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INVESTIGATION OF STRUCTURAL AND OPTICAL PROPERTIES OF SINGLE PHASE CZTS THIN FILMS SYNTHESIZED BY SPIN COATING TECHNIQUE

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ABSTRACT

In the present work, the $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films are prepared by spin coating technique. The phase purity of prepared film is confirmed by X-ray diffractometer technique. The CZTS thin film shows single phase of kesterite structure with a dominant peak at 28.7° corresponds to the plane (112) which also confirmed by Raman peak at 331 cm^{-1} . The coefficient of absorption and direct band gap values of 10^4 cm^{-1} and 1.50 eV , respectively are determined by UV-Visible spectrophotometer technique. The optical results show that prepared thin film is ideal for solar cell applications. The SEM images shows that a uniform and homogeneous film is prepared which has an average particle size of 36.0 nm . Furthermore, the surface morphology and roughness determined by the AFM technique confirm that a smooth thin film of CZTS is prepared. The Hall measurements showed the p-type conductivity with carrier concentration $\sim 1.55 \times 10^{16}\text{ cm}^{-3}$, conductivity $\sim 65.08 \times 10^{-2}\ \Omega^{-1}\text{cm}^{-1}$, and hall mobility $\sim 26.15\text{ cm}^2/\text{Vs}$ at room temperature. Therefore the present research work provides a good quality CZTS thin film prepared by sol-gel assisted spin coating technique, which is cost-effective and also applicable for large scale production.

Keywords: Thin film, Sol-gel process, X-ray diffraction, Raman, Solar cell

1. INTRODUCTION

The solar cell is an important part of a clean and renewal energy generation system, which converts solar energy into electric energy [1]. For largescale power generation, thin film based solar cells are viable option. Copper Indium Selenide (CIS), Cadmium Telluride (CdTe), and Copper Indium Gallium Selenide (CIGS) are good absorbing materials for thin film solar cells due to their moderate efficiencies, but these materials are costly and toxic in nature [2-11]. To solve these problems $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a promising absorbing material because all the elements of CZTS are earth-abundant, non-toxic and environmentally friendly. Also, CZTS is a p-type direct band-gap semiconducting material having wide band gap $1.4\text{-}1.5\text{ eV}$ and high absorption coefficient (10^4 cm^{-1}) [12-15]. These CZTS thin films can be deposited by various techniques such as spin coating [16], dip coating [17], pulsed laser deposition [18], SILAR method [19], thermal evaporation [20], spray pyrolysis [21], DC and RF magnetron sputtering [22-23] and electro-deposition [24]. Sol-gel rooted spin coating is a relatively easy, cost-effective, and direct liquid deposition non-vacuum technique which has a lot of potential for largescale production [25]. The synthesis of a single-phase CZTS thin film for photovoltaic/solar

cell applications is a major problem. Yan *et al.* [26] synthesized $\text{Cu}_2\text{ZnSnS}_4$ thin film on FTO glass substrates using solvothermal method and claimed that prepared films contain lots of uniform spherical shaped particles with a mean diameter of about 5300 \AA . Furthermore, the prepared $\text{Cu}_2\text{ZnSnS}_4$ films show kesterite structure and optical energy band gap value of the films was measured at 1.51 eV . Ansari *et al.* [27] prepared CZTS thin film on glass slides using ultrasonically assisted chemical vapor deposition (CVD) method. According to XRD & Raman investigations, single-phase CZTS film is formed at 325°C temperature. The film has shown secondary phases of SnS_2 and Cu_{2x}S at 350°C and at the temperature below 325°C , well crystallized CZTS phase was not achieved. Swami *et al.* [28] prepared $\text{Cu}_2\text{ZnSnS}_4$ thin film on soda-lime glass using a spin coating technique and XRD analysis confirmed a kesterite structure with diffraction peaks corresponds to the (112), (220) and (312) planes. The main peak was also confirmed by Raman spectra at 333 cm^{-1} . According to SEM analysis, the thin film's surface was uniform. The coefficient of absorption of CZTS film was 10^4 cm^{-1} with a 1.5 eV optical band gap.

In the present research, we have prepared a single-phase CZTS thin film on ordinary glass

slide using the spin coating method. The surface morphology, structural and optical characteristics of the prepared film has also been investigated.

2. MATERIALS AND METHODS

2.1 Synthesis

The sol-gel solution was prepared by dissolving 0.0350 M of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and 0.02 M of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 50 mL Dimethyl formamide (DMF) solvent. The prepared solution was magnetically stirred at 1200 rpm on a hot plate at 45°C for 4h . Then 0.0350 M of ZnCl_2 and 0.1560 M of $\text{SC}(\text{NH}_2)_2$ were added to the above solution. Also, 2 mL of monoethanolamine was added to the above solution which helps in dissolving the metal salts completely. The final solution was further stirred by magnetic stirring for 1h at 50°C to get a transparent yellow.

2.2 Preparation of film

The prepared sol was deposited on a cleaned glass slide by spin coater at 2500 rpm . The glass substrate was cleaned before deposition by using acetone, isopropyl alcohol and deionized water respectively. The deposited thin film was baked on a hot plate at 100°C for 3 min . This procedure was repeated 5- 6 times to get thin films of required thickness. Finally, the prepared films were annealed in air for 15 minutes at 300°C .

2.3 Characterization

The prepared CZTS thin film was characterized by various techniques. The phase purity of the film was confirmed by X-ray diffractometer (PANalytical X'Pert Powder). The elemental composition was determined by using a FESEM (Nova Nano FE-SEM 450), whereas, SEM (ZEISS) was used to analyze surface morphology. The optical absorbance of $\text{Cu}_2\text{ZnSnS}_4$ thin films was determined using a UV-Vis spectrophotometer (LAMBDA 750 Perkin Elmer) in the $290\text{-}800\text{ nm}$ wavelength range. Raman spectrum was obtained using Raman spectroscopy (STR 500 CONFOCAL MICRO) at room temperature. These spectra were recorded using the 532 nm wavelength emission line of Argon ion laser. The atomic force microscopy (AFM) (Bruker) was used to determine the surface topography.

3. RESULTS AND DISCUSSION

3.1 Structural analysis

The XRD pattern of prepared CZTS thin film is shown in **Figure 1(a)**. The profile matching of obtained XRD data was done with JCPDS # 00-026-0575 file. The diffraction peaks at 28.70° , 36.26° , 46.73° and 56.54° are corresponded to the planes (112), (202), (220) and (312). The peak correspond to the plane (112) is the most intense peak. The XRD pattern completely matches with a reference pattern of kesterite CZTS phase (JCPDS # 00-

026-0575) having tetragonal structure with space group *I-42* which confirms that the high purity film is prepared without having any other secondary sulphide compounds. Therefore, we have prepared a single-phase $\text{Cu}_2\text{ZnSnS}_4$ thin film having a tetragonal structure. The lattice parameters were calculated by the formula:

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

and the values are $a = 5.37\text{\AA}$, $b = 5.37\text{\AA}$ and $c = 10.93\text{\AA}$. The unit cell volume for tetragonal structure is 315.18\AA^3 calculated by formula $V = a^2c$. The average crystal size (D) of the prepared thin film was calculated from

diffraction peak of (112) plane by using Debye–Scherer formula:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

and the value was found 11.61 nm.

The tetragonal distortion was calculated using following formula:

$$\Delta = 2 - \frac{c}{a}$$

and the value came out to -0.033 .

The dislocation density (δ) for $\text{Cu}_2\text{ZnSnS}_4$ thin film was calculated by using Williamson and Smallman's formula:

$$\delta = \frac{1}{D^2}$$

and the value is 0.007 nm^{-2} .

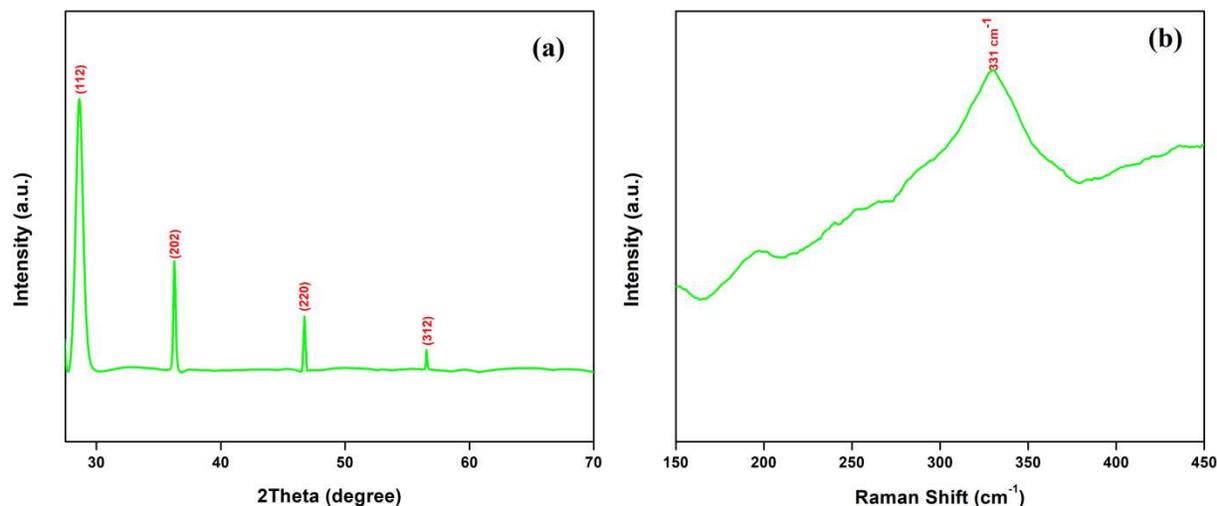


Figure 1: (a) XRD spectra of $\text{Cu}_2\text{ZnSnS}_4$ film, and (b) Raman spectra of $\text{Cu}_2\text{ZnSnS}_4$ film

The Raman spectrum of a prepared $\text{Cu}_2\text{ZnSnS}_4$ thin film is shown in the **Figure 1(b)**. A single peak centered at Raman shift of about 331 cm^{-1} was detected which most likely

corresponds to the kesterite structure of CZTS [29]. In the Raman spectra, no other peaks correspond to Cu_{2-x}S [30], Cu_2SnS_3 [31], Sn_2S_3 [32], and ZnS [33] species were

detected. Therefore, the Raman spectra also support the phase purity of the CZTS thin film and free from the contaminants such as $\text{Cu}_2\text{-xS}$, Cu_2SnS_3 , Sn_2S_3 , ZnS that are generally found.

3.2 Elemental composition

The elemental compositions of CZTS thin films were determined by EDS analysis and results are shown in **Figure 2**. A typical EDS spectrum shows peaks corresponding to Cu,

Zn, Sn, and S which indicates the presence of Cu, Sn, Zn & S elements in the film. The atomic percentages of these elements are shown in the inset table of **Figure 2**. The low atomic / weight percentage of sulfur as compared to the theoretical values may be due to the loss of sulfur content during annealing process. Therefore, to enhance compositional properties of CZTS thin films sulfurisation treatment is required.

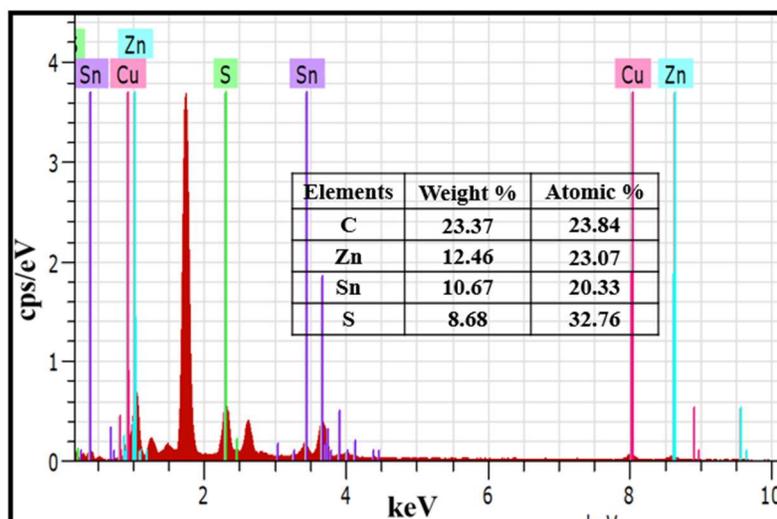


Figure 2: EDS graph of the CZTS thin film and elemental composition in inset table

3.3 Optical Properties

The optical properties of the synthesized thin film were calculated through transmittance and wavelength data taken from UV-Visible spectroscopy in the 290-800 nm wavelength range. Using the Transmittance (T) data, the Absorbance (A) has been calculated using the relation:

$$A = 2 - \log (\%T)$$

The graph between % transmittance vs. wavelength, and absorbance vs. wavelength are displayed in **Figures 3(a) & 3(b)**, respectively. The Absorption coefficient (α) of thin film can be calculated using the relation [34]:

$$\alpha = 2.303 \frac{A}{t}$$

where A and t represent the absorbance and thickness of thin film, respectively. Using the above relation, the calculated value of absorption coefficient for this thin film is found $\sim 10^4 \text{ cm}^{-1}$. Tauc formula was used for

calculating optical energy band gap value of these samples [35]:

$$(\alpha h\nu)^2 = \beta(h\nu - E_g)$$

where α , β and E_g represent absorption coefficient, energy independent constant and band gap energy, respectively.

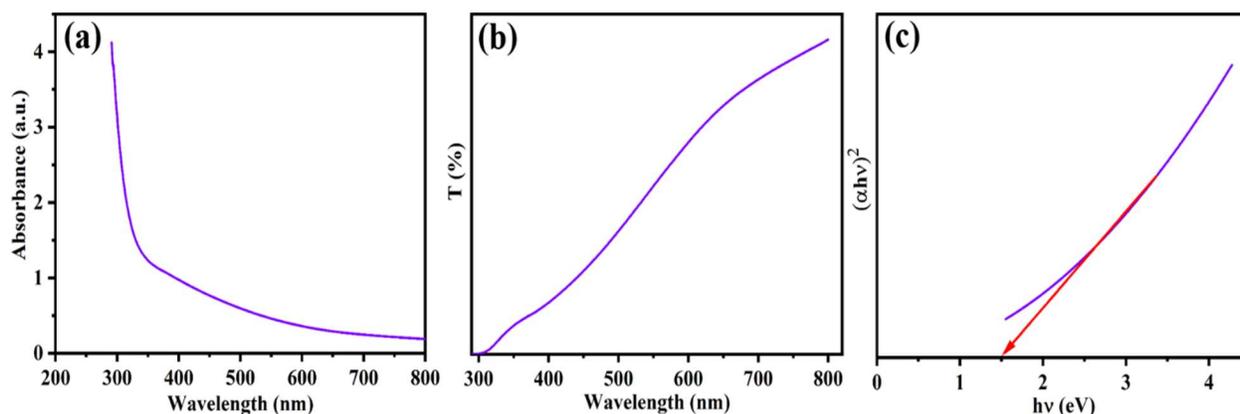


Figure 3: (a) Transmittance vs. wavelength, (b) Absorbance vs. wavelength, and (c) $(\alpha h\nu)^2$ vs. $(h\nu)$ graph of CZTS thin film

The graph between $h\nu$ and $(\alpha h\nu)^2$ is shown in **Figure 3(c)**. Linear extrapolation of graph between $(h\nu)$ and $(\alpha h\nu)^2$, to $h\nu$ axis provides band gap value (E_g). The observed value of optical energy band gap from the above plot is found about 1.50 eV . The calculated value of the band gap is comparable with known thin-film solar cell band gap values ($1.45\text{-}1.50 \text{ eV}$) [36], and corresponds to the absorber material's ideal band gap. Based on the optical properties, it can be inferred that the synthesized CZTS films are ideal for solar cell applications.

3.4 Surface analysis

The surface morphology of prepared thin film was observed by scanning electron microscope (SEM) as shown in **Figure 4**. Agglomerated particles with average diameters of about 36 nm can be seen in the high magnification image shown in **Figure 4(b)**. Thus, the SEM images of CZTS thin film indicate that the thin film has deposited uniformly over the entire substrate. Hence, the prepared thin films may be employed as good absorber layer materials for solar cell applications.

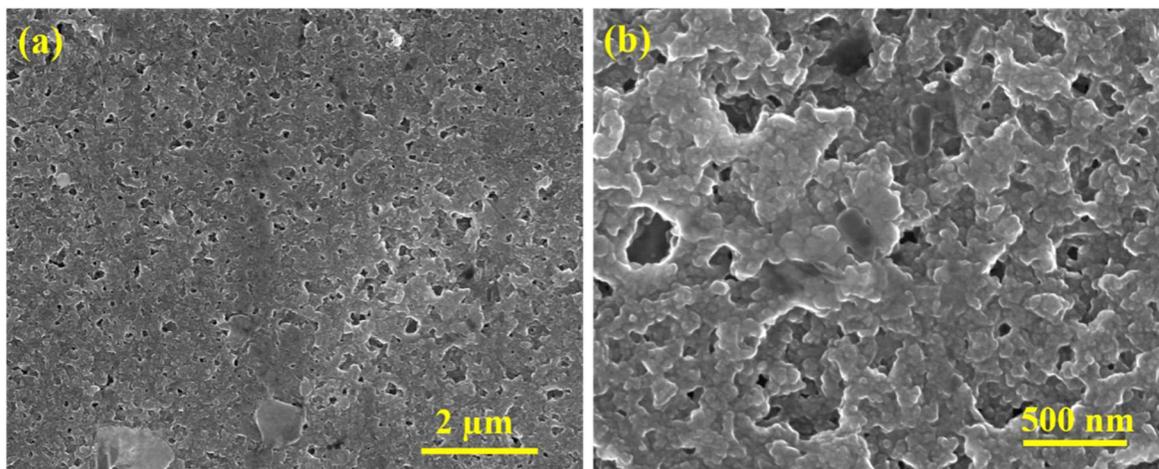


Figure 4: SEM images of as-synthesized $\text{Cu}_2\text{ZnSnS}_4$ thin film at (a) low magnification, (b) high magnification

AFM technique was used to observe 2D and 3D micrographs of prepared CZTS thin films, and results are displayed in **Figure 5 (a & b)**. The surface is uniformly covered with the particles of spherical shape as shown in the micrographs (**Figure 5a**). The surface seems

to be flat, with a vertical height between $+57.9 \text{ nm}$ (highest) and -49.9 nm (lowest). The average & root mean square (rms) roughness based on AFM micrographs were found to be 1.623 nm and 2.190 nm , respectively.

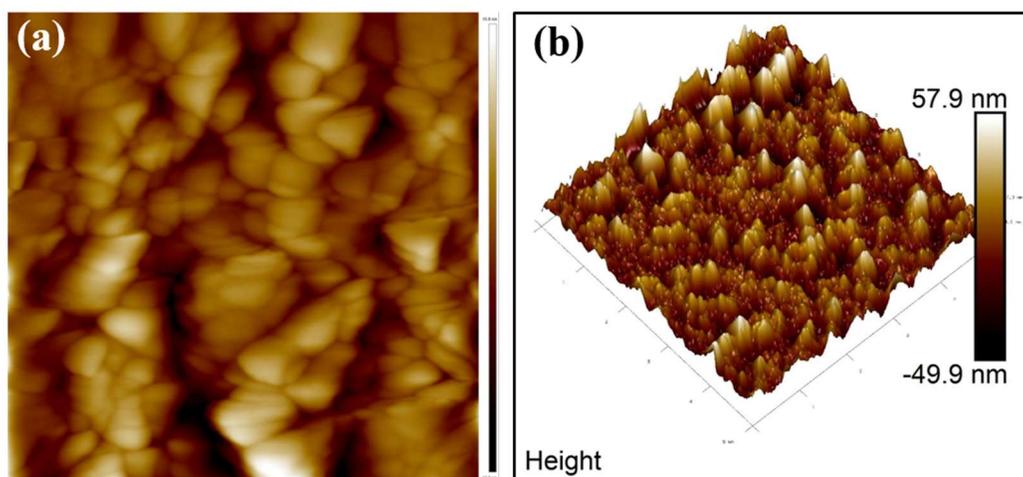


Figure 5: AFM micrographs for $\text{Cu}_2\text{ZnSnS}_4$ thin film (a) 2D micrograph, and (b) 3D micrograph

3.5 Electrical properties

The Hall measurements of the synthesized CZTS thin films have been performed at room temperature with a magnetic field intensity of

0.556 T and a current of 0.005 mA current. The positive value of Hall coefficient revealed that the synthesized thin film is a p-type semiconductor. The carrier concentration,

conductivity, resistivity, and hall mobility of synthesized thin films are obtained as $\sim 1.55 \times 10^{16} \text{ cm}^{-3}$, $\sim 65.08 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$, $\sim 0.015 \times 10^2 \Omega \text{ cm}$, and $\sim 26.15 \text{ cm}^2/\text{Vs}$, respectively.

4. CONCLUSION

In the present work, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin film has been successfully prepared through spin coating technique using the sol-gel process. The XRD results shows the CZTS thin films have a kesterite structure with a dominant peak at 28.7° corresponding to the plane (112). The Raman spectrum shows a single intense peak at 331 cm^{-1} . The absence of other Raman peaks confirms that the single phase CZTS thin film is prepared. Therefore, Raman spectra of CZTS thin films confirm the X-ray diffraction results. The deposited thin film shows p-type conductivity with absorption coefficient $\sim 10^4 \text{ cm}^{-1}$, carrier concentration $\sim 1.55 \times 10^{16} \text{ cm}^{-3}$, conductivity $\sim 65.08 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$, resistivity $\sim 0.015 \times 10^2 \Omega \text{ cm}$ and hall mobility $\sim 26.15 \text{ cm}^2/\text{Vs}$ at room temperature. The band gap of the thin film is found about 1.50 eV which is in the good agreement with the ideal value of band gap for absorbing material. The SEM results show the uniformity of the film with average particle size of about 36 nm . The AFM micrographs show the nearly flat surface of prepared thin films. The both AFM

and SEM results confirm that there are no local fractures or pinholes in the film. Therefore, the surfaces of prepared films are smooth, consistent, and tightly packed. As a result, the suggested inorganic sol-gel process offers a promising path for the quick, low-cost, and large-scale production of CZTS thin films.

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