Synthesis and characterization of ecofriendly and large-area honeycomb-like \( \text{Cu}_2\text{ZnSnS}_4 \) thin films for solar cell applications using chemical bath deposition method

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Abstract. In view of care and concern for society to provide sustainable energy by renewable solar photovoltaic technology using various absorbers is being highly reliable. Among all absorbers, recently the \( \text{Cu}_2\text{ZnSnS}_4 \) (CZTS) thin films have prompted the significant attention of researchers as low-cost and high-quality photovoltaic absorber semiconducting material owing to its high absorption coefficient, optimum band gap, nontoxic nature and naturally abundant elements with high expectations of greener synthesis and renewable solar to electrical conversion. Considering this eco-friendly approach we focus on synthesis, characterization and photo electrochemical application of \( \text{Cu}_2\text{ZnSnS}_4 \) (CZTS) thin films by cost effective chemical bath deposition technique. The films were characterized using various techniques like XRD, scanning electron microscopy, optical absorbance, electrical conductivity, photoluminescence, and PEC studies. The investigation revealed a poly-crystalline, stable kasterite structure of CZTS thin films in a good stoichiometric and with an excellent uniform, large area typical honeycomb-like morphology.

1. Introduction

The increasing serious environmental problems and energy crisis due to continuous consumption of fossil fuel makes researcher to focus on renewable energy sources. Nowadays the solar photovoltaic (PV) is considered as a promising, environment best energy supply option because sunlight is abundant and clean energy source which does not evolve any harmful emission of gases.

The current PV market has been dominated by silicon, cadmium telluride (CdTe) and copper indium gallium di-selenide (CIGS) as absorber materials. However there are certain disadvantages with these materials in detail silicon based solar cells having high processing cost, indirect band gap, etc. [1]. The CIGS and CdTe composed of rare, costlier elements [2]. Hence Si, CIGS and CdTe materials will not considered as long term environment friendlier materials. The present solar cell technology needs to develop new alternative is of low cost, eco-friendly, non-toxic, highly efficient material that can replace the existing scenario. In this regard, \( \text{Cu}_2\text{ZnSnS}_4 \) (CZTS) has been considered as promising absorber materials in PV technology because of their excellent optoelectronic properties. The CZTS is the p-type semiconductor material with favorable band gap of 1.5 eV, having as high as absorption coefficient over \( 10^4 \text{ cm}^{-1} \) and low thermal conductivity [3-5]. The composition of CZTS is naturally earth abundant, nontoxic and readily affordable in comparisons to CIGS and CdTe. The CZTS shows two structures fundamentally kasterite (space group I4) and stannite (space group I42m). These two structures having different arrangements of Cu\(^{+1}\) and Zn\(^{+2}\) atoms in the crystal structure. [6]. However, CZTS exhibit stability in Kasterite structure because it is thermodynamically more stable [7]. Further CZTS is quaternary semiconductor compound which is actually derivative of the
chalcopyrites (CuInS$_2$/CuGaS$_2$) obtained by replacing In or Ga. Overall CZTS is a supreme and supernatural light absorber material as an alternative for CIGS and CdTe as low-cost absorber layers.

So far CZTS thin films have been prepared by a number of techniques such as RF magnetron sputtering [8], thermal evaporation [9], atom electron-beam-evaporation [10], pulsed laser deposition [11], etc but these methods require vacuum chambers large power supplies and specially designed complicated equipments. Moreover, the solvents used are mostly hazardous to the environment. Other non-vacuum methods involves sol-gel [12], spray pyrolysis [13], chemical vapor deposition [14], spin coating technique, [15], electrodeposition methods [16], nanoparticle methods [17], silar method [18] etc. These nonvacuum methods possess some disadvantages like the association with low-quality films, impurities, and low efficiency. To date, the solar cell based on pure CZTS, have achieved power conversion efficiency as high as 9.2 % [19]. Hence there is need for improvement because CZTS is foremost perspective supernatural material to develop low cost, eco-friendly thin film solar cells with highest efficiency.

The chemical bath deposition method has paying attention because of its simplicity, low-temperature processes and no need of costlier equipments [20]. It does not need to use toxic solvents or ligands like hydrazine etc. and hence relied as environment sustainable method. In this report we focus on synthesis of CZTS using a simple chemical bath method its characterization and application as photo absorber in a PEC. This is the first attempt, to synthesis of polycrystalline, kasterite CZTS thin films having typical honeycomb-like morphology having large surface area which is highly applicable for solar cells. The films were characterized by X-Ray diffraction, optical absorbance, photoluminescence, electrical conductivity, scanning electron microscopy and EDS techniques and PEC studies.

2. Experimental Methods

2.1 Preparation of reagents
The chemicals were used for deposition of films of standard grade which includes copper sulphate [Cu (SO$_4$).5H$_2$O], zinc sulphate (ZnSO$_4$.H$_2$O), stannic chloride (SnCl$_4$.5H$_2$O), liquor ammonia (25% liq.NH$_3$), sodium sulfite (Na$_2$SO$_3$), sulfur powder (Aldrich) etc. All the solutions were prepared by using double distilled water. The specially sodium thiosulphate (Na$_2$S$_2$O$_3$) solution was prepared by refluxing of sulfur powder and sodium sulphite in proportion of 3.5 and 15 g respectively in 200 ml of double distilled water for 6 h at 363 K [21]. The resulting solution was stored in an airtight container after removing impurities properly like undissolved sulphur. The films were deposited on non-conducting micro-glass slides (Blue Star, India) having dimensions of 75 x 25 x 1.35 mm. The cleaning of slides were done by keeping in beaker containing chromic acid for about sufficient time. Then rinsed by acetone and water (double distilled) prior to deposition of CZTS films.

2.2 Deposition of Thin Films
To deposit CZTS thin films, 8 ml copper sulphate (0.25 M) of solution, 4 ml ZnSO$_4$ (0.25 M), 4 ml SnCl$_4$ (0.25 M) were taken in 250 mL beaker. Then addition of liquor ammonia (40 mL) was done slowly drop by drop and followed by stirring constantly so as to obtain stable complex. The ammonia worked as complexing agent. After few minutes to this complexed solution specially prepared sodium thiosulphate 16 mL was added slowly. Then final addition of double distilled water was done so as to maintain final volume up to 180 mL. The excess ammonia was used to maintain pH of the solution at 10. Then in an oil bath the beaker of reaction solution was taken and then clean glass slides were vertically positioned with help of specially designed substrate holder. This substrate holder was rotated with a specifically speed of control upto 40 rpm. The oil bath was then subjected to increase in temperature up to 40 °c slowly for a period of 180 minutes. During this time it was observed that complete deposition on the slides, taken out, followed by washing by distilled water several times. Then films were kept to dry in nature. Then films were potted in desiccators containing CaCl2 to remove moisture.
2.3 Characterization
The structural study of films were done by using XRD with diffraction angle (2θ) and in range of 10–80°. For this characterization Philips PW-1710 diffractometer with CuKα1 (λ = 1.54056 Å) radiation was used. A ‘dc’ four probes (equal spacing) method using silver paste was used to measure electrical conductance of CZTS thin films. The optical absorption characterization was recorded by UV 3600 Shimadzu UV-VIS-NIR double beam spectrophotometer in the wavelength range 400–1200 nm. The Jasco spectrofluorometer (FP-8300, Japan) was used for photoluminescence study at an excitation wavelength of 530 nm. The surface morphology and other microscopic observation study with the help of Scanning electron microscopy (SEM) images obtained from JEOL JSM-6360. The PEC study of CZTS films were done by Keithley Model-4200 (SCS).

3 Results and Discussion

3.1 Growth mechanism
To obtain a high quality and reproducible films, repetitions of experiment was performed to optimize various parameters like pH, concentration of solutions, temperature etc. We observed for getting excellent quality films the pH of solution 10.5 and temperature: 40 °C. The duration of the film deposition was 180 min, and the speed of rotation ~ 40 rpm. At initial stage (at 25 °C) the reaction mixture was a clear homogeneous solution. The decomposition of sodium thiosulphate occurred at slow increase in temperature, and metal complexes in presence of alkaline medium. This dissociation causes the generations of ions like cations and sulphur ions which combine on the substrate followed by an ion-by-ion combination procedure causes the good quality of thin film. The slow release of cations and sulphur ions. We assume that CZTS films were deposited via a well-known coprecipitation technique. The weight difference density consideration method used to measure thickness of the CZTS thin films and which was found to be 0.9 μm. The proposed reactions mechanism of growth of the thin film is shown below:

$$\text{CuSO}_4 \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} \quad (1)$$

Here, Cu$^{2+}$ reacts to sodium thiosulphate forms copper thiosulphate complex which dissociates into Cu$^{+}$ ions [22].

$$2\text{Cu}^{2+} + 4\text{Na}_2\text{S}_2\text{O}_3 \rightarrow 2[\text{Cu}(\text{S}_2\text{O}_3)]^+ + [\text{S}_4\text{O}_6^2]^+ + 8\text{Na}^+ \quad (2)$$

$$[\text{Cu(S}_2\text{O}_3)]^- \rightarrow \text{Cu}^+ + \text{S}_2\text{O}_3^{2-} \quad (3)$$

$$\text{ZnSO}_4 \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} \quad (4)$$

$$\text{SnCl}_4 \rightarrow \text{Sn}^{4+} + 4\text{Cl}^- \quad (5)$$

$$\text{Na}_2\text{S}_2\text{O}_3 + 2\text{OH}^- \rightarrow \text{S}^{2-} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \quad (6)$$

The overall ionic reaction is,

$$\text{Cu}^+ + \text{Zn}^{2+} + \text{Sn}^{4+} + 4\text{S}^{2-} \rightarrow \text{Cu}_2\text{ZnSnS}_4 \quad (7)$$

3.2 Structural characterization
The structural study of the CZTS thin film was carried out by X-Ray diffraction analysis. The Fig.1a. shows XRD patterns of the annealed at 200 °C in the air (for 2 h) of CZTS film. It shows diffraction peaks of CZTS thin film at 2θ angles; 20.2, 28.5, 33.0, 47.5 and 56.85 corresponding diffraction originating plane having indices of (101), (112), (200), (220) and (303) as per JCPDS card number 26-0575 for CZTS. The main diffraction peaks indexed to (112), (200), (220) and (303) planes are well defined and narrow peaks indicates polycrystalline and Kasterite CZTS structure (JCPDS 26-0575) [23]. The formation of CZTS film is in Kasterite structure which is most thermodynamically stable form of CZTS than any other structural phases of CZTS. The sharpness of major peaks along with kasterite and crystalline phase which concluded that CBD method is applied at low temperature to produce films of uniform composition. The annealed CZTS film shows an excellent increase in the diffraction peaks intensity as compared to as deposited films which indicating that the annealed CZTS
film is in a highly crystallized form than as-deposited CZTS film. There were no other impurity phases were observed in XRD analysis of CZTS samples.

![X-ray diffraction patterns of annealed CZTS thin films](image)

**Figure 1** X-ray diffraction patterns of annealed CZTS thin films

### 3.3 Morphological Analysis

Scanning electron microscopy is the most useful fundamental tool technique for the study of surface morphology and microstructure of the thin films as these directly concerned with their optical properties. The typical honeycomb-like surface morphology with an almost identical texture was exhibited by the annealed CZTS films. The size and shapes of the individual parts are found to be quite homogeneous and larger in thickness. The Fig. 2a shows the CZTS thin film at 500 X magnification which shows smooth, homogeneous, well adhered, interconnected, honeycomb-like morphology. Basically it is seen that interconnection pattern of cores of hexagon or pentagon or polygon of honeycomb structure. The Fig. 2b shows film at 10000 X the magnification shows enlarged view of honeycomb core interconnected with each other. It is seen clearly from uniform surface morphology of films without any cracks and pores harmonized distribution of the CZTS through the film. The wonderful and unique honeycomb like morphology shows no existence of any impurities like binary or ternary components. This type of characteristic honeycomb morphology exhibits a large-area surface which is helpful to collect effectively solar radiations falling on it. [24]
3.4 Optical properties of CZTS
In thin film technology band gap of a solar absorber material plays a crucial role because it has potential characteristic to convert sunlight into electricity. Hence to find out band gap of material in view of improving cell efficiency solar cells, the optical study of the thin films is of very much fundamental. With the help of double beam spectrophotometer at the wavelength range of 400 to 1200 nm the variation of optical absorption spectrum of the CZTS thin film was obtained at room temperature. The reflectance and refraction losses were neglected. It can be concluded from Fig. 3a of UV-visible spectrum, the CZTS material shows high absorbance. The Lambert law is specifically used to calculate the optical absorption spectrum of the material [25].

\[ \ln \left( \frac{I_0}{I} \right) = 2.303 \frac{A}{d} = \alpha d \]  

Where \( I_0 \) and \( I \) are the intensities of the incident and transmitted light, respectively; \( A \) is the optical absorption, \( \alpha \) is the absorption coefficient and \( d \) is the thickness of the film. We observed an optical absorption coefficient of CZTS thin film in the order of \( 10^4 \text{ cm}^{-1} \) which is good agreement with earlier reports of literature. The Figure 3b shows variation of the absorption coefficient function i.e. \( \propto = f (h\nu) \) with wavelength. According to S. Mushtaq et al the connection of absorption coefficient and photon energy near the absorption edge is studied and band gap calculated by following relation [26].

\[ \alpha h\nu = B(h\nu - E_g) x \]  

Where \( B \) is edge width parameter and it is a constant, \( h\nu \) is the wavelength of the light used, \( E_g \) is the band gap of the material and \( x \) is a factor which determines transitions involved. (The \( x = 1/2 \) indicates direct allowed transition) To find what type of transition involved Eq. (9) rearranged to linear line equation, \( y = mx + c \), gives \( y = (h\nu)2 \), \( x = h\nu \), the linear portion of which when extrapolated to the x-axis, gives the optical band gap (Eg) of 1.5 eV at room temperature. This value of the band gap is good agreement with the reported value of CZTS (1.5 eV) [3-5]. This estimated band gap is recognized as stable and ideal band gap energy value for applications in thin film solar cells with high conversion efficiency.

3.5 Electrical conductivity
The electrical conductivity is dependent large grain size of material like CZTS which causes positive increase in current and electron transport. The temperature range was used to measure electrical resistivity of the as-deposited CZTS thin film in between 27 \( ^\circ \text{C} \) to 150 \( ^\circ \text{C} \). With gradual increase in temperature causes the decrease in resistivity of material which strongly proves the semiconducting nature of the CZTS thin film material. The electronic properties of thin film materials depend on the
nature of impurities and structure of material [27]. In addition an electronic property of materials also strongly depends on type of conductivity which can be determined from the Arrhenius relation:

\[ \rho = \rho_0 \exp\left(\frac{-E_a}{kT}\right) \]  

(10)

where \( E_a \) is the activation energy, \( k \) is the Boltzmann constant; \( T \) is the absolute temperature, and \( \rho \) and \( \rho_0 \) are the resistivity and specific resistivity, respectively. We observed nature of plot of the log \( \rho \) vs. inverse absolute temperature is linear which indicates that only one type of conduction mechanism (Fig. 4). The activation energy calculated from the slope of above plot of the CZTS film found to be 0.588 eV. The CZTS film showed a positive polarity toward the cold end under influence of thermoeffect which was generated when a temperature gradient was applied across the length of CZTS. This strongly indicating the p-type semiconducting behaviour of CZTS thin films [28]. The electrical properties of CBD deposited CZTS good agreement in view of in thin film solar cell applications.

Fig. 4  log conductivity vs. inverse absolute temp

3.6 Photoluminescence (PL) studies
Photoluminescence (PL) spectroscopy attracted attention of researchers due to its potential to differentiate the quality of semiconductors. This technique helpful to examine presence of defects, doping level, homogeneity, and stoichiometry of material [29]. The PL spectrum of the CZTS at an excitation wavelength of 530 nm at room temperature shows a strong peak at a wavelength of 825 nm (i.e.1.50 eV) and a small peak shoulder at 780 nm (1.58 eV). This representation is as shown in Fig. 5. The strong emission at 1.50 eV appeared very good agreement to that of CZTS PL absorption measurements [30]. The another emission at 1.58 eV appears which is also associated with CZTS.

Fig. 5 PL spectrum of CZTS thin film

3.7 PEC measurement-
The CZTS thin films have been obtained from the FTO-coated substrate of size 12*50* 1mm size. The CZTS photo electrode with 1cm3 unmasked surfaces and graphite rod as a counter electrode was used in PEC analysis. The 0.1 M iodine redox solution in 0.1 M KOH solution was used as electrolyte. The distance between two electrodes was kept at least 3 mm. The PEC was characterized by measuring current-voltage characteristics (I-V) in dark as well as light, and power output characteristics (under illumination). The Figure 6. shows variation of current density-voltage curve CZTS thin films at room temperature. The photocurrent increases with steady increase in negative potential, which clearly confirms that p-type nature of CZTS film [31]. The conversion efficiency (\( \eta \)) is defined as the ratio of
power output to power input. The power output is the product of $V_m I_m$. As power input is known (i.e. 100 mW) the power conversion efficiency ($\eta$) can be calculated by following relation.

$$\eta = \frac{\text{Power output}}{\text{Input power}} = \frac{V_m I_m}{\text{Input power}} \quad (11)$$

The analysis of PEC data revealed stable power conversion efficiency ($\eta$) 4.60 % with open circuit voltage ($V_{oc}$) 500 mV; a short circuit current ($I_{sc}$) 20.0 mA/cm$^2$ and fill factor is 0.46 of as deposited CZTS film. This power conversion efficiency of CZTS which is in good agreement with reported efficiency [32].

![Figure 6 Current - voltage (I-V) characteristics of CZTS thin films](image)

### 4 Conclusion

A simplest and low cost CBD method applied to synthesis earthabundent and non toxic CZTS thin films at low temperature. A unique, distinctive honeycomb-like morphology of CZTS were observed. The CZTS film shows a ideal band gap of 1.5 eV. The single type of conduction mechanism is observed by conductivity measurement. It is worth to report that from XRD, SEM, UV-VIS, Electrical and PL analysis that CZTS thin films synthesized with polycrystalline and highly stable kasterite structure without any secondary phases and specially avoiding by use of hazardous solvents and chemicals. The typical honeycomb like morphology possesses a large surface area which is highly applicable for in thin film solar cells. A PEC cell fabricated using CZTS showed 4.60 % conversion efficiency.

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