Influence of H\(_2\)S on the growth of sputter deposited Cu\(_2\)ZnSnS\(_4\) thin film

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Abstract. Cu\(_2\)ZnSnS\(_4\) (CZTS) is considered as a suitable absorber layer for thin film solar cells. In the present study, the effect of flow rates of H\(_2\)S on the fabrication of CZTS thin films are studied in detail. RF magnetron sputtering in the presence of Ar and H\(_2\)S gas was adopted to deposit sulphides of Cu, Sn and Zn, followed by annealing at higher temperature in H\(_2\)S ambience in the same chamber to complete the crystallization process. Raman spectra showed peaks corresponding to kesterite CZTS and new impurity peaks observed while the H\(_2\)S flow rate increases. XRD result helped to identify various secondary phases present along with CZTS phase. It was revealed by FESEM images that the samples prepared at different H\(_2\)S flow rates exhibiting different nano shapes. Compositional study indicated that the Zn/Sn ratio decreases with H\(_2\)S flow rate. Surface roughness was calculated by AFM technique and big sulphur aggregates were present on the surface of the sample prepared at high H\(_2\)S flow rate. Optical bandgap value of the CZTS films was varied from 1.28 to 1.74 eV and electrical parameters were calculated for samples prepared at lower H\(_2\)S flow rate. This study presents the importance of choosing appropriate H\(_2\)S flow rates for the fabrication of CZTS thin films.

1. Introduction

The kesterite structured Cu\(_2\)ZnSnS\(_4\) (CZTS), a quaternary semiconductor, has been emerged as a promising absorber layer for thin film solar cell due to its desirable optoelectronic properties. CZTS is an earth abundant and non-toxic p-type semiconductor with direct bandgap of around 1.5 eV, absorption coefficient more than 10\(^{5}\) cm\(^{-1}\) [1]. Even though the predicted photovoltaic conversion efficiency of CZTS solar cell is 34\%, the highest efficiency attained so far is 12.6 \% only, which makes this material to be studied further [2]. One of the major challenges in the fabrication of CZTS is the formation of secondary phases such as Cu\(_2\)S, ZnS, SnS, SnS\(_2\) and Cu\(_2\)SnS\(_3\) [3]. CZTS thin films have been synthesized by several methods such as electron beam evaporation [4], thermal evaporation [5], DC and RF sputtering [6,7], pulsed laser deposition [8], successive ionic layer adsorption and reaction (SILAR) [9], sequential electro deposition [10] and sol-gel spin coating [11]. Among these, sputtering method is a widely preferred technique for large scale deposition due to its high deposition rate, uniformity, reproducibility and flexibility in tuning compositions [12,13].
Numerous studies have been conducted to improve the quality of CZTS thin films through the optimization of different growth parameters such as composition of the precursors [14], stacking order and thickness of precursors [15,16], pre annealing and ramping rate of annealing [17,18], sulfurization temperature and time [19,20] etc. Optimizing the sulfurization condition is one of the major approaches to achieve good quality CZTS films and researchers adopted different sulfurization methods. Generally, sulfurization processes of the films are carried out either with elemental sulphur powder or in the presence of H$_2$S gas. Annealing with H$_2$S gas gives an advantage of fabricating CZTS film under the controlled sulphur partial pressure. Moreover, there are reports of crystalline quality improvement with H$_2$S gas compared to elemental sulphur [21]. Awadallah et al fabricated CZTS films through sol-gel sulfurization with H$_2$S gas [22]. Rujun and co-workers prepared CZTS films by sulfurizing the stacked precursors in H$_2$S + N$_2$ gas and the phase formation was investigated by varying the temperature [23]. In a recent work, Idris and co-workers studied the effect of flow rate of H$_2$S on the properties of CZTS thin film by sulfurizing ZnS/Sn/Cu sequence by a two-step process. The surface of samples which are subjected to sulfurization at higher flow rate of H$_2$S was found to be more homogeneous and free of cavities [24]. However, the fabrication of CZTS films in H$_2$S ambience is not much explored and the formation mechanisms are not clearly investigated.

In the present study, we report the influence of the H$_2$S gas in the formation of CZTS thin films which are obtained by the sequential sputtering of Cu, Sn and Zn in Ar + H$_2$S ambience followed by sulfurization with different flow rate of H$_2$S in the same sputtering chamber. The Sn layer was selected as a middle layer to eliminate the loss of volatile Sn. Substrate temperatures during sputtering and post annealing were fixed to 200°C and 500°C respectively [25].

2. Experimental

Copper (99.95%), Zinc (99.9%) and Tin (99.9%) metallic targets of 2 inch diameter (Testbourn Ltd. UK) was sputtered sequentially onto a glass substrate in a custom designed RF magnetron sputtering system in the presence of H$_2$S and Argon gas. The substrate was ultrasonically cleaned in acetone, IPA and DI water respectively, for 15 min each and then dried in N$_2$ gas. The base and working pressure of the sputtering chamber were 2×10$^{-6}$ and 8×10$^{-3}$ mbar respectively. The substrate holder was rotated at 5 rpm and the substrate was kept at a distance of 10 cm from the target. Ar and H$_2$S gases were injected into the chamber in different ratios and the deposition was carried out at RF powers of 50 W for all the targets. The substrate temperature was kept at 200 °C during the sputtering and immediately after the sputtering, the substrate temperature was increased to 500 °C at a ramp rate of 30 °C per min. The annealing was done for 1 hour in H$_2$S ambience at ~2 × 10$^{-2}$ mbar pressure followed by natural cooling.

The stacking order Cu/Sn/Zn was selected considering the volatile nature of Sn, as it may evaporate quickly if it is the upper layer and CuS may form easily in Cu capped stacking order. The sputtering time for the deposition of Cu, Sn and Zn were fixed at 32, 17 and 6 min respectively to get a total thickness of around 600 nm. To understand the H$_2$S flow rate dependence, Ar:H$_2$S gas ratios were varied, keeping Ar + H$_2$S = 20 sccm. Four samples were prepared with H$_2$S flow rate of 2, 3, 5 and 8 sccm (Samples named as HS2, HS3, HS5 and HS8 respectively). The total thickness of each stack was around 500 nm.

Deposited CZTS thin films were subjected to different structural, morphological and optical studies. Raman spectra were recorded using Horiba LABRAM HR Raman spectrometer excited with the 514 nm line of an Ar$^+$ laser and XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The film morphology and elemental analysis were studied using Carl Zeiss field emission scanning electron microscopy (FESEM) equipped with an EDS analyser and AFM images were obtained using Keysight 5500 Scanning Probe Microscope in non-contact mode. Transmission spectra were recorded with ParkinElmer Lambda 365 UV/Vis spectrophotometer. The electrical studies were performed using Hall effect measurements at room temperature.
3. Result and Discussion

The reaction mechanism of Cu, Zn and Sn metals in H₂S ambience can be written as,

\[ \text{Sn} + 2\text{H}_2\text{S} \rightarrow \text{SnS}_2 + 2\text{H}_2 \]

\[ \text{Zn} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2 \]

\[ 2\text{Cu} + \text{H}_2\text{S} \rightarrow \text{Cu}_2\text{S} + \text{H}_2 \]

\[ \text{SnS}_2 + \text{ZnS} + \text{Cu}_2\text{S} \rightarrow \text{Cu}_2\text{ZnSnS}_4 \]

![Figure 1. Raman spectra of CZTS (samples HS2, HS3, HS5 and HS8) thin films.](image)

Raman spectroscopy is a powerful tool for detecting impurity phases in CZTS, because in the XRD pattern there is an overlap between the peaks of CZTS and some of the binary/ternary phases. Figure 1 shows the Raman spectra of CZTS thin films deposited at different H₂S flow rates. For the samples HS2 and HS3, spectra show major peak at 330 cm⁻¹ with weaker peaks at 286 cm⁻¹, 364 cm⁻¹ and 660 cm⁻¹. The peak at 364 cm⁻¹ is attributed to the E(LO) mode and all other peaks corresponded to the vibrational A symmetry modes of kesterite CZTS [26]. The main A mode of Kesterite, stems from the vibration of S atom, has been reported between 330-338 cm⁻¹ depending the synthesis method and 337-338 cm⁻¹ is the most commonly reported value for the good quality single phase Kesterite CZTS films [27]. There is a shift for this major CZTS peak to 333 cm⁻¹ in sample HS5 with a shoulder peak at 311 cm⁻¹ which is ascribed to the SnS₂ phase [28]. The sample HS8 consists of three distinct peaks at 334 cm⁻¹, 313 cm⁻¹ and 228 cm⁻¹ which are assigned to kesterite CZTS, SnS₂ and SnS respectively [29]. As H₂S flow rate increases, there is a clear shift for major CZTS peaks from 330 cm⁻¹ to 334 cm⁻¹ indicating the improvement in the crystalline quality of CZTS [30]. However, the intensity of this peak gets weaker owing to the reduced amount of CZTS due to the change in stoichiometry as H₂S flow rate increases. Moreover new peaks of SnS₂ and SnS are emerging with H₂S flow rate which indicates the presence of high tin content in the sample. It was observed that while the H₂S flow increases to 5 sccm, adhesion of the film was poor resulting peel off from the substrate.
It is challenging to fabricate CZTS without secondary phases. Therefore XRD is employed for further phase identification of CZTS thin films. XRD patterns are given in Figure 2 and phases corresponding to each peak are listed in Table 1. It can be seen that all of the CZTS films consisted of a diffraction peak at $2\theta = 28.6^\circ$ which is attributed to the (112) plane of CZTS phase (ICCD 00-026-0575) and the intensity of this peak is very low in samples prepared at high $H_2S$ flow rate. The other characteristic peak of CZTS at $2\theta = 47.6^\circ$ is present in all the samples except HS8. The diffraction peak at $2\theta = 36.6^\circ$ present in sample HS2 is also assigned to the CZTS phase. In addition to the CZTS phase, all samples exhibited binary and ternary secondary phases. Both HS2 and HS3 samples revealed the existence of secondary phases like $Cu_2S$ (ICCD 00-053-0522), $CuS_2$ (ICCD 00-018-0381), $Cu_3SnS_4$ (ICCD 00-036-0217) and $Cu_3SnS_4$ (ICCD 00-027-0198) and the samples HS5 and HS8 exhibited peaks of $CuS_2$, $Cu_2S$, $Cu_4SnS_4$ (ICCD 00-027-0196), $SnS$ (ICCD 00-039-0354) and $SnS_2$ (ICDD 00-023-0677). $CuS$ based secondary phases obtained in XRD could not be detected in Raman spectra due to the low penetration depth of laser. The distribution of Cu to the surface of the film may be low since Cu layer was at the bottom of our stacking order. In comparison, samples prepared at lower $H_2S$ flow rates exhibit diffraction peaks of $CuS$ related secondary phases along with CZTS phase. Whereas sample HS5 and HS8 have Sn related secondary phases in addition to CZTS phase. The presence of $SnS$ and $SnS_2$ in these samples was revealed in the Raman analysis also.

Table 1. Materials correspond to diffraction angle of XRD.

| Sample | $2\theta(\degree)$ | Material  | Sample | $2\theta(\degree)$ | Material  |
|--------|-------------------|-----------|--------|-------------------|-----------|
| HS2    | 28.69             | CZTS      | HS3    | 18.48             | $Cu_3SnS_4$ |
| 30.79  | $Cu_4SnS_6$       |           | 27.56  | $Cu_3SnS_4$       |           |
| 32.09  | $Cu_2S$           |           | 28.68  | CZTS              |           |
| 36.61  | CZTS              |           | 32.17  | $Cu_3S$           |           |
| 39.45  | $Cu_3SnS_4$       |           | 33.20  | $Cu_3S$           |           |
| 43.07  | $Cu_4SnS_4$       |           | 39.45  | $Cu_3SnS_3$       |           |
| 45.06  | $Cu_3SnS_4$       |           | 45.86  | $Cu_2S$           |           |
| 45.84  | $Cu_2S$           |           | 47.58  | CZTS              |           |
| 47.608 | CZTS              |           | 48.55  | $Cu_3SnS_4$       |           |
| 51.42  | $Cu_3SnS_4$       |           | 53.66  | $Cu_3S$           |           |
| 53.68  | $Cu_3S$           |           | 54.44  | $Cu_3S$           |           |
| 54.36  | $Cu_3S$           |           | 56.43  | $Cu_3SnS_4$       |           |
| 56.56  | $Cu_3SnS_4$       |           | 66.94  | $Cu_3S$           |           |
Field emission scanning electron microscope with EDS was used to study the surface properties and to find out the elemental composition of CZTS thin films. The atomic percentage and atomic ratios of CZTS thin film samples fabricated at different H₂S flow rate are given in Table 2. It has been reported that the CZTS absorber layer with Copper-poor (Cu/(Zn + Sn) < 1) and Zinc-rich (Zn/Sn > 1) compositions are ideal for photovoltaic applications [31]. The composition Cu/(Zn + Sn) ≈ 0.8 and Zn/Sn ≈ 1.2 is suggested as the most suitable for high performance solar cell [32]. It can be seen in Table 2, with an increase of the H₂S flow rate, the atomic percentage of zinc is decreasing drastically, which indicates that the sputtering rate of zinc is very poor in the H₂S ambience while comparing with that of other metals copper and tin. Further study is needed to find out the reason behind the low sputtering rate of zinc. All of the CZTS films are found highly Sn-rich contrary to our expectation as Sn loss is a commonly observed process in the fabrication of CZTS. These can be explained by the fact that Sn is depositing as SnS₂ by the sputtering of Sn at 200°C in the presence of H₂S which is not volatile as metallic tin and this SnS₂ contributes to the further formation of CZTS. Whereas Sn loss is happening in two step process during temperature ramping due to the volatile nature of Sn. As a result of Sn-rich and Zn-poor composition, all our CTZS films are away from stoichiometry. Elemental mapping of the samples was examined and only HS8, prepared at higher H₂S ambience, consists of sulphur aggregates on the surface as seen in the Figure 3. Since the melting point of sulphur is very low it should have evaporated at higher temperature of 500 °C. The existence of sulphur can be explained through the formation process of SnS which is present in the sample prepared with high H₂S flow rate. Generally the formation of SnS is observed at a higher temperature, much above 500 °C, by the thermal decomposition of SnS₂ into SnS and Sulfur. But this is not the case here since the temperature never exceeded 500 °C and also the temperature is given in H₂S ambience. Zhang and co-workers reported that formation of SnS is favourable even in low temperature if the H₂S concentration is very high [33]. The H₂ released from H₂S acts as a strong reducing agent and decomposes SnS₂ in to SnS and Sulfur. This sulfur resides on the surface of the film as aggregates.

Table 2. Elemental compositions of CZTS films

| Sample | Cu  | Sn  | Zn  | S   | Cu/(Zn + Sn) | Zn/Sn |
|--------|-----|-----|-----|-----|--------------|-------|
| HS2    | 17.51 | 28.14 | 11.01 | 43.49 | 0.45         | 0.39  |
| HS3    | 19.19 | 22.50 | 6.17  | 51.90 | 0.67         | 0.27  |
| HS5    | 19.62 | 28.68 | 2.48  | 49.04 | 0.63         | 0.09  |
| HS8    | 18.18 | 27.69 | 2     | 52.2  | 0.61         | 0.08  |
**Figure 3.** EDS mapping of CZTS samples HS2, HS3, HS5 and HS8.

**Figure 4.** FESEM images of samples HS2, HS3, HS5 and HS8
Figure 4 presents the FESEM images of CZTS thin film samples and the magnified views of structures are given as an inset. As shown in the image, the surface morphologies of the films are not similar and consist of different nano structures with homogeneous surface as the flow rate of H₂S vary from 2 sccm to 8 sccm. The sample HS2, prepared at a lower H₂S flow rate consist of a flower like structure and morphology changed to nano flakes with sharp edges at higher flow rate. It has been reported that Sn has a tendency to form nano structures in the presence of sulphur [34]. Since EDS results confirmed the high atomic ratio of Sn in deposited films, we can conclude that the excess amount of Sn present in our sample is responsible for the formation of different nano structures. This result confirms that variation in H₂S atmosphere plays a crucial role in the formation of CZTS films.

![FESEM images of CZTS thin film samples](image)

**Figure 5.** AFM images of samples HS2, HS3, HS5 and HS8

Surface topography of CZTS thin films is studied by non-contact atomic force microscopy. The 2D and 3D AFM images of the films deposited at various gas flows are shown in Figure 5. While these images are examined, it is seen that the grains are homogeneous and uniform for the samples with a lower H₂S flow, whereas samples deposited at a higher H₂S flow have big aggregates on surfaces. Surface roughness value is an important parameter for solar cell application and below 50 nm is the desirable value. The root mean square (RMS) and average roughness values of the samples are given in Table 3. The rms roughness values are found varying from 44.4 nm to 26.1 nm as the H₂S gas flow increases from 2 to 5 sccm whereas sample HS8 showed increased rms roughness value of 131 nm due to the formation of big sulphur cluster.

![AFM images of CZTS thin film samples](image)
Table 3. Surface roughness values of CZTS films

| Sample | RMS (nm) | Mean (nm) |
|--------|----------|-----------|
| HS2    | 44.4     | 34.2      |
| HS3    | 26.1     | 20.8      |
| HS5    | 26.1     | 20.6      |
| HS8    | 131      | 102       |

Transmittance spectra of CZTS thin films for the wavelength ranging from 300 to 1100 nm is shown in Figure 6(a). The optical bandgap is calculated by extrapolating the straight line portion in the plot of \((\alpha h\nu)^2\) versus photon energy \((h\nu)\) and values are found to be 1.45, 1.62, 1.74 and 1.28 eV for samples HS2, HS3, HS5 and HS8 respectively as seen in Figure 6(b). The lower bandgap for HS8 is due to the comparatively high concentration of SnS secondary phase which is having very low bandgap energy of 1.07 eV. The sample HS5 has a little higher bandgap value of 1.74 eV due to the presence of high band gap (2.3 eV) SnS$_2$ phase.

**Figure 6.** (a) Transmission spectra of CZTS thin film samples HS2, HS3, HS5 and HS8 (b) Tauc plot of CZTS film samples HS2 and HS3.

Electrical properties of the samples HS2 and HS3 were studied using Hall effect set-up. Films were p-type in nature and Table 4 shows the parameters sheet resistance, carrier density and mobility. HS3 exhibit higher mobility and sheet resistance with a carrier concentration of $4.9 \times 10^{18}$ cm$^{-3}$. Hall measurements of other two samples were not done due to its peal off nature.

Table 4. Electrical parameters of CZTS films HS2 and HS3.

| Sample name | Sheet resistance (Ω) | Carrier density(cm$^{-3}$) | Mobility (cm$^2$/Vs) | Carrier type |
|-------------|----------------------|-----------------------------|----------------------|--------------|
| HS2         | 647                  | $1.72 \pm 0.4 \times 10^{20}$ | $1.2 \pm 0.26$       | P            |
| HS3         | 2289                 | $4.94 \pm 1.01 \times 10^{18}$ | $11.14 \pm 2.29$     | P            |

4. Conclusion
To summarize, CZTS thin films were grown by RF magnetron sputtering by sequentially depositing copper, tin and zinc in the presence of H$_2$S + Ar gas at 200 °C, followed by post annealing at 500 °C in H$_2$S ambience. Studies were carried out by changing the flow rate of H$_2$S to identify the impact of gas flow in the growth process. Raman spectra revealed the formation of CZTS phase in all the samples and confirmed the emergence of secondary phases of SnS$_2$ and SnS peaks while the H$_2$S flow rate
increases. Various secondary phases were identified from XRD analysis in addition to CZTS phase and noted that Cu-S related phases are dominant in the films prepared in lower H₂S flow rate whereas Sn related phases are formed while the H₂S flow rate increases. These secondary phases occur because of non-stoichiometric compound caused by the Zn-poor and Sn-rich composition as evident from EDS analysis. It is observed that there is a significant loss of Zn while H₂S flow rate increases and Sn loss was not happening since the sputtering was carried out in H₂S ambience. It was revealed by FESEM images that the CZTS films had different morphologies depending on different flow rate of H₂S. Films fabricated at higher H₂S flow rate contain sulphur aggregates due to the decomposition of SnS₂ into SnS and Sulfur. Since non-stoichiometric compound are not favourable for photovoltaic applications a further optimization is needed to fabricate stoichiometric CZTS thin films by eliminating the formation of secondary phases. However, this study demonstrates the importance of choosing H₂S flow rate as it is a crucial factor in the fabrication process of CZTS thin films. The understanding of critical role of H₂S atmosphere may help researchers in improving the quality of CZTS thin films.

References

[1] Kumar M, Dubey A, Adhikari N, Venkatesan S and Qiao Q. Strategic review of secondary phases, defects and defect-complexes in kesterite CZTS-Se solar cells 2015 Energy Environ. sci. 8 3134-3159.

[2] Wang W, Winkler M T, Gunawan O, Gokmen T, Todorov T K, Zhu Y and Mitzi D B, Device characteristics of CZTSSe thin-film solar cells with 12.6 % efficiency 2014 Adv. Energy Mater. 4 1301465.

[3] Jung H R, Shin S W, Gurav K, Gang M G, Lee J Y, Moon J H and Kim J H, Evolution of detrimental secondary phases in unstable Cu₂ZnSnS₄ films during annealing 2016 Electron. Mater. Lett. 12 139-146.

[4] Peksu E, Terlemezoglu M, Parlak M and Karaagac H, Characterization of one-step deposited Cu₂ZnSnS₄ thin films derived from a single crystalline powder 2019 Renew. Energy 143 1133-1142.

[5] Shi C W, Shi G Y, Chen Z, Yang P F, Yao M, Deposition of Cu₂ZnSnS₄ thin films by vacuum thermal evaporation from single quaternary compound source 2012 Mater.Lett. 73 89-91.

[6] Li J, Zhang Y, Wang H and et al., On the growth process of Cu₂ZnSn(S/Se)₄ absorber layer formed by selenizing Cu-Zn-Sn-Sn precursors and its photovoltaic performance 2015 Sol. Energy Mat. Sol. Cells 132 363-371.

[7] Wang J, Li S, Cai J, Shen B, Ren Y and Qin G, Cu₂ZnSnS₄ thin films: facile and cost effective preparation by RF-magnetron sputtering and texture control 2013 J. Alloy.Compd. 552 418-422.

[8] Vanalakar S A, Agawane G L, Shin S W et al., A review on pulsed laser deposited CZTS thin films for solar cell applications 2015 J. Alloys Compd. 619 109-121.

[9] Henry J, Mohanraj K and Sivakumar G, Electrical and optical properties of CZTS thin films prepared by SILAR method 2018 J. Asian Ceram. Soc. 4 81-84.

[10] Tao J, Chen L, Cao H, et al., Co-electrodeposited Cu₂ZnSnS₄ thin-film solar cells with over 7 % efficiency fabricated via fine tuning of the Zn content in absorber layers 2016 J. Mater. Chem. A 4 3798- 3805.

[11] Haass S G, Diethelm M, Werner M, Bissig B, Romanyuk Y E, Tiwari A N, 11.2 % efficient solution processed kesterite solar cell with a low voltage deficit 2015 Adv. Energy Mater. 5 1-7.

[12] Dalapati G K, Masudy-Panah S, Chua S T, Sharma M, Wong T I, Tan H R and Chi D, Color tunable low cost transparent heat reflector using copper and titanium oxide for energy saving applications 2016 Sci. Rep. 6 20182.
[13] Selvakumar N, Biswas A, Rajaguru K, Gouda G M, Barshilia H C. Nanometer thick tunable AlHfN coating for solar thermal applications: transition from absorber to antireflection coating 2015 Sol. Energy Mater. Sol. Cells 137 219-226.

[14] Zhuk S, Kushwaha A, Wong T K S, Panah S M, Smirnov A and Dalapati G K. Critical review on sputter-deposited Cu2ZnSnS4 based thin film photovoltaic technology focusing on device architecture and absorber quality on the solar cell performance 2017 Sol. Energy Mater. Sol. Cells 171 239-252.

[15] Thota N, Gurubhaskar M, Anantha Sunil P, Prathap P, Subbaiah Y P V and Tiwari A. Effect of metal layer stacking order on the growth of Cu2ZnSnS4 thin films 2017 Applied Surface Science 396 644-651.

[16] Dalapati G K et al. Impact of molybdenum out diffusion and interface quality on the performance of sputter grown CZTS based solar cells 2017 Sci. rep 7 1350.

[17] Jiang J, Zhang L, Wang W, Huang X and Hong R. The role of pre-annealing in the sulfurization of Cu-Zn-Sn stacked metal layer prepared by magnetron sputtering 2018 Material Science in semiconductor processing 83 125-132.

[18] Ge J, Yu Y H, Zhang C J, Zuo S H, Jiang J C, Ma J H, Yang P X and Chu J H. Comparative study of the influence of two distinct sulfurization ramping rates on the properties of Cu2ZnSnS4 thin films 2012 Appl Surf Sci. 258 7250-7254.

[19] Zhao Q, Hao R, Liu S, Yang M, Liu X, Chang F and Lu Y. Fabrication and characterization of Cu2ZnSnS4 thin films by sputtering a single target at different temperature 2017 Physica B 523 62-66.

[20] Jiang J, Zhang L, Wang W, Huang X and Hong R. The role of pre-annealing in the sulfurization of Cu-Zn-Sn stacked metal layer prepared by magnetron sputtering 2018 Materials science in semiconductor processing 83 125-132.

[21] Scragg J J, Dale P J and Peter L M. Synthesis and characterization of Cu2ZnSnS4 absorber layers by an electrodeposition-annealing route 2009 Thin solid films 517 2481-2484.

[22] Awadallah O and Cheng Z. Formation of sol-gel based Cu2ZnSnS4 thin films using ppm-level hydrogen sulphide 2017 Thin solid films 625 122-130.

[23] Sun R, Zhuang D, Zhao M, Zhang N, Xie M, Wei Y, Ren G, Wu Y, Gong Q and Wei J. Phase formation of Cu2ZnSnS4 thin films by sulfurizing stacked precursors by sputtering from Cu-Zn and Cu-Sn targets 2019 Thin Solid Films 690 137561.

[24] Akyuz I, Atay F, Aydin R and Kose S. Production and characterization of CZTS films: On the role of H2S flow rate 2015 Solar energy 194 709-715.

[25] Zhao Q, Hao R, Liu S, Yang M, Liu X, Chang F, Lu Y and Wang S. Fabrication and characterization of Cu2ZnSnS4 thin films by sputtering a single target at different temperature 2017 Physica B 523 62-66.

[26] Fernandes P A, Salome P M P and da Cunha A F. Study of polycrystalline CuZnSnS4 films by Raman scattering 2011 J. Alloy. Comp. 509 7600-7606.

[27] Parkin J P, Price L S, Hibbert T G and Molloy K C. The first single source deposition of tin sulphide coatings on glass: aerosol-assisted chemical vapour deposition using [Sn(SCH2CH2Si)]3 2001 J. Matter. Chem. 11 1486-1490.

[28] Ahn J H, Lee M, Heo H, Sung J H, Kim K, Hwang Hand Jo M. Deterministic Two-Dimensional Polymorphism Growth of Hexagonal n-Type SnS2 and Orthorhombic p-Type SnS Crystals 2015 Nano Lett. 15 3703-3708.

[29] Sinsermsuksakul P, Heo J, Noh W, Hock A S and Gordon R G. Atomic layer deposition of tin monosulphide thin films 2011 Adv. Energy Mater. 1 1116-1125.

[30] Zhao Q, Hao R, Liu S, Yang m, Liu X, Chang F and Lu Y. Fabrication and characterization of Cu2ZnSnS4 thin films by sputtering a single target at different temperature 2017 Physica B 523 62-66.

[31] Katagiri H, Jimbo K, Maw W S, Oishi K, Yamazaki M, Araki H and Takeuchi A. Development of CZTS-based thin film solar cells 2009 Thin Solid Films 7 2455-2460.
[32] Chen S, Walsh A, Gong X G and Wei S H, Classification of lattice defects in the kesterite Cu$_2$ZnSnS$_4$ and Cu$_2$ZnSnSe$_4$ earth-abundant solar cell absorbers 2013 Adv. Mater. 11 1522-1539.

[33] Zhang H, Balaji Y, Mehta A N, Heyns M, Caymax M, Radu I, Vandervorst W and Delabie A, Formation mechanism of 2D SnS$_2$ and SnS by chemical vapor deposition using SnCl$_4$ and H$_2$S 2018 J. Mater. Chem. C 6 6172.

[34] Singh O P, Parmar R, Gour K S, Dalai M K, Tawale J, Singh S P, Singh V N, Synthesis and characterisation of petal type CZTS by stacked layer reactive sputtering Superlattice. Microst. 88 281-286.

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