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Structure, morphology and optical parameters of spray deposited CZTS thin films for solar cell applications

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Abstract

Objectives: To develop simple method for Cu_2ZnSnS_4 (CZTS) thin film deposition suitable for solar cell device application. **Method:** Cu_2ZnSnS_4 (CZTS) thin film was deposited by using simple chemical spray pyrolysis technique for substrate temperature (270±5) °C. Analytical reagent Grade 0.025 M Copper chloride ($CuCl_2$), 0.0125 M zinc chloride ($ZnCl_2$), 0.0125 M Tin chloride ($SnCl_4.5H_2O$) and 0.05 M Thiourea (SC $(NH_2)_2$) were used as sources of copper (cu^+), zinc ($Zn^{+)}$, tin (Sn^+) and sulfur (S^-) ions respectively. The structure, morphology and optical band gap of the film were investigated by using X-ray Diffractometer (XRD), Scanning Electron Micrograph (SEM) and UV-Visible spectroscopy respectively. Energy dispersive X-ray Analysis (EDX) was used for elemental analysis of deposited CZTS film. **Findings:** The XRD spectra showed that CZTS film exhibit polycrystalline tetragonal crystal structure with preferential orientation along (112) plane. The crystallite size calculated using full width at half maximum (FWHM) of (112) peak was to be $36.82\ nm$. SEM image revealed that film composed of regular arrangement of spherical granules of average size 1.61 μm. The purity of the CZTS phase was confirmed by elemental analysis. The calculated energy band gap (Eg) by using Tauc's plot was about 1.62 eV. The dc resistvity estimated by using IV characteristics of the CZTS film was to be 2.3×10^{-2} Ω-cm. It is concluded that CZTS film prepared using present deposition technique can be used for solar cell device applications.

Keywords: Chemical spray technique; CZTS Thin Films; band gap; structure of CZTS; electrical resistivity; elemental analysis

1 Introduction

In past four decades scientists all over the world are continuously taking efforts to develop high efficiency, solar cell devices. In recent years researchers are much more interested to develop 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.). Extensive work have been reported on Cu_2 (InGa) Se2 based thin film solar cells of conversion efficiency up to 20.6 %. However, Indium (In) and Germanium (Ge) elements are toxic, less abundant, and expensive which limits the large scale production of devices[1]. Cu_2ZnSnS_4 (CZTS) compound 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 were non-toxic, higher abundance and very economic and Cu_2ZnSnS_4 (CZTS) is one of the most promising quaternary materials exhibited 9.6 % conversion efficiency[4]. CZTS is therefore a suitable candidate to replace the CIGS as an absorber layer for 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.

Several techniques have been employed by the researchers in the preparation of CZTS thin films, such as Radio Frequency (R. F.) sputtering[5], SILAR method[6], Sol-gel method[7], pulsed laser deposition[8], Co electro deposition[9], etc. 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[10–12].

2 Material and Method

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 was obtained by mixing solutions of 0.025 M Copper chloride ($CuCl_2$), 0.0125 M Zinc chloride ($ZnCl_2$), 0.0125 M Tin chloride ($SnCl_4.5(H_2O)$) and 0.05 M Thiourea ($SC(NH_2)_2$). The molarities of the reagents were optimized previously[13]. All the solutions were prepared in ethanol medium because deionized water converts $SnCl_4.5$ (H_2O) into tin hydroxyl $Sn(OH)_4$ and free Sn^+ ions were not available for CZTS phase formation. The pure ethanol medium was therefore used for all three cationic solutions, and thiourea solution was prepared by using 50% ethanol and water. The experiment show that turbidity of mixture was depends on amount of thiourea addition. The above prepared solutions were stirrer for one and half hour. Three cationic solutions were mixed together one by one with stirring continue and then thiourea solution was added slowly such that the turbid mixture become clear homogenous precursor. This precursor was sprayed on the substrate maintained at desire temperature on hot plate by locally available perfume atomizer. The temperature of hot plate was controlled by digital temperature controller. The distance 30 cm. of spraying nozzle form substrate, spray rate of 5 ml per second and substrate temperature (275±5)°C were kept fixed. After deposition CZTS film was annealed for two hour at 275°C in muffle furnace. The annealed film sample was subjected to XRD, SEM, EDX and UV–Visible for Characterizations. The structure, morphology, optical properties and electrical properties have been investigated and the results were reported in this paper.

3 Results and Discussion

3.1 Physical Characterization

The thickness (t) of the deposited CZTS film was calculated by using weight and difference method by following well-known relation.

$$t = \frac{m}{\rho A} \tag{1}$$

Where, m (*gm*) is the deposited mass, ρ ($\frac{gm}{cm3}$) is density of deposited material and A ($cm2$) is the area of deposited film. The thickness of CZTS film obtained was to be 351 μm.

3.2 Structure of CZTS Thin film

XRD spectra were recorded by using MiniFlex II X-Ray Diffractometer in the scanning range of 20-80º. Figure 1 shows the XRD patterns of CZTS films. XRD pattern represents the polycrystalline Kasterite crystal structure with Bragg's reflections at (2θ~28.57º, 32.06 º, 47.38○ and 56.05○) which are assigned to (112), (200), (220) and (312)

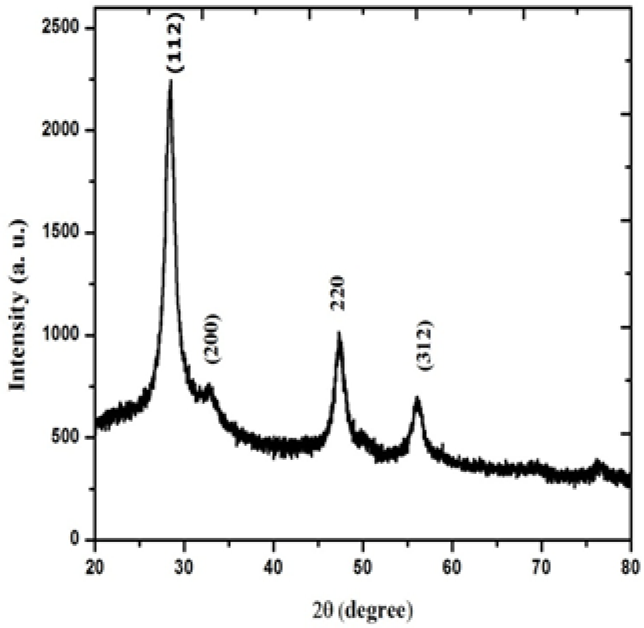

Fig 1. XRD spectra of CZTS thin film

lattice planes respectively. Similar structure have been reported by Diwate, K et al.(2017)[14].

These values are in good agreement with the International Center of Diffraction Data (ICDD) card number (26-0575). The full width at half maximum (FWHM) was obtained from Lorentzian fit of (112) preferential peak. The crystallite size (D) was calculated using following Sucherrer relation[15] and displayed in Table 1.

$$D = \frac{0.94\lambda}{\beta cos\theta} \tag{2}$$

Where, λ is wavelength of X-ray (0.1504nm), β is full width at half maximum and θ is Brag's angle (degree). The calculated crystallite size was to be 36.82 nm for CZTS film. This shows that the film was composed of CZTS nano Crystals. The lattice parameters 'a' and 'c' for tetragonal unit cell have been estimated by using following relation[16].

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \tag{3}$$

where d is the lattice plane space and (hkl) the miller indices corresponding to XRD peaks. The estimated values of lattice constants 'a' and 'c' were to be 5.4202 A^o and 10.932A^o respectively. The values of lattice parameters were similar to the standard values (a = 5.435 A^o, c = 10.843 A^o) obtained from JCPDS Card No: 26-0575.

Table 1. Brag's angle, interplaner distance and crystallite size of CZTS thin film

Film Sample	2θ	d values	FWHM (β)	D (nm)
CZTS	28.41483	3.1511	2.32056	36.82

3.3 Surface Morphology of CZTS Thin film

Figure 2 shows Scanning Electron Micrographs (SEM) of deposited CZTS thin film. The film Sample was scanned at magnification 5000X. SEM image revealed that whole surface was uniformly covered with spherical granules. The CZTS spherical granules are arranged in regular fashion with some void spaces. The average grain size 1.63 μm was obtained by using linear intercept method. The average grain size was found to be larger than crystallite size obtained from XRD data. The increase of grain size is due to agglomeration of CZTS crystallites.

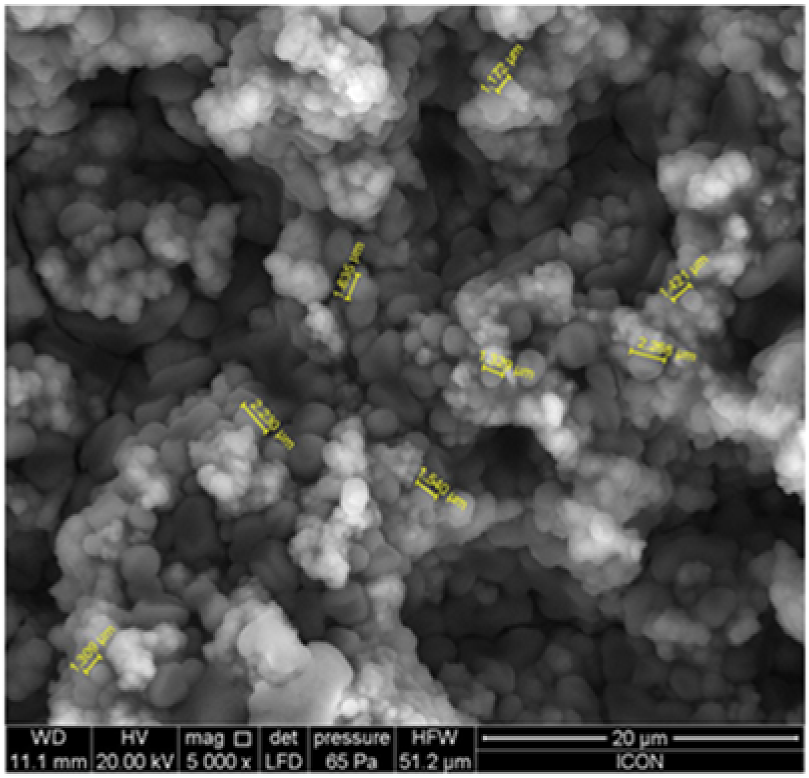

Fig 2. SEM image of CZTS film

3.4 Elemental Analysis of CZTS Thin films

Elemental analysis of CZTS sample was carried out using Energy-Dispersive X-ray Analysis (EDX). Figure 3 shows EDX spectrum of CZTS film. Figure 3 showed that prepared sample composed by Copper, Zinc and Tin and Sulfur elements. The initial and final weight as well as atomic % was shown in Table 2.

Initial and final weight and atomic % are nearly equal which confirm that film composed of Cu_2ZnSnS_4 phase formation**.**

Table 2. Initial and final weight% and atomic %

Element	Initial Weight %	Initial Atomic %	Final Weight %	Final Atomic %	Grain size (μm)
S K	29.04	50.00	28.67	49.22	
SnL	28.03	12.50	26.41	12.25	
CuK	26.86	25.00	28.67	24.84	1.613
ZnK	16.07	12.50	16.25	13.69	
Total	100	100	100	100	

3.5 Optical absorption study and band gap

Optical absorption spectra of CZTS film was recorded in (350–999) nm spectral range of electromagnetic spectrum by using double beam UV–visible spectrophotometer Systronics 2201. Figure 4 shows the variation of opti-

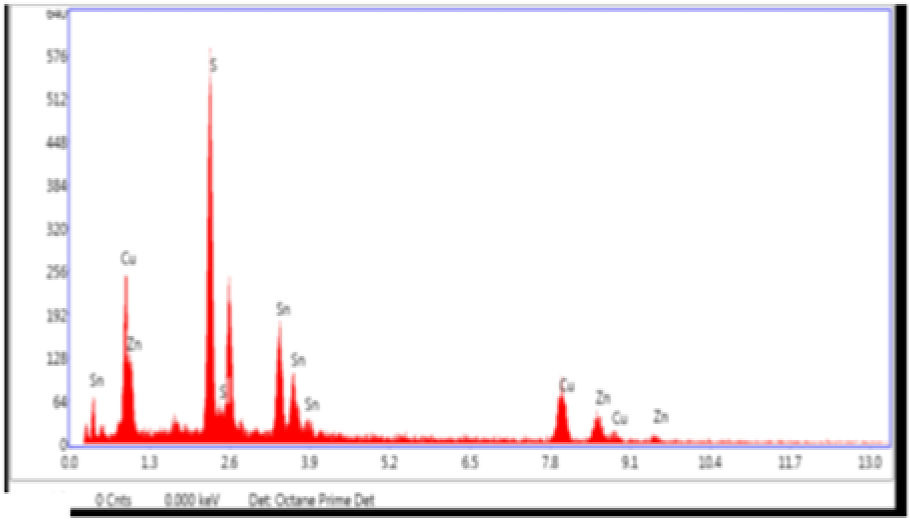

Fig 3. EDX Spectra of deposited CZTS thin film

cal absorption with wavelength (nm) of deposited CZTS film. It was noticed that the optical absorption of CZTS films decreased exponentially with increase in wavelength in the range 350 -800 nm, and then increased slowly at higher wavelengths. The film exhibits higher absorption coefficient α and is of the order of $\geq 10^4 cm^{-1}$. Tauc relation explains the variation of the absorption coefficient α is linked to the band gap Eg of the material. Tauc relation was given below[17].

$$\alpha hv = A\,(hv - E_g)^n \tag{3}$$

Where (Eg) 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. The optical band gap was estimated by Tauc's plots. Figure 5 shows the Tauc plot in which a graph of $(\alpha h\nu)^2$ versus $(h\nu)$ is plotted. The extrapolation of linear portion of the Tauc's curve to α= 0 axis gives the value of the direct optical band gap of the deposited CZTS film[18].

The band gap obtained was about 1.62 . The obtained band gap was slightly large as compared to reported in the literature. This may be due to annealing effect, microstructural variation in the morphology and nature and the amount of secondary phases if any which were not reflected in XRD and optical absorption[19,20]. The CZTS film exhibits excellent Kieserite XRD pattern, absorption coefficient greater than $10^4 cm^{-1}$ and band gap about 1.62 eV can be used in solar cell device application. The similar findings were reported in earlier literature[18,20].

3.6 Room temperature resistivity of CZTS Thin film

The room temperature resistivity was estimated by using I-V curve. Figure 6 shows I-V characteristics curve of CZTS thin film. 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).

$$Rs = 4.53\,\frac{\triangle V}{\triangle I} \tag{4}$$

The calculated sheet resistance was to be 67.16Ω. The D. C. resistivity ρ of the CZTS film was estimsted by using equation (5).

$$\rho = Rs\ \times t \tag{5}$$

The dc resistivity of CZTS thin film was to be 23.57×10^{-3} Ω-cm or 2.3×10^{-2} Ω-cm. The similar results have been reported in the earlier work by other researcher[21].

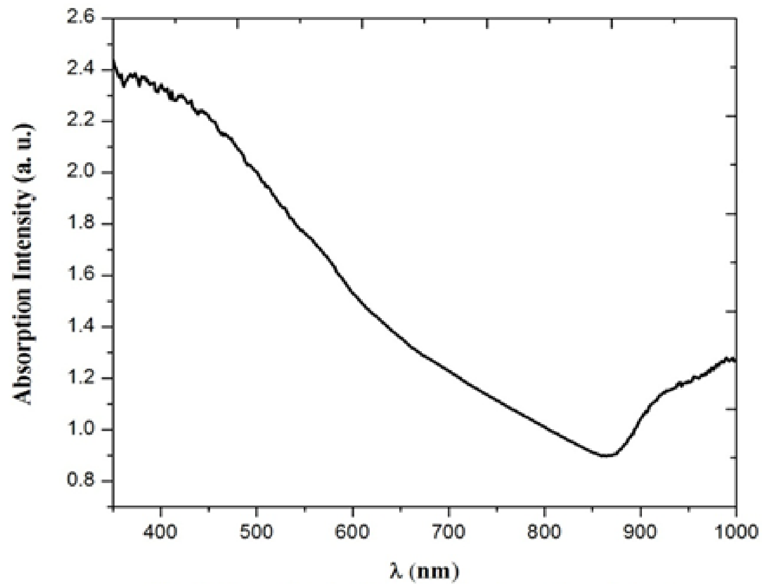

Fig 4. Absorption spectra of CZTS film

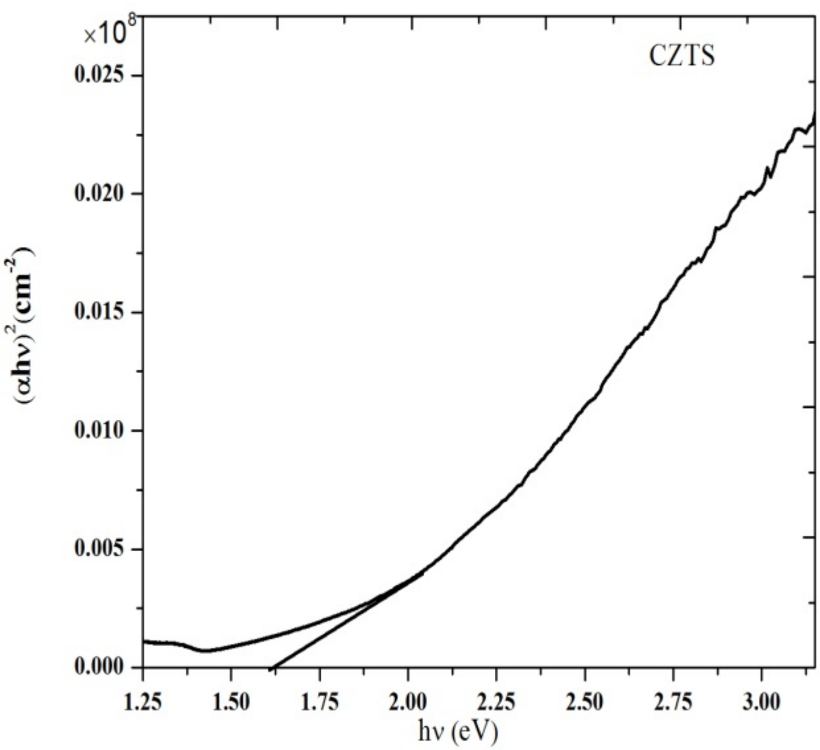

Fig 5. Tauc Plot of CZTS thin film

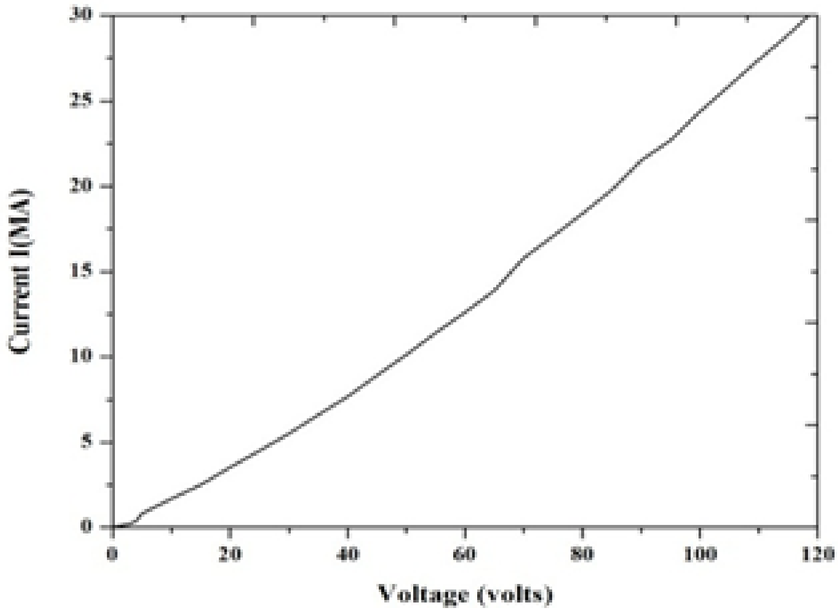

Fig 6. Room Temperature IV characteristics of CZTS

4 Conclusion

CZTS thin film was deposited on simple soda lime glass substrates by chemical spray pyrolysis technique using locally available perfume atomizer. The XRD results showed that prepared films were polycrystalline, tetragonal crystal structure. The crystallite size estimated was to be 36.82 nm. SEM micrographs confirm that spherical grains of CZTS crystals were agglomerated in regular fashion with some void spaces. EDAX analysis was confirmed that purity and stoichiometry of prepared CZTS films. The calculated direct energy band gap (Eg) was about 1.62 *eV*, the room temperature dc electrical resistivity obtained from I-V characteristics was about 2.3×10^{-2} Ω-cm. The fabrication of solar cell of the type (CZTS/CdS) is needed to study the conversion efficiency and it is the future work. On the basis of overall results and discussion, it was concluded that presently deposited CZTS sample exhibits Kasterite crystal structure of 36.82 nm crystallite size, higher absorption coefficient $\geq 10^4 cm^{-1}$ and with band gap of about 1.62 *eV* which can be used as better candidates for solar cell device application.

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