__Original Research Article__

Effect of thiourea concentration on structural, optical and electrical properties of Cu_2ZnSnS_4 thin films prepared by using spray pyrolysis

ABSTRACT

Thin films of Cu_2ZnSnS_4 (CZTS) with different molar concentrations of thiourea were prepared on glass substrates using spray pyrolysis technique. The structural, optical and electrical properties of the CZTS thin films were investigated using X-ray diffraction (XRD), UV-vis spectroscopy and sheet resistance measurement respectively. The XRD analysis demonstrated the polycrystalline nature of the CZTS. We observed better crystallanity in CZTS film prepared with thiourea concentration of 0.20M and optical band gap value at this concentration was observed to be 1.60 eV. The optical study showed that band gap increased with an increase in thiourea concentration. The sheet resistance of the sample prepared with 0.20 M concentration of thiourea was 10.73 Kohm/□.

Keywords: CZTS thin films, spray pyrolysis, X-ray diffraction, thiourea concentration,

1. INTRODUCTION

Copper Indium Gallium Selenide ($CuInGaSe_2$ or CIGS) is considered one of the most promising absorbent layers in solar cell fabrication [1, 2]. The US National Renewable Energy Laboratory (NREL) reported that CIGS thin film solar cell exhibited a conversion efficiency of 22.6% [3]. However, the use of less abundant elements such as, In and Ga, limits the development of CIGS solar cell due to high production cost [4, 5]. Presently, copper zinc tin sulfide (Cu_2ZnSnS_4 or CZTS) is emerging as a substituent for CIGS that overcomes this drawback. The crystal structure of CZTS is like the chalcopyrite semiconductor CIGS [6].

The quaternary compound copper zinc tin sulfide (CZTS) generally exists as a p-type semiconductor with a tunable band gap ranging from 1.4 eV to 1.7 eV [7]. The most valuable property of this compound is that it has an absorption coefficient greater than 10^4 cm^{-1} [8]. Furthermore, the constituent elements of this compound are inexpensive, readily available and environment friendly. These factors make CZTS a potential material for the photo-absorbing layer in the fabrication of low cost thin film solar cells. Report shows that CZTS based solar cells achieved an efficiency of 9.5% [3].

Thin films of CZTS can be prepared by using various techniques such as pulsed laser deposition [9], radio frequency magnetron sputtering [10], spray pyrolysis [11-15], electrochemical deposition [16], thermal evaporation [17], etc. Because of simplicity, versatile, low cost and scalable to mass production we have used spray deposition technique for preparation of CZTS film. In this paper, we report the structural, optical and electrical properties of CZTS thin films prepared by using spray pyrolysis. The concentrations of thiourea were varied in the precursor solutions during the preparation of the CZTS films to investigate the effect of thiourea on properties of CZTS film.

2. MATERIALS AND METHODS

CZTS thin films were deposited using a homemade spray pyrolysis deposition unit. Firstly, aqueous solutions of 0.05M Cupric Chloride dihydrated($CuCl_2.2H_2O$) as a source of Cu, 0.025M Zinc Acetate dihydrated[Zn $(CH_3COO)_2$. $2H_2O$] as a source of Zn, 0.025M Tin Chloride dihydrated($SnCl_2$. $2H_2O$) as a source of Sn and various molar concentration of thiourea [$CS(NH_2)_2$] as a source of S were prepared. Then, these separate solutions were mixed with continuous stirring for 15 minutes which resulted in a clear transparent and homogeneous precursor solution [18]. All the chemicals used in this work were of AR grade. The prepared solution was sprayed on the hot substrate with the help of a locally available general-purpose nebulizer. The solution was sprayed at a flow rate of 2 ml/min with the compressed air for 3 minutes. The aerosols generated by the nebulizer passed through the glass nozzle, which was nearly half a centimeter in diameter, to the hot substrate. The distance between nozzle and substrate was fixed at 1.5 cm. The temperature of substrate was fixed at optimized temperature of 310°C using a J-Tec model-903 temperature controller.

In this experiment, the concentration of thiourea was varied from 0.20 to 0.35 M in the precursor solution. The structural characterization of the as-prepared CZTS thin films was performed using X-ray diffraction (XRD) technique employing X-ray wavelength, λ= 0.15405 nm, and the diffraction angle was varied from 10° to 80°. The optical properties were explored by measuring transmittance (T%) of the films with Ocean Optics Spectrophotometer USB 2000, Singapore. To study the electrical properties, the sheet resistances were measured using a four-probe technique in Vander Pauw configuration.

3. RESULTS AND DISCUSSION

3.1 Structural Characterization – Fig 1(a) shows the XRD pattern of a CZTS thin film fabricated with 0.20 M thiourea concentration at a temperature of 310℃. The peaks observed at 2θ= 28.53°, 47.48°, and 56.35° correspond to (112), (220), and (312) planes, respectively of CZTS with kesterite structure with reference to JCPDS card# 26-0575. Additionally, the broad peak at 2θ = 26.09° is possibly due to presence of amorphous phase of Cu_4SnS_4 corresponding to (220) plane. This was determined through a comparison of d-spacing made with respect to JCPDS card# 29-0584 as illustrated below in Table 1. The symbol "d" denotes this broad peak, shown in the inset of Fig 1(a). Fig1(b) shows the XRD pattern of CZTS film prepared with 0.35 M thiourea at the same substrate temperature of 310℃. The pattern also shows the similar peaks but at slightly shifted positions. The peak position, full width half maximum and relative intensities of all the observed peaks in the captured XRD patterns were achieved by Gaussian fit.

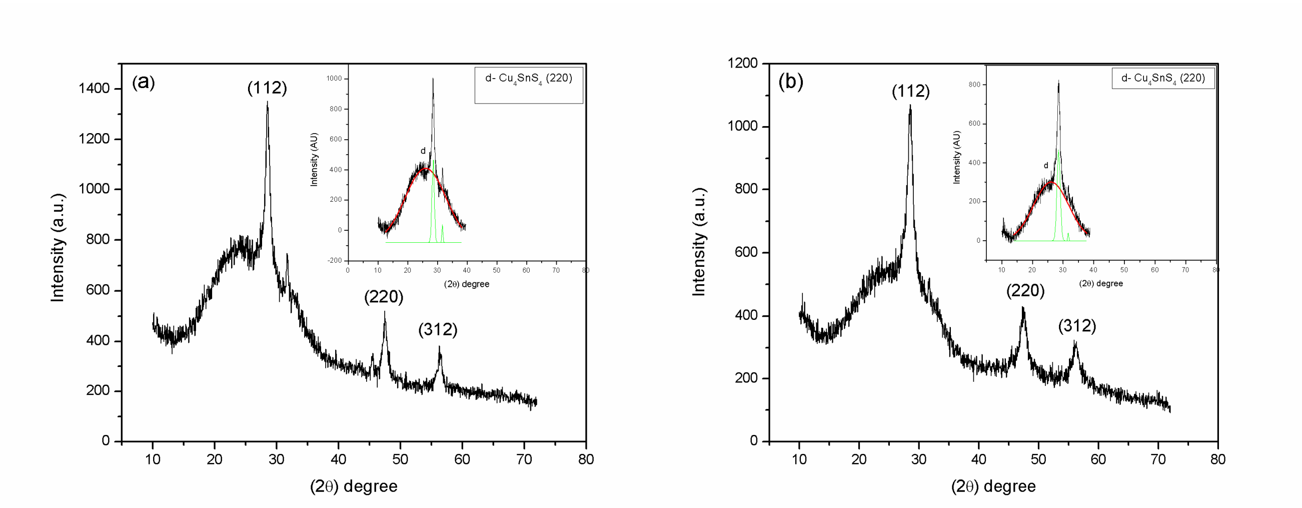

Fig.1. XRD pattern of CZTS thin films prepared with (a) 0.20M and (b) 0.35M thiourea. Insets to the figures show the Gaussian fit for the broad peak.

The peaks at 28°, 47° and 56° were present in both the figures. It indicates no dramatic changes in the structure of CZTS films prepared with two different thiourea concentrations. The comparison of observed 2θ(d spacing) shows that as the concentration of thiourea in the precursor solution increased from 0.20M

(Fig 1(a)) to 0.35M (Fig 1(b)), the 2θ values slightly shifted as shown in Table 1. For both concentrations, a broad peak at diffraction angle of about 26° was observed. This may be due to presence of an amorphous phase of Cu_4SnS_4. Since, the experiment was performed in non-vacuum conditions, so we cannot ignore atmospheric oxygen for the formation of metal oxides, i.e. ZnO. Improvement in crystallinity and minimization of secondary phase formations can be made by sulfurizing the deposited CZTS films with H_2S treatment at 550℃ for an hour in vacuum conditio n [19].

Table1. Peak position, observed and JCPDS- d spacing and (hkl) values obtained from XRD patterns of Fig 1(a) and 1(b).

Figure	S.No.	Peak position (2θ) degree	Observed 'd' value	'd' value from JCPDS	JCPDS card number	(hkl)	phases
1(a)	1	26.09	3.3446	3.3420	29-0584	(220)	Cu_4SnS_4
	2	28.53	3.1250	3.1260	26-0575	(112)	CZTS
	3	47.48	1.9130	1.9190	26-0575	(220)	CZTS
	4	56.35	1.6314	1.6360	26-0575	(312)	CZTS
1(b)	5	26.62	3.3446	3.3420	29-0584	(220)	Cu_4SnS_4
	6	28.49	3.1303	3.1260	26-0575	(112)	CZTS
	7	47.45	1.9145	1.9190	26-0575	(220)	CZTS
	8	56.20	1.6354	1.6360	26-0575	(312)	CZTS

The crystallite size,D, of CZTS films was calculated using the Debye Scherrer's equation [20],

$$D = \frac{0.94\lambda}{\beta cos\theta} \tag{1}$$

where λ, β, and θ represent the wavelength of X-ray, full width half maximum (FWHM) measured in radian and diffraction angle, respectively. The calculated values of relative intensities, FWHM, the D, dislocation density (δ), and texture coefficient (T_c) of above observed peaks were tabulated in Table 2. It shows slight shift in intensities of all the peaks due to change in thiourea concentration. The FWHM of all the observed peaks increases as the thiourea concentration increases from 0.20 M to 0.35 M and hence the crystallite size decreases. The crystallite sizes of 11 nm and 7 nm were observed for film prepared with 0.20 M thiourea and 0.35 M concentrations, respectively. It indicates that the sample prepared with 0.20 M has better crystallinity than with 0.35 M of thiourea. Similar behaviour of decrease in crystallite size for increase in thiourea concentration was detected by Kiran Diwate et. al. [21]. Since instrumental line broadening and stresses are not taken into account, the correct grain sizes may be greater than above mentioned values in our results. The decrease in crystallite size with increase in concentration of thiourea might be due to decrease in crystallinity of the film.The dislocation density ($\delta=1/D^2$), which gives the crystallographic defect or irregularity within a crystal structure, was found to increase with increase in thiourea concentration as shown in Table 2.

The texture coefficient was calculated using the equation [20]

$$T_{c(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{\frac{1}{n}\sum_n I_{(hkl)}/I_{0(hkl)}} \tag{2}$$

where $T_{c(hkl)}$ is the texture coefficient of (hkl) plane, $I_{(hkl)}$ is the intensity measured for (hkl) plane, $I_{0(hkl)}$ is the intensity of (hkl) plane taken from the standard data in JCPDS card fitting in the X-ray diffraction pattern material, and n is the diffraction peak number. Calculation shows texture coefficient values of greater than 1 for diffraction angles of both 28.53° and 56.35°. It infers that the samples show a preferential orientation along (112) direction. A closer look at the variation of T_c with thiourea concentration reveals that as thiourea concentration increases, T_c for diffraction angle 28.53° decreases from 1.3326 to 1.3147 (shown in Table 2). It shows that the orientation along (112) direction decreases with increase in thiourea concentration.

Table2. Calculation of crystallite size, dislocation density and texture coefficient of CZTS films

Thiourea conc. (M)	Observed d values (Å)	Observed Relative Intensity (%)	JCPDS d values (Å)	JCPDS Relative Intensity (%)	FWHM (degree)	D (nm)	δ (×10^2 nm)$^{-2}$	$T_{c(hkl)}$
0.20M	3.1250	100	3.1260	100	0.7722	11	0.8899	1.3326
	1.9130	26	1.9190	90	0.8756	10	1.0203	0.5478
	1.6314	15	1.6360	25	0.8426	11	0.8734	1.1194
0.35M	3.1303	100	3.1260	100	1.1857	7	2.1003	1.3147
	1.9145	29	1.9190	90	1.2212	7	1.9778	0.5078
	1.6354	18	1.6360	25	1.4052	6	2.4414	1.1077

3.2 Optical Characterization - Fig 2(a) represents the absorbance spectra of the CZTS films prepared with different thiourea concentrations as a function of wavelength. It clearly depicts that absorbance starts to increase sharply at around 750 nm which is due to fundamental absorption of CZTS. A comparative study on variation of absorbance with thiourea concentration shows that absorbance is higher for the sample prepared with 0.20 M thiourea than other thiourea concentrations. This might be due to greater amount of CZTS phase formation and better crystallanity of CZTS film prepared with 0.20 M thiourea concentration than other concentrations. This result is found to be consistent with the structural analysis as discussed earlier through the observation of intense peaks in the XRD pattern of CZTS film prepared with 0.20M thiourea concentration. The direct band gap (E_g) of the each sample was determined by fitting the absorption data to the direct transition equation [22].

$$(\alpha h\nu)^2 = E_d\left(h\nu - E_g\right) \qquad (3)$$

where α is the optical absorption coefficient, $h\nu$ is the photon energy, E_g is the direct band gap,and E_d is a constant.

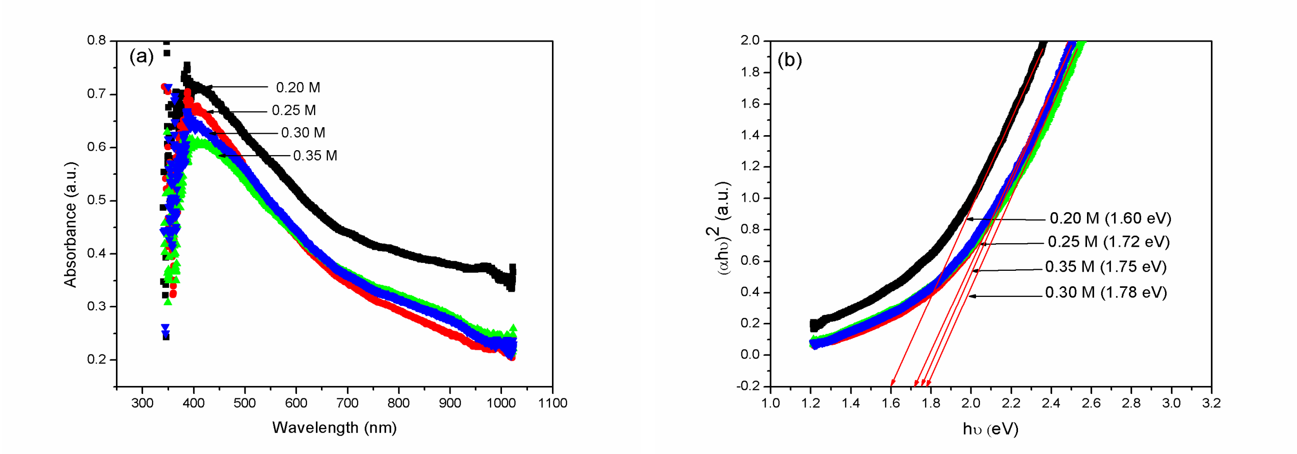

Fig.2. (a) Absorbance spectra and (b) band gaps of CZTS films prepared with different concentrations of thiourea.

Fig 2(b) shows the variation of $(\alpha h\nu)^2$ with photon energy, $h\nu$ (eV) of the prepared CZTS films. The optical band gap (E_g) of the films was determined by extrapolating the linear portion of $(\alpha h\nu)^2$ versus '$h\nu$' curve to $(\alpha h\nu)^2 = 0$ in the high absorption region. The band gap of CZTS film was found to be increased from 1.60 eV to 1.78 eV as the thiourea concentration increased from 0.20 M to 0.35 M as shown in Table 3. The observed smallest band gap of 1.60 eV for film prepared with 0.20 M thiourea was slightly higher than that reported by Kumar et al., [23]. The observation of increased band gap as thiourea concentration was increasing is possibly due to a decrease of particle size, which is consistent with our XRD results. The XRD results show as thiourea concentration increased from 0.20 M to 0.35 M the particle size decreased from 11 nm to 7 nm, which may lead to an increase in band gap. The greater value of band gap can be reduced by post sulfurization process.

Table 3. Band gap of CZTS films

S.N	Thiourea Concentration (M)	Band gap (eV)
1.	0.20 M	1.60 eV
2.	0.25 M	1.72 eV
3.	0.30 M	1.78 eV
4.	0.35 M	1.75 eV

3.3 Electrical Characterization - Fig 3 shows the variation of sheet resistance of CZTS films prepared with different thiourea concentrations. The sheet resistance was measured by using the four probe method [24].The result shows that as thiourea concentration increases, the sheet resistance of the CZTS film increases. This trend is possibly due to formation of larger particle size of CZTS films prepared with 0.20 M thiourea concentration, than films prepared with other higher concentrations of thiourea: 0.25 M, 0.30 M and 0.35 M. As thiourea concentration increases, the particle size decreases which may lead to increase in grain boundaries. As charge carriers are scattered at the grain boundaries, this may increase in resistivity of the material as well as sheet resistance of film deposited.

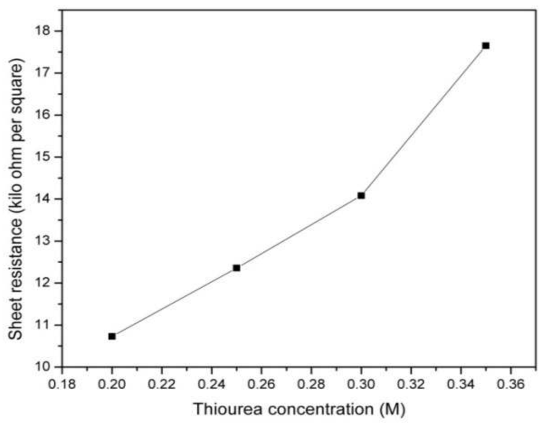

Fig.3.Sheet resistances of CZTS films prepared with different thiourea concentrations.

4. CONCLUSION

Thin films of CZTS were deposited on glass substrates by spray pyrolysis method. X-ray diffraction analysis confirmed that the deposited films were CZTS with kesterite structure. As the thiourea concentration increased from 0.20 M to 0.35 M the crystallite size of CZTS was decreased from 11 nm to 7 nm. The lowest band gap of CZTS film prepared with 0.20 M thiourea was 1.60 eV. Additionally, the band gap increased from 1.60 to 1.75eV as thiourea concentration increased from 0.20M to 0.35M.

Electrical measurements showed increase in sheet resistance of CZTS film from 10.73 to 17.65kohm/□ when the thiourea concentration was increased from 0.20 to 0.35M.

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