



INFLUENCE OF HEATING RATE ON THE STRUCTURAL AND OPTICAL PROPERTIES OF SILVER AND GERMANIUM CO-DOPED CZTS THIN FILM

Yavuz ATASOY^{1*} , Ali ÇİRİŞ² , Mehmet Ali OLĞAR³ 

^{1,2,3} Nigde Omer Halisdemir University, Nanotechnology Research Center, 51240, Nigde, Türkiye

¹Nigde Ömer Halisdemir University, Nigde Zübeyde Hanım Health Services Vocational High School, 51240 Nigde, Türkiye

³Nigde Omer Halisdemir University, Department of Physics, 51240, Nigde, Türkiye

ABSTRACT

The effect of heating rate on the structural and optical properties of Ag+Ge co-doped CZTS thin film were investigated and compared with the undoped CZTS sample. The undoped and Ag+Ge co-doped CZTS samples obtained by two-stage technique consisting of the sequential deposition of the precursor stacks by sputtering system and sulfurization of these layers at elevated temperature in the RTP system by employing heating rate of 1°C/s, 2°C/s and 3°C/s. Ag and Ge co-doped precursor stack as well as undoped stack demonstrated Cu-poor, Zn-rich composition. In addition, the dopant ratio of the Ag+Ge co-doped stack was close to the targeted content considering to EDS measurement. Regardless of the employed heating rate or the doping process, all of the samples crystallized in a kesterite structure. However, it was confirmed by XRD measurements that high heating rates caused phase separation in kesterite phase formation. On the other hand, The Raman peaks assigned to Cu-vacancy and Cu_{Zn} antisite defects formation inhibited with incorporating Ag and Ge into the CZTS structure. Ag and Ge co-doped CZTS sample produced with a heating ramp rate of 1°C/s showed better structural and optical results among them.

Keywords: Ag and Ge co-doping, CZTS Thin Film, Sputtering, Rapid Thermal Processing, Heating Rate

1. INTRODUCTION

The Cu-based kesterite compounds such as Cu₂ZnSnS₄ (CZTS), Cu₂ZnSnSe₄ (CZTSe) Cu₂ZnSn(S,Se)₄ (CZTSSe) are shown as alternatives to the absorber layers used in the mature thin-film-based solar cell technologies (CuIn_{1-x}Ga_x(S,Se)₂ (CIGS) and CdTe), since kesterite materials contain earth abundant and non-toxic elements. Moreover, kesterite thin films also demonstrate similar characteristics to those they are compared to. i.e. having high absorption coefficient (10⁴-10⁵ cm⁻¹), closer ideal direct band gap (1.5 eV) and p-type conductivity which make them an appropriate candidate for photovoltaic applications [1, 2]. However, it is known that the experimental photo conversion efficiency obtained from CZTSSe-based solar cells (~13%) is lower than the theoretical value (~33%), as well as CIGS (23.1%) and CdTe (22.9%) solar cells [3, 4]. This difference is mostly attributed to the low Voc [5]. The formation of high acceptor defects concentration such as V_{Cu} and Cu_{Zn} due to Cu-Zn disorder that occur during the formation of the kesterite structure is referred to the Voc deficiency [6]. On the other hand, deep defect levels originating from the formation of unstable Sn⁺² ions have been widely reported as a reason of low efficiency of the CZTSSe devices [7].

To overcome these defects related to issues mentioned above, alloying of kesterite material is one of the main approach that used. In this context, the cation replacement of copper (Cu) with silver (Ag) or tin (Sn) with germanium (Ge) in CZTSSe have been mostly reported in the literature. For example, it has been reported that partial replacement of Ag with Cu decreases the V_{Cu} and Cu_{Zn} defects, induces better surface morphology with a larger grains and controls the thickness of the MoS₂ [8]. Such improvements in the structure of the films contributes to enhance the cell efficiency. Besides, it has also been revealed by some reported studies that, the concentration of defects in the structure decreased, the crystalline quality improved and grain boundary recombination decreased by Ge doping in CZTSSe thin film [7]. Apart from these, there have been limited amount of work focused on double cation substitution in CZTSSe structures to simultaneously cope with the Cu-Zn disorder and Sn-related problems [9, 10]. In addition, it has been revealed that Ag and Li co-doping strategy improves performance of CZTSe based thin film solar cell by reducing poor electrical conductivity [11].

In this study, we reported Ag and Ge co-doped CZTS thin films prepared by Rapid Thermal Processing (RTP) method for the first time. In order to find the optimum growth process, the effect of heating rate on the structural and optical properties of Ag and Ge co-doped CZTS thin films investigated. For comparison, undoped CZTS thin films were also produced.

* Corresponding author, e-mail: yavuzatasoy@ohu.edu.tr (Y. Atasoy)

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2. MATERIAL AND METHOD

Undoped (CZTS) and Ag-Ge co-doped CZTS (ACZGTS) thin films were grown by the two-stage method. First of all, precursor films were constructed on Soda-Lime Glass (SLG) substrates by DC and RF magnetron sputtering system employing high purity ZnS (5N), Cu (5N), Sn (5N), Ag (4N) and Ge (5N) sputter targets. Then, the precursor stacks were annealed under sulfur atmosphere using the RTP method with different heating rates to form Ag and Ge co-doped CZTS kesterite structure. For deposition of precursor stacks of undoped and Ag+Ge co-doped samples, SLG substrates were cleaned through standard procedure, were placed into the sputtering chamber, and then SLG/Mo/ZnS/Cu/Sn/Cu and SLG/Mo/ZnS/CuSn/Cu/Ag/Ge stacks were obtained with using high purity sputtering targets, respectively. The SLG/Mo/ZnS/CuSn/Cu stack was used in the present study due to promising results were obtained using this structure in our previous study [12]. Finally, the stacks were sulfurized at 550°C for 1 min by using different heating rates of 1°C/s, 2°C/s and 3°C/s. It is well-known that the RTP is more attractive method for large scale production due to higher throughput and low energy consumption compared to Conventional Thermal Processing (CTP) method and it is also more favorable due to the fact that the shorter annealing time prevent the decomposition reactions and elemental loss in CZTS compounds [13]. The detailed information about the deposition process can be found elsewhere [9, 14].

The chemical composition of the precursor stacks were investigated by Energy Dispersive X-ray Spectroscopy measurements (EDS). The polycrystalline properties of the thin films were determined by X-ray diffraction (XRD) and Raman spectroscopy (excitation wavelength of 633 nm) methods. The optical properties of the samples were studied by optical transmission measurement.

3. RESULTS AND DISCUSSION

The chemical composition of the undoped and Ag+Ge co-doped precursor layers was given in Table 1. Two stacks were found to be Cu-poor (Cu+Ag/Zn+Ge+Sn) and Zn-rich (Zn/Ge+Sn) composition with the ratio of about 0.9 and over 1.30, respectively. The Cu-poor and Zn-rich chemical composition is desired property in CZTS-based thin film solar cell applications since such composition contributes to form Cu vacancies (V_{Cu}) and Cu_{Zn} anti-site defects, which strengths the p-type conductivity, improves the Cu and Zn cation ordering in the lattice, and enhances the separation of photo-generated electron-hole pairs [15].

According to the doping concentration of the Ag and Ge co-doped stack, it was seen that Ag and Ge ratio was about 6% and 11%, respectively that was close to the targeted dopants ratio (10%). Regardless of the deposition process, the chemical compositions of the samples demonstrate that the doped stack has been successfully formed even if it contained six different elements.

Table 1. EDS results of undoped and Ag+Ge co-doped precursor stacks

Precursor	Atomic Compositions (%)						Atomic Ratios			
	Cu	Ag	Zn	Sn	Ge	S	$\frac{(Cu+Ag)}{(Zn+Ge+Sn)}$	$\frac{Zn}{(Ge+Sn)}$	$\frac{Ag}{(Ag+Cu)}$	$\frac{Ge}{(Ge+Sn)}$
Undoped	36.0	-	24.2	14.9	-	24.9	0.92	1.60	-	-
Ag and Ge co-doped	31.4	1.7	22.4	14.5	1.9	28.1	0.85	1.36	0.06	0.11

XRD patterns of CZTS and ACZGTS thin films produced by sulfurization of undoped SLG/ZnS/CuSn/Cu and co-doped SLG/ZnS/CuSn/Cu/Ag/Ge and structures for 1 min at 550°C are given in Figure 1(a-b), respectively. It was observed in XRD patterns of the samples that irrespective of dopants and heating rate crystallized in the kesterite structure. Dominant diffraction peaks of the samples in the XRD patterns are at angles of around $2\theta = 28.45^\circ$, 47.50° , and 56.30° which belong to the (112), (220/204) and (312/116) crystal planes of the kesterite CZTS phase, respectively (JCPDS 00-26-0575). Apart from these peaks, the trace of low-intensity characteristic peaks that occur in the crystal planes of (002), (200), (008) and (332) that are also attributed to the kesterite phase. Extended patterns in the range of $2\theta = 28-29^\circ$ correspond to the (112)-peaks of the XRD patterns demonstrated in Figure 1(a-b) are given in Figure 2(a-b). It was determined that the (112) peak positions of the CZTS samples did not change with the increasing heating rate as well as the Ag+Ge co-doped CZTS samples ones. Vegard's law states that

there is a linear relationship between the crystal lattice constant and the concentrations of the elements involved in the structure [16]. This shifts in the XRD peak position inversely proportional to the ionic radius of the dopant atom that replaces the host atom in the lattice. In our case, it is expected that the Bragg angle, 2θ , shifts to lower angle by the replacement of Cu with Ag (larger radius) into the CZTS structure, while it shifts to a higher angle by the replacement of Sn with Ge (smaller radius) [17, 18]. Considering the differences between the ionic radii of the Ag and Ge contributions in the lattice and the atomic ratios in the stack of the samples produced at 550°C , it was determined that the shifts in the peak position compensated each other and presented the same diffraction pattern.

When the effects of the heating rate on the XRD pattern of undoped CZTS thin films were examined closely, it was concluded that the value of the full width at the half-maximum as known an indicator of crystallization degree decreased ($0.170^\circ \rightarrow 0.155^\circ \rightarrow 0.150^\circ$) with the increasing heating rate ($1^\circ\text{C/s} \rightarrow 2^\circ\text{C/s} \rightarrow 3^\circ\text{C/s}$). Although the increase in the heating rate improved the crystal quality, it was determined that there was a relative decrease in the (112) peak intensity of these samples and a shoulder peak was formed at around $2\theta = 29.55^\circ$, which corresponds to the ZnS phase (JCPDS 00-002-0564). In contrast, the Ag and Ge co-doped CZTS thin film produced at 1°C/s with a half-maximum width of 0.17° shown the best crystal quality among them. As a result of XRD measurements, the optimum heating rate for the growth of undoped and Ag+Ge co-doped CZTS thin films is 1°C/s .

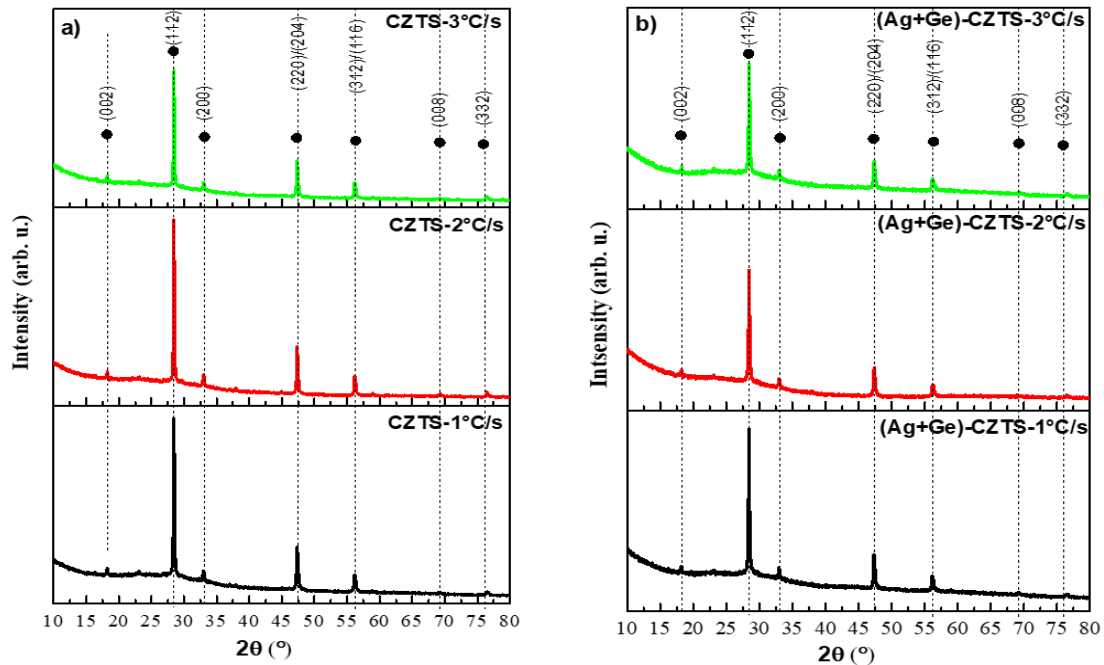


Figure 1. XRD spectra of a) undoped, b) Ag+Ge co-doped CZTS thin films formed with various heating rates.

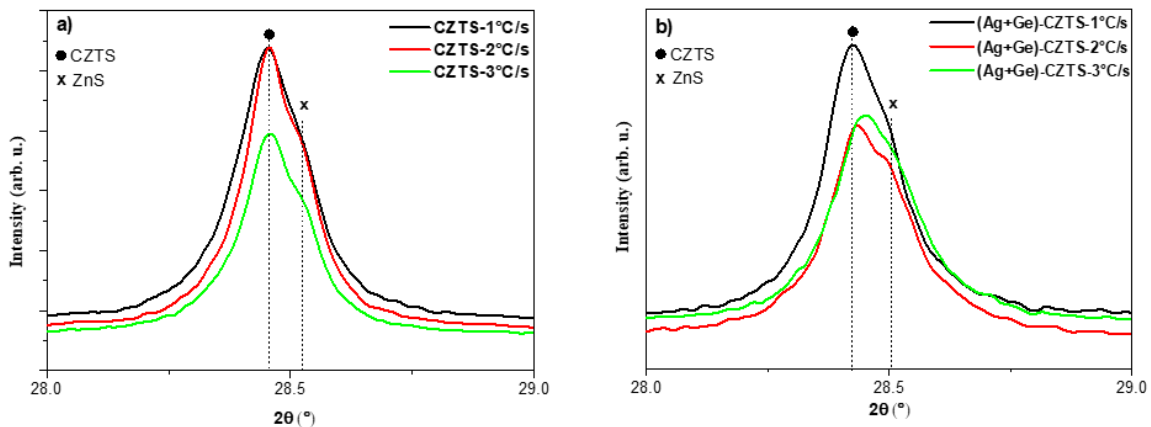


Figure 2. Extended XRD patterns of a) undoped, b) Ag+Ge co-doped CZTS thin films formed with various heating rates.

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Raman spectra of undoped and Ag+Ge co-doped CZTS samples produced by employing various heating rates are shown in Figure 3 (a-b). In Raman spectra taken in the range of 200-500 cm^{-1} , a dominant peak at about 336 cm^{-1} (corresponds to the A1 mode of the kesterite structure) occurred regardless of the heating rate for all of the samples [19]. For undoped CZTS samples, the peaks formed at 264, 286 and 366 cm^{-1} of the kesterite phase are marked in the figure and are in accordance with the previous studies [20, 21]. In addition to these, along with a peak formed at 304 cm^{-1} which is attributed to the CTS phase, the Raman peaks at 287 and 367 cm^{-1} associated with V_{Cu} and Cu_{Zn} defects appeared, respectively [22, 23]. Besides, although ZnS phase was observed in the XRD pattern of the samples, it was not detected with Raman spectroscopy measurement due to the insufficient energy of the excitation wavelength of the laser. When the Raman spectra of Ag and Ge co-doped CZTS film were examined, it was determined that the Raman modes of the kesterite phase varied with the heating rate, except for the main peak around 336 cm^{-1} . Apart from this, Ag-S or Ge-S related secondary phases did not emerged, depending on the dopants. The Raman peaks associated to V_{Cu} and Cu_{Zn} defects concentration decreased by introducing Ag and Ge into the structure. Also, there was no change in the main peak position. However, similar to the XRD results, it is expected that there will be shifts in the main peak position (336 cm^{-1}) with introducing Ag and Ge into the structure separately. It is thought that the Raman peak position of the A1 mode remains constant since the lattice volume did not shrink or expand due to the fact that amount of the Ag and Ge content in the lattice structure are low and close to each other. The Raman peak intensities of the sample produced with 1 $^{\circ}\text{C/s}$ are relatively higher by twofold indicates the improved crystal quality. Overall, according to the Raman measurements, the optimum heating rate for the growth of Ag and Ge co-doped CZTS thin film was determined as 1 $^{\circ}\text{C/s}$.

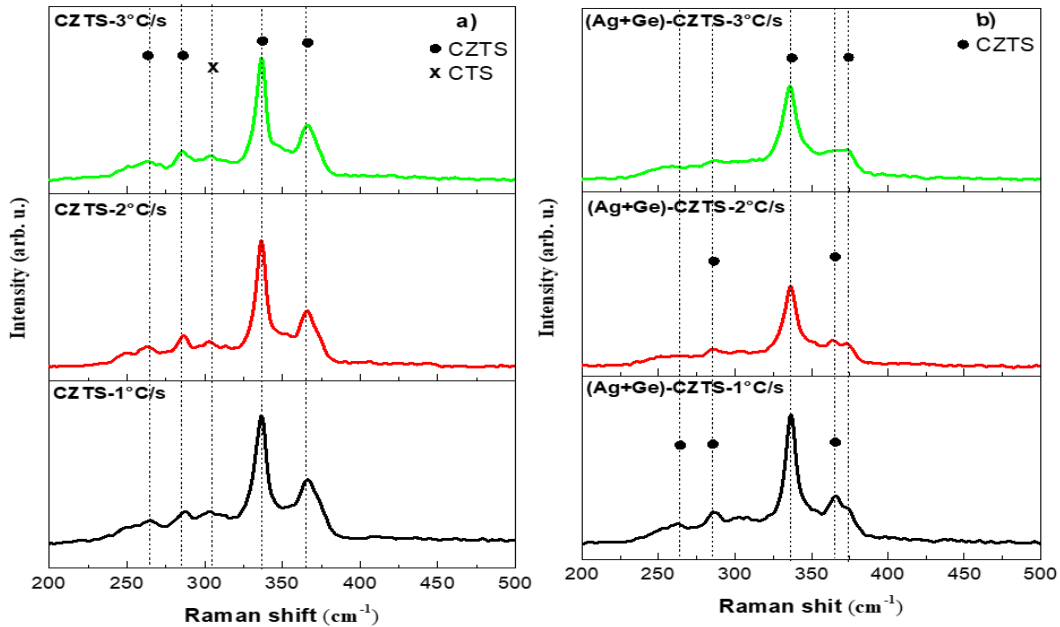


Figure 3. Raman spectra of a) undoped, b) Ag+Ge co-doped CZTS thin films formed employing various heating rates.

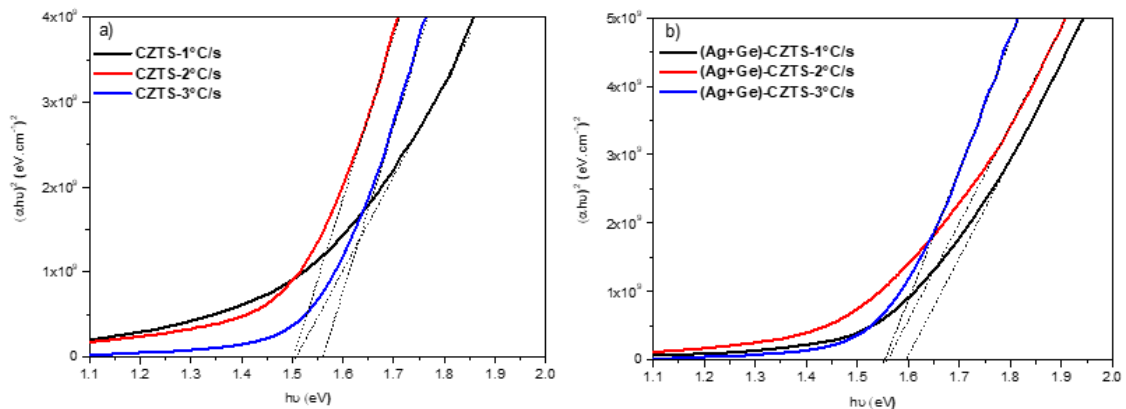


Figure 4. Determination band gap of a) undoped, b) Ag+Ge co-doped CZTS thin films from $(\alpha h\nu)^2 - (h\nu)$ curves.

The transmission data were taken in the wavelength range of 400-1200 nm of the CZTS samples grown by employing various heating rates. The optical direct bandgap of the samples was determined using Tauc plot equation of $(\alpha hv) = A(hv - E_g)^{1/2}$ with known absorption coefficients calculated from transmission data [24]. Then, the direct bandgap values of the undoped and Ag+Ge co-doped samples were obtained from the points where the linear region of the curve intersect on the hv - axis. While the band gap value of undoped CZTS thin films produced at 1°C/s and 2°C/s was found to be 1.5 eV, this value increased up to 1.56 eV with the heating rate of 3°C/s [25]. In contrast, the bandgap values of the Ag and Ge co-doped CZTS thin film produced at higher heating rates (2-3°C/s) did not show a substantial change. On the other hand, it was determined that the bandgap energy increased to 1.6 eV with an increase of 0.1 eV compared to undoped CZTS with the sample produced by 1°C/s. This may be due to the fact that the doping atoms cannot sufficiently introduce into the lattice structure for the samples produced at higher heating rates. Optical measurements show that the annealing time of 1 minute is sufficient to obtain the desired structure for the Ag and Ge co-doped sample sulfurized at 550°C with the heating rate of 1°C/s.

4. CONCLUSION

The effect of heating rate on the structural and optical properties of Ag+Ge co-doped CZTS thin film were studied and compared with undoped CZTS structure. The precursor stacks formed by the sequential deposition of Cu, Sn, ZnS, Ag and Ge layers via sputtering system, then were sulfurized at 550°C for 1 minute in the RTP system employing various heating rates. The EDS measurements indicated that Ag and Ge co-doped precursor stack have a Cu-poor, Zn-rich chemical composition with a close targeted dopant content. Although the kesterite CZTS structure took place in all of the samples according to XRD patterns and Raman spectra, secondary phase formation and crystal quality changed with the employing different heating rate. Overall, Ag and Ge co-doped CZTS sample produced with a heating rate of 1°C/s revealed better results due to formation single phase and successfully incorporation of Ag and Ge ions into the kesterite structure. In our future works, we will focus on investigating the effect of different ratios of cation replacement on the properties of CZTS thin film as well as device performance.

SIMILARITY RATE: 13%

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REFERENCES

- [1] K. Jimbo *et al.*, "Cu₂ZnSnS₄-type thin film solar cells using abundant materials," *Thin solid films*, vol. 515, no. 15, pp. 5997-5999, 2007.
- [2] K. Ito, *Copper zinc tin sulfide-based thin-film solar cells*. John Wiley & Sons, 2014.
- [3] M. A. Green *et al.*, "Solar cell efficiency tables (Version 61)," *Progress in Photovoltaics: Research and Applications*, 2023.
- [4] W. Shockley and H. J. Queisser, "Detailed Balance Limit of Efficiency of p-n Junction Solar Cells," (in English), *J. Appl. Phys.*, vol. 32, no. 3, pp. 510-519, 1961, doi: 10.1063/1.1736034.
- [5] Y. E. Romanyuk *et al.*, "Doping and alloying of kesterites," *Journal of Physics: Energy*, vol. 1, no. 4, p. 044004, 2019.
- [6] S. G. Haass, M. Diethelm, M. Werner, B. Bissig, Y. E. Romanyuk, and A. N. Tiwari, "11.2% efficient solution processed kesterite solar cell with a low voltage deficit," *Advanced Energy Materials*, vol. 5, no. 18, p. 1500712, 2015.
- [7] S. Giraldo *et al.*, "Cu₂ZnSnSe₄ solar cells with 10.6% efficiency through innovative absorber engineering with Ge superficial nanolayer," *Progress in Photovoltaics: Research and Applications*, vol. 24, no. 10, pp. 1359-1367, 2016.
- [8] S. Yang *et al.*, "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*, vol. 30, pp. 11171-11180, 2019.
- [9] Y. Atasoy, "Effect of annealing temperature on the microstructural and optical properties of newly developed (Ag, Cu) ₂Zn (Sn, Ge) Se₄ thin films," *Applied Physics A*, vol. 128, no. 11, p. 1030, 2022.
- [10] L. Qiu, J. Xu, and X. Tian, "Fabrication of Ag and Mn co-doped Cu₂ZnSnS₄ thin film," *Nanomaterials*, vol. 9, no. 11, p. 1520, 2019.

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- [11] X. Zhao *et al.*, "Lithium-assisted synergistic engineering of charge transport both in GBs and GI for Ag-substituted Cu₂ZnSn(S, Se)₄ solar cells," *Journal of Energy Chemistry*, vol. 50, pp. 9-15, 2020.
- [12] A. Yagmyrov, S. Erkan, B. Başol, R. Zan, and M. Olgar, "Impact of the ZnS layer position in a stacked precursor film on the properties of CZTS films grown on flexible molybdenum substrates," *Optical Materials*, vol. 136, p. 113423, 2023.
- [13] A. Fairbrother *et al.*, "Precursor stack ordering effects in Cu₂ZnSnSe₄ thin films prepared by rapid thermal processing," *The Journal of Physical Chemistry C*, vol. 118, no. 31, pp. 17291-17298, 2014.
- [14] M. Olgar, A. Sarp, A. Seyhan, and R. Zan, "Impact of stacking order and annealing temperature on properties of CZTS thin films and solar cell performance," *Renewable Energy*, vol. 179, pp. 1865-1874, 2021.
- [15] S. Y. Chen, X. G. Gong, A. Walsh, and S. H. Wei, "Defect physics of the kesterite thin-film solar cell absorber Cu₂ZnSnS₄," (in English), *Appl Phys Lett*, vol. 96, no. 2, p. 021902, Jan 11 2010, doi: Artn 02190210.1063/1.3275796.
- [16] A. R. Denton and N. W. Ashcroft, "Vegard's law," *Phys. Rev. A*, vol. 43, no. 6, p. 3161, 1991.
- [17] N. Saini, J. K. Larsen, K. V. Sopiha, J. Keller, N. Ross, and C. Platzer-Björkman, "Germanium incorporation in Cu₂ZnSnS₄ and formation of a Sn–Ge gradient," *physica status solidi (a)*, vol. 216, no. 22, p. 1900492, 2019.
- [18] H. Cui, X. Liu, F. Liu, X. Hao, N. Song, and C. Yan, "Boosting Cu₂ZnSnS₄ solar cells efficiency by a thin Ag intermediate layer between absorber and back contact," *Appl Phys Lett*, vol. 104, no. 4, p. 041115, 2014.
- [19] M. Y. Valakh *et al.*, "Raman scattering and disorder effect in Cu₂ZnSnS₄," *physica status solidi (RRL)–Rapid Research Letters*, vol. 7, no. 4, pp. 258-261, 2013.
- [20] S. Yazici *et al.*, "Growth of Cu₂ZnSnS₄ absorber layer on flexible metallic substrates for thin film solar cell applications," (in English), *Thin Solid Films*, vol. 589, pp. 563-573, Aug 31 2015, doi: 10.1016/j.tsf.2015.06.028.
- [21] M. Olgar, A. Seyhan, A. Sarp, and R. Zan, "The choice of Zn or ZnS layer in the stacked precursors for preparation of Cu₂ZnSnS₄ (CZTS) thin films," *Superlattices and Microstructures*, vol. 146, p. 106669, 2020.
- [22] J. J. Scragg, L. Choubrac, A. Lafond, T. Ericson, and C. Platzer-Björkman, "A low-temperature order-disorder transition in Cu₂ZnSnS₄ thin films," *Applied Physics Letters*, vol. 104, no. 4, p. 041911, 2014.
- [23] H. D. Shelke, A. C. Lokhande, V. S. Raut, A. M. Patil, J. H. Kim, and C. D. Lokhande, "Facile synthesis of Cu₂SnS₃ thin films grown by SILAR method: effect of film thickness," *Journal of Materials Science: Materials in Electronics*, vol. 28, pp. 7912-7921, 2017.
- [24] J. Tauc, "Optical properties and electronic structure of amorphous Ge and Si," *Mater. Res. Bull.*, vol. 3, no. 1, pp. 37-46, 1968.
- [25] B. A. Schubert *et al.*, "Cu₂ZnSnS₄ thin film solar cells by fast coevaporation," *Progress in Photovoltaics: Research and Applications*, vol. 19, no. 1, pp. 93-96, 2011.

