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RESEARCH ARTICLE

Growth of Cu_2ZnSnS_4 Thin Film Solar Cells Using Chemical Synthesis

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Abstract

Objectives: Cu_2ZnSnS_4 thin film solar cell is fabricated by using the chemical spray pyrolysis method. **Method:** CZTS thin films were successfully deposited by employing the eco-friendly and cost-effective chemical spray pyrolysis method. X-ray diffraction (XRD) and Raman spectroscopy are used to investigate the structural properties of the prepared samples. The surface morphology of the deposited films is studied using a scanning electron microscope. An energy dispersive spectrometer is used to know the chemical compositions of the deposited films. A double beam spectrophotometer is used to study the optical characteristics of these films. The hot probe technique is used to confirm the nature of the conductivity of the deposited films. **Findings:** The XRD spectra of the thin films reveal the polycrystalline nature with the kesterite structure of the thin films. The optical band gap is found to be 1.52 eV and the absorption coefficient value of these films is found to be $\geq 10^4$ cm^{-1}. The nature of conductivity is identified to be p-type. Finally, Cu_2ZnSnS_4 thin film solar cell is fabricated with the substrate configuration glass/Mo/CZTS/CdS/Ag which exhibited an open circuit voltage and short circuit current of 156 mV and 1.82 mA/cm^2 respectively. **Novelty:** The growth of Cu_2ZnSnS_4 thin films is studied by varying the distance between the spray nozzle and glass substrate from 25 to 35 cm in steps of 5 cm and maintaining all other parameters as constant. Finally, the Cu_2ZnSnS_4 thin film solar cell is prepared in a substrate as well as a superstrate configuration.

Keywords: Thin films; Absorber layers; Spray technique; Solar cell; Cu2ZnSnS4

1 Introduction

The increase in industrialization, urbanization and hasty growth in the population increased the utilization of electricity and the electric power requirement. At present, the typical power consumption is about 10 TW and is predicted to be 30 TW by 2050 [(1)]. Currently, the energy supply is attained from fossil fuels, which are going to be exhausted in the coming decades. Hence there is a need to look for alternate renewable resources that are readily available and environmentally friendly. In this context, solar energy is an important and potential renewable energy source.

For the past few decades, photovoltaic investigations are focused on ternary and quaternary chalcopyrite semiconductors such as $CuInSe_2$, $CuGaSe_2$, $CuInGaSe_2$ (CIGS), and $CuIn(SSe)_2$. Thin film heterojunction photovoltaic cells using CIGS as absorber layers exhibited a record efficiency of about 22.9 % and are a good alternative for Si-solar cells[2]. The scarcity and massive cost of gallium and indium limit their future market use. To achieve low-cost and efficient commercial thin film solar cells, there is a need to work on other alternative compound materials. In this context, Cu_2ZnSnS_4 (CZTS), a quaternary compound semiconductor is proved as an alternative absorber layer to CIGS thin films. The elements present in these absorber layers are eco-friendly as well as non-toxic in nature[3,4]. CZTS thin films have splendid physical properties like direct bandgap (1.5 eV), higher absorption coefficient value ($\geq 10^4$ cm^{-1}), tetragonal structure and p-type conductivity[4]. Its fundamental constituents (Cu, Zn, Sn, and S) are abundant and inexpensive; as a result, it is possible to fabricate efficient and affordable thin film solar cells.

Chang and his co-workers fabricated CZTS thin films by co-sputtering technique followed by sulfurization and reported 11% as maximum conversion efficiency[5]. To enhance the solar cell conversion efficiency and industrial feasibility of CZTS, more research is required on it. Cu_2ZnSnS_4 thin films were grown by various techniques like pulsed laser deposition[6], co-sputtering[7], electrodeposition[8], chemical bath deposition[9], spray pyrolysis[10,11], sol-gel[12], spin coating[13], etc. Spray pyrolysis is eco-friendly, one of the low-cost techniques and highly suitable for massive production[14,15]. This technique was adopted in the present investigation to deposit the CZTS thin films. In the present paper, the growth of CZTS thin films was discussed by varying the distance between the spray nozzle to the glass substrate. The compositional, structural, morphological, optical, and electrical properties of as-deposited CZTS thin films were described. Finally, by using the chemical method an effort was made to fabricate a typical Cu_2ZnSnS_4 absorber based thin film solar cell.

2 Experimental methods and materials

Cu_2ZnSnS_4 thin films were successfully deposited onto chemically and ultrasonically cleaned soda-lime glass substrates by using the chemical spray pyrolysis approach. The Cu_2ZnSnS_4 thin films were obtained by spraying an aqueous solution containing salts of $CuCl_2.2H_2O$, $(CH_3CO_2)_2Zn.2H_2O$, $SnCl_4.5H_2O$, and $(NH_2)_2(CS)$ with a molar ratio of 1.8:1:1:10[16]. The starting solution contained excess thiourea than the requirement stoichiometric value to reimburse the loss of sulphur concentration during the experimentation. In the present study, the pH of the aqueous solution was around 3.5. The deposition process was carried out at an optimized temperature of 643 K[16,17]. The temperature was maintained constant throughout the experimentation with the help of a digital temperature controller. The spray nozzle and the electric heater were enclosed in a fume cupboard. To eradicate the hot vapours of the solvent and gas fumes, an exhaust fan was attached to the fume cupboard. Movable glass doors were fixed at the front side of the cupboard and are closed during the process of spray pyrolysis. The prepared aqueous solution was sprayed onto the soda-lime glass substrate at a constant spray rate of 10 ml/min. The growth of Cu_2ZnSnS_4 thin films was studied by varying the spray nozzle to substrate distance. These distances were maintained as 25, 30, and 35 cm respectively. The spray nozzle was supported by sturdy support that could be lifted and lowered to change the distance between the nozzle and the substrate. For optimal coverage of the droplet cone on the glass substrates, the nozzle to substrate distance was varied between 25-35 cm in steps of 5 cm.

2.1 Material Characterization

A powder X-ray diffractometer (BRUKER) was used to analyze the films by using Cu-Kα radiation. Micro Raman spectra of these films were recorded with the help of an Argon ion laser beam of λ = 514.3 nm in backscattering mode. The surface morphology of CZTS films was studied with the help of a scanning electron microscope (CARL ZEISS). The energy dispersive spectrometer was used for the elemental analysis of these samples. Energy dispersive spectra were recorded using an excitation voltage of 20 kV. Using a Perkin Elmer UV–Vis–NIR double-beam spectrometer, the spectral transmittance and reflectance curves of the deposited films were recorded between the wavelength range of 300-1500 nm. The hot probe technique was used to identify the nature of the deposited films. CdS films were used as a buffer layer and were deposited by chemical bath deposition.

3 Results and discussion

The spray deposited Cu_2ZnSnS_4 films are observed to be extremely adherent. The thickness of the deposited films was measured by finding the mass of the film with a digital microbalance and using a bulk density. Thickness (t) of the film = $\frac{m}{a\,X\,d}$, where m = mass of the deposited thin film, a = area of thin film, and d = density of CZTS. As the spray nozzle to substrate distance increases the thickness of the films was found to be decreased and is tabulated in Table 1. This might be due to the few spraying

droplets got evaporated before reaching the glass substrates as the distance between the spray nozzle to substrate increases.

Table 1. Thickness of CZTS thin films deposited at various distances

S. No.	Distance between the nozzle and glass substrates (cm)	Thickness (nm)
1	25	530
2	30	452
3	35	395

The elemental composition of deposited CZTS thin films at various distances of the nozzle to glass substrates was tabulated in Table 2. From Table 2, it is clear that there is a significant variation in stoichiometry. The elemental composition ratio of these films reveals that the deposited films were Cu-poor, Zn-rich, and S-deficient. There was significant variation in the sulphur composition in the film identified with the change in the distance from the spray nozzle to glass substrates. This might be due to the volatility nature of sulphur being more at higher substrate temperatures, as the distance between the nozzle to glass substrates was increased, the sulphur composition in the films was reduced. However, Cu-poor and Zn-rich conditions are highly favorable for the optimized performance of Cu_2ZnSnS_4 solar cells[18].

Table 2. Elemental composition of CZTS thin films deposited at various distances between the nozzle and glass substrates

Distance (cm)	Chemical composition (in at.%)				Ratio of composition		
	Cu%	Zn%	Sn%	S%	Cu/(Zn+Sn)	Zn/Sn	S/Metal
25	26.4	14.9	13.0	45.7	0.94	1.14	0.84
30	26.3	15.4	13.2	45.1	0.92	1.17	0.82
35	26.8	15.9	13.7	43.6	0.90	1.16	0.77

The XRD patterns of CZTS films grown by varying the distance between the spray nozzle and glass substrate were shown in Figure 1. The films were found to be polycrystalline with a kesterite structure, as evidenced by the XRD pattern. The 2θ values and lattice parameters deduced from d-spacings were tabulated in Table 3. These values were in accordance with reported data[13,19] as well as the JCPDS Card No. 26-0575. CZTS films grown at 25 cm were found to be low crystallinity. This might be due to a large number of droplet particles in the cone reaching the glass substrates as a result the thermal energy might be not sufficient to form the proper crystallization[20]. The intensity of the peaks increased significantly when the distance between the nozzle and the substrates was increased, as seen in the XRD spectra. The intensity ratio of $I_{(112)}/I_{(220)}$ increases as the distance between the nozzle and the substrate distance is fixed at 30 cm and 35 cm. As the distance between the spray nozzle and the glass substrate is increased, the solvent evaporates from the aerosol droplets during its transit towards the substrate. This results in the shrinking of droplet size which enhances the crystallinity in the film[20]. The films grown at 35 cm were found to contain $Cu_{2-x}S$ [JCPDS Card No. 34-0660] as a minor impurity phase along with CZTS.

Scherer's formula was used to calculate the crystallite size (L) of the film. Here $L = \frac{0.9\,\lambda}{\beta\, cos\theta}$, where λ = 0.15406 nm (Cu-Kα radiation), β is Full Width at Half Maximum of the peak reflected from (112) plane and θ is the diffraction angle of the resultant peak[21]. The crystallite sizes of the deposited CZTS films were found to be around 36 nm.

Table 3. 2θ and lattice parameters of CZTS thin films deposited at various distances between the nozzle and glass substrates

Distance (cm)	2θ (deg)			a (nm)	c (nm)
25	28.54°	47.37°	56.32°	0.542	1.079
30	28.53°	47.34°	56.19°	0.542	1.080
35	28.51°	47.36°	56.21°	0.543	1.082

The typical micro Raman spectra of CZTS films grown at a distance of 30 cm was shown in Figure 2. The two modes were

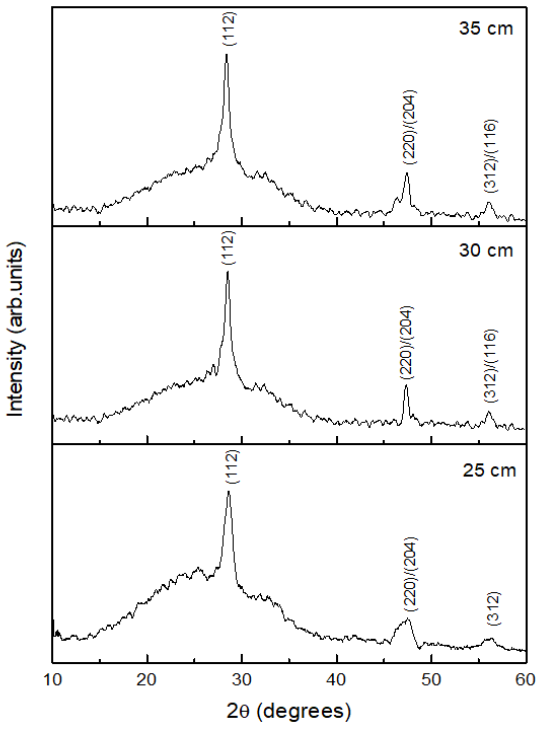

Fig 1. XRD pattern of CZTS films deposited at various distances between the spray nozzle and glass substrates

obtained at 290 and 339 cm^{-1}. These two Raman modes confirm the existence of the CZTS with the kesterite phase[22]. These results have concurred with the XRD studies.

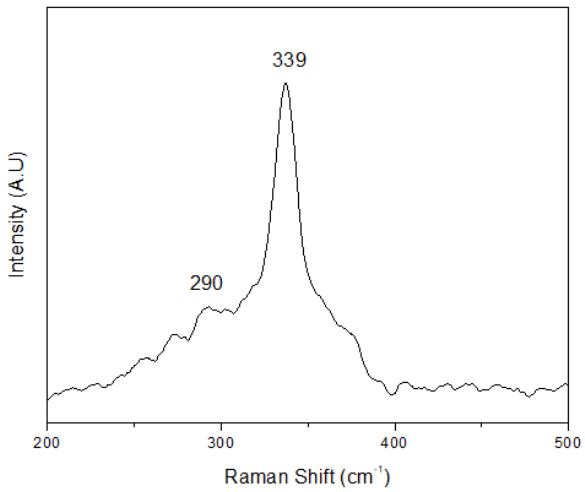

Fig 2. Micro Raman spectra of CZTS films grown at a 30 cm distance between the spray nozzle and glass substrates

The scanning electron micrographs of the grown CZTS films at various distances between the spray nozzle and glass substrates were shown in Figure 3. In the present investigation, it was observed that the distance between the spray nozzle and glass substrate was influencing the growth of the samples. The distinct grains were observed in the films deposited at a distance of 30 cm and their distribution was homogeneous. Also, a few needle-like grains can be seen in the micrograph. To

enhance the efficiency of thin film solar cells, improving the grain sizes of the absorber layer is necessary [23].

Films grown at 25 cm were found to be smeary and lacking in well-defined grains. XRD spectra of these films also confirm the little bit of poor crystallinity. Films grown at a distance of 35 cm were found to be porous and little pinholes were seen.

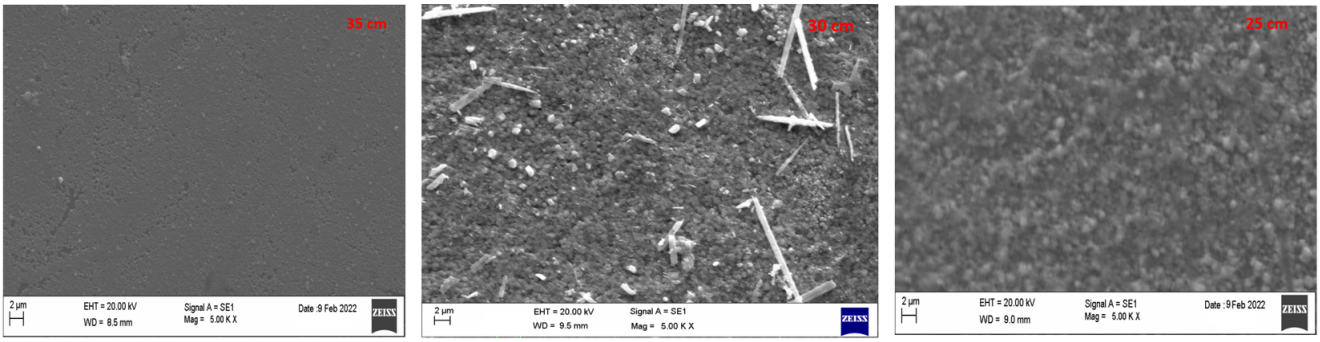

Fig 3. SEM micrographs of CZTS films deposited at various distances between the spray nozzle and glass substrates

The typical transmittance spectra of CZTS films grown at 30 cm was shown in Figure 4. Near the fundamental absorption edge, there is a sharp decrease in transmittance, which indicates that the optical transition is direct. By using this spectral data, the optical absorption coefficient (α) of CZTS films was obtained by using a simple mathematical formula $\alpha = \frac{1}{t} \ln \left[\frac{(1-R)^2}{T} \right]$ where T, R, and t are spectral transmittance, spectral reflectance, and thickness of the CZTS film [21]. In the direct optical transitions, the absorption process is described by the equation $(\alpha h\nu) = A(h\nu\text{-}E_g)^{1/2}$ where A is constant [21]. The optical absorption coefficient of CZTS films was found to be greater than $10^4 cm^{-1}$ [24]. The bandgap of these films was found using the Tauc plot. The straight-line fit indicates that the optical transition of these films exhibits a direct band gap. Figure 5 represents the band gap of CZTS films grown at 25 cm and 30 cm. The band gap of these films was obtained from the intercept on the $h\nu$-axis and was found to be 1.47 eV and 1.52 eV respectively. The band gap of films deposited at 35 cm was found to be 1.46 eV. The obtained values are concord with the optical band gap reported earlier [25] and this material is appropriate for photovoltaic conversion.

Van der Pauw technique was used for room temperature electrical resistivity studies, and it was found to be 28 Ω-cm. The hot probe technique confirms that the deposited films exhibit p-type nature.

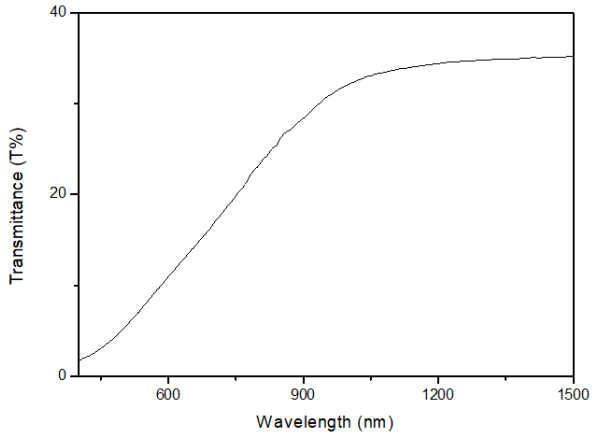

Fig 4. Spectral transmittance of CZTS films grown at a 30 cm distance between the nozzle and glass substrates

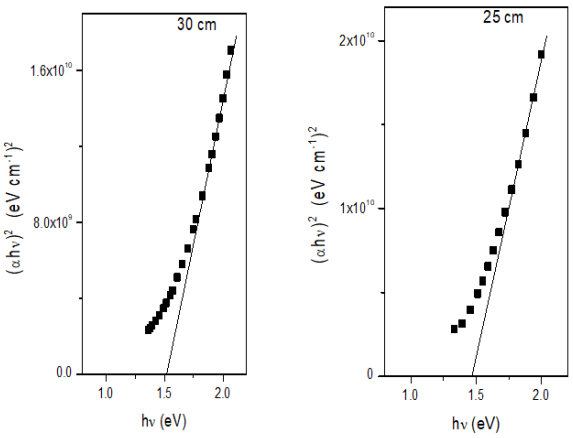

Fig 5. Band gap of CZTS thin films deposited at 25 cm and 30 cm

Finally, a typical Cu_2ZnSnS_4 solar cell was fabricated in the sequence glass/Mo/CZTS/CdS/Ag. CZTS film grown on Mo-glass substrate at a distance of the spray nozzle and substrate distance of 30 cm was used as an absorber layer. The chemical bath deposited CdS films were used as a buffer layer. The chemical bath temperature was maintained at 333 K[17]. For the formation of a metallurgical junction between Cu_2ZnSnS_4/CdS thin films, these layers were heated in a vacuum furnace at 423 K for about 15 minutes. Finally, a top contact was made with the help of Ag metal. Cu_2ZnSnS_4 thin film solar cells were also prepared in superstrate configuration in the sequence glass/ZnO:Al/CdS/CZTS/Ag.

J-V characteristics of Cu_2ZnSnS_4 thin film solar cells were shown in Figure 6. The photovoltaic properties of these cells were shown in Table 4. The obtained cell performance was too low. The low performance might be due to poor crystallinity, secondary phases might be present in amorphous nature along with CZTS, and non-optimized film thickness. Efforts are under progress to attain sensible efficiency.

Table 4. Photovoltaic properties of Cu_2ZnSnS_4 thin film solar cells

Cell configuration	V_{oc} (mV)	I_{Sc} (mA/cm^2)
Substrate configuration	156	1.82
Superstrate configuration	112	1.11

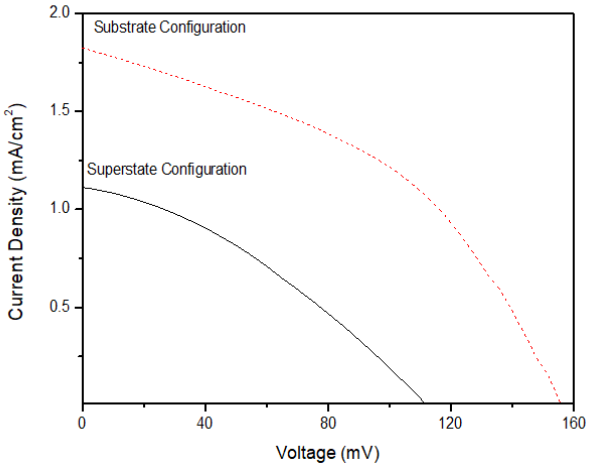

Fig 6. I-V characteristics of Cu_2ZnSnS_4 thin films solar cells

4 Conclusions

The polycrystalline Cu_2ZnSnS_4 thin films were successfully grown at a constant spray rate of 10 ml/min and the spray nozzle to substrate distance varied between 25 to 35 cm. An extremely adherent and uniform Cu_2ZnSnS_4 thin film were grown at a distance of 30 cm. The deposited films are exhibiting kesterite structure. The lattice parameters were found to be $c \approx 2a$. Raman spectra confirm the deposited Cu_2ZnSnS_4 films with the kesterite phase. Well-defined uniform grains per unit area were identified when the films were formed at a distance of 30 cm from the nozzle to the substrate. The optical band gap of these films is close to 1.5 eV which indicates that this material is appropriate for photovoltaic conversion. Efforts are being made to achieve a reasonable level of efficiency.

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