

## Thermal Annealing Effect on Improved Structural, Morphological, Optical and Electrical Properties of $\text{Cu}_2\text{ZnSnS}_4$ Thin Film

Sandip V. Mahajan<sup>1</sup>, Sanjay R. Kamable<sup>1</sup>, Vishwajit R. Mhaske<sup>2</sup>, Anil D. Adsare<sup>3</sup>

<sup>1</sup>Department of Physics, Shikshan Maharashtra Dnyandeo Mohekar College, Kalamb, Osmanabad, Maharashtra, India

<sup>2</sup>Department of Botany, Shikshan Maharashtra Dnyandeo Mohekar College, Kalamb, Osmanabad, Maharashtra, India

<sup>3</sup>Department of Botany, Arts, Commerce and Science College, Maregaon, Dist. Yavatmal, Maharashtra, India

### ABSTRACT

Low-cost  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) absorber layer thin films have been prepared by Successive Ionic Layer Adsorption and Reaction method (SILAR). CZTS thin film prepared at room temperature without any toxic components or precursors. After synthesis thin films have annealed at 250 °C for 60 min to remove defects and improve the crystallinity. The crystal structure was studied by X-ray diffraction (XRD) characterization equipment. The as-grown CZTS thin films have shown amorphous structure but due to annealing effect improvement in crystallinity with a slight increase in peak intensity were observed. CZTS annealed thin film crystallite size is 15nm. A porous and granular structure of morphology of as-grown CZTS thin film has been confirmed by Scanning Electron Microscopy (SEM). Annealing effect decrease porosity and increase compact of the surface of a thin film. Optical properties show the increases the absorbance and decrease the band gap of as-grown and annealed samples respectively. Enhancement of current under the light condition has confirmed by I-V characteristics method. Higher optical absorption in visible light and enhancement of current up to mA is suitable characteristics of good absorber layer for solar cells application.

**Keywords :** Low Cost, CZTS, Absorber, Porous, Solar Cells.

### I. INTRODUCTION

Semiconducting kesterite CZTS thin films are currently under intensive investigation for efficient solar cells. Current  $\text{CuInGaS}$  (CIGS) and  $\text{CdTe}$  materials have reached high efficiencies, but it has serious issues of cost, toxicity and rare materials [1]. CZTS is emerging candidate as replaced CIGS thin film with In and Ga replaced by Zn and Sn. Direct band gap ( $\sim 1.45\text{eV}$ ) of CZTS thin film is suitable for solar energy conversion. CZTS thin film is also a high

absorption coefficient  $\sim 10^4\text{cm}^{-1}$ . Quaternary CZTS thin films have been reported as produced by pulsed laser ablation [3], DC sputtering [4], Co Sputtering [5], chemical spray deposition [2,6], Printing technique [7], Vacuum deposition technique [8], Sol Gel sulfurization [9,10], spin coating technique [11], electron beam evaporation [12], electroplating [13], hot injection method [14], Chemical Bath Deposition [1-3], Successive Ionic Layer Adsorption and Reaction method [4]. However, these methods have some

drawbacks such as expensive precursors, complicated apparatus and even toxic byproducts evolved during their synthesis. SILAR method has some advantages like it is inexpensive, large area deposition, easy handling, environmentally friendly and room temperature growth. To fabricate solar cell modules at a truly competitive cost, the SILAR method is a most attractive process to cut down the expenses. Mostly ternary and quaternary materials are shown amorphous structure prepared by SILAR method at room temperature. Annealing effect has removed the defects and increase intensity peaks due to crystallinity are increased [16].

In the present research paper, we report the synthesis of CZTS thin film by SILAR method at room temperature and after preparation samples annealed at 250 °C. The soft chemically prepared as grown and annealed CZTS thin films studied by structural, morphological, optical and electric properties have been investigated.

## II. METHODS AND MATERIAL

CZTS thin films have been prepared by SILAR method on silica glass substrates. The growth of CZTS thin was carried out at room temperature. The solutions of 0.1M CuSO<sub>4</sub>, 0.05M ZnCl<sub>2</sub>, 0.05M SnCl<sub>4</sub> and 0.4M S<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub> were separately prepared in distilled water with analytical grade reagents. The ammonia and Triethanolamine (TEA) used as complexing agents to control precipitation in cationic reaction. Cu, Zn and Sn as used cationic precursors and S as an anionic precursor. 5 ml of TEA was added each cationic solution and stirred few min. Few drops of ammonia were also added in cationic solution to maintain reaction basic media up to ~11 pH. All cationic solutions were mixed together. The substrates were immersed in cationic solution 10 sec and dipped in distilled water to remove the loose ions then substrates were immersed in anionic solution 20 sec

and dipped in distilled water. Successive cycles repeated at 60 times to get the uniform film.

The X-ray diffraction of the thin film samples was measured on Bruker AXS, Germany (D8 Advanced) X-ray Diffractometer by using monochromatic CuK $\alpha$  radiation in the range of 2 $\theta$  from 20-60°. Surface morphology of the samples was studied using Scanning Electron Microscope (JEOL). UV-Visible spectrum was recorded on Perkin Elmer spectrophotometer (Perkin-Elmer Lambda 25 UV Vis Spectrophotometer). Electrical measurements of CZTS thin film was studied by the current-voltage (I-V) characteristics [LAB equipment model 24 (2004)].

## III. RESULTS AND DISCUSSION

The X-ray diffraction is a widely used technique to investigate the structure and phase of the material. Fig. 1 shows the typical XRD pattern obtained for as-grown and annealed CZTS thin films. The formation of CZTS kesterite structure was confirmed by comparing the obtained XRD pattern with standard JCPDS data (JCPDS # 26 0575). The XRD analysis of as-grown CZTS thin film shows amorphous behavior but after annealing CZTS thin film revealed small diffraction peaks at 2 $\theta$  values 28.60°, 47.32° and 58.1° which were assigned to (112), (220) and (224) reflection planes respectively [16]. The average crystallite size has been calculated from the X-ray diffraction pattern using the Debye-Scherrer's formula given in Eq. (1).

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

Where D is the crystallite size, k is shape constant,  $\beta$  is the full width at half maximum (FWHM) and  $\lambda$  is the wavelength of the X-rays. The crystallite size of annealed CZTS thin film is to be 15 nm.

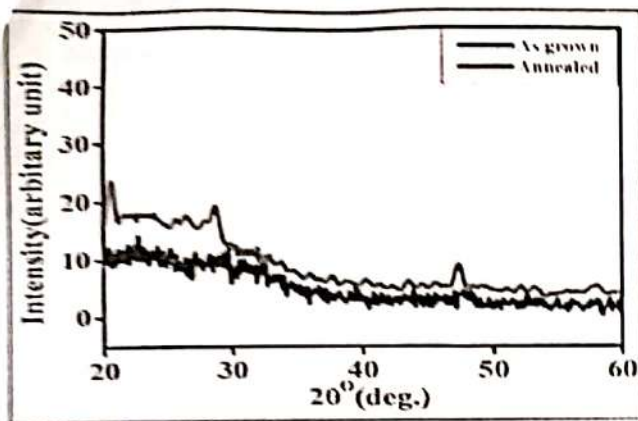


Fig.1 XRD pattern of as-grown and annealed CZTS thin film.

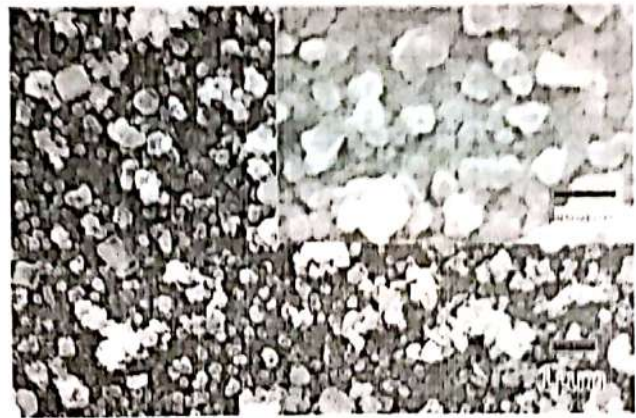
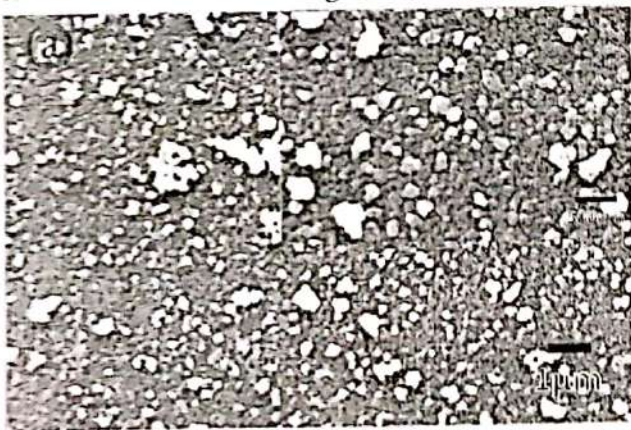


Fig. 2: FESEM images of as grown (a) and annealed (b) CZTS thin films.

### Surface morphology study

The surface morphology of CZTS thin films was carried out by Field Emission Scanning Electron Microscopy (FE-SEM) technique. The FE-SEM images show a smooth and homogeneous surface with the formation of granular crystallites but after annealing compactness of the surface increases and few of which came together to form agglomerates as shown in Fig. 2(a) and (b) respectively [1]. The inset images in Fig. 2(a) and (b) shows higher resolution images of the CZTS thin film for as-grown and annealed samples respectively. The FE-SEM images show the irregular shape particles turns into some cubic like structure due to annealing effect. Along with compactness in the surface annealing also increases the homogeneity in the surface this may be attributed to the binding of surface atoms after annealing.



### Optical study

The UV-Vis spectrophotometer was used to characterize the optical absorbance and to obtain the band gap of CZTS thin films. Fig. 3 shows the optical spectra and the band gap of (a) as grown and (b) annealed CZTS thin films. The theory of optical absorption gives the relationship between the absorption coefficient ( $\alpha$ ) and the photon energy ( $h\nu$ ) for direct or indirect allowed transition given in following Eq. (2),

$$\alpha = \frac{\alpha_0(h\nu - E_g)^n}{h\nu} \quad (2)$$

Both CZTS thin films show higher absorption in the visible region. Thermal annealing effect decreases the band gap of the material and it is correlated with the crystallinity of the material. Band gap values of as-grown and annealed thin film were found to be 1.58 eV and 1.56 eV respectively [16]. The decrease in band gap is assigned to the increase in crystallite size of the CZTS thin films as it increases the absorption

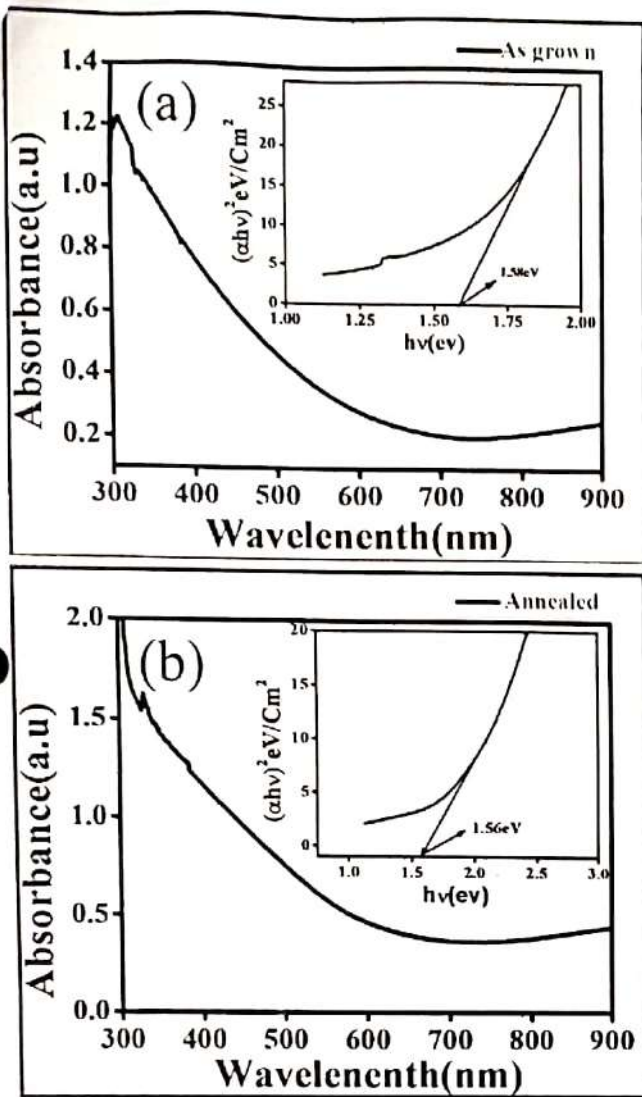


Fig. 3: Absorption of as-grown (a) and annealed (b) CZTS thin films and inserted own band gap.

thin films reveal photo sensing nature of the CZTS thin film as there is an increase in current after light illumination is observed [16].

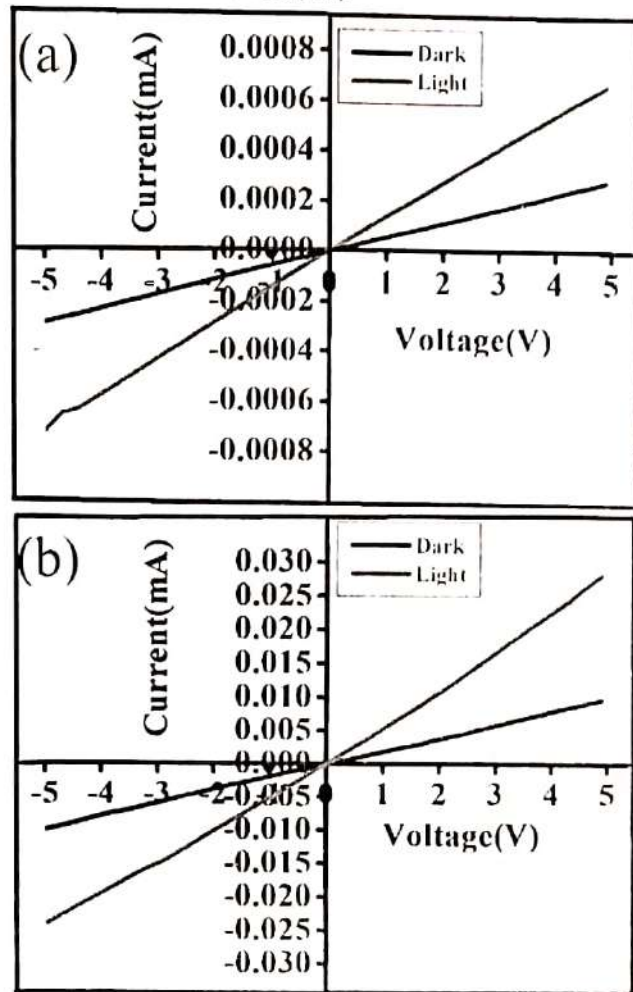


Fig.4 I-V characteristics of as-grown (a) and annealed (b) CZTS thin films.

### Electrical Study

The electrical properties of the prepared CZTS thin film were investigated by I-V characteristic curve in dark and under illumination of light. Fig. 4(a) and (b) shows I-V characteristics data of as-grown and annealed CZTS thin films respectively in the applied voltage range of  $\pm 5$  V. Both CZTS thin films under dark and under light illumination of  $100 \text{ mW/cm}^2$  light results in higher current in the order of milliamperes. I-V curve shows straight line passing through origin indicates ohmic nature of the metal semiconductor contacts for CZTS thin films. Both the

### IV. CONCLUSION

We have successfully synthesized CZTS thin films by SILAR method at room temperature on a glass substrate. Thermal Annealing effect on structural, morphological, optical and electrical properties of CZTS thin film has been reported. As grown CZTS thin film show amorphous structure, which after annealing turns into crystalline with increased peak intensity. The estimated crystallite size of annealed CZTS thin film was found to be  $\sim 15 \text{ nm}$ . As grown

thin films compared to annealed film have more agglomeration of nanoparticles due to the compactness of thin film surface. The band gap value decreases and electrical current increases after annealing due to increased crystallinity in the material. From the reported results we can conclude that annealing effect induces favorable changes in the CZTS thin film.

## V. REFERENCES

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