This is because most of the incoming photons from the sun are absorbed by a film of very less thickness than required in Si-based solar cells. The CIGS and CdTe thin-film materials are the most studied structures in thin-film solar cell technology. With their high cell efficiency, they have reached a level that can compete with Si solar cells [1, 2]. However, the scarcity of some elements such as In and Ga in the nature and the presence of toxic elements such as Cd cause a decrease in interest in these compounds. In this context, CZTS(e)-based thin-film solar cells have been studied intensively in the recent time. The abundance of the elements it contains in the nature and its environmental friendliness make studying this material so attractive. The main reasons that make this compound attractive for using as an absorber layer in thin-film solar cells are its 1.4-1.6 eV optical direct band gap, high absorption coefficient, and p-type electrical conductivity [3, 4].

Although the theoretical maximum cell efficiency of CZTS(e) based thin film solar cells is above 30%, the current record cell efficiency is around 13% [5, 6]. One of the main reasons for this difference is the formation of undesired secondary phases and defect levels due to the fact that it consists of at least 4 elements, and accordingly low V_{oc} values are obtained. One of the main methods for solving these problems is the cation substitution within the structure. The replacement of Cu with Ag, Sn with Ge is one of the most widely used strategy in the literature [7]. It has been reported that the replacement of small amount of Ag with Cu reduces the disorder of Cu and Zn atoms, limits the formation of Cu_{Zn} anti-site defects, and improves the cell efficiency by reducing the band tailing and potential fluctuations in the structure [8]. Yang et al. reported that partial replacement of Cu by Ag reduces acceptor levels related the defects in $(Cu_{1-x}Ag_{x})_2ZnSnS_4$ thin films with having better surface morphology and optimum MoS_2 thickness, resulting in significant increase in solar cell

---

[1]*Niğde Ömer Halisdemir University, Faculty of Arts and Sciences, Department of Physics, 51240, Niğde, Türkiye,* [2]*Niğde Ömer Halisdemir University, Nanotechnology Application and Research Center, 51240, Niğde, Türkiye,* [3]*Niğde Ömer Halisdemir University, Niğde Zübeyde Hanım Vocational School of Health Services, 51240, Niğde, Türkiye*
#Corresponding author: mehmetaliolgar@ohu.edu.tr, yavuzatasoy@ohu.edu.tr

Keywords: CZTS, Ag-CZTS, Ge-CZTS, Sputtering, Thin film

Received: 27 April 2023 | Accepted: 18 May 2023 | Published online: 25 June 2023

efficiency [9]. On the other hand, the replacement of a small amount of Ge with Sn is seen as another factor that improves the cell performance. This is because the Ge^{+4} cation has more stable oxidation states than the Sn^{+4} ion. Therefore, from Ge to Sn displacement contributes to the reduction of Sn-S(e)-based secondary phases, the reduction of Sn-based deep defects, and the reduction of recombination centers for charge carriers [9]. In this context, within the scope of this study, Ag-doped CZTS (Ag-CZTS) and Ge-doped CZTS (Ge-CZTS) thin films were produced by using the Glass/Mo/ZnS/CuSn/Cu layer structure for the first time separately for Ag and Ge doping processes, and compared with undoped CZTS structure.

2. Results and Discussion

The atomic percentage and some atomic ratios of the elements contained in undoped and doped CZTS thin films were determined by EDX technique and obtained results given in Table 1. It was aimed to obtain more accurate composition information by taking the EDX measurements of all samples from large areas (~125x125 μm^2). It was observed that all produced CZTS films had Cu-poor and Zn-rich composition regardless of the doping process. The (Cu+Ag)/(Zn+Sn+Ge) ratio was found to be in the range of 0.84-0.94, while the ratio of Zn/(Sn+Ge) was found to vary from 1.07 to 1.56. Considering a complex structure consisting of at least four different elements, it was observed that the composition of precursor layers produced were very close to the targeted values. When the doping concentration rates were examined, it was observed that the Ag concentration was around 4%, while the Ge concentration was around 13%. Although the doping ratio for both elements was thought to be around 10%, it was seen that while the Ge doping was close to the desired level, the Ag-doping was not. However, these atomic ratios still show that the doping process was carried out successfully.

The XRD pattern of the CZTS, Ag-CZTS and Ge-CZTS thin films produced by sulfurization of the undoped, Ag-doped and Ge-doped precursor layers at 550°C for 1 min are given in Figure 1. It was observed that all thin films produced independently of Ag or Ge doping crystallized in the kesterite CZTS phase. Dominant diffraction peaks were seen in the XRD patterns of undoped CZTS thin films at angles of approximately 2θ = 28.43°, 47.50° and 56.30°. It was determined that these peaks belong to the (112), (220/204) and (312/116) diffraction planes of the kesterite CZTS phase, respectively (JCPDS 00-26-0575). Apart from these peaks, it was determined that low-intensity characteristic peaks appeared for the (002) and (200) diffraction planes, which were also attributed to the kesterite CZTS phase. Besides these phases, a peak of Mo (00-042-1120) phase was detected at 2θ=40.5° angle position coming from the substrate. Any secondary phase(s) was not detected except for the kesterite CZTS peaks. The XRD patterns of Ag-CZTS and Ge-CZTS thin films revealed similar diffraction pattern.

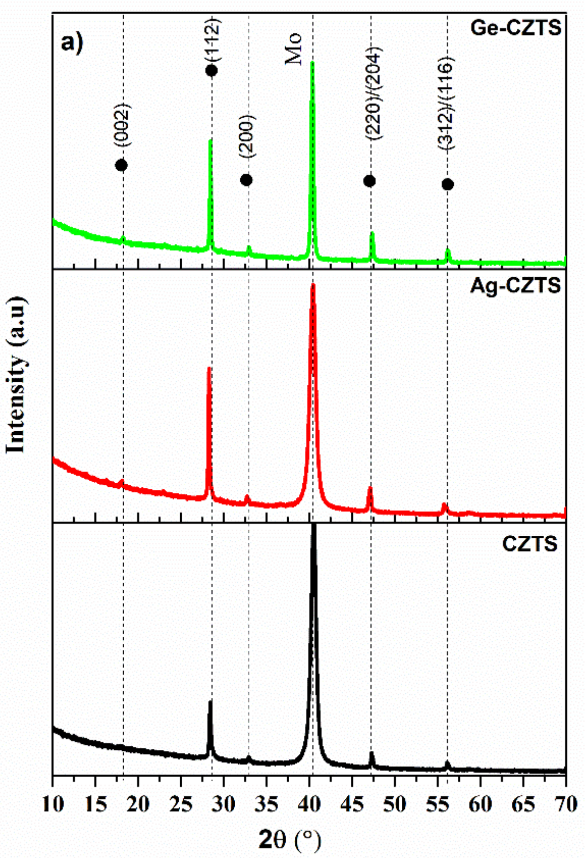

Figure 1. XRD patterns of pure CZTS, Ag-CZTS and Ge-CZTS thin films.

Therefore, extended diffraction patterns in the range of 2θ= 28-29° belonging to the (112) main peaks of the XRD patterns shown in Figure 1 are given in Figure 2. It is expected that the characteristic peaks in the XRD pattern will shift towards lower diffraction angles with the increase of the d interplanetary distance depending on the ionic radius of the doping ion entering the kesterite lattice structure, and the peak positions will shift towards higher angles with the decrease of the d distance. In accordance with Vegard's law, the peak (112) of Cu_2ZnGeS_4, which contains completely Ge, is at 2θ= 29.10° (JCPDS 00-025-0327) and the peak (112) of Ag_2ZnSnS_4, which contains completely Ag, is recorded at 2θ= 27.20° (JCPDS 00-035-0544) [10-12]. When the shift in the (112) peak positions of Ag-CZTS and Ge-CZTS was examined and compared with the undoped CZTS, a shift was seen in the peaks as expected by doping Ag and Ge in CZTS thin film. While the position of (112) diffraction peak was found to be around at 2θ= 28.43° for undoped CZTS thin film, the diffraction peak position of Ag-CZTS and Ge-CZTS thin films were found as 28.28° and 28.45°, respectively. While Ag-doping was found to cause a shift towards lower diffraction angle, the Ge doping gave rise to a slight shift towards higher diffraction angle. Such result verified incorporation of Ag and Ge in the host lattice of the kesterite CZTS structure.

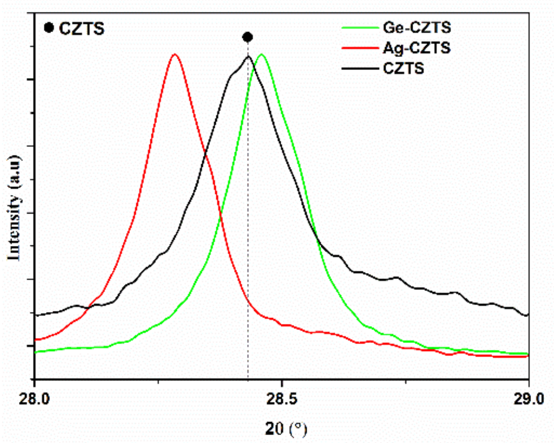

Figure 2. XRD patterns of undoped and Ag/Ge doped CZTS thin films in the range of 2θ= 28-29°.

Raman analyses were employed as a complementary method to the XRD measurement of the samples that were performed in the range of 200-500 cm^{-1} and are shown in Figure 3. As can be seen in the figure, a dominant peak corresponding to the A1 mode of the kesterite structure is observed at around 337 cm^{-1} in the spectra of undoped and doped CZTS samples, independent of the doping process. It was noted that the low-intensity peaks attributed to the kesterite CZTS phase appeared in the spectra marked on the figure. In addition to kesterite CZTS phase, Cu_2SnS_3 (CTS) phase was detected only in undoped CZTS spectra at 303 cm^{-1} [13]. Ag/Ge alloying was found to limit the formation of undesired secondary phases having detrimental effect on potential solar cell performance [14].

The optical transmission measurements were taken in the wavelength range of 300-1200 nm of undoped, Ag and Ge doped CZTS samples produced by sulfurization at 550°C for 1 min so as to see the effect of the doping process on the optical band gap of films. The absorption coefficients of the samples were calculated using these measurements. The band gap energy of semiconductor samples was calculated using the absorption coefficient formula;

$$(\alpha h\nu)=A(h\nu - E_g)^n \qquad (1)$$

where α is absorption coefficient, A is constant, E_g is optical band gap, and n is ½ for direct optical transitions.

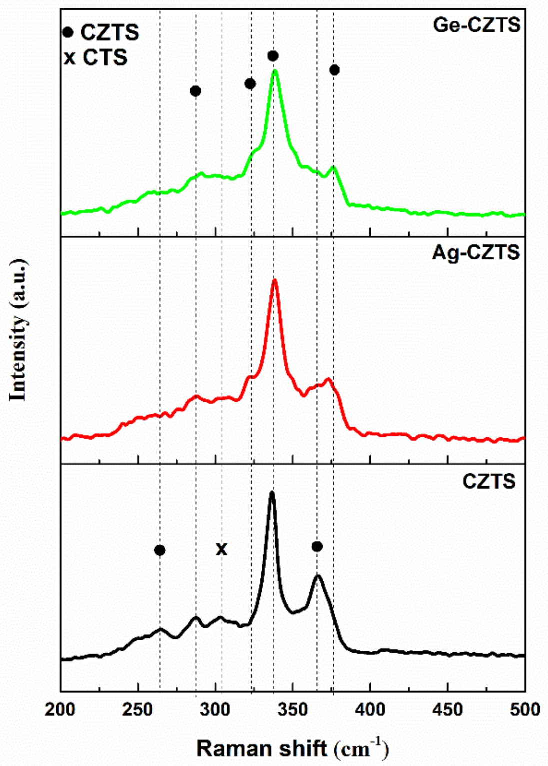

Figure 3. Raman spectra of undoped, Ag-doped and Ge-doped CZTS thin films.

E_g was determined using the Tauc equation [15]. Accordingly, $(\alpha h\nu)^2$ - $(h\nu)$ graphs of the samples were drawn using Equation (1). Then, the optical band gap values of the samples were determined from the points where the linear parts of the curves in the graph intersect on the horizontal axis. The band gap values of the samples were calculated with the help of $(\alpha h\nu)^2$ - $(h\nu)$ curves given in Figure 4.

When these curves were examined, it was observed that the band gap of undoped, Ge and Ag doped CZTS thin films were found to be 1.50, 1.52 and 1.55 eV, respectively. Such values are compatible with the reported literature for CZTS thin films [16, 17].

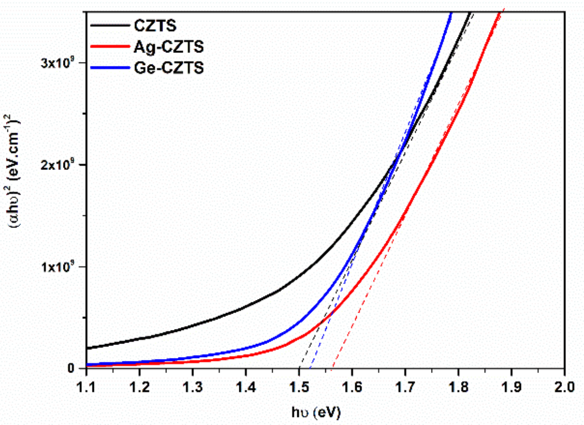

Figure 4. Determination of undoped, Ag-doped and Ge-doped CZTS thin films from $(\alpha h\nu)^2$ - $(h\nu)$ curves.

Table 1. Chemical composition of undoped CZTS, Ag-CZTS and Ge-CZTS.

Sample	Cu %	Ag %	Zn %	Sn %	Ge %	S %	(Cu+Ag) / (Sn+Zn+Ge)	Zn/ (Sn+Ge)	Ag/ (Ag+Cu)	Ge/ (Ge+Sn)
CZTS	17.84	-	11.75	9.23	-	61.18	0.89	1.27	-	-
Ag-CZTS	17.57	0.80	13.32	8.51	-	59.81	0.84	1.56	0.04	-
Ge-CZTS	20.61	-	11.27	9.15	1.40	57.58	0.94	1.07	-	0.13

3. Conclusion

Undoped, Ag-doped, and Ge-doped CZTS thin films were fabricated by sputtering method and sulfurization process carried out by RTA technique. All samples demonstrated Cu-poor and Zn-rich chemical composition. In addition, doped CZTS samples revealed 4% Ag and 13% Ge atomic concentration. XRD and Raman measurements verified occurrence of kesterite CZTS phase regardless of the doping process. However, doped CZTS samples showed purer structure in term of absence of CTS phase according to Raman spectra. Optical band gap of doped CZTS samples (1.52 and 1.55 eV) exhibited higher value with respect to undoped CZTS sample (1.50 eV). As a result of our findings, the doping process of the samples was carried out successfully and the doping process yielded a purer CZTS structure, which may improve the cell efficiency of potential fabricated solar cell.

Method

Undoped and doped CZTS thin films were produced by the two-step method. In the first stage of the production, Cu (5N), ZnS (4N), Sn (4N), Ag (4N), and Ge (4N) layers were deposited on Mo-coated glass substrates by sputtering method. In the second stage of the production process, the films were exposed to short annealing period under a sulfur atmosphere employing the Rapid Thermal Annealing (RTA) method so as to obtain CZTS structure. Before the film production, the substrates were cleaned by passing through the standard cleaning step (acetone, isopropanol, and DI water). Afterwards, clean substrates were placed in the sputtering chamber, and a Glass/Mo/ZnS/CuSn/Cu stacked structure was created by using ZnS, Cu and Sn sputter targets, respectively. More experimental details can be found elsewhere [18]. After doing the similar processes for Ag and Ge doped layered structures, Ag and Ge layers were coated as the top layers. Three different precursor structures, Glass/Mo/ZnS/CuSn/Cu (undoped), Glass/Mo/ZnS/CuSn/Cu/Ag (Ag-doped) and Glass/Mo/ZnS/CuSn/Cu/Ge (Ge-doped), were formed. The production of CZTS, Ag-CZTS and Ge-CZTS films was completed by annealing these precursor structures for 1 min at 550 °C with the RTA method under sulfur atmosphere. The structural properties of the produced films were determined by XRD (PANalytical-EMPYREAN) and Raman spectroscopy (Renishaw inVia Raman spectroscopy, excitation wavelength of 633 nm) measurements. The chemical compositions of the films were determined by Energy Dispersive X-ray Spectroscopy (ZEISS EVO 40, EDX) measurements. The optical properties of the films were examined by optical transmission measurement (J. A. Woollam Co., Inc. Elipsometer) so as to determining the optical band gaps.

Acknowledgements

This research was supported by grants from Research Projects Unit of Niğde Ömer Halisdemir University (FMT 2022/6-BAGEP).

Authors' contributions:

M.A. Olğar: Methodology, Writing - Original Draft, Validation, Investigation, Writing - review & editing, R. Zan: Validation, Investigation, A. Çiriş: Validation, Investigation Y.Atasoy: Conceptualization, Methodology, Validation, Investigation, Writing - review & editing.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

[1] Nakamura, M., Yamaguchi, K., Kimoto, Y., Yasaki, Y., Kato, T., and Sugimoto, H. "Cd-Free Cu(In,Ga)(Se,S)2 Thin-Film Solar Cell With Record Efficiency of 23.35%", IEEE Journal of Photovoltaics **9** (6) 1863-1867 (2019).

[2] Green, M.A., Dunlop, E.D., Siefer, G., Yoshita, M., Kopidakis, N., Bothe, K., and Hao, X.J. "Solar cell efficiency tables (Version 61)", Progress in Photovoltaics **31** (1) 3-16 (2023).

[3] Olgar, M.A., Seyhan, A., Sarp, A.O., and Zan, R. "Impact of sulfurization parameters on properties of CZTS thin films grown using quaternary target", Journal of Materials Science: Materials in Electronics **31** (22) 20620-20631 (2020).

[4] Jimbo, K., Kimura, R., Kamimura, T., Yamada, S., Maw, W.S., Araki, H., Oishi, K., and Katagiri, H. "Cu_2ZnSnS_4-type thin film solar cells using abundant materials", Thin Solid Films **515** (15) 5997-5999 (2007).

[5] Shockley, W. and Queisser, H.J. "Detailed Balance Limit of Efficiency of p-n Junction Solar Cells", Journal of Applied Physics **32** (3) 510-519 (1961).

[6] Gong, Y., Zhang, Y., Zhu, Q., Zhou, Y., Qiu, R., Niu, C., Yan, W., Huang, W., and Xin, H. "Identifying the origin of the V oc deficit of kesterite solar cells from the two grain growth mechanisms induced by Sn 2+ and Sn 4+ precursors in DMSO solution", Energy & Environmental Science **14** (4) 2369-2380 (2021).

[7] Atasoy, Y. "Effect of annealing temperature on the microstructural and optical properties of newly developed (Ag, Cu) 2Zn (Sn, Ge) Se4 thin films", Applied Physics A **128** (11) 1030 (2022).

[8] Hages, C.J., Koeper, M.J., and Agrawal, R. "Optoelectronic and material properties of nanocrystal-based CZTSe absorbers with Ag-alloying", Solar Energy Materials and Solar Cells **145** 342-348 (2016).

[9] Chen, S., Walsh, A., Gong, X.G., and Wei, S.H. "Classification of lattice defects in the kesterite Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ earth-abundant solar cell absorbers", Adv Mater **25** (11) 1522-39 (2013).

[10] Denton, A.R. and Ashcroft, N.W. "Vegard's law", Physical review A **43** (6) 3161 (1991).

[11] Cui, H., Liu, X., Liu, F., Hao, X., Song, N., and Yan, C. "Boosting Cu2ZnSnS4 solar cells efficiency by a thin Ag intermediate layer between absorber and back contact", Applied Physics Letters **104** (4) 041115 (2014).

[12] Saini, N., Larsen, J.K., Sopiha, K.V., Keller, J., Ross, N., and Platzer-Björkman, C. "Germanium incorporation in Cu2ZnSnS4 and formation of a Sn–Ge gradient", physica status solidi (a) **216** (22) 1900492 (2019).

[13] Olgar, M.A., Başol, B.M., Tomakin, M., and Bacaksız, E. "Phase transformation in Cu_2SnS_3 (CTS) thin films through pre-treatment in sulfur atmosphere", Journal of Materials Science: Materials in Electronics **32** (8) 10018-10027 (2021).

[14] Altamura, G. and Vidal, J. "Impact of minor phases on the performances of CZTSSe thin-film solar cells", Chemistry of Materials **28** (11) 3540-3563 (2016).

[15] Tauc, J. "Optical properties and electronic structure of amorphous Ge and Si", Materials Research Bulletin **3** (1) 37-46 (1968).

[16] Yang, S., Wang, S., Liao, H., Xu, X., Tang, Z., Li, X., Wang, T., Li, X., and Liu, D. "The impact of different Ag/(Ag+ Cu) ratios on the properties of (Cu 1− x Ag x) 2 ZnSnS 4 thin films", Journal of Materials Science: Materials in Electronics **30** 11171-11180 (2019).

[17] Sanchez, T., Regalado-Pérez, E., Mathew, X., Sanchez, M., Sanchez, Y., Saucedo, E., and Mathews, N. "Ge doped Cu2ZnSnS4: An investigation on absorber recrystallization and opto-electronic properties of solar cell", Solar Energy Materials and Solar Cells **198** 44-52 (2019).

[18] Olgar, M., Sarp, A., Seyhan, A., and Zan, R. "Impact of stacking order and annealing temperature on properties of CZTS thin films and solar cell performance", Renewable Energy **179** 1865-1874 (2021).