Photoelectrochemical Properties of Spray Deposited $\text{Cu}_2\text{ZnSnS}_4$ Photoelectrode: Enhancement in Photoconversion Efficiency with Film Thickness

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Abstract

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were deposited using the spray pyrolysis method at different deposition conditions. The effects of molarity of precursor solution and film thickness on structural, morphological, composition, optical and photoelectrochemical cell (PEC) performance of CZTS thin films were investigated. The X-ray diffraction study showed that the polycrystalline nature of the kesterite phase CZTS with a tetragonal structure and the average crystallite size was estimated around 26 nm. The scanning electron microscope (SEM) analysis revealed uniform, dense and compact film deposited on the substrate surface. The films exhibited a direct energy band gap (E_g) around 1.54 eV, and the elemental composition ratio was found to be $\text{Cu}/(\text{Zn}+\text{Sn}) = 0.97$ and $\text{Zn}/\text{Sn} = 1.04$. The effect of elemental composition and the thickness of CZTS films on photoelectrochemical properties were investigated. The PEC cell fabricated using CZTS photoelectrode exhibited a photocurrent density of 11.12 mA/cm^2 with a power conversion efficiency of 2.70%.

Keywords: CZTS thin films; Photoelectrochemical cell; Solar cell; Photovoltaic properties.

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1. Introduction

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) semiconductor has emerged as a high potential photovoltaic material. The interest in (CZTS) semiconductor thin films have been growing over the last few decades. The recent advancements in cadmium telluride (CdTe) and copper indium gallium sulfide (CIGS) thin film solar cell have resulted in commercial photovoltaic devices.^[1-3] However, there are few limitations for the large scale use of CdTe and CIGS based technology due to the limited availability of In, Ga and Te as well as the large processing cost. Therefore, the major challenge of thin film technology is to develop solar cells using non-toxic, earth-abundant materials and low-cost deposition technique. The CZTS semiconductor could be a suitable alternative because it exhibit similar properties as that

of its competent materials like CdTe, CIGS/Se, etc. The main advantage of CZTS material is that the constituent elements are non-toxic and earth-abundant. The CZTS compound exists in kesterite phase with space group $\Gamma 4$ and $\Gamma 42m$ ^[4,5] and has a tetragonal structure. The structure can be simply explained as a cubic closely packed array of sulfur as anion and cations positioning at one-half of the tetragonal voids, with a stacking similar to zinc blend with the lattice constant, $a = 5.46 \text{ \AA}$ and $c = 10.93 \text{ \AA}$.^[5] The direct band gap of CZTS material is 1.51 eV,^[6,7] which is close to the optimum value of the band gap for solar cells. The high optical absorption coefficient about 10^4 cm^{-1} makes CZTS suitable to be used as a light absorber layer in the thin film solar cells.^[8]

CZTS thin films are deposited using a variety of methods that mainly include sputtering,^[9,10] thermal and vacuum evaporation,^[11-12] ion beam sputtering,^[13] sputtering with a sequential evaporation,^[14] electrodeposition,^[15] successive ionic layer adsorption and reaction (SILAR)^[16,17] etc. The CZTS films deposited using vacuum based processes achieved the considerable photoconversion efficiencies of around 1.08%, 3.99%, 6.77%^[6,10,12] and 10.8%.^[18] Also, the CZTS powder with various microstructures were synthesized using hydrothermal/solvothermal process, and then doctor bladed coated, drop casted or spin coated was used to form uniform

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layers. Solution-based approaches are also used to form CZTS thin films, in which the constituent elemental precursor solution is prepared and then spin coated is used to form CZTS layer. The highest efficiency of 12.6% has been reported using the solution-processed CZTSSe absorber layer.^[19]

Among all the deposition methods explained above, the spray pyrolysis technique is a famous method for the deposition of a variety of conducting and semiconducting materials. Using a spray pyrolysis deposition technique, different kinds of thin and thick films, ceramic coatings, and powders can be deposited. Unlike many other film deposition techniques, spray pyrolysis represents a straight forward and relatively cost-effective processing method. For example, Larramona *et al.*^[20] have reported 5% photoconversion efficiency by using spray deposition method and using colloidal dispersion of Cu-Zn-Sn-S in water and ethanol. In the present work, we report on the deposition and characterization of CZTS thin films. The film composition and film thickness on the physical properties of CZTS thin films were investigated. The effects of film compositional and film thickness on photoelectrochemical properties of the CZTS films were investigated.

2. Experimental Section

2.1 Chemicals

AR grade cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), thiourea ($(\text{NH}_2)_2\text{CS}$), hydrochloric acid (36% HCl), and sodium sulfate (Na_2SO_4) were purchased from S. D. fine Chem. Ltd., Mumbai and used without any further purification.

2.2 Thin film deposition using a spray pyrolysis method

The CZTS thin films were deposited by varying the molarity of precursor solution. Initially, aqueous solution was prepared by dissolving (0.01 M) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, (0.005 M) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, (0.005 M) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.04 M $(\text{NH}_2)_2\text{CS}$ in distilled water. The solution was mixed in the ratio Cu:Zn:Sn:S = 2:1:1:4. Excess thiourea was used to compensate the loss of sulfur during the formation of CZTS thin films.^[19] Few drops of concentrated HCl (36%) were added into the precursor solution to lower the pH (< 4). Then 80 mL of the resulting solution was sprayed onto a glass substrate at a rate of 5 mL/min using air as a carrier gas. The distance between the substrate temperature and spray nozzle was fixed to 25 cm. The substrate temperature was maintained at 400 °C.^[21] The formed CZTS film was named as CZTS1. The experiment was repeated with precursor concentrations of (0.02/0.03 M) ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), (0.01/0.015 M) $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, (0.01/0.015 M) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and (0.08/0.12 M) $(\text{NH}_2)_2\text{CS}$. All other experimental conditions were maintained the same and the sample was named as CZTS2/CZTS3 respectively. Finally, using the composition of CZTS2 sample and spraying 60 (T1), 80(T2) and 100(T3) mL of the precursor solution, thin films of different thicknesses were obtained. The films prepared by spraying 120 mL of solution were not uniform and adherent,

therefore were not considered for further characterizations.

2.3 Characterization techniques

For phase identification and to calculate various structure parameters of CZTS thin films, X-ray diffraction (XRD) patterns were recorded using XPERT-PROMPD X-ray diffractometer, with Cu K_α radiations of wavelength 1.5404 Å in 2θ range between 20–70°. The chemical composition and morphology of the CZTS thin film were analyzed by using energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM, JEOL JSM-IT300). The 3-D surface morphologies of CZTS thin films were analyzed using MFP-3D-AFM technique. The optical properties of the thin films were studied by UV-Vis (PerkinElmer) absorbance spectrophotometer at room temperature. The film thickness was measured using a surface step profiler (Dektak XT Profilometer).

3. Results and discussion

3.1 X-ray diffraction studies

Fig. 1 XRD pattern of CZTS thin films deposited by changing the molarity of the precursor solution.

Fig. 2 The XRD pattern CZTS films of different film thickness.

Fig. 1 depicts the XRD pattern of CZTS1, CZTS2 and CZTS3 samples. From the XRD pattern, it is revealed that the films were polycrystalline in nature. The diffraction peaks observed in the XRD pattern at $2\theta = 28.47, 33.1, 47.8$ and 56.3° could be attributed to the (112), (200), (220) and (312) planes of kesterite phase of CZTS (Reference: JCPDS file no. 26-0575). At lower precursor concentrations, the diffraction peaks were boarded at the base and less in intensity, whereas those

at higher concentrations were narrow with enhanced intensities. The crystalline nature of the thin film was found to be improved with increasing the precursor concentration.

Fig. 2 shows the XRD patterns of CZTS films of 0.698, 1.041 and 1.541 μm thickness. From the XRD pattern, it is seen that at the lower thickness, the films were poorly crystalline and only (112) plane showed its appearance. However, as the film thickness was increased, the enhancement in the intensity of (112), (220) and (312) peak was observed. The (112) peak intensity was higher for 1.541 μm thin film, which indicated the preferred orientation of film growth along (112) plane. The intensity of (002) peak is relatively low at a low spray volume; however, it is increased at 100 mL of spray volume. The thickness of light absorber layer of solar cell device plays a vital role in the performance of the device. Katagiry *et al.*^[22] studied the effect of the thickness of the CZTS absorber on the device performance by using the E-beam evaporation method. The photo-conversion efficiency of CZTS absorber layer was reported to be 1.46% with 0.95 μm layer.

Fig. 3 The SEM images of CZTS thin films deposited using different concentrations of precursors: a) CZTS1, b) CZTS2, and c) CZTS3.

Table 1. Structural parameters of CZTS thin films deposited using different molarities of precursor solution.

Sample name	FWHM (deg.)	d spacing (Å)	Lattice parameters (Å)		D-S D (nm)
			a	c	
CZTS1	0.50	3.130	5.406	10.873	15.38
CZTS2	0.42	3.130	5.409	10.873	19.27
CZTS3	0.30	3.131	5.406	10.886	25.30

(deg. - degree)

Table 2. Details of XRD patterns of spray deposited CZTS thin films of different thickness.

Film thickness (μm)	FWHM (deg.)	d spacing (Å)	Lattice parameters (Å)		D-S D (nm)
			a	c	
0.698 (T1)	0.60	3.120	5.407	10.801	13.18
1.041 (T2)	0.55	3.161	5.410	10.719	19.25
1.541 (T3)	0.45	3.137	5.403	10.800	28.16

The crystallite size calculated using the Debye-Scherrer formula was found to be 16 to 27 nm. The observed small variation in particle size may be due to the improved crystalline nature of the film. The estimated lattice parameters and crystallite size are in good agreement with the earlier report.^[23-25] The crystallite parameters corresponding to principle peak along the (112) plane are summarized in Table 1.

3.2 Morphological studies

Fig. 4 The SEM images of CZTS thin films deposited at different film thickness a) T1, b) T2, c) T3.

Fig. 4(a-c) shows the SEM images of CZTS thin films deposited using different molar concentrations. All the films were uniform, homogeneous, compact and showed spherical grains uniformly distributed over the substrate. The film surface was observed to be smooth, without any cracks and voids with well-defined interconnected grains. The surface agglomeration is observed relatively large in the Fig. 4(c) at the higher molar concentration. Fig. 4(a-c) depicts the SEM images of CZTS samples of different film thickness. For lower

thicknesses, the surface of the film was observed to be smooth, compact and homogenous. As the film thickness is increased, due to the particle agglomeration, the grain size was enhanced and the micron-sized interconnected sphere of CZTS grains was formed.^[22] Valdes *et al.*^[25] reported the compact structure of CZTS thin film at the same range of substrate temperature.

3.3 Composition analysis

Table 3. Chemical composition of elements (at.%) of CZTS thin films prepared at various precursor concentration.

Sample Name	Cu	Zn	Sn	S	Zn/Sn	$\frac{\text{Cu}}{\text{Zn} + \text{Sn}}$
CZTS1	27.5	16.8	12.48	43.22	1.34	0.93
CZTS2	25.44	12.53	11.2	50.83	1.11	1.07
CZTS3	22.55	13.5	12.3	51.65	1.09	0.87

Table 4. Chemical composition of elements (at.%) of CZTS thin films prepared using various film thickness.

Film thickness (μm)	Cu	Zn	Sn	S	Zn/Sn	$\frac{\text{Cu}}{\text{Zn} + \text{Sn}}$
0.698 (T1)	23.83	15.42	14.27	49.41	1.01	0.94
1.041 (T2)	24.37	13.46	12.81	49.34	1.11	1.07
1.541 (T3)	24.79	13.53	12.38	50.83	1.04	0.97

The compositional analysis of CZTS thin films deposited using different molarities of precursor solution are given in Table 3. The observed composition ratios of Cu/(Zn+Sn) for CZTS1, CZTS2 and CZTS3 films were 0.93, 1.07 and 0.87 respectively, whereas the Zn/Sn ratios for these samples were 1.34, 1.11 and 1.09, respectively. For high-performance CZTS based solar cells, the optimum composition ratio of Cu/(Zn+Sn) and Zn/Sn was reported to be about 0.75 ~ 0.95 and 1.1~1.4, respectively.^[26, 27] The sulfur content in the CZTS film was observed to be increased with increasing the molar concentration. The films deposited under the CZTS2 condition were fairly close to the optimized composition.^[26,27] Kumar *et al.*^[28] studied the effect of copper concentration on the physical properties of CZTS thin films and showed that the atomic composition of copper (Cu) in CZTS film was increased with increasing the copper concentration in the precursor solution. The compositional analysis of CZTS film of different film thicknesses is shown in Table 4. From the values shown in the Table 4, it is clear that the composition ratios for all the films are near to the optimum values.

3.4 AFM study of CZTS thin film

Fig. 5 3D surface topographic images (AFM) of CZTS thin films deposited using different solution concentrations, i.e., CZTS1, CZTS2, CZTS3.

The surface topography of the CZTS thin film was studied by using atomic force microscopy (AFM) technique. Fig. 5 shows the 3D AFM images of CZTS1, CZTS2 and CZTS3 samples. It is revealed from AFM images that the film surface exhibits the uniform spherical clusters of size in the range of 50 – 300 nm in diameter. During the deposition process, small droplets are vaporized above the substrate and bigger ones are condensed on the substrate, resulting in variation in the grain size to micro-crystallites.^[29] At higher precursor concentrations, an agglomeration of tiny crystals took place that results in the formation of micro-crystallites on the substrates. The 3D micrograph showed that the average roughness of CZTS1, CZTS2 and CZTS3 thin film samples is about 9.4, 10.42, and 16.67 nm, respectively. The surface roughness was observed to be increased as the precursor concentration was increased.

Fig. 6 3D Surface topographic images (AFM) of spray deposited CZTS thin film with the thickness of 0.698 (T1) μm , 1.041 μm (T2) and 1.541 μm (T3)

Fig. 6 depicts the 3D AFM images of CZTS thin films of 0.698, 1.041 and 1.541 μm thickness. Based on 3D AFM micrographs, the average roughness of the CZTS films for 0.698, 1.041 and 1.541 μm thickness was found to be 10.42, 16.46 and 29.88 nm respectively. It was revealed that, the average roughness of the film was increased with increasing the film thickness. From the AFM micrograph, the CZTS clusters of size around 100-200 nm were observed.

Fig. 7 The $(\alpha h\nu)^2$ vs $(h\nu)$ plot of spray deposited CZTS thin films for a) different molar concentration, and b) different film thickness.

3.5 Optical absorption studies

In order to evaluate the band gap energy, the absorbance of CZTS thin film was recorded. The band gap of CZTS thin films was estimated by extrapolating the linear region of $(\alpha h\nu)^2$ vs $(h\nu)$ curve on the energy axis. The band gap values were found to be 1.48, 1.52, 1.67 eV for the CZTS1, CZTS2 and CZTS3 samples respectively (Fig.7(a)). The estimated band gap of CZTS3 sample is found to be 1.67 eV, which is more than the optimum value. This may be because of the compositional variation as evident from the EDS analysis. The variation of the band gap of CZTS films of three different film thicknesses is shown in Fig. 7(b). The estimated band gap values were found to be 1.44, 1.5 and 1.56 eV for 0.698, 1.041 and 1.541 μm film thickness, respectively. The estimated band gap values are in good agreement with the reported values.^[30-33] Rajeshmon *et al.*^[34] and Seboue *et al.*^[35] reported that the CZTS films prepared using copper chloride, zinc acetate and stannous chloride precursors had estimated the band gap values around 1.3 and 1.79 eV.

4 Photoelectrochemical (PEC) properties of CZTS photoelectrode

Fig. 8 The schematic of three-electrode PEC cell measurement system.

One of the most convenient and efficient way of harvesting light energy into electrical energy is the thin film solid-liquid junction cell, commonly known as photoelectrochemical (PEC) cell. The main advantage of PEC is that they are much cheaper than the conventional solid-state devices. PEC cell offers good electrical contact between semiconductor and electrolyte. Also with the appropriate redox couple in the electrolyte, the Fermi energy in the electrolyte can be controlled and a barrier height can be tuned to the desired level. In the PEC cell, the light energy is directly converted into chemical energy of the PEC reaction product and therefore the energy storage problem can be solved with proper energy conversion. The schematic of three-electrode PEC measurement system is shown in Fig. 8. The photoelectrochemical (PEC) properties of CZTS photoelectrode deposited on FTO substrate was investigated. The PEC properties were investigated using a CH electrochemical analyzer instrument, with a three-electrode system consisting of CZTS/FTO as a photoelectrode electrode, Pt as a counter electrode and Ag/AgCl as a reference electrode. Three electrodes were immersed in the redox mediator containing 0.5 M aqueous solution of Na_2SO_4 ($\text{pH} = 6$) solution under illumination. The sample ($1 \times 1 \text{ cm}^2$) was irradiated from the semiconductor electrolyte interface with AM 1.5 G illumination (100 W/cm^2). The contact between FTO and metallic screw and CZTS/FTO is ohmic and quasiohmic.^[36, 37] Various cell parameters like short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and photovoltaic conversion efficiency (η) of the PEC cell performance of CZTS photoelectrode deposited on FTO substrate were estimated using the following equation and summarized in Table 5.

$$\text{FF} = \frac{I_{\text{max}} V_{\text{max}}}{J_{\text{sc}} V_{\text{sc}}} \quad (1)$$

$$\eta(\%) = \frac{I_{\text{sc}} V_{\text{ov}}}{P_{\text{in}}} \times \text{FF} \times 100 \quad (2)$$

where FF is fill factor, η is photoconversion efficiency, I_{max} is

the maximum current density, $V_{\max}$ is the maximum voltage, I_{sc} is short-circuit current density and V_{oc} is the open-circuit potential. The P_{in} is the input power in Watt/cm².

Fig. 9 Current–Voltage curve (J–V) under the illumination of PEC cell fabricated using sprayed CZTS/FTO photoelectrodes of different CZTS film thicknesses.

Fig. 9 depicts the current density –voltage curve (J–V) under the illumination of PEC cell fabricated using sprayed CZTS thin films of different film thickness. It was observed that, as the film thickness was increased, the photocurrent was increased, leading to an increased efficiency of the PEC cell. For the film with a thickness of 1.541 μm , the current density (J_{sc}) and open-circuit voltage (V_{ov}) were observed to be 11.12 mA and 0.58 V, respectively, with a fill factor (FF) of 42% and photoconversion efficiency about 2.70%. Shinde *et al.*^[38] studied the photoelectrochemical cell performance of CZTS cell deposited using SILAR method and reported 0.88% photoconversion efficiency. Bhosle *et al.*^[36] studied the effect of substrate temperature on the photoelectrochemical performance of CZTS thin films and reported the highest efficiency of 0.86 % for 500 °C substrate temperature. Suryavanshi *et al.*^[37] reported 3.81% photoconversion efficiency of CZTS thin film deposited using the SILAR method. It was reported that the higher photocurrent observed (15.23 mA/cm²) was because of the large grain size of the CZTS material consisting of poor copper film composition.

The photoconversion efficiency is strongly dependent on the grain size of the absorber layer. The large grain size enhances the minority carrier diffusion length and built in potential of the semiconductor device.^[39] From Table 5, it is clear that the photoconversion efficiency was increased with an increase in the film thickness. This improvement in the efficiency at higher film thickness may be due to the improved crystallinity and large grains of the CZTS films. It is seen from Table 4 that the films are Cu poor in composition. The reduction in Cu results in the removal of Cu based binary phases and leads to the optimized (Cu/Zn+Sn) composition ratio. Chen *et al.*^[40] reported the existence of the Cu (V_{Cu}) vacancy and Cu substituted Zn sites (Cu_{Zn}) in the CZTS

compound. Because the Cu_{Zn} state is relatively deeper than V_{Cu} state, V_{Cu} improves the photoconversion efficiency of CZTS/FTO photoelectrode. The Cu poor composition of the film enhances the V_{Cu} formation and suppresses the Cn_{Zn} formation, resulting in a higher short circuit current (J_{sc}).

Table 5. Various output parameters for the PEC cell fabricated using spray deposited CZTS/FTO electrode.

Thickness (μm)	Cu/(Zn+Sn)	Zn/Sn	V_{oc} (mV)	J_{sc} (mA)	FF (%)	η (%)
0.698	0.94	1.01	0.54	8.10	31	1.35
1.041	1.07	1.11	0.57	9.05	34	1.75
1.541	0.97	1.04	0.58	11.12	42	2.70

5. Conclusion

The CZTS thin films were successfully deposited using versatile spray pyrolysis technique. The effects of molarity of the precursor solution and film thickness on the physical properties of CZTS thin films were investigated. All the CZTS films exhibited the kesterite phase with a preferential orientation along the (112) direction. The direct optical band gap of CZTS films deposited under optimized conditions was found to be 1.55 eV with an optical absorption coefficient of $> 10^4 \text{ cm}^{-1}$ suitable for its use as a light absorber layer of the solar cell. The films deposited at a higher precursor concentration were found to be nearly stoichiometric. The thickness dependent photoelectrochemical performance of the CZTS working electrode was investigated. For the film with a thickness of 1.541 μm , the short-circuit current (J_{sc}) and open-circuit voltage (V_{ov}) were observed to be 11.12 mA and 0.57 V, respectively, with a fill factor (FF) of 42%, leading to a photoconversion efficiency of about 2.70%. The good crystalline nature of thin film, large grain size and suitable elemental composition of elements (Cu poor composition) in CZTS thin films may have increased the photoconversion efficiency. The present work gives an insight that the sprayed CZTS thin films could be used as a light absorber layer in the CZTS based solar cell.

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Conflict of Interest

There are no conflicts to declare.

Support information

Not applicable

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