EFFECT OF COPPER CONCENTRATION ON STRUCTURE MORPHOLOGY AND OPTICAL BAND GAP OF SPRAY DEPOSITED CZTS THIN FILMS

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ABSTRACT

Cu2ZnSnS4 (CZTS) films were deposited for five different molarity of Copper chloride ($CuCl_2$) by using simple chemical spray pyrolysis technique at substrate temperature of (275±5)°C. Analytical Grade; Copper chloride ($CuCl_2$), zinc chloride ($ZnCl_2$), tin chloride ($SnCl_4.5H_2O$) and thiourea (SC $(NH_2)_2$) were used as sources of copper (cu^+), zinc (Zn^+), tin (Sn^+) and sulfur (S^-) ions respectively. A set of five CZTS films was deposited using five different molarity of $CuCl_2$. The structure, morphology and optical properties of deposited CZTS films were studied using X-ray difractometer (XRD), Scanning Electron Micrographs (SEM) and UV-Visible spectroscopy respectively. The XRD spectra showed that all films are polycrystalline tetragonal crystal structure with Kesterite phase. The crystallite size estimated using full width at half maximum (FWHM) of (112) peak was increased with increase in concentration Cu^+ ions. Optical band gap shows similar variation as that of crystallite size.

Keywords: CZTS Thin Films, Chemical Spray technique, XRD, band gap, Optical Parameters.

I. INTRODUCTION

Thin film solar cells based on chalcoegnide compound of stoichiometry Cu_2(MII(MIV) S, Se$)_4$ (MII=Mn, Fe, Ni, Zn, Cd, Hg) and MIV =(In, Ge, Sn.) have got vital impotence because Copper indium gallium selenide (CIGS) was well established, stable solar cell systems. Extensive work have been reported on CIGS [Cu_2 (InGa) S4] and Cu_2 (InGa) Se_4 based thin film solar cells of conversion efficiency up to 20.3 %. However Indium (In) and Germanium (Ge) elements are toxic, less abundance, and expensive which limits the large scale production of devices [1]. Cu_2ZnSnS_4 (CZTS) is quaternary p-type semiconductor has direct optical band gap about 1.2-1.5 eV and absorption coefficient 10^4 cm^{-1} very similar to CIGS type thin film solar cells [2-3]. The elements used in fabrication of CZTS material are non-toxic, higher abundance and cheap in cost. Newest report show 11.1% and 12.6 % conversion efficiency of CZTS based solar cells [4-5], CZTS is to be therefore a suitable candidate to be used as an absorber layer thin film solar cell devices. In above point of view, researchers have much encouraged to fabricate low cost and large scale CZTS based solar cell devices.

The elemental variation plays vital role to obtain good stoichiometric CZTS films with pure kesterite phase. Numbers of reports were available on the structural properties of the CZTS thin films and on the elemental composition variation. The variation of copper concentration on the structural and phase purity of the CZTS have been reported in the earlier literature [6]. The copper rich CZTS nanoparticles were prepared by a simple hydrothermal method with different concentration ratios of sulfur and copper and the results were reported in the literature [7]. Several other techniques have been reported by the researchers in the preparation of CZTS thin films, such as Radio Frequency (R. F.) sputtering [8], Sol-Gel sulfurization method [9], pulsed laser deposition [10], electron beam evaporation [11], etc. However the no reports were available on synthesis of CZTS thin films using different concentration Copper ion by chemical sprays pyrolysis method. Most of the methods of preparation need sulfurization process after the CZTS deposition. In this article we explore simple low cost spray pyrolysis technique using perfume atomizer without sulfurization for preparation CZTS films.

II. EXPERIMENTAL

CZTS thin films were deposited on simple soda lime glass substrates. The substrates were cleaned ultrasonically using acetone, ethanol and distilled water and dried by hair drier. The precursor solution was obtained by mixing specific molarity solutions of reagents such as copper chloride ($CuCl_2$), zinc chloride ($ZnCl_2$), stannic chloride ($SnCl_4.5(H_2O)$) and thiourea ($SC(NH_2)_2$). The preparation of precursor the cationic solutions are prepared in pure ethanol medium. Thiourea solution was prepared by using 50% ethanol and water to avoide the formation of tin hydroxyl $Sn(OH)_4$. To study the effect of Cu^+ concentration the molarity of $CuCl_2$ was varied as 0.015, 0.02, 0.025, 0.03, 0.035 M and molarities of ZnCl2 and $SnCl_4$ 5 (H_2O) were kept fixed as 0.015M. The molarity of thiourea was kept fixed as 0.06 M. The above prepared solutions are stirrer for one sand half hour. Thus set of five precursors were prepared for five different molarity of $CuCl_2$. The precursors were sprayed on substrate maintained at desire temperature on hot plate by locally available perfume atomizer. The temperature of hot plate is controlled by digital temperature controller. The distance 30 cm of spraying nozzle form substrate and spray rate 5 ml per second and spraying time 45 second were kept constant. A set of five CZTS films were prepared for different molarity of $CuCl_2$. The deposited were removed after cooled down to room temperature. The deposited CZTS thin films are characterized by variety of characterizations and their results were discussed in this report.

III. RESULTS AND DISCUSSION

3.1 Physical Characterization

The thickness (t) of the deposited CZTS films is calculated by using weight and difference method [12], using following well known relation.

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

Where, m is the deposited mass in grams (*gm*), ϱ *is* density of deposited material in grams per cubic centimeter (gm/cm^3)and A is the area of deposited film in cm^2. The variation of film thickness with Cu^+ ions concentration was shown in Figure 1.

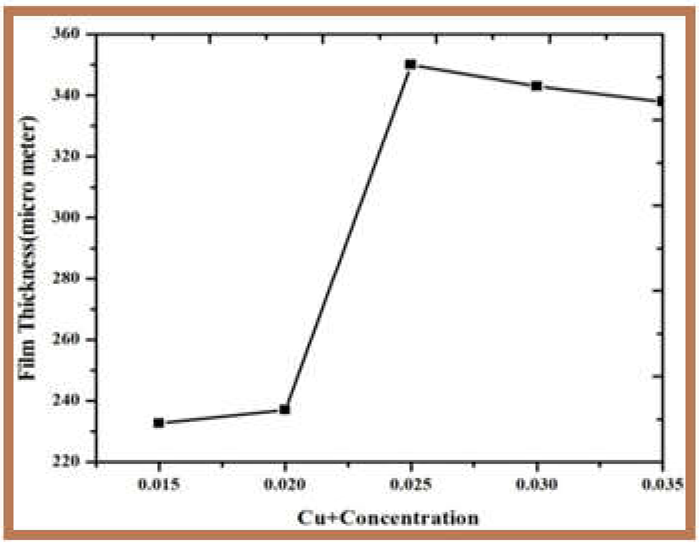

Figure 1. Film Thickness of CZTS films plotted Verses Cu^+ ion concentration

Film thickness was increased with increase in Cu^+ ion concentration. The maximum value of film thickness was to be 351 μm for 0.015M copper concentration beyond 0.15 M copper concentration value thickness was decreased. This confirm that copper ion concentration or molarity of $CuCl_2$ plays significant role in growing CZTS film and maintaining stoichiometry of the composition

3.2 Structural Study

XRD spectra were recorded by using MiniFlex II X-Ray Diffractometer in the range 20°-80°. Figure 1 shows the XRD pattern of deposited CZTS thin films. XRD patterns for all films show three major peaks at Brag's angles 2θ~28.57°, 47.38° and 56.05° which are assigned by (112), (220) and (312) lattice planes respectively. These values are well matched with standard diffraction data of card number (26-0575) which represents kestrites crystal structure. This show that present XRD pattern confirmed the kesterites crystal phase with tetragonal polycrystalline crystal structure. Absence of the impurity and secondary peaks gives the formation of the pure and good quality CZTS thin films similar findings have been reported in earlier literature [13]. The XRD spectra show that the intensity of (112) peak was increased with increase in molarity of $CuCl_2$. However on increasing molarity of CuCl2 beyond 0.03 M, height of XRD peak gets decreased. This concluded that crystallinity of CZTS films was depends on molarity of $CuCl_2$. Thus Cu^+ ion concentration plays important role to maintain the stoichiometry and crystallinity of CZTS films. The full width at half maximum (FWHM) was obtained from Lorentzian fit of (112) preferential peak for calculation of crystallite size. The crystallite size was calculated using following Sucherrer's relation [14] and displayed in Table 1.

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

The crystallite size estimated shows that all the films are composed of nano sized CZTS crystals. The crystallite size was increased with increase in molarity of $CuCl_2$. The maximum crystallite size was obtained for 0.03 M copper concentration molarity.

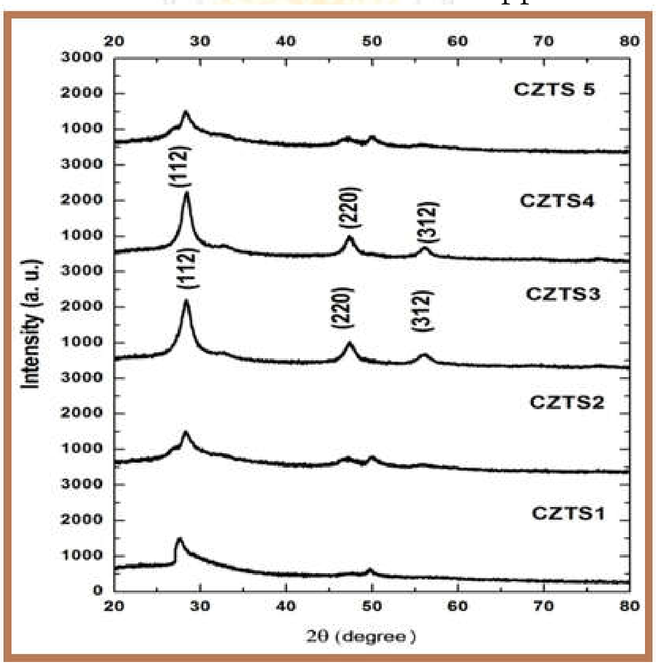

Figure 2. XRD Patten of CZTS Thin films

However the crystallite size was observed decreased for further increase in Copper concentration. Similar finding have been reported in the literature [13].

Table 1. XRD Data, FWHM and Crystallite Size

Sample film	2θ	d values	FWHM (β)	D (nm)
CZTS1	28.3529	3.145	13.61069	10.66
CZTS2	28.37571	3.1469	2.569298	33.25
CZTS3	28.41483	3.1511	2.32056	36.82
CZTS4	28.63008	3.1449	2.31412	38.12
CZTS5	28.63016	3.1551	4.595373	20.51

2θ= Brag angle in degree, d=Interplaning spacing in degree,
β = FWHM in radians, D= Crystallite size in nanometers.

3.3 Surface Morphology of CZTS4 Thin Films

Figure 3 show the Scanning Electron micrograph (SEM) of Sample CZTS4.

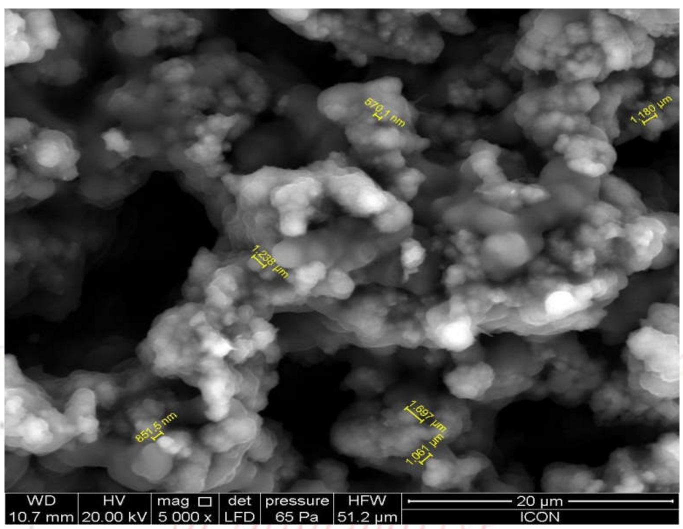

Figure 3. SEM micrograph of CZTS 4 Thin film

Sample was scanned at 5000X magnification. SEM image revealed that whole surface is uniformly covered with spherical granules with some void spaces. The spherical granules are arranged in regular fashion. The average grain size of spherical granules estimated by using linear intercept method was to be 1.1073 µm. The average grain size is larger than crystallite size obtained from XRD data. The increase of grain size is due to agglomeration of CZTS crystallites.

3.4 Elemental Analysis:

Elemental analysis of CZTS4 sample was carried out using Energy-Dispersive X-ray Analysis (EDX). The figure 4 shows the EDAX spectra. The figure 4 revealed that prepared sample composed by Copper, Zinc and Tin and Sulfur elements.

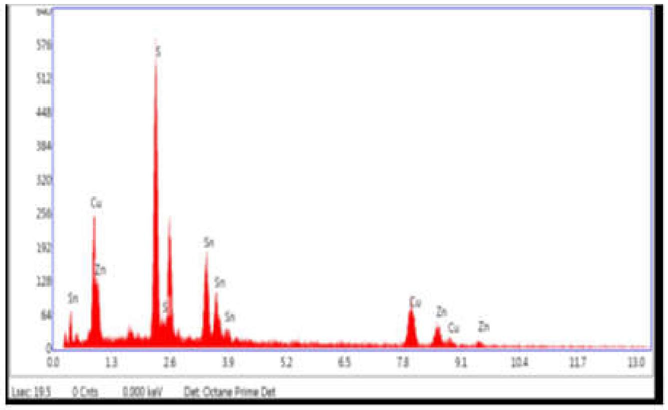

Figure 4. EDX Spectra of CZTS4 thin film

The initial and final weight as well as atomic % was shown in Table 3. Initial and final weight % and atomic % are nearly equal which confirm the stoichiometry of Cu_2ZnSnS_4 phase. EDX analysis shows that there was no any impurities present in the deposited sample.

Table 2. Initial and Final Atomic Weight % of CZTS 3 Thin Film Sample

Element	Initial		Final		Grain size (µm)
	Weight %	Atomic %	Weight %	Atomic %	
S K	29.04	50.00	28.67	49.22	1.1073
SnL	28.03	12.50	26.41	12.25	
CuK	26.86	25.00	28.67	24.84	
ZnK	16.07	12.50	16.25	13.69	
Total	100	100	100	100	

3.5 Optical Study

Optical absorption spectra of CZTS films were recorded in spectral range of (350–999) nm by using double beam UV–visible spectrophotometer Systronics 2201. The variation of optical absorption with wavelength (nm) was shown in Figure 4. It is noticed that the optical absorption for all CZTS films decreased exponentially as wavelength increased in the range 350 -800 nm, and then increases slowly at higher wavelengths.

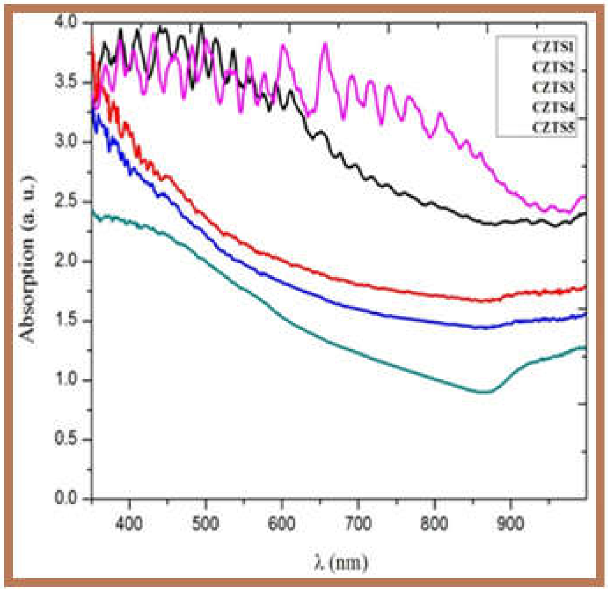

Figure 5. Absorption spectra of CZTS Thin Films

The absorption was observed decreased with increase in copper concentration from sample CZTS1 to CZTS4 and for CZTS5 it shows abrupt increase. The optical band gap is obtained by using Tauc equation (3) [15].

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

where (E_g) the optical energy gap of the film, (A) is a constant, ($h\nu$) is the incident photon energy and n is a numeric value equal to (1/2) for allowed direct transition.

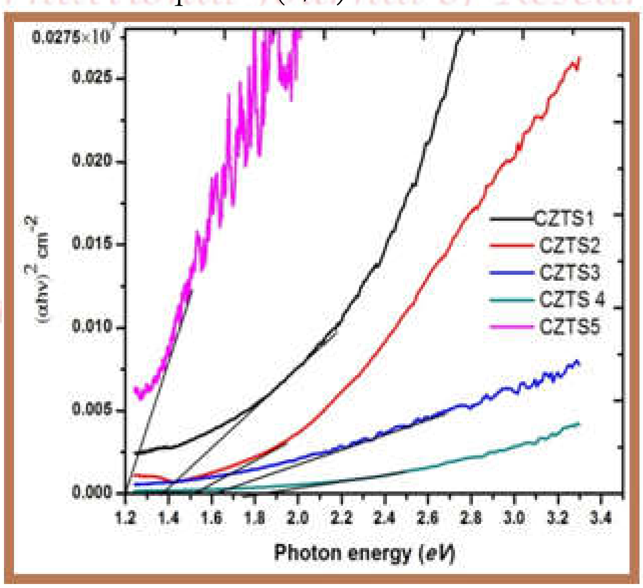

Figure 6. Tauc's Plots of CZTS films

All the films shows higher absorption coefficient of the order of $\geq 10^4$ cm^{-1}. The optical band gap was estimated by Tauc's plots as shown in Figure **5** where a graph of $(\alpha h\nu)^2$

versus (hν) is plotted and the extrapolating linear portion of the curve gives the value of the direct optical band gap of the deposited CZTS films [16].

All film samples (CZTS1, CZTS2, CZTS3, CZTS4 and CZTS5) exhibit optical band gaps 1.4 1.52, 1.162, 1.8 and 1.2 *eV* respectively. The figure 7 shows plot between molarity of $CuCl_2$ and band gap.

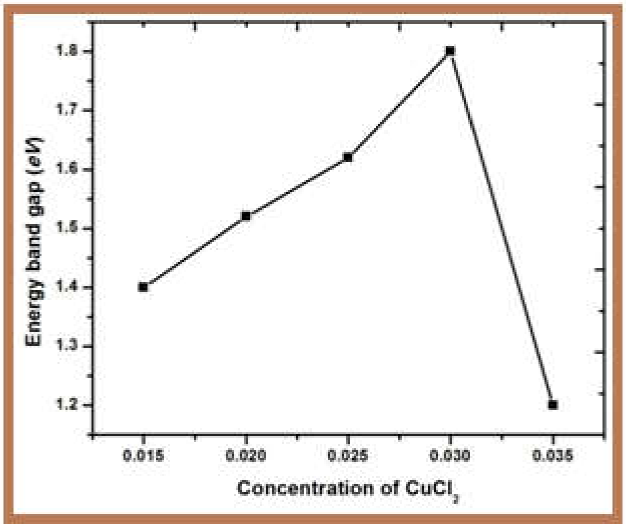

Figure 7. Variation of Band gap Verse $CuCl_2$ concentration

The optical; band was increased with increase in crystallite size and molarity of $CuCl_2$. However sample CZTS5 shows decrease in band gap as compared to other samples. The variation of band gap is related to variation in crystallite size of CZTS deposited material, which is in agreement with report presented by other researchers [17].

IV. CONCLUSION

CZTS thin films were deposited on simple soda lime glass substrates by chemical spray pyrolysis technique using locally available perfume atomizer. The XRD results showed that the prepared films are polycrystalline having tetragonal structure. The crystallite size estimated by using Lorentz fit of (112) peak and Scherrer's formula showed that all the films composed by nano sized CZTS crystals. The crystallite size and film thickness was increased with increase in molarity of $Cucl_2$. SEM micrographs confirm that spherical grains of CZTS crystals agglomerated in regular fashion. EDAX analysis was confirmed that purity and stoichiometry of prepared CZTS films. The direct energy band gap (Eg) was in the range between (1.2 and 1.8) eV. The overall results and discussion it is concluded the Copper concentration was plays vital role to achieve pure kestriste stoichiometric CZTS thin films. The CZTS4 film sample deposited for 0.03 M copper concentration exhibit maximum crystallite size 38 nm, excellent surface morphology, higher absorption coefficient $\geq 10^4$ $cm^{-1}$and higher band gap1.8eV can be used as a good candidates as an absorber layer in solar cells Provided that the electrical characterizations and PEC measurements are to be study and it is the future work.

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