Original Research Article

Effect of Thiourea Concentration on Structural, Optical and Electrical Properties of Cu2ZnSnS¬4 Thin Films Prepared by Spray Pyrolysis Setup

ABSTRACT

Aims: Thin films of Cu_2ZnSnS_4 (CZTS) were prepared on glass substrate by spray pyrolysis technique.
Study design: The effects of Thiourea variation on CZTS thin films were investigated.
Place and Duration of Study: Department of Physics in Patan Multiple Campus, Patandhoka, Lalitpur and Central Department of Physics, Kirtipur, Kathmandu, between June 2013 and December 2014.
Methodology: The structural, optical and electrical characterization of the CZTS thin films were carried out by X-ray diffraction (XRD), UV-Visible spectrum and sheet resistance measurements respectively.
Results: XRD study shows polycrystalline nature of CZTS films. We get better crystallinity at thiourea concentration of 0.20M. The optical study shows that band gap increases with the increase in thiourea concentration. At thiourea concentration of 0.20M, the optical band gap is found to be 1.60 eV. Sheet resistance measurement at various concentrations of Thoiurea shows that it has minimum value of 10.73 KΩ/□ for the sample prepared with Thiourea concentration 0.20M.

Conclusion: The increase in Thiourea concentration into the parent solution decreased the crystallinity of the prepared film.

Keywords: [Cu_2ZnSnS_4, Thin films, Spray pyrolysis, Thiourea, Characterization]

1. INTRODUCTION

$CuInGaSe_2$ (CIGS) is considered as one of the most promising absorbent layer in solar cell [1, 2]. US National Renewable Energy Laboratory (NREL) reported that CIGS thin film solar cells exhibited a conversion efficiency of 20.5%[3]. But the use of less abundant element In and Ga limits the development of CIGS solar cell due to high production cost [4,5]. To overcome the drawbacks, CZTS is emerging as a substituent for CIGS. The crystal structure of CZTS is similar to the chalcopyrite semiconductor CIGS [6].

The quaternary compound copper zinc tin sulfide (Cu_2ZnSnS_4: CZTS), generally exists as a p-type semiconductor with tunable band gap ranging from 1.4eV to 1.7eV [7]. Its attention grabbing property is its possession of a high absorption coefficient, which is greater than 10^4 cm^{-1} [8]. The constituent elements of this compound are cheap, easily available and environment friendly which made CZTS a potential material to act as a photo-absorbing layer in the fabrication of low cost thin film solar cells. It was reported that CZTS solar cell achieves an efficiency of 8.5±0.2 % [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 [11-13], electro-deposition [14], evaporation [15] etc. In this work, we report the results of study on structural, optical and electrical properties of CZTS films prepared by spray pyrolysis technique. We varied the thiourea concentration in the parent solution during the preparation of CZTS films.

2. MATERIAL AND METHODS

We deposited CZTS thin films using a homemade spray pyrolysis set up. Firstly, we prepared 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

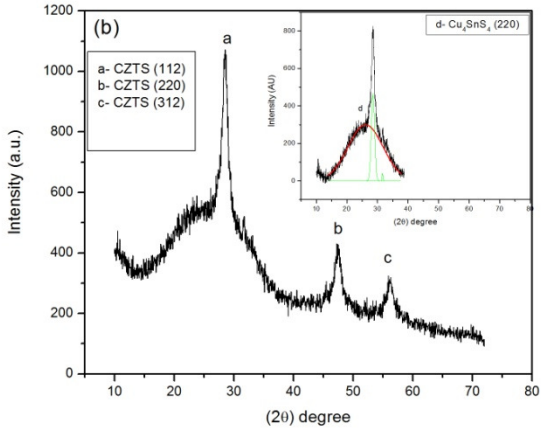
source of Sn and various molar concentration of Thiourea [$CS(NH_2)_2$] as a source of S respectively. Then, we mixed the solutions with continuously stirring for 15minutes that results a clear transparent and homogeneous precursor solution [16]. All the chemicals used in this work are of AR grade. The prepared solution sprayed into the hot substrate with the help of a nebulizer. The aerosols generated by nebulizer are allowed to pass through the glass nozzle nearly half a centimeter in diameter to the hot substrate. Distance between nozzle and substrate was fixed at 1.5cm. The temperature of substrate was fixed at 310^{o}C using a temperature controller J-Tec model-903.

In this experiment, we varied the thiourea concentration in the parent solution. The structural characterization of the as-prepared CZTS thin films were performed using X-ray diffraction (XRD) technique employing X-ray wavelength λ= 0.15405nm and the diffraction angle was varied from 10^{o} to 80^{o}. The optical properties were investigated by measuring transmittance T% of the films with Ocean Optics Spectrophotometer USB 2000, Singapore. To study its electrical properties sheet resistances were measured by using a four probe technique.

3. RESULTS AND DISCUSSION

3.1 Structural Characterization - Figure1a shows the XRD pattern of CZTS thin film fabricated with 0.20M Thiourea concentration into the parent solution at a temperature of 310℃. The peaks observed at 2θ= 28.5352^{o}, 47.4897^{o}, and 56.3556^{o}corresponds to (112), (220), and (312) planes respectively of CZTS with kesterite structure with reference to JCPDS card# 26-0575. In this figure, the peaks at 2θ= 28.5352^{o}, 47.4897^{o}, and 56.3556^{o}are labeled as a, b, and c respectively. Additionally, the presence of a broad peak at 2θ = 26.0907^{o} is possibly due to presence of amorphous phase of Cu_4SnS_4corresponding to (220) plane when comparison of d-spacing has been made with respect to JCPDS card# 29-0584 as described in the table 1 below. This broad peak is denoted by symbol d shown in the inset of figure 1a. Figure1(b) shows the XRD pattern of CZTS film prepared with 0.35M Thiourea at the same temperature of 310℃. The pattern also shows the similar peaks but at very slightly shifted in positions. All the peak positions were obtained by Gaussian fit of the observed peaks in XRD pattern.

The peaks at 2θ= 28.5352°, 47.4897°, and 56.3556° were observed in both figures. It indicates the presence of polycrystalline CZTS film with reference to JCPDS file no. 26-0575. The comparison of observed 2θ (d spacing) shows that as the concentration of Thiourea in the parent solution increased from 0.20M (figure 1a) to 0.35M (figure 1b), the 2θ values were found to be only slightly shifted as shown in table 1. For both concentrations a broad peak at diffraction angle of ~ 26° was observed. This may possibly be due to presence of amorphous phase of Cu_4SnS_4 during preparation with reference to JCPDS card #29-0584. Since, the experiment was performed in non-vacuum condition; we cannot ignore atmospheric oxygen for the formation of oxide of metal i.e ZnO. Improvement in crystallinity and minimization of secondary phase formations can be done by sulfurizing the deposited CZTS films with H_2S treatment at 550℃ for an hour in vacuum condition.



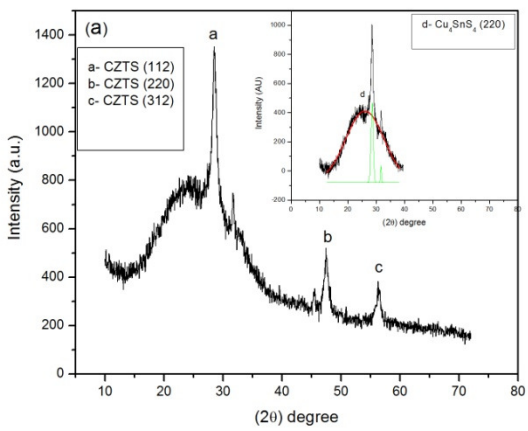


Fig.1. XRD pattern of CZTS thin films prepared with (a) 0.20M and (b) 0.35M Thiourea. Insets to the figures show the Gaussian fit for the broad peak.

We calculated the crystallite size of CZTS films using the Debye Scherrer's equation [17],

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

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 intensity, FWHM, the crystallite size (D), dislocation density (δ), and texture coefficient (T_c) of above observed four peaks were tabulated in Table 2. It shows that the intensities of all the peaks were found to be only slightly shifted for the change of thiourea concentration. The FWHM of all observed peaks have increased as the thiourea concentration was increased from 0.20M to 0.35M and hence decreased the grain size (D) of CZTS films. It indicates that the sample prepared with 0.20M has better crystallinity than sample prepared with 0.35M of thiourea.The grain size of 11 nm and 7nm were observed for film prepared with 0.20 M thiourea and 0.35M concentration respectively. Since instrumental line broadening and stresses are not taken into account, the correct grain size may be greater than above mentioned value. Decrease in grain size with increase in concentration of thiourea might be due to decrease in crystallinity of the prepared film with increase in thiourea concentration. The dislocation density 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.

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

Figure	S.N.	Peak position (2θ) degree	Observed 'd' value	'd' value from JCPDS	JCPDS card number	(hkl)	phases
1(a)	1	26.0907	3.3446	3.3420	29-0584	(220)	Cu_4SnS_4
	2	28.5352	3.1250	3.1260	26-0575	(112)	CZTS
	3	47.4897	1.9130	1.9190	26-0575	(220)	CZTS
	4	56.3556	1.6314	1.6360	26-0575	(312)	CZTS
1(b)	5	26.6277	3.3446	3.3420	29-0584	(220)	Cu_4SnS_4
	6	28.4926	3.1303	3.1260	26-0575	(112)	CZTS
	7	47.4506	1.9145	1.9190	26-0575	(220)	CZTS
	8	56.2022	1.6354	1.6360	26-0575	(312)	CZTS

Table2. Calculation of grain size, dislocation density and texture coefficient

Thiourea conc. (M)	Observed d values (Å)	Observed Relative Intensity (%)	JCPDS d values (Å)	JCPDS Relative Intensity (%)	FWHM (degree)	D (nm)	δ ($\times 10^2$ 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

The texture coefficient is calculated using the equation [17]

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

where $T_{c(hkl)}$is the texture coefficient of (hkl) plane, $I_{(hkl)}$is the intensity measured for (hkl) plane, $I_{o(hkl)}$is the intensity of (hkl) plane taken from the standard data in PDF card fitting in the X-ray diffraction pattern material, n is the diffraction peak number. Calculation shows texture coefficient values of greater than 1 for the diffraction angle of 28.5352° and 56.3556°. It infers that the sample showed a preferential orientation along (112) direction. A close look on variation of T_c with Thiourea concentration reveals that as thiourea concentration increases, T_c for diffraction angle 28.5352° decreases from 1.3326 to 1.3147 which is shown in table2. It shows the orientation along (112) direction decreases with increase in thiourea concentration.

3.2 Optical Characterization – Figure 2a represents the absorbance of the CZTS films prepared with different Thiourea concentration as a function of wavelength. From this figure we see 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 the absorbance is high for the sample prepared with 0.20 M Thiourea compared to other Thiourea concentrations. This might be due to greater amount of CZTS phase formation and better crystallanity nature of CZTS than with other concentrations. This result is found to be consistent with the structural analysis as discussed earlier for observation of intense peaks in the XRD pattern of CZTS film prepared with 0.20M Thiourea concentration. Figure 2b shows the variation of $(\alpha h\nu)^2$ with photon energy, $h\nu$ (eV) of prepared CZTS films. The band gap of CZTS film was found to be increased from 1.60 to 1.78 eV as the Thiourea concentration increased from 0.20M to 0.35M shown in table 3. The observed smallest band gap of 1.60 eV for film prepared with 0.20M Thiourea was slightly higher than that reported by Kumar et al., [18]. An observation of increased band gap for increasing the Thiourea concentration is possibly due to decrease of particle size which is consistent with our XRD results. The XRD result shows as the Thiourea concentration increased from 0.20M to 0.35M the particle size was found to be decreased from 11 nm to 7 nm which may lead to increase the band gap. The greater value of band gap can be reduced by post sulfurization process.

Fig.2.(a) Absorbance spectra and (b) band gaps of CZTS films prepared with different concentrations of Thiourea in the parent solution.

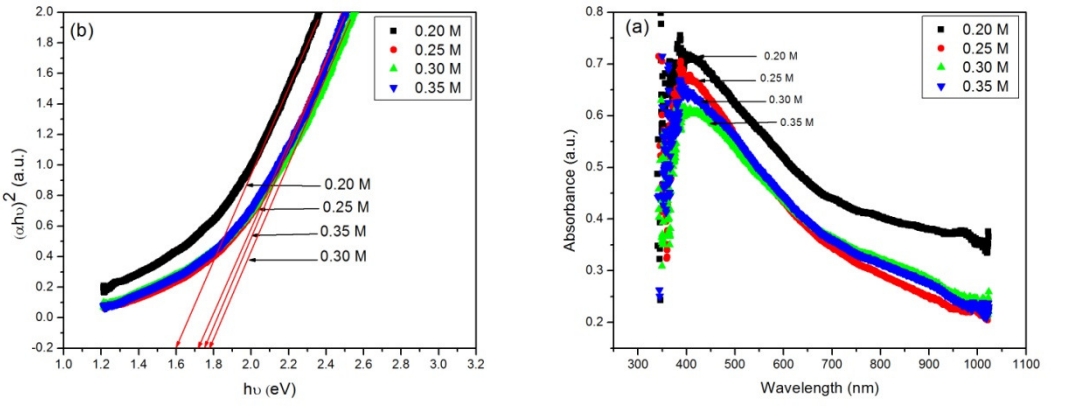


Table 3. Band gap of CZTS films

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 – Figure 3 shows the variation of sheet resistance of CZTS films prepared with Thiourea concentrations in the parent solution. The result shows that as the Thiourea concentration increased, the sheet resistance of the CZTS film was found to be increased. This trend is possibly due to formation of larger particle size with CZTS film of 0.20M that enhanced film crystallanity than films prepared with other higher values of Thiourea concentration: 0.25M, 0.30M and 0.35M. When Thiourea concentration was increased the particle size decreased, that leads to increase in grain boundaries. As charge carriers are scattered at the grain boundaries, that may increase resistivity of the material as well as sheet resistance of film deposited.

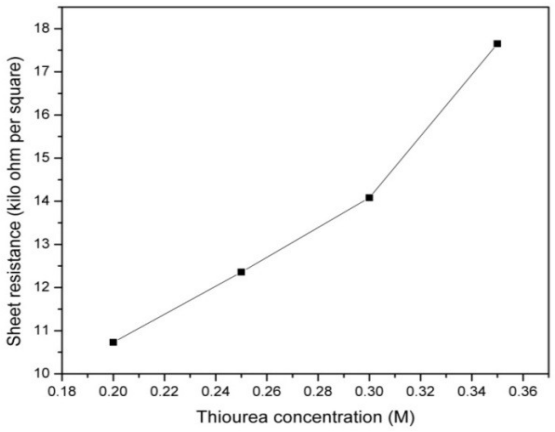


Fig.3.Sheet resistances of CZTS films prepared with various amounts of Thiourea.

4. CONCLUSION

Thin films of CZTS were prepared by spraying a solution over hot glass substrates. X-ray diffraction study of as-prepared films indicates that the deposited film was of kesterite structure. The increase in Thiourea concentration into the parent solution decreased the crystallite size from 11nm to 7 nm. The lowest band gap of CZTS film prepared with 0.20M thiourea was of 1.60 eV. This was found to be increased from 1.60 eV to 1.75eV as the Thiourea concentration increased from 0.20M to 0.35M consisting with changes in crystallite size in XRD study. Electrical measurements show that sheet resistance of CZTS film increased from 10.73kohm/□ to 17.65kohm/□ when the Thiourea concentration was increased from 0.20M to 0.35M.

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