



# Effect of copper concentration and spray rate on the properties Cu<sub>2</sub>ZnSnS<sub>4</sub> thin films deposited using spray pyrolysis



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## ABSTRACT

Polycrystalline Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) thin films were prepared using chemical spray pyrolysis. We examined the influence of concentration of copper in spray solution and spray rate on the properties of the films. Choice of copper concentration in the precursor solution was found to have a pivotal role in adjusting composition, band gap and resistivity of sprayed CZTS thin films. Nearly stoichiometric CZTS thin films with desirable band gap were obtained by using copper concentration of 0.015 M. Spray rate also has crucial role in adjusting properties like band gap of the films. Higher spray rates resulted in rougher films with secondary phases of copper sulfide. Secondary phases were also observed at low spray rate of 2 ml/min. Good films without any secondary phases and having band gap of 1.5 eV were obtained at the spray rate of 6 ml/min.

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## 1. Introduction

Recently considerable work is being carried out on the quaternary compound semiconductor Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) so as to optimize its opto-electronic properties for using as absorber layer of thin film solar cells [1]. This is mainly due to its direct band gap, high optical absorption coefficient, intrinsic p-type conductivity as well as non-toxicity [2]. Moreover all the constituents of CZTS are abundant in the earth's crust reducing concerns of materials costs. CZTS is derived from the copper indium gallium selenide (CIGS) structure by the isoelectronic substitution of two In (or Ga, respectively) atoms by one Zn and one Sn atom. As a consequence, CZTS has some similar properties as CIGS [3].

There are a variety of techniques reported for the deposition of CZTS thin films like vacuum techniques involving sequential deposition of constituent metallic layers followed by sulfurization [4], sputtering [5], PLD [6] and non-vacuum techniques like electrochemical deposition [7], sol-gel [8], spray pyrolysis [9] or deposition based on nanoparticle solutions [10]. CZTS thin films deposited using spray pyrolysis has been of increased interest these days as the method is simple with the potential for large-area deposition with fine control over elemental stoichiometry and

thickness; this enables significant cost reduction compared to other techniques [11]. In spray deposition, properties of the deposited films depend on several parameters of which the major ones are substrate temperature, spray rate and concentration of precursors. In our previous work, we reported the effect of precursor solution on the properties of spray pyrolyzed CZTS films [9]. The right choice of tin precursor was found to be stannic chloride. Present report details the effect of variation in spray rate and copper concentrations in the precursor solution on the properties of spray pyrolyzed CZTS thin films.

## 2. Experimental details

### 2.1. Preparation of CZTS films

CZTS film deposition was carried out using an indigenously developed chemical spray pyrolysis unit [12]. Precursors used were copper chloride (CuCl<sub>2</sub>·2H<sub>2</sub>O), zinc chloride (ZnCl<sub>2</sub>), stannic chloride (SnCl<sub>4</sub>·5H<sub>2</sub>O) and thiourea (CS(NH<sub>2</sub>)<sub>2</sub>) which were dissolved in water and sprayed on to the preheated soda lime glass (SLG) substrates. To prepare copper varied samples, substrate temperature, spray rate and volume of solution were fixed at 350 °C, 8 ml/min and 140 ml, respectively; while molarity of copper chloride was varied from 0.01 M to 0.03 M in steps of 0.005 M. Molarities of ZnCl<sub>2</sub>, SnCl<sub>4</sub>·5H<sub>2</sub>O and CS(NH<sub>2</sub>)<sub>2</sub> in the spray solution were 0.01, 0.01 and 0.12 M, respectively. Samples were named according to the molarity of copper chloride in the precursor solution as C-0.01, C-0.015, C-0.02, C-0.025 and C-0.03.

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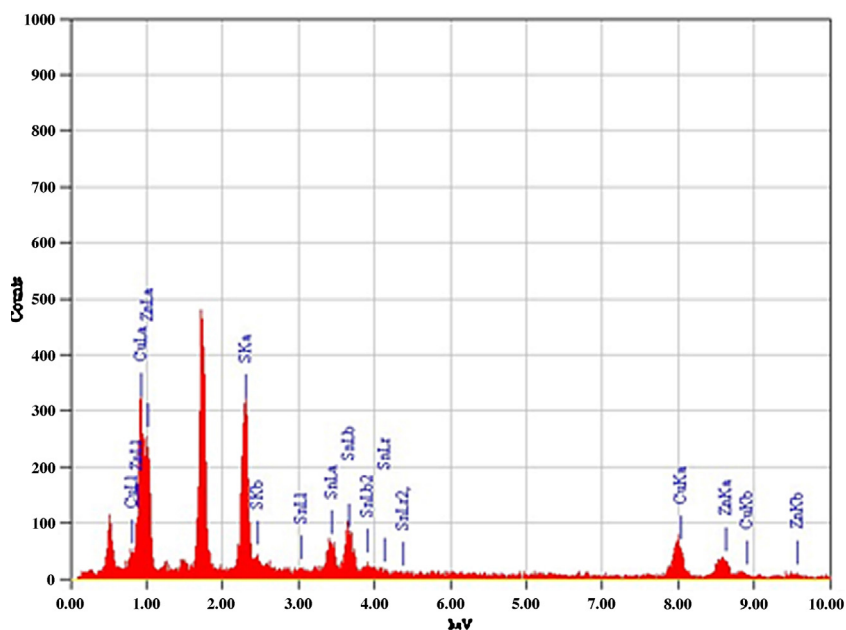


Fig. 1. EDAX spectrum of stoichiometric CZTS film (C-0.015).

To study the effect of spray rate, the parameters such as substrate temperature and volume of solution were fixed as mentioned before while the spray rate alone was varied in steps of 2 ml/min (from 2 to 10 ml/min). Cu:Zn:Sn:S ratio in the precursor solution is taken as 1.5:1:1:12. These samples were named as C2, C4, C6, C8 and C10, respectively.

## 2.2. Characterization of CZTS films

Film thickness was measured using Dektak-6M stylus profilometer. X-ray diffraction (XRD) was carried out using Rigaku (D.Max.C) X-ray diffractometer (having  $\text{CuK}\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) radiation and Ni filter operated at 30 kV and 20 mA). Raman studies were carried out in back scattering mode at room temperature using micro Raman system from Jobin Yvon Horiba LABRAM-HR visible (400–1100 nm) with spectral resolution of  $1 \text{ cm}^{-1}$ . Argon ion laser of wavelength 488 nm was used as the excitation source. Surface morphology of the CZTS thin films was studied with scanning electron microscope (SEM) (JEOL, JSM-840). The elemental composition of films was determined using energy dispersive X-ray (EDAX) analyzer attached to the SEM. Optical absorption studies were carried out using a UV–vis–NIR Spectrophotometer (JASCO V-570 model). Resistivity of the films was measured using the two probe method employing Keithley Source Measure Unit (SMU, K236).

## 3. Results and discussion

### 3.1. Effect of copper concentration

#### 3.1.1. Compositional analysis

In order to confirm whether we could achieve stoichiometry through the variation of copper concentration, compositional

analysis using EDAX was done. For each sample, measurement was taken from different points on the surface and their mean values are taken. As expected, copper incorporation in the film increased with increase in copper concentration in the precursor solution and the results are tabulated in Table 1. For C-0.015 we got almost stoichiometric CZTS film. From the EDAX spectrum of the stoichiometric CZTS film shown in Fig. 1 peaks indicating the presence of copper, zinc, tin and sulfur could be clearly seen. Peaks due to silicon and oxygen could also be seen which were from the SLG substrate.

#### 3.1.2. Structural analysis using XRD and Raman spectroscopy

Since the copper concentration was increased considerably in the precursor solution, there is a chance of formation of secondary phases in the deposited films. In order to understand this, XRD and Raman analysis were carried out for all the copper varied samples. Fig. 2 shows the XRD pattern of CZTS films deposited with different copper concentrations. From XRD, it is observed that all the samples were polycrystalline with diffraction peaks corresponding to the (1 1 2), (2 0 0), (2 2 0) and (3 1 2) planes of characteristic 'kesterite' structure. The  $d$ -values coincided with that of CZTS (JCPDS card no. 26-0575) with preferential orientation along the (1 1 2) plane. As the concentration of copper increases secondary phase corresponding to  $\text{Cu}_x\text{S}$  phase is visible in the pattern (JCPDS card no. 42-0564) and the intensity of the peaks corresponding to CZTS increased. From compositional analysis it was found that copper concentration in the film is high for samples C-0.025 and C-0.03. As evident from XRD, secondary  $\text{Cu}_x\text{S}$  phase is also prominent in these samples. Crystallite size of the samples was calculated using 'Scherrer formula' and this was maximum for the nearly stoichiometric film C-0.015 ( $\sim 30 \text{ nm}$ ) (Table 2).

Table 1  
Elemental composition of CZTS films prepared by varying the copper concentration.

Sample	Cu (at.%)	Zn (at.%)	Sn (at.%)	S (at.%)	Cu/Zn + Sn	Zn/Sn	S/metal
C-0.01	20.6	17.5	13.2	48.7	0.67	1.33	0.95
C-0.015	25.2	13.2	12.4	49.2	0.98	1.06	0.97
C-0.02	26.0	13.4	16.3	44.3	0.87	0.82	0.80
C-0.025	30.2	10.3	12.3	47.2	1.33	0.84	0.89
C-0.03	33.2	8.8	8.2	49.8	1.95	1.07	0.99

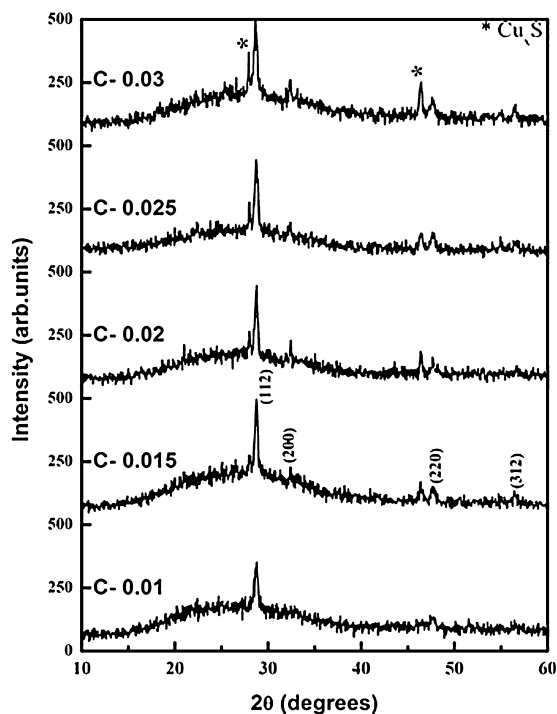


Fig. 2. X-ray diffractograms of CZTS samples prepared with different copper concentrations.

Presence of secondary phases in these films was also confirmed by Raman microprobe measurements. Fig. 3 shows the Raman spectra of CZTS films deposited with various copper concentrations. For samples C-0.01 and C-0.015, the Raman spectrum has dominant peak at  $338\text{ cm}^{-1}$  and a shoulder at  $351\text{ cm}^{-1}$  spectral region which

indicates formation of CZTS [13]. As copper concentration increases beyond 0.015 M, a peak at  $475\text{ cm}^{-1}$  due to the  $\text{Cu}_x\text{S}$  phase appears and its intensity increases as copper concentration increases. This peak at  $475\text{ cm}^{-1}$  is reported earlier in case of CZTS films prepared using spray pyrolysis [14] and other methods also [15]. For C-0.03 sample, the characteristic CZTS peak was suppressed almost completely and the prominent peak is due to the  $\text{Cu}_x\text{S}$  phase. This observation is in contrary to the XRD results for this sample in which a strong peak of CZTS is observed along with that of copper sulfide. This discrepancy is only due to the difference in analysis depth of the two techniques and suggests that the copper sulfide phase formed gets segregated over the surface of the sample, and with increase in copper concentration in the precursor leads to the formation of a thicker layer of  $\text{Cu}_x\text{S}$  over the surface, preventing the detection of the underlying CZTS phase using Raman scattering.

### 3.1.3. Morphological studies

Fig. 4 shows the SEM image of CZTS thin films prepared with various copper concentrations. It is well known that efficiency of polycrystalline thin film solar cell increases with increasing grain size of absorber layer, and therefore, larger grains are required for improving the device efficiency [16]. In the present work, it is obvious from the SEM images that, as the copper concentration increases there is improvement in grain morphology and size. Increase in grain size could be clearly seen when copper concentration increases from 0.01 M to 0.015 M. Beyond that agglomeration of grains occurs. Similar observation was reported earlier for copper variation in spray deposited CZTS films [17].

### 3.1.4. Optical studies

Optical band gap was deduced from  $(\alpha h\nu)^2$  versus  $h\nu$  plot (Fig. 5) and it reduced from 1.55 to 1.21 eV as the copper concentration increases from 0.01 M to 0.03 M (see inset of Fig. 5). Similar range of band gap values was reported earlier by Tanaka et al. [18]

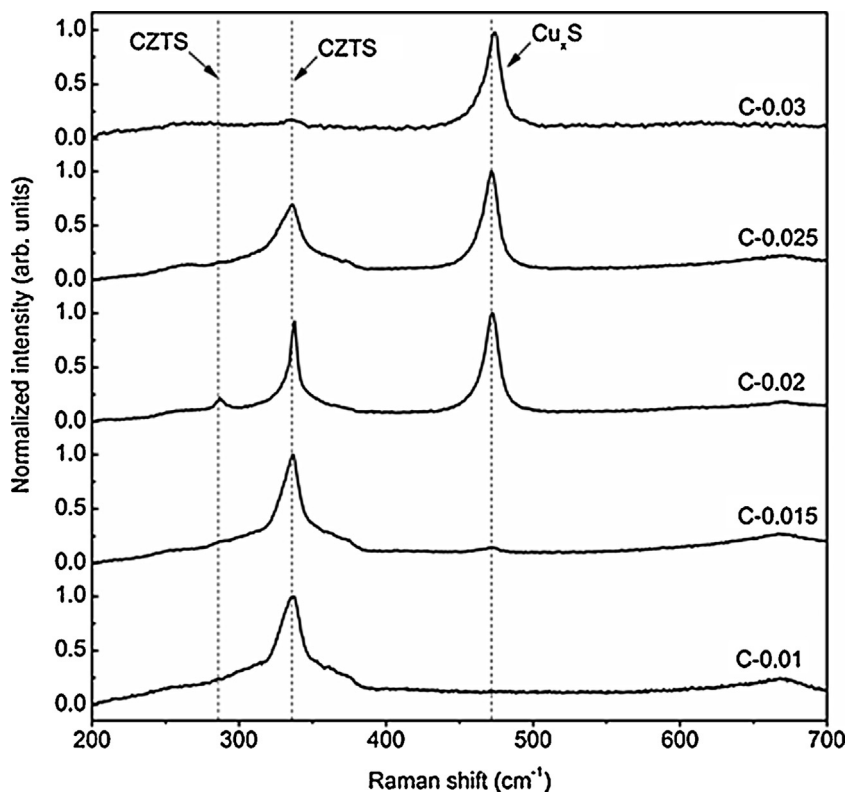


Fig. 3. Raman scattering spectra of CZTS samples prepared with different copper concentrations.

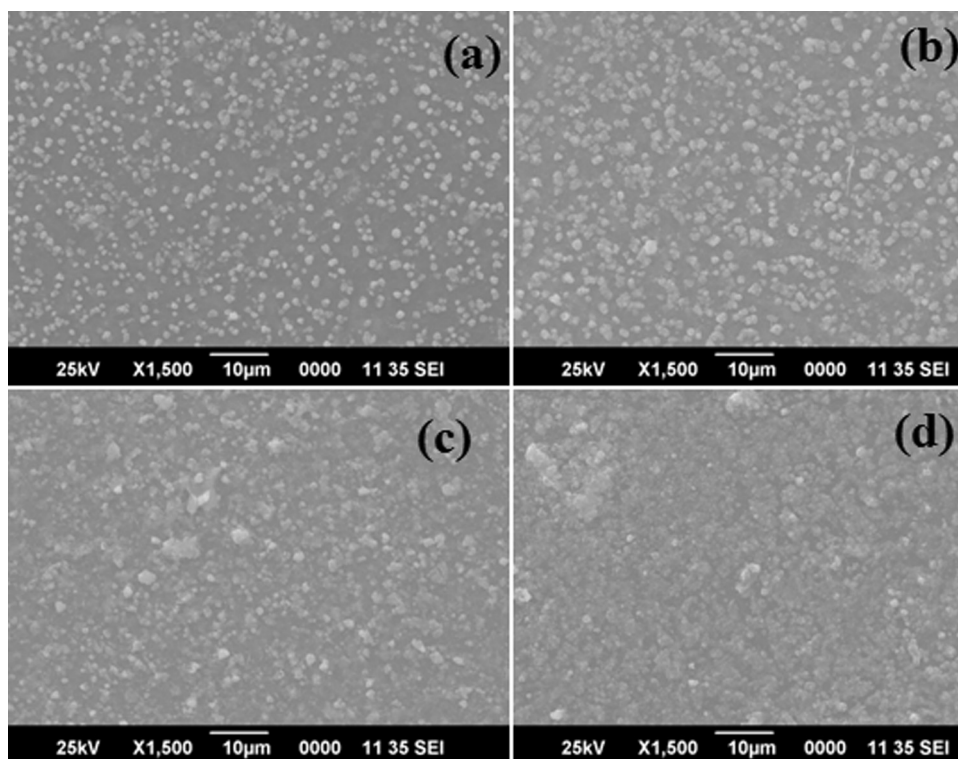


Fig. 4. SEM micrographs of CZTS samples prepared with different copper concentrations. (a) C-0.01, (b) C-0.015, (c) C-0.02 and (d) C-0.03.

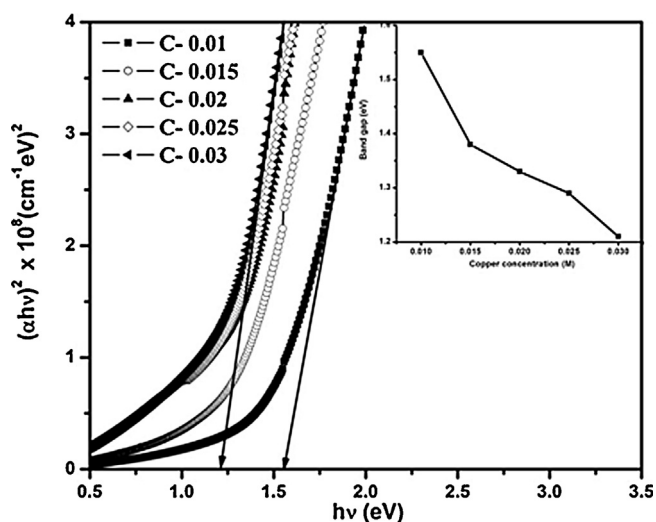


Fig. 5.  $(\alpha hv)^2$  versus  $h\nu$  graph of CZTS samples prepared with different copper concentrations.

for CZTS thin films. Decrease in band gap with increase in copper concentration was also observed by Kumar et al. [17] for sprayed CZTS thin films and by Tuttle et al. [19] in the case of  $\text{CuInSe}_2$  thin films. Another observation is that absorption edge becomes less

and less sharp and the absorption tail becomes more and more elevated as the copper concentration is increased in the films. This may be due to low energy absorption as a result of the presence of binary compounds of Cu and S which were confirmed from structural analysis. Similar observations of elevated absorption tail were made earlier for electron beam evaporated CZTS thin films when the  $\text{Cu}/(\text{Zn} + \text{Sn})$  ratio increased beyond 0.94 [20].

### 3.1.5. Electrical studies

Sheet resistance of the samples (measured using two probe technique) decreased with increase in copper concentration while thickness and roughness of the samples increased. However, resistivity of the films calculated from sheet resistance and thickness, decreases with increase in copper concentration (Table 3). All the samples showed p-type conductivity.

## 3.2. Effect of spray rate

### 3.2.1. Structural characterization

X-ray diffraction patterns of the CZTS films deposited at different spray rates were shown in Fig. 6. For sample C2 in addition to peaks corresponding to CZTS phase there are peaks corresponding to secondary phases such as  $\text{Cu}_{1.8}\text{S}$  (JCPDS card no. 47-1748) and  $\text{Cu}_x\text{S}$  (JCPDS card no. 42-0564). Also for high spray rate (sample C10) there is formation of  $\text{Cu}_x\text{S}$  phase as indicated by the peak at

Table 2  
XRD data of CZTS samples prepared by varying copper concentration.

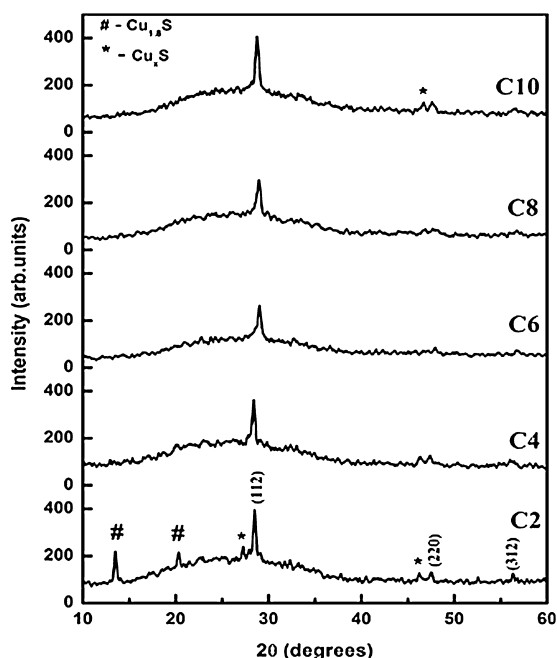
Sample	Preferential orientation	$2\theta$ (degrees)	$d$ -value (Å)	FWHM (degrees)	Crystallite size (nm)	Secondary phases observed
C-0.01	(1 1 2)	28.82	3.094	0.31	26.5	$\text{Cu}_x\text{S}$
C-0.015	(1 1 2)	28.99	3.077	0.28	29.6	$\text{Cu}_x\text{S}$
C-0.02	(1 1 2)	28.84	3.093	0.30	27.3	$\text{Cu}_x\text{S}$
C-0.025	(1 1 2)	28.84	3.093	0.34	23.8	$\text{Cu}_x\text{S}$
C-0.03	(1 1 2)	28.84	3.093	0.29	28.1	$\text{Cu}_x\text{S}$
Standard values (JCPDS Card No. 26-0575)		28.53	3.126			

**Table 3**  
Thickness, roughness and resistivity of CZTS samples prepared with different copper concentrations.

Sample name	Sheet resistance ( $\Omega/\square$ )	Thickness (nm)	Roughness (nm)	Resistivity ( $\Omega\text{ cm}$ )
C-0.01	9280	875	216	$8.12 \times 10^{-1}$
C-0.015	376	1010	238	$3.8 \times 10^{-2}$
C-0.02	154	1165	277	$1.8 \times 10^{-2}$
C-0.025	91	1320	331	$1.2 \times 10^{-2}$
C-0.03	43	1530	373	$6.6 \times 10^{-3}$

**Table 4**  
XRD data of CZTS samples prepared by varying the spray rate.

Sample	Preferential orientation	$2\theta$ (degrees)	$d$ -value ( $\text{\AA}$ )	FWHM (degrees)	Crystallite size (nm)	Secondary phases observed
C2	112	28.50	3.129	0.23	35.3	$\text{Cu}_{1.8}\text{S}$ , $\text{Cu}_x\text{S}$
C4	112	28.46	3.133	0.23	35.1	$\text{Cu}_x\text{S}$
C6	112	28.64	3.114	0.25	33.3	Nil
C8	112	28.58	3.120	0.24	34.8	$\text{Cu}_x\text{S}$
C10	112	28.60	3.118	0.23	35	$\text{Cu}_x\text{S}$
Standard values (JCPDS Card No. 26-0575)		28.53	3.126	–	–	–



**Fig. 6.** X-ray diffractograms of samples prepared at different spray rates.

46.2°. Sample C6 is devoid of any secondary phases. Crystallite size of the films decreased as the spray rate increased up to 6 ml/min and then slightly increases (Table 4). Similar decrease in crystallite size with increase in spray rate is observed in the case of sprayed  $\text{CuInS}_2$  films also [21].

### 3.2.2. Optical studies

$(\alpha h\nu)^2$  versus  $h\nu$  plot of CZTS films deposited at different spray rates are shown in Fig. 7. For C2, the band gap obtained is 1.6 eV and the absorption in the tail region was extremely elevated. As

the spray rate increases band gap decreased and the elevation of absorption tail also decreased. At the spray rate of 6 ml/min (sample C6) the band gap was 1.5 eV, suitable for photovoltaic energy conversion. Beyond 6 ml/min there are two linear portions in the  $\alpha h\nu^2$  versus  $h\nu$  plot, which indicates two band gaps, one due to the CZTS phase (at  $\sim 1.4$  eV) other due to  $\text{Cu}_x\text{S}$  phase ( $\sim 1.8$  eV). The (direct) optical band gap of  $\text{Cu}_x\text{S}$  reported earlier in literature is in the range 1.7–2.16 eV based on the value of 'x' [22].

### 3.2.3. Electrical studies

Resistivity of the films was calculated from sheet resistance and thickness. Thickness of the samples was increased from 650 nm to 880 nm when the spray rate increased from 2 ml/min to 10 ml/min. Resistivity values increased steadily up to 6 ml/min and then slightly decreases (Table 5). This increase in resistance might be due to the decrease in crystallinity with spray rate. Roughness of the films also increases with spray rate resulting in the surface being uneven. This is usually expected in spray deposited films [21].

## 4. Summary

Effect of copper concentration in the precursor solution and the spray rate on the properties of CZTS thin films deposited using spray pyrolysis was investigated. Initially, the influence of copper concentration was studied by preparing CZTS films by varying the molarity of copper chloride from 0.01 M to 0.03 M in steps of 0.005 M fixing all the other spray parameters. Referring to the structural analysis described previously, it may be understood that the crystallite size, composition and morphology of CZTS films depends strongly on the concentration of copper in the starting solution. Band gap of the films was also influenced by the amount of copper in the solution. It can be seen as decreasing from 1.55 eV for low copper concentration to 1.22 eV for high concentration. Resistivity of the films also decreases with increase in the amount of copper in the precursor solution. CZTS films that are nearly stoichiometric and

**Table 5**  
Sheet resistance, thickness, roughness and resistivity of the CZTS samples prepared at different spray rates.

Sample name	Sheet resistance ( $\Omega/\square$ )	Thickness (nm)	Roughness (nm)	Resistivity ( $\Omega\text{ cm}$ )
C2	71	650	152	$4.6 \times 10^{-3}$
C4	281	690	164	$1.9 \times 10^{-2}$
C6	619	775	171	$4.8 \times 10^{-2}$
C8	378	820	186	$3.1 \times 10^{-2}$
C10	296	880	195	$2.8 \times 10^{-2}$

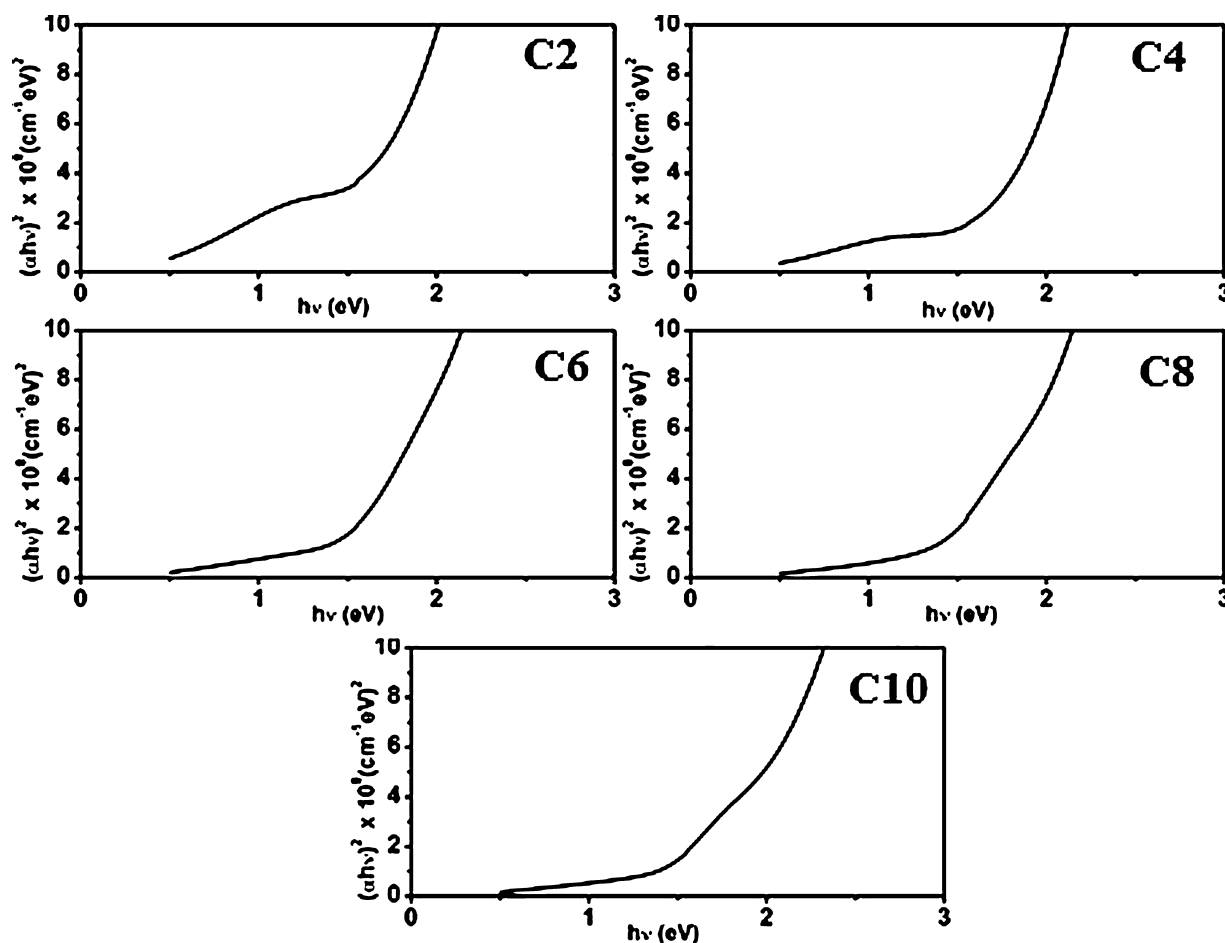


Fig. 7.  $(\alpha hv)^2$  versus  $h\nu$  graph of CZTS samples prepared at different spray rates.

having a band gap of 1.4 eV was obtained for a copper concentration of 0.015 M.

The influence of spray rate on the properties of CZTS thin films deposited through spray pyrolysis was investigated by varying the spray rate from 2 to 10 ml/min in steps of 2 ml/min. Higher spray rates has detrimental effect on the film morphology, making films more rough and uneven. Moreover, secondary phases were also observed at higher spray rates. The analysis of film properties prepared at various spray rates revealed that the spray rate of 6 ml/min is suitable for our deposition conditions.

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#### References

- [1] M.P. Suryawanshi, G.L. Agavane, S.M. Bhosale, S.W. Shin, P.S. Patil, J.H. Kim, A.V. Moholkar, CZTS based thin film solar cells: a status review, *Mater. Technol.* 28 (2013) 98–109.
- [2] T.K. Chaudhuri, D. Tiwari, Earth abundant non-toxic  $\text{Cu}_2\text{ZnSnS}_4$  thin films by direct liquid coating from metal–thiourea precursor solution, *Sol. Energy Mater. Sol. Cells* 101 (2012) 46–50.
- [3] S. Botti, D. Kammerlander, M.A.L. Marques, Band structures of  $\text{Cu}_2\text{ZnSnS}_4$  and  $\text{Cu}_2\text{ZnSnSe}_4$  from many-body methods, *Appl. Phys. Lett.* 98 (2011) 241915.
- [4] H. Katagiri, K. Saitoh, T. Washio, H. Shinohara, T. Kurumadani, S. Miyajima, Development of thin film solar cell based on  $\text{Cu}_2\text{ZnSnS}_4$  thin films, *Sol. Energy Mater. Sol. Cells* 65 (2001) 141–148.
- [5] S.W. Shin, S.M. Pawar, C.Y. Park, J.H. Yun, J.H. Moon, J.H. Kim, J.Y. Lee, Studies on  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) absorber layer using different stacking orders in precursor thin films, *Sol. Energy Mater. Sol. Cells* 95 (2011) 3202–3206.
- [6] L. Sun, J. He, H. Kong, F. Yue, P. Yang, J. Chu, Structural, composition and optical properties of  $\text{Cu}_2\text{ZnSnS}_4$  thin films deposited by pulsed laser deposition method, *Sol. Energy Mater. Sol. Cells* 95 (2011) 2907–2913.
- [7] J. Iljina, R. Zhang, M. Ganchev, T. Raadik, O. Volobujeva, M. Altoaar, R. Traksmaa, E. Mellikov, Formation of  $\text{Cu}_2\text{ZnSnS}_4$  absorber layers for solar cells by electrodeposition–annealing route, *Thin Solid Films* 537 (2013) 85–89.
- [8] H. Park, Y.H. Hwang, B.S. Bae, Sol–gel processed  $\text{Cu}_2\text{ZnSnS}_4$  thin films for a photovoltaic absorber layer without sulfurization, *J. Sol–Gel Sci. Technol.* 65 (2013) 23–27.
- [9] V.G. Rajeshmon, C. SudhaKartha, K.P. Vijayakumar, C. Sanjeeviraja, T. Abe, Y. Kashiwaba, Role of precursor solution in controlling the opto-electronic properties of spray pyrolysed  $\text{Cu}_2\text{ZnSnS}_4$  thin films, *Sol. Energy* 85 (2011) 249–255.
- [10] Q. Guo, H.W. Willhouse, R. Agarwal, Synthesis of  $\text{Cu}_2\text{ZnSnS}_4$  Nanocrystal ink and its use for solar cells, *J. Am. Chem. Soc.* 131 (2009) 11672–11673.
- [11] M. Espindola-Rodriguez, M. Placidi, O. Vigil-Galan, V. Izquierdo-Roca, X. Fontane, A. Fairbrother, D. Sylla, E. Saucedo, A. Perez-Rodriguez, Compositional optimization of photovoltaic grade  $\text{Cu}_2\text{ZnSnS}_4$  films grown by pneumatic spray pyrolysis, *Thin Solid Films* 535 (2013) 67–72.
- [12] T. Sebastian, M. Gopinath, C. SudhaKartha, K.P. Vijayakumar, T. Abe, Y. Kashiwaba, Role of substrate temperature in controlling the properties of sprayed  $\text{CuInS}_2$  absorbers, *Sol. Energy* 83 (2009) 1683–1688.
- [13] P.A. Fernandes, P.M.P. Salome, A.F. da Cunha, Growth and Raman scattering characterization of  $\text{Cu}_2\text{ZnSnS}_4$  thin films, *Thin Solid Films* 517 (2009) 2519–2523.
- [14] H. Yoo, J. Kim, Comparative study of  $\text{Cu}_2\text{ZnSnS}_4$  film growth, *Sol. Energy Mater. Sol. Cells* 95 (2011) 239–244.
- [15] H. Yoo, J. Kim, Growth of  $\text{Cu}_2\text{ZnSnS}_4$  thin films using sulfurization of stacked metallic films, *Thin Solid Films* 518 (2010) 6567–6572.
- [16] K. Tanaka, N. Moritake, H. Uchiki, Preparation of  $\text{Cu}_2\text{ZnSnS}_4$  thin films by sulfurizing sol–gel deposited precursors, *Sol. Energy Mater. Sol. Cells* 91 (2007) 1199–1201.

- [17] Y.B. Kishore Kumar, P. UdayBhaskar, G. Suresh Babu, V. Sundara Raja, Effect of copper salt and thiourea concentrations on the formation of  $\text{Cu}_2\text{ZnSnS}_4$  thin films by spray pyrolysis, *Phys. Stat. Sol. A* 207 (2010) 149–156.
- [18] K. Tanaka, N. Moritake, M. Oonuki, H. Uchiki, Preannealing of precursors of  $\text{Cu}_2\text{ZnSnS}_4$  thin films prepared by sol–gel sulfurizing method, *Jpn. J. Appl. Phys.* 47 (2008) 598–601.
- [19] J. Tuttle, D. Albin, J. Goral, C. Kennedy, R. Noufi, Effect of composition and substrate temperature on the electro-optical properties of thin-film  $\text{CuInSe}_2$  and  $\text{CuGaSe}_2$ , *Sol. Cells* 24 (1988) 67–79.
- [20] T. Kobayashi, K. Jimbo, K. Tsuchida, S. Shinoda, T. Oyanagi, H. Katagiri, Investigation of  $\text{Cu}_2\text{ZnSnS}_4$  based thin film solar cells using abundant materials, *Jpn. J. Appl. Phys.* 44 (2005) 783–787.
- [21] T. Sebastian, R. Jayakrishnan, C. SudhaKantha, K.P. Vijayakumar, Characterization of spray pyrolysed  $\text{CuInS}_2$  thin films, *Open Surf. Sci. J.* 1 (2009) 1–6.
- [22] A.C. Ratogi, S. Salkalachen, Optical absorption behaviour of evaporated  $\text{Cu}_x\text{S}$  thin films, *Thin Solid Films* 97 (1982) 191–199.