

Efect of annealing time on the composition, microstructure and band gap of copper zinc tin sulfide thin films

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ABSTRACT

In this study, CZTS thin films were deposited by co-sputtering Cu, ZnS and SnS targets and sulfurizing it in H₂S atmosphere at 550 °C. It has been observed that by varying the sulfurization time from 5 to 40 min, the secondary phases got eliminated and stoichiometric film is obtained. This leads to change in the optical band gap from 1.67 to 1.51 eV. The crystallite size calculated using the broadening in the (112) peak of the X-ray diffraction spectra also changed with the sulfurization time from 15.0 to 21.7 nm. Broadening and shift in the Raman peaks have also been observed. Changes in grain size have been observed in scanning electron microscopic studies. In short, the increased band gap reported in literatures may be due to the presence of impurities (except for particles where quantum confinement is applicable; with size less than ~ 7 nm). The above conclusion is based on careful analysis of XRD and Raman data. This study shall help in characterizing CZTS thin film properly, growing high quality CZTS thin films for the realization of high efficiency and durable CZTS based solar cell. Copyright © 2015 VBRI Press.

Keywords: CZTS; Raman shift; co-sputtering; bandgap variation.



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Introduction

Cu₂ZnSnS₄ (CZTS), made entirely of abundant materials, has attracted a great interest due to its potential applications in sustainable thin-film solar cell devices [1-4]. It is a p-type semiconductor with a favorable band gap (~ 1.5 eV) and a high absorption coefficient (10⁴ cm⁻¹) which minimizes the quantity of material used in devices [5-10]. These advantages make CZTS a possible substitute to

Cu(In, Ga)Se₂ thin film solar cells and could be used to reduce the cost of material for large scale production of thin film solar cell. Solar cells based on CZTSSe have achieved efficiency as high as 12.6% using highly toxic and very unstable hydrazine based approach [11] while thin film solar cell based on CIGS have achieved a much higher efficiency of 20.4% [12]. Based on the reported value of efficiency of CZTS based thin film solar cell, there is a lake of scope to carry out research for improving the efficiency.

Various techniques have been reported for the deposition of CZTS thin film for solar cell application. Using non-vacuum techniques, 12.6% lab level efficiency have been reported and using vacuum based techniques, 9.2% (sputtering technique) efficiency have been achieved [11, 13]. In both the techniques, it is difficult to control the formation of secondary phases. The formation of secondary phases mostly depends on the composition (non-stoichiometric) and on annealing/sulfurization/selenization process. Various secondary and ternary phases with varying band gaps are produced during the sulfurization; like, CuS: 2.10-2.55 eV, Cu₂S: 1.21 eV (indirect), ZnS: 3.44-3.84 eV, SnS₂: 2.22-2.35 eV, SnS: 1.34 eV, CuO: 1.2-1.9 eV, ZnO: 3.37 eV, SnO₂: 3.8 eV, respectively [14-20]. Presence of such large number of impurities can deteriorate the optoelectronic properties of the material. Therefore, it is utmost important to avoid or remove the formation of these impurities. It is necessary to ramp up the temperature and avoid the 300-350 °C region in order to minimize the possibility of formation of Cu₂SnS₃, because it is easier to convert the binary to quaternary but difficult to convert the Cu₂SnS₃ to quaternary. Formation of oxides can be avoided by carrying out sulfurization in inert/ hydrogen containing atmosphere. Apart from sulfurization temperature, sulfurization time plays an important role in deciding the phase purity of the CZTS. In the present study, CZTS thin films have been made by sputtering Cu, SnS and ZnS targets and sulfurizing it in H₂S. The samples were annealed for 5, 15, 25, 40 min in H₂S to investigate the effect of annealing duration. Through systematic study it has been shown that 40 min annealing is the optimum time for achieving stoichiometric CZTS without any defect. Also, through careful examination of XRD and Raman data, it has been shown that presence of impurities can alter the band gap of the CZTS.

It should be noted that although the effect of sulfurization time and temperature on the phase and structure of CZTS have been reported [21-29], in those studies, the metallic films were deposited by e-beam evaporation, electrodeposition or sputtering from metallic targets [5, 21-24]. Few studies focused on finding out the optimum condition for obtaining completely sulfurized film have also been reported [25-28]. The intermediate steps provide the information about the mechanism of formation of CZTS [25]. In the present study, CZTS thin films have been deposited by co-sputtering Cu, ZnS and SnS targets and sulfurizing it at 550 °C. Thus, films were already having sulfur into it and therefore annealing even for 5 min at 550 °C in H₂S atmosphere was sufficient to obtain crystalline CZTS phase (revealed by GAXRD and Raman studies). It is shown that secondary phase were present in the sample even up to the annealing time of 30 min and were completely removed when sample was annealed for

40 min in H₂S atmosphere. Increasing the sulfurization time also leads to increase in the crystallite size. A bandgap variation from 1.67 eV to 1.51 eV is observed for samples annealed for 5 min to 40 min. It has been shown that the variation in the bandgap is due to the presence of secondary phase in the sample. By increasing the sulfurization time, the secondary phases got converted into the quaternary phase CZTS and a band gap of 1.51 was observed for the pure CZTS phase. Thus, this study suggests that pure CZTS phase could be grown by optimizing the sulfurization time. The results shall be useful for growing good quality CZTS thin films and hence enhancing the efficiency of CZTS based solar cell.

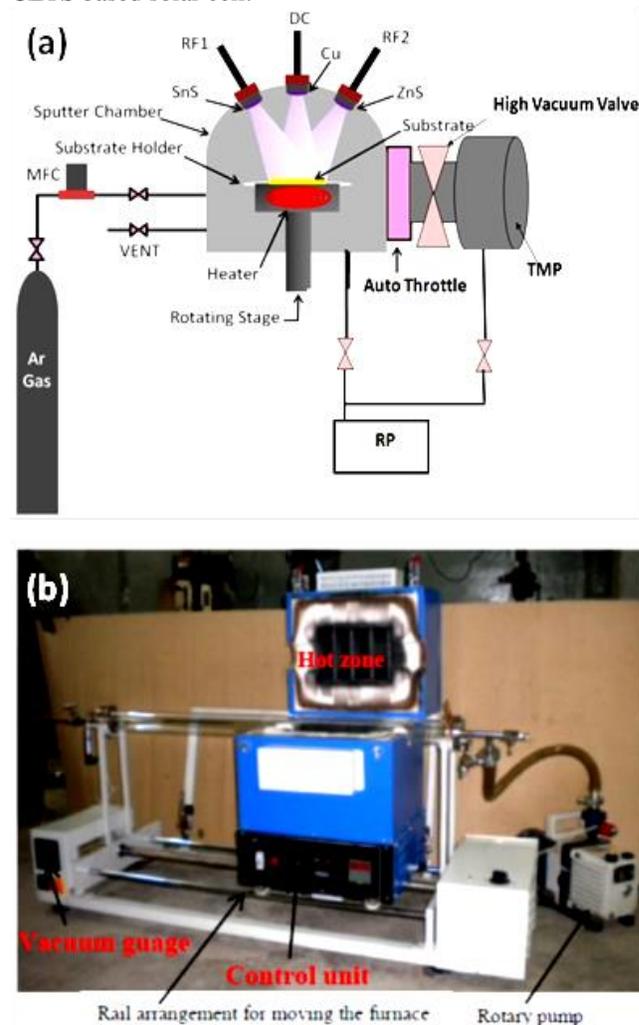


Fig. 1. (a) Co-sputtering system used for sputtering Cu, ZnS and SnS and (b) sulfurization system used for sulfurizing the samples.

Experimental

Materials

All the three targets Cu, ZnS and SnS (obtained from Vin Karola USA, 2 inch diameter, 3 mm thickness) were 99.99% or more pure. H₂S gas (diluted with 85 vol % Ar) with 99.99% purity and Ar (99.9999% pure) were purchased from BOC India limited, India. N₂ gas (99.9% pure), reagent grade acetone and propanol were supplied by the local supplier in India.

Material synthesis and method

CZTS thin films were deposited on soda lime glass (SLG) by co-sputtering Cu, ZnS and SnS targets and sulfurizing them in H_2S at 550°C for 5 min (S1), 15 min (S2), 30 min (S3) and 40 min (S4). The flow rate of H_2S (15%, diluted with Argon) was controlled by mass flow controller and kept at 30 sccm. The tube was evacuated to 10^{-3} mbar using rotary pump and then was purged with N_2 gas for 30 min. This was done in order to eliminate the presence of O_2 in the tube which may affect the quality of CZTS film during sulfurization. The samples were inserted into the hot zone when the temperature of hot zone was 550°C and the samples were taken out immediately from the hot zone after given of sulfurization time. Cu was sputtered using 12 W DC power and ZnS and SnS were sputtered using 75 W and 55 W RF power, respectively. The schematic diagram of the sputtering system and sulfurization unit used are shown in **Fig. 1a** and **1b**, respectively. A spilt-furnace mounted on rail was used for sulfurization. The furnace can slide over rail, and it can be opened up for faster cooling.

Prior to deposition, soda-lime glass (SLG) substrates were cleaned in acetone, propanol and deionized water. All films were deposited at room temperature. A base vacuum of 1.0×10^{-6} mbar was achieved using turbo molecular pump [30]. During the deposition of CZTS layer, pressure and Ar (6N pure) gas flow rate were maintained at 5.0×10^{-3} mbar and 60 sccm, respectively. The target substrate distance was 15 cm. The angles of all three sputtering guns were set at 30° with respect to horizontal axis for focusing the guns at the center of rotation table. Substrate table was rotated at 10 RPM in order to obtain uniform films. The sputtering time was adjusted to obtain $1.3 \mu\text{m}$ thick CZTS films.

Characterization tools

Optical properties were studied using UV-VIS spectrophotometer (Model: Shimadzu UV-VIS 1800). Structural properties were studied using XRD (Philips X'pert pro X-ray diffractometer) and Raman spectroscopy (Renishaw in Via Raman spectrometer). GAXRD (with glancing angle 1°) is used to analyze the phase and to calculate the crystallite size. Surface morphologies of the films were studied using scanning electron microscopy (model: Zeiss EVO-50) and elemental composition were analyzed using energy dispersive spectroscopy (EDS) attached with SEM.

Results and discussion

Optical characterization

Transmittance spectra of all the samples (S1 –S4) are shown in **Fig. 2a** and the optical absorbance spectra and Tauc's plot (inset images) of the annealed CZTS thin films are shown in **Fig. 2b, c, d** and **e**. The absorption coefficient for all the samples is $\sim 10^4 \text{ cm}^{-1}$. These are consistent with other reports for CZTS [5-10]. The estimated direct optical band gap were obtained by extrapolating the linear region of the $(\alpha h\nu)^2$ versus $h\nu$ plot to $\alpha = 0$. Samples S1, S2, S3 and S4 have optical band gap values of 1.67 eV, 1.66 eV, 1.54 eV and 1.51 eV, respectively. The samples S1, S2, S3 and S4 were annealed in H_2S atmosphere for 5 min, 15 min,

30 min and 40 min. The optical band gap values of samples decreased upon increasing the sulfurization time and was ~ 1.51 eV for film annealed for 40 min which is close to the reported value of 1.50 for CZTS thin film samples [5-10]. This may be due to the elimination of secondary phases having higher band gap. The presence of secondary phases having higher band gap may show an increase in the measured optical band gap of the materials.

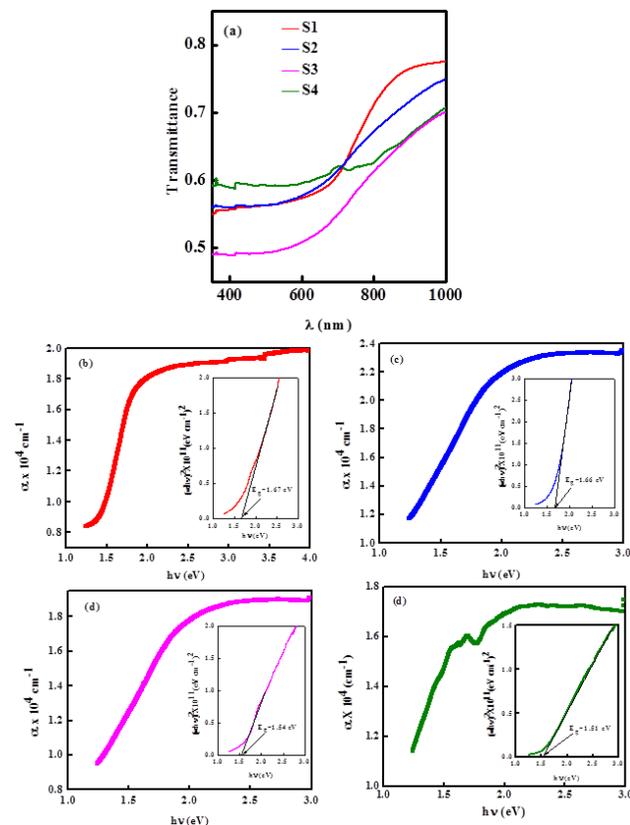


Fig. 2. (a) Transmittance spectra, (b), (c), (d) and (e) photon energy vs. optical absorbance plot. Inset shows Tauc's plot of CZTS thin film samples for S1, S2, S3 and S4.

Structural characterization

The structural properties of CZTS thin film were studied using GAXRD. The GAXRD patterns of CZTS samples S1, S2, S3 and S4 are shown in **Fig. 3a**. The peak intensity was plotted on log scale in order to detect low intensity peaks. Peaks corresponding to (110), (112), (103), (200), (211), (202), (105), (220), (312), (224), (008) and (332) planes of CZTS are present in all the samples and are similar to the reported values [24]. One extra peak corresponding to CuS phase was observed in samples S1, S2 and S3 (marked as star * in **Fig. 3a**). The intensity of peak corresponding to CuS phase decreases with increase in annealing time. Peak corresponding to CuS was not present in the XRD of sample S4. The formation of CuS phase in CZTS thin film leads to the variation in bandgap from the reported value of bandgap for CZTS [9]. The change in the band gap depends upon the amount of impurity present. The band gap value steadily decreases from samples S1 to S4. With increase in the annealing time, the amount of CuS phase decreases which results in the decrease in the band gap. The band gap for sample S4 was 1.51 eV, which is close to the value

reported for CZTS. This shows that undesirable CuS phase can be eliminated by increasing the annealing time. Conventionally, to remove CuS phase from surface of CZTS thin film, samples are etched with an extremely toxic KCN solution [9]. In the present case this has been achieved simply by increasing the annealing time. By increasing the annealing time, film crystallinity also improved. It is clear from the GAXRD patterns that CZTS thin films are having good crystallinity and the growth is oriented along (112) direction. Crystallite size were calculated using the Scherer formula

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where, λ (in nm) is the wavelength of X-ray used, β is the full width at half maximum and θ (in degree) is the Bragg angle. The (112) peak was used to calculate the crystallite size of samples. Fig. 3b shows the magnified view of the (112) peak. The crystallite size varies from 15 nm to 21.7 nm for samples S1 to S4. The calculated values of the crystallite size are given in Table 1.

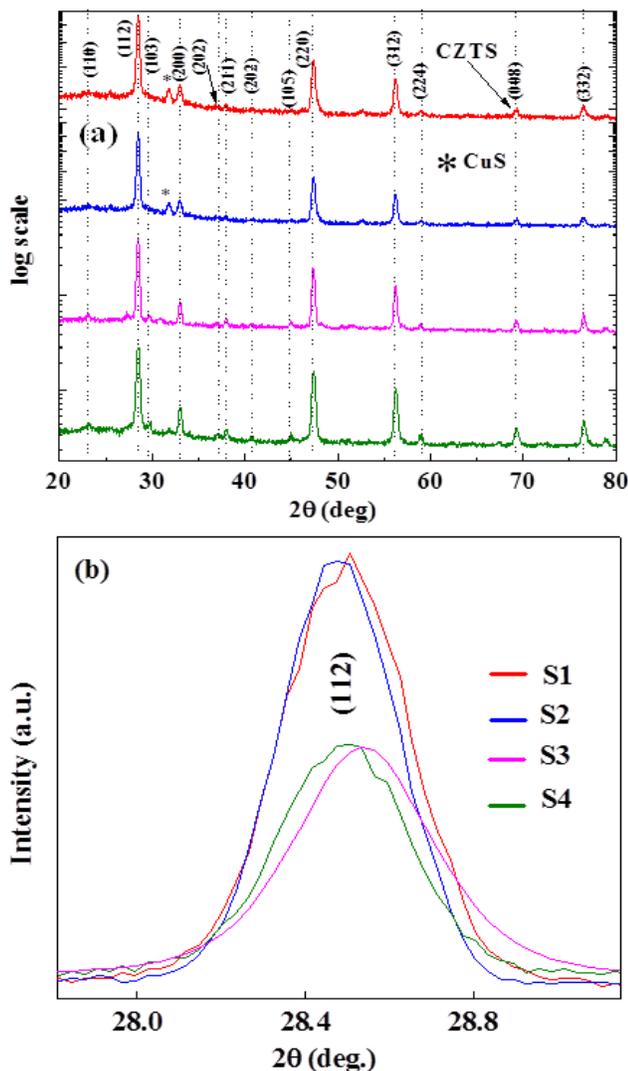


Fig. 3. (a) GAXRD pattern of CZTS thin film samples and (b) magnified view of (112) peak.

Table 1. Effect of sulfurization time on the crystallite size, Raman peak position, FWHM of Raman peaks and optical band gap of CZTS thin film samples.

Samples	Sulfurization time (min)	XRD (crystallite size, nm)	Raman A1 peak (cm^{-1})	FWHM (cm^{-1})	Optical E_g (eV)
S1	5	15.0	333.6	13.82	1.67
S2	15	17.5	335.0	9.21	1.66
S3	30	20.7	336.0	7.92	1.54
S4	40	21.7	338.0	6.27	1.51

The structural properties of CZTS thin films were further analyzed using Raman spectroscopy. The results of Raman spectroscopy of CZTS films are shown in Fig. 4a.

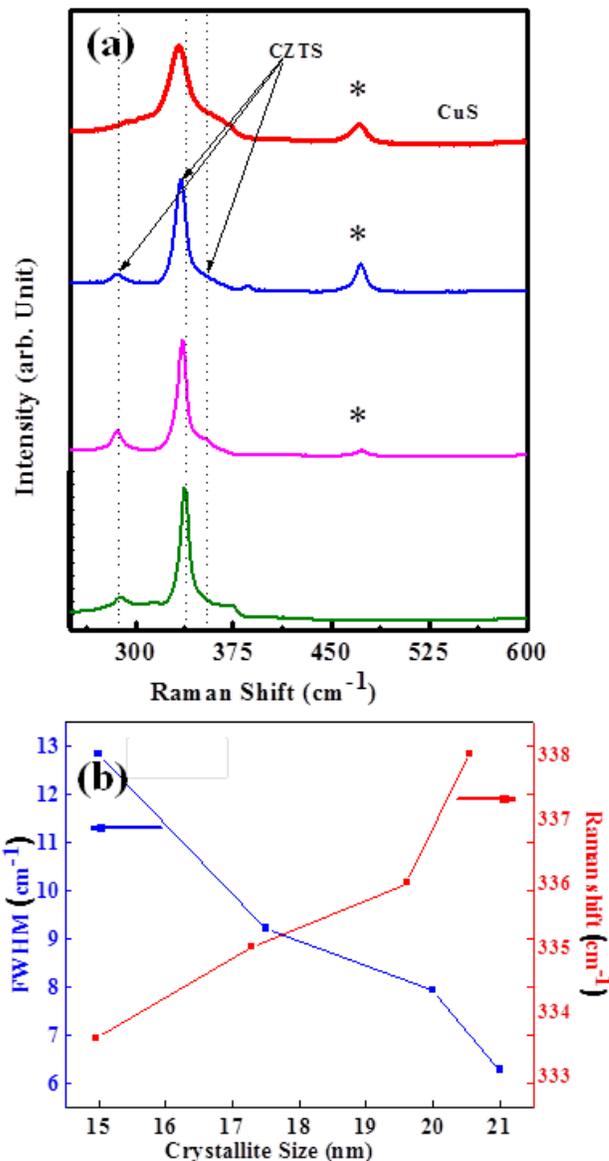


Fig. 4. (a) Raman spectra of CZTS thin films and (b) crystallite size vs. FWHM and shift in Raman peak position.

Spectrum for all the samples (S1, S2, S3 and S4) shows main CZTS peak at 338, 288 and 353 cm^{-1} . The highest intensity peaks in Raman spectra shift towards higher wavenumber with increase in the sulfurization time. The

peak positions for samples S1, S2, S3 and S4 are 333.6, 335, 336, and 338 cm^{-1} , respectively. This peak shift in Raman spectra shows the improvement in the crystallinity of CZTS phase. CuS phase which were observed in the GAXRD analysis in samples S1, S2, and S3 are also detected in Raman spectrum analysis at 474 cm^{-1} . In sample S4, Raman peak related to CuS phase was absent. Thus, GAXRD and Raman analysis confirm that sample S4 has pure CZTS phase only. The elimination of CuS phase in sample S4 may be due to the decomposition of CuS during long term sulfurization at 550 °C, as the melting point of CuS is nearly 500 °C. With increase in sulfurization time, CuS decomposes slowly, which is revealed by decrease in the intensity of corresponding peak in GAXRD and Raman studies. Peak shift and peak broadening for different samples are calculated and the plotted with respect to crystallite size (shown in Fig. 4b) and the data are presented in Table 1. These changes in the Raman peak positions and broadening may be due to the variation in the crystallite size [31-33]. Finally, it is concluded that optimizing the annealing time is important to obtain the pure CZTS phase.

Fig. 5 shows the SEM micrographs of the surface of the annealed CZTS thin films (S1 to S4) sulfurized for 5 min, 15 min, 30 min and 40 min, respectively at 550 °C.

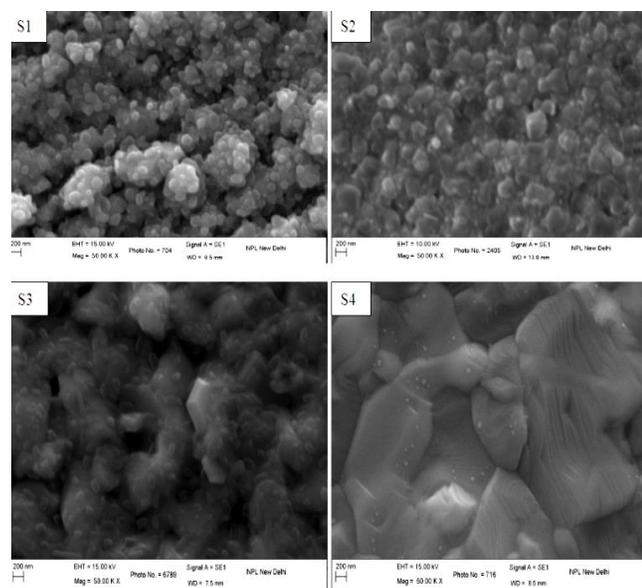


Fig. 5. Surface morphologies of CZTS thin film samples S1, S2 S3 and S4.

From the micrographs it is clear that the grain size increases with increase in the sulfurization time. It is clearly seen in SEM micrograph of sample S4 that grain size is larger than other thin film samples and grains are very compact which may be helpful in improving the efficiency of device. The EDS analysis (shown in Fig. 6) showed that the film consisted of Cu, Zn, Sn and S elements. Peak corresponding to Si was also detected in EDS analysis. The presence of Si may be due to the silicon detector used in the EDS measurements. A nearly stoichiometric elemental composition was observed in EDS analysis. The elemental composition obtained from EDS studies are presented in Table 2. It should be noted that for making high efficiency

thin film solar cells, it is necessary to make pure phase material without impurities of secondary and ternary phases. In the present study, co-sputtering and post sulfurization has been used for obtaining CZTS thin films having good optical, morphological and structural properties.

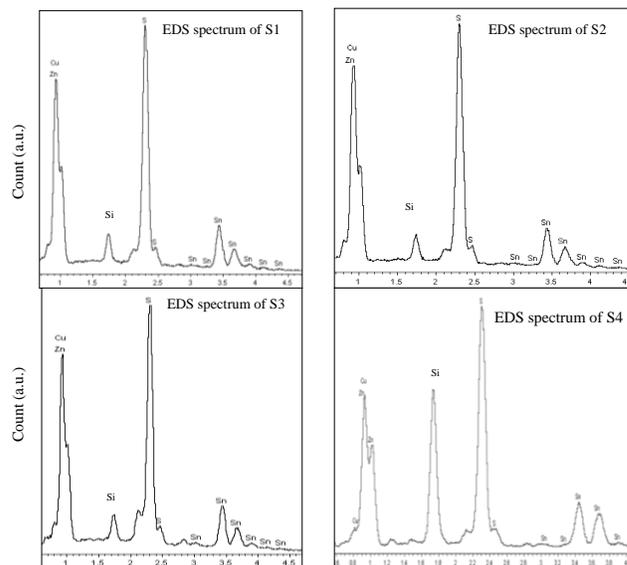


Fig. 6. EDS spectra of CZTS samples S1, S2, S3 and S4.

Table 2. Atomic % of elements present in CZTS thin film samples.

Samples	Cu (at %)	Zn (at %)	Sn (at %)	Zn/Sn	Cu/(Zn+Sn)	S (at %)	S/(Cu+Zn+Sn)
S1	26.02	13.74	12.83	1.07	0.979	47.42	0.901
S2	26.35	13.84	12.99	1.065	0.982	46.82	0.879
S3	26.76	13.99	13.33	1.05	0.979	45.99	0.850
S4	25.82	12.76	8.71	1.46	1.20	52.71	1.11

Conclusion

CZTS thin films have been deposited by co-sputtering Cu, ZnS and SnS targets and sulfurizing the film for 5, 15, 30 and 40 min in H_2S at 550°C. The effect of sulfurization time on the phase formation, crystallite size, optical band gap, shifts in Raman peak position and broadening in the Raman peaks of CZTS thin films were investigated. The film crystallinity improved with increase in the sulfurization time. The crystallite size (using the (112) peak of GAXRD) varied from 15.0 nm to 21.7 nm with increase in sulfurization time. The optical band gap of CZTS also varied from 1.67 eV to 1.51 eV with increase in the sulfurization time from 5 min to 40 min, respectively. The variation in bandgap is due to the formation of CuS impurity phase in CZTS thin film annealed for shorter times. Shifts in the Raman peak position and broadening have been observed with increase in the sulfurization time. CuS impurity phase have been removed just by increasing the annealing time and without use of extremely toxic solution, KCN which is a conventional way to remove CuS. The optimized sulfurization condition for obtaining pure CZTS thin film shall be useful in realizing the increased efficiency of CZTS based thin film solar cell.

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