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Effect of Substrate Temperature on Structure, optical and Electrical Properties of Spray Deposited CZTS Thin films

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Abstract:
Cu_2ZnSnS_4 (CZTS) films were deposited for different substrate temperatures by using simple chemical locally built spray deposition technique. Copper chloride ($CuCl_2$), Zinc chloride ($ZnCl_2$), Tin chloride ($SnCl_4.5H_2O$) and thiourea ($SC(NH_2)_2$) were used as Cu^+, Zn^+, Sn^+ and S^- ion sources respectively. A set of five CZTS films was deposited using five different substrate temperatures (175, 200, 250, 275, and 300°C). The structure, Morphology, Elemental analysis and Optical properties were studied using X-ray diffratometer (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDX) and UV-Visible Systronic Double Beam (2201) Spectrophotometer, techniques respectively. The XRD spectra showed that all films are polycrystalline and exhibit kesterite tetragonal crystal structure with preferential orientation along (112) direction. The calculated crystallite size was increased with increase in substrate temperature. The surface morphology of CZTS films was improved with increase in substrate temperature. The film sample deposited for 275℃ represent excellent spherical granules CZTS crystals of increasing size from 640 nm to 1.8 μm arranged in regular fashion with some void spaces. The purity of the composition was investigated using Elemental analysis of the deposited films. The optical band gap was estimated using Tauc plots. The band gap obtained was to be in the range of 1.4 to 1.6eV. The calculated energy band gap (*Eg*) by using Tauc's plot was about 1.62eV. The dc electrical resistivity estimated by using IV characteristics of the CZTS film was to be in the range .5622×10^{-2} to 9.746×10^{-2} $\Omega - cm$.

Key words: CZTS thin films, Spray pyrolysis, XRD, Optical band gap, Absorption coefficient, Electrical resistivity

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1. Introduction

Extensive work have been reported on CIGS [$Cu_2(InGe)S_4$] and $Cu_2(InGe)Se_4$ based thin film solar cells of higher conversion efficiency up to 20.3 %. However Indium and Germanium elements are toxic, less abundance, and expensive which limits the large scale production of devices [1–4]. CdTe solar cell technology was also an alternatively good system in terms of photovoltaic solar cells performance [5-7]. However, CdTe based solar cell technology suffers from the use of potentially unsafe substance in both absorber layer (CdTe) and window material (CdS) they create the problems of safe disposal of non-functioning, outdated CdTe solar cells. Recently copper, zinc, tin and sulfur (CZTS) thin film based solar cells with comparatively cheap in cost because higher abundant of zinc and tin element are found to be more suitable for the large-scale application [9–12]. CZTS is an important compound as an absorber material and exhibits superior optical and electronic properties, as well as a suitable band gap (1.2 to 1.6 eV). CZTS has a higher light absorption coefficient ≥ 10^4 cm^{-1} in the visible region of electromagnetic spectrum, and its theoretical power conversion efficiency (PCE) is more than 30% [13–15].

The methods employed for preparation of CZTS film, were mainly; sputtering [16], Sol. gel [17], thermal evaporation [18], electro deposition [19,], pulsed laser deposition [20]. These techniques require high temperature annealing and sulfurization processes. Chemical spray pyrolysis (CSP) is an important preparation method for CZTS thin films because of its simplicity to prepare highly crystalline, large area thin films without sulfurization. In CSP method stoichiometry of CZTS is very sensitive to the concentrations of precursors in the spraying solutions and does not require sulfurization however it require substrate temperature optimization. In present paper we report therefore influence of substrate temperature on structure, morphology and optical properties. The dc electrical resistivity is to be investigated using IV characteristics of CZTS thin films prepared by present chemical spray pyrolysis method.

2. Material and Methods

In present work, copper chloride ($CuCl_2$), zinc chloride ($ZnCl_2$), tin chloride ($SnCl_4$) and thiourea [$(NH_2)_2CS$] were used as precursor materials to deposit CZTS films by using home-made chemical spray pyrolysis technique onto soda lime glass (SLG) substrate [21]. All the chemicals used were of analytical grade of 99.99 % purity. The precursor was prepared by mixing of previously optimized molar concentration of 0.025 M $CuCl_2.2H_2O$, 0.0125 M $ZnCl_2.2H_2O$, 0.0125 M $SnCl_4.5H_2O$ and 0.05 M (NH2)2CS. The substrate temperature was kept at desired value as 175, 200, 250, 275 and 300℃. The cationic solutions were stirrer for one and half hour. Three cationic solutions were mixed together one by one with stirring continue and then (NH2)2CS solution was added slowly such that mixture initially became turbid. The addition of (NH2)2CS was continued till the clear homogenous precursor was obtained. This clear homogeneous precursor was sprayed on the substrate maintained at desire temperature on hot plate by locally available perfume atomizer. A set of five samples was deposited for five different substrate temperatures (175, 200, 250, 275, and 300℃). The substrate temperature was controlled by automatic digital temperature controller. The distance 30 cm. of spraying nozzle form substrate and spray rate of 5 ml per second were optimized previously [22]. On deposition samples were allowed to cool to room temperature and then used for the characterization. Thickness (t) of films was determined by weight and difference method using following well known relation.

$$t = \frac{m}{\rho A} \qquad (1)$$

Where, m (gm) is the deposited mass, ρ ($gm/cm3$) is density of deposited material and A ($cm2$) is the area of deposited film. X-ray diffraction patterns were obtained by Mini Flex II- X-ray diffractometer using $CuK\alpha$ line (λ = 1.54056 Å) at a grazing angle of 1^0 and scan range 10-80°. The average crystallite size was estimated using the following classical Scherrer's formula [23].

$$D = \frac{0.94\lambda}{\beta \csc\theta} \qquad (2)$$

Where, λ is equal to 1.54056 Å wavelength of X-ray used, β is full width at half maximum and θ is Brag's angle of diffraction.

The optical band gap of CZTS films were obtained from absorption spectra of the films deposited on soda-lime glass. The absorption spectra were recorded using Systronics Double Beam (2201) UV-Visible spectrophotometer in the range 250-1000 nm. The Band gap was estimated using following Tauc's relation [24]

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \qquad (3)$$

The room temperature resistivity of deposited CZTS thin films was investigated by using IV curves. The sheet Resistance [25] was calculated from the slope of IV Characteristic using relation (4).

$$R_s = 4{:}\,53\frac{\Delta V}{\Delta I}\,\Omega \quad (4)$$

The D. C. resistivity ρ of the CZTS film was estimated by using equation (5).

$$\rho = R_s \times t\,\Omega - cm \quad (5)$$

(5)

where *t* is the thickness of the film.

3 Results and Discussion

3.1 Variation of film thickness

The results corresponding to thickness measurements of CZTS films prepared at different substrate temperature is shown in Figure 1. Figure revealed that as substrate temperature increased from 175 ℃ to 275 ℃ film thickness was increased from 326 μm to 367μm. However, further increased in substrate temperature to 300℃, thickness of CZTS film decreased to 356μm. These results suggest that the growth of CZTS films depends upon substrate temperature. The optimum temperature for growth of CZTS film was to be 275℃.

3.2 X-ray diffraction analysis

Figure 2 show XRD patterns of CZTS films deposited at different substrate temperature. It is evident from figure that the XRD pattern show three preferential peaks at $2\theta = 28.40$, 47.30 and 55.32^o corresponding to (112), (220) and (312) crystal planes. The XRD pattern was compared with standard JCPDS data card no. 26-0575 and confirmed that deposited CZTS thin films exhibit kesterite crystal structure of tetragonal phase [22].

The XRD study indicates that deposited CZTS films are polycrystalline.. The crystallite size calculated from Scherrer's formula by Lorentz fitting of dominant (112) peak. The calculated crystallites size was listed in table 1. The crystallite size increases with increase in substrate temperature. However temperature above 275℃ crystallite size and crysallinity were observed to be deceased. This shows that both crystallinity and crystallite size were depends on substrate temperature.

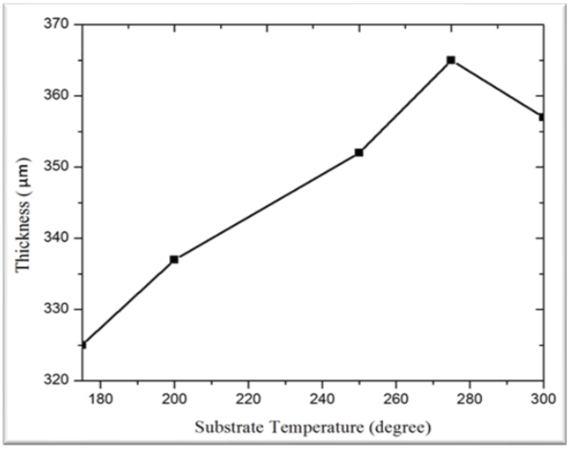

Fig.1. Plot of Variation of Film Thickness Verses substrate temperature

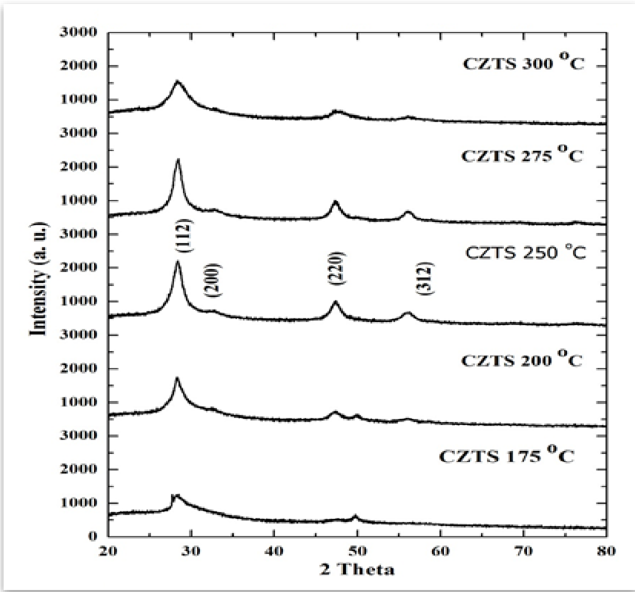

Fig.2. XRD Spectra of spray deposited CZTS Thin Films

Table 1. Crystallite size (D) calculated using Lorentz fitting

Sample	2θ (degree)	β (degree)	θ	β radians	D
$CZTS$ 175 ℃	28.3859	12.49949	14.19295	0.247714	26.1611
$CZTS$ 200 ℃	28.62607	6.19265	14.31304	0.24981	52.36157
$CZTS$ 250℃	28.3753	5.2717	14.18765	0.247621	62.05257
$CZTS$ 275 ℃	28.4126	5.064	14.2063	0.247947	64.51286
$CZTS$ 300 ℃	28.4985	6.2124	14.24925	0.248696	52.42875

3.3 Scanning electron microscopy (SEM) analysis

Figure 3 show the scanning electron micrographs (SEM) of CZTS thin films prepared at different substrate temperatures. In case of CZTS film prepared at 175 ℃ (Fig. 3.(a)) represents uniformly coated surface over which CZTS granules average size of 644 nm were distributed. As the temperature increases the surface morphology of CZTS films was found improved into spherical granules of CZTS crystals of increasing size from 640 nm to 1.8 μm represented by figures 3(a) to 3(d) of CZTS samples deposited at 175 to 275℃ substrate temperatures. The film samples CZTS deposited 250℃, and 275℃ represented by figures 3 (c and d) composed of excellent spherical granules of CZTS crystals arranged in regular fashion with some void spaces. The increase in particle size as compared to crystallite size from XRD data may be due to agglomeration of CZTS crystallites. The film deposited at 300 ℃ shows similar morphology as that of sample prepared at 175 ℃ substrate temperature. This type of similarity was also observed in XRD spectra of samples deposited at 175 and 300℃ substrate temperatures.

3.4 Elemental Analysis

The EDX spectra of film sample CZTS (275℃) was shown in figure 4. Elemental composition of Cu, Zn, tin and S of CZTS thin films prepared at different substrate temperatures are presented in Table 2. The films samples deposited for 175, 200 and 300 ℃ are inherently sulphur rich. However, the samples deposited for 250 and 275℃ shows equal initial and final atomic % which is essential for stoichiometric combination of CZTS phase formation. This effect is also reflects in XRD and SEM images of the samples.

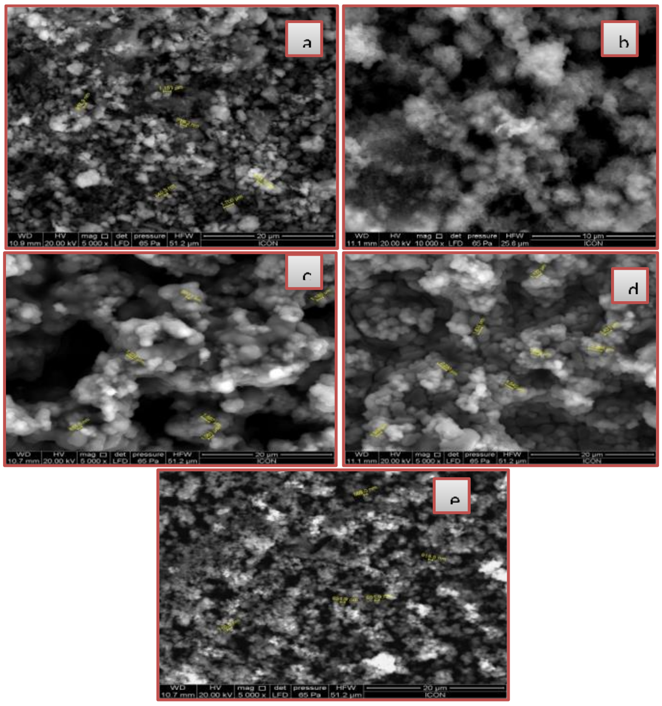

Fig.3. SEM micrographs of Spray Deposited CZTS Thin films

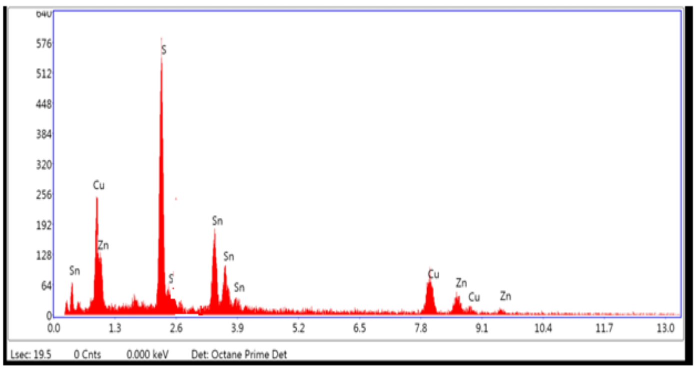

Fig.4. EDX Spectra of CZTS (275℃) Sample

Table 2. Elemental composition of CZTS films

Substrate Temperature	Atomic % of the composition			
	Cu	Zn	Sn	S
175℃	15.17	7.43	9.76	67.63
200℃	17.90	8.92	7.08	66.09
250℃	25.30	11.93	12.52	50.25
275℃	25.00	12.5	12.5	50.00
300℃	15.78	11.03	14.48	58.71

3.5 UV Visible study

Figure 5 shows the plot of absorption coefficient (α cm^{-1}) versus the photon energy (eV) for CZTS thin films deposited by varying substrate temperature. It can be seen that all the films have relatively high absorption coefficients between 10^4 cm^{-1} and 10^5 cm^{-1} in the near-IR and the visible spectral range. It is also noted that the absorption coefficient decreased for thin films deposited with increasing substrate temperature, especially for 175 ℃ to 275℃ however film deposited for 300℃ substrate temperature shows sudden increase in absorption coefficient.

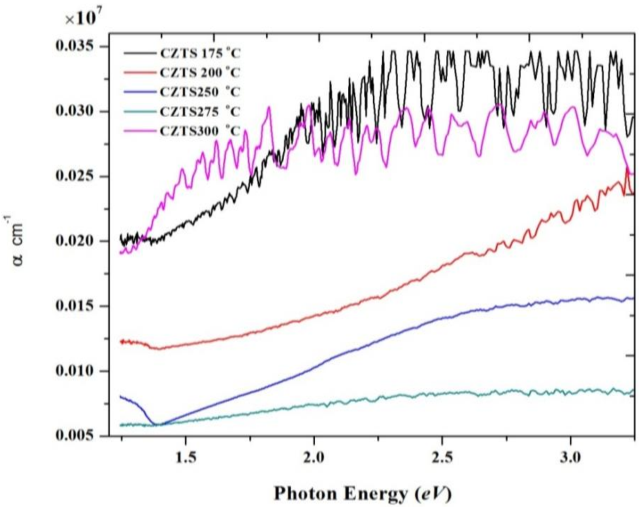

Fig. 5. Absorption Coefficient (α) is plotted verses Photon Energy

Tauc's plots of CZTS thin films have been shown in Figure 6. The band gap values obtained from Tauc's plots were found in the range 1.4 eV to 1.65eV. The variation of band gap verses substrate temperature was presented in figure 7. The band gap was decreased with increase in crystallite size and increase in substrate temperature as revealed from XRD analysis (Table 1). The observed band gap values of CZTS thin films shows similar range (1.45 eV to 1.6 eV) as proposed by other reports [26, 27]. This shows that optical band gap of CZTS thin films may be effectively tuned by varying substrate temperature.

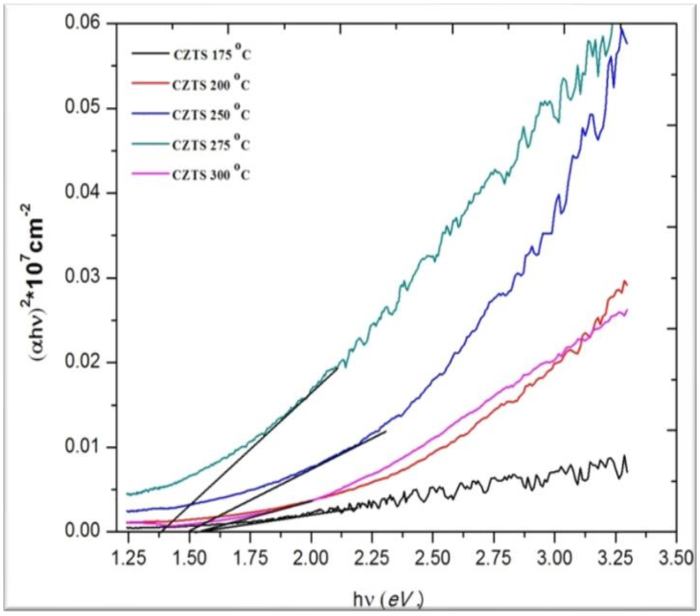

Fig.6. Tauc's Plots for CZTS thin films

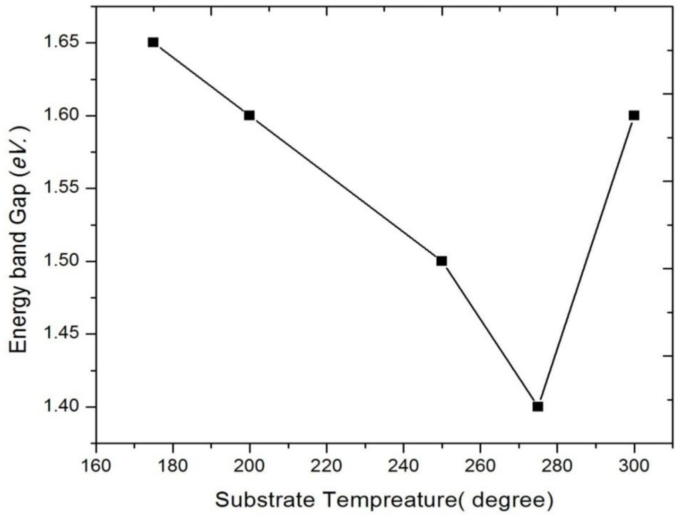

Fig.7. Plot of Variation of Band gap Verses Substrate Temperature

3.6 Room temperature resistivity of CZTS Thin film

The room temperature dc- electrical resistivity was estimated by using I-V curve. Figure 8 shows I-V characteristics curve of deposited CZTS thin films. The I-V curve shows linear and ohmic behavior for CZTS thin films. The sheet Resistance was calculated from the slope of IV Characteristic using relation (4).

Table 3. Resistivity of deposited CZTS thin films

Film Sample	Thickness (µm)	Sheet resistance R_s (Ω)	Resistivity ρ (Ω-cm)
CZTS (175 ºC)	3.26	29.9	9.746×10^{-2}
CZTS (200 ºC)	3.37	18.1	6.09×10^{-2}
CZTS (250 ºC)	3.51	14.2	4.98×10^{-2}
CZTS (275 ºC)	3.67	1.532	0.5622×10^{-2}
CZTS (300 ºC)	3.56	5.96	2.98×10^{-2}

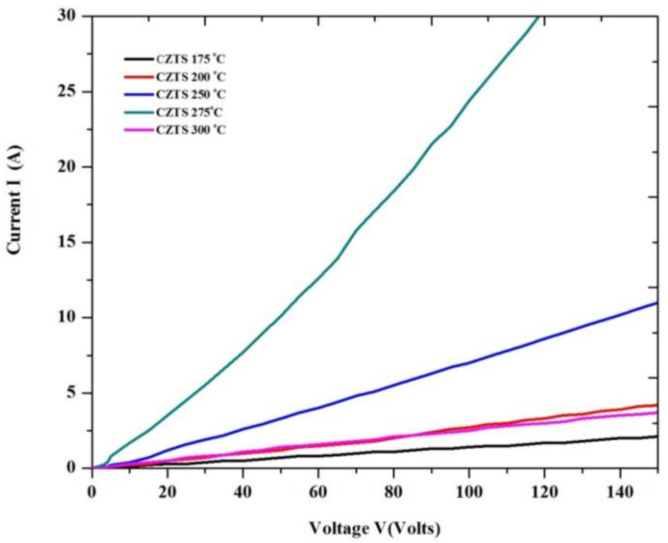

Fig. 8. Room Temperature IV Characteristics of CZTS Thin Films

The calculated sheet resistance was to be in the 1.532 to 29.9Ω range . The D. C. resistivity ρ of the CZTS films was estimated by using equation (5). The dc-electrical resistivity of CZTS thin film was to be order of 10^{-2} Ω-cm. The similar results have been reported in the earlier work by other researcher (25). The film sample deposited for 275 ℃ exhibit low dc-electrical resistivity as compared to other CZTS samples.

4. Conclusion

CZTS thin films have been prepared by using chemical spray pyrolysis technique by varying substrate temperature. Influence of substrate temperature variation on structure, morphology and optical properties of CZTS films have been investigated by using variety of techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Visible spectroscopy, etc. The formation of CZTS has been confirmed by XRD and elemental analysis. The XRD analysis reveals formation of kesterite tetragonal CZTS phase with preferential orientation along (112) direction. The SEM images show that microstructure of CZTS films was improved by varying substrate temperature. The elemental analysis confirm that purity and stoichiometry of CZTS phase of deposited films. The entire CZTS films shows absorption coefficient (α) is higher than order of 10^4 cm^{-1}. All CZTS thin films exhibit optical band gap was to be in the range 1.4-1.65eV. The dc electrical resistivity was to be in the range 0.5622×10^{-2} to 9.746×10^{-2} $\Omega - cm$. On the basis of results discussed in the report it was concluded that film sample deposited for 275 ℃ exhibit significant crystallinity, higher crystallite size 64 nm good elemental stoichiometry, higher absorption coefficient$\geq 10^4\, cm^{-1}$ and optical band gap 1.4 eV and dc electrical resistivity was about 0.5622 $\times 10^{-2}$ $\Omega - cm$ suitable for device application.

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