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Modification Of Optoelectronic Properties Of Sprayed CZTS Thin Films Through Spray Rate Variation

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Abstract. Effect of spray rate on structural, optical and electrical properties of spray pyrolysed Cu_2ZnSnS_4 (CZTS) thin films was investigated. We deposited films by varying spray rate from 2 ml/min to 10 ml/min in steps of 2 ml/min. For very low and high spray rates presence of secondary phases could be observed while for the films prepared at a spray rate of 6 ml/min were devoid of secondary phases. As spray rate increases band gap decreased. Samples prepared at 6 ml/min had optimum band gap of 1.5 eV. All the samples were observed to be p-type. Resistivity values increased steadily up to 6 ml/min and then slightly decreased. From the present work, CZTS films prepared at a spray rate of 6 ml/min is found to be ideal for absorber layer in solar cell.

Keywords: Spray coating techniques, X-ray diffraction, Optical properties, CZTS.
PACS: 81.15.Rs, 61.05.cp, 74.25.Gz, 73.61.Le;

INTRODUCTION

Cu_2ZnSnS_4 (CZTS) is a compound semiconductor that is currently being investigated as an 'indium-free' alternative to the $Cu(In,Ga)Se_2$ absorber layer in thin film solar cells. Indium is considerably less abundant and more expensive than either zinc or tin. CZTS has direct band gap of 1.5 eV and absorption coefficient > 10^4 cm^{-1} making it suitable for an absorber layer [1]. These films have been prepared using several experimental techniques such as atom beam sputtering [1], RF magnetron sputtering [2], hybrid sputtering [3], photochemical deposition [4], thermal evaporation [5], electrodeposition [6], pulsed laser deposition [7], spray pyrolysis [8], sulfurization of electron-beam evaporated precursors [9] etc. Among these, spray pyrolysis is cost effective and scalable technique. In the present work we report characterization of spray pyrolysed CZTS thin films deposited at different spray rates.

EXPERIMENTAL

CZTS films were deposited on cleaned soda lime glass substrates, using indigenously fabricated automated spray machine. Aqueous solution containing cupric chloride ($CuCl_2.2H_2O$), zinc acetate ($Zn(CH_3COO)_2.2H_2O$), stannic chloride ($SnCl_4.5H_2O$) and thiourea ($CS(NH_2)_2$) was sprayed onto the substrate kept at 623 K, using compressed air (pressure~1.5 bar) as the carrier gas. Spray rate was varied as 2 ml/min, 4 ml/min, 6 ml/min, 8 ml/min and 10 ml/min. These samples were named as C2, C4, C6, C8 and C10 respectively. Cu:Zn:Sn:S ratio in the precursor solution was taken as 1.5:1:1:12. Concentration of thiourea was made 3 times larger than the required quantity to maintain stoichiometry, to compensate for the loss of sulphur during pyrolysis. Structural analysis of the films was carried out using Rigaku (D. Max. C) X-ray diffractometer (employing Cu-Kα line (λ=1.5405 Å) and Ni filter) operated at 30 kV and 20 mA. Thickness and roughness of the films were measured using stylus profiler (Dektak 6M). Optical properties were studied using UV-Vis-NIR spectrophotometer (Jasco V-570 Model). Electrical studies were conducted using Keithley 236 Source Measure Unit (SMU).

RESULTS AND DISCUSSION

Structural Studies

X-Ray diffractograms of the films prepared at different spray rates are depicted in figure 1. Peaks corresponding to the (112), (220) and (312) planes of CZTS could be observed at 2θ values 28.52^0, 47.4^0 and

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56.2^0 respectively. These are characteristic of the 'kesterite' structure of CZTS. Preferential orientation was along the (112) direction. For C2, in addition to peaks corresponding to CZTS phase, there are peaks corresponding to secondary phases such as $Cu_{1.8}S$ (JCPDS card no. 47-1748) and Cu_xS (JCPDS card no. 42-0564). Also for high spray rate (C10) there is formation of Cu_xS phase as indicated by the peak at 46.2^o. Sample C6 is devoid of all such secondary phases. Grain size decreased as the spray rate increased up to 8 ml/min and then there was slight increase. Similar decrease in grain size with increase in spray rate is observed in the case of sprayed $CuInS_2$ films also [10].

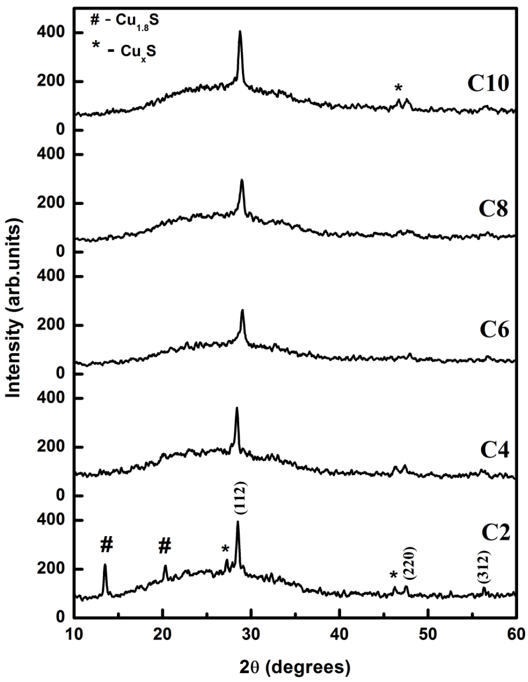

FIGURE 1. X-ray Diffractograms Of Sprayed Cu_2ZnSnS_4 Thin Films Prepared At Different Spray Rates.

Optical Studies

$\alpha h\upsilon^2$ versus $h\upsilon$ plot of CZTS films deposited at different spray rates is shown in figure 2. For C2 the band gap obtained is 1.6 eV and we can see that the absorption of the tail region was extremely elevated. This elevation means there is absorption in the lower energy region than the bandgap energy. This might be due to the presence of binary compounds of Cu and S which were confirmed from XRD analysis. Similar observations of elevated absorption tail were made earlier for E-B evaporated CZTS thin films when the Cu/(Zn+Sn) ratio increased beyond 0.94 [11]. As the spray rate increases band gap decreased resulting in decrease of absorption tail too. At a spray rate of 6 ml/min (C6) the band gap was 1.5 eV, suitable for photovoltaic energy conversion. Beyond 6ml/ min there was two linear portion in the $\alpha h\upsilon^2$ versus $h\upsilon$ plot, which indicates two band gaps; one is due to the CZTS phase (at ~1.4 eV) other one is due to Cu_xS phase (~ 1.8 eV). Direct optical band gap of Cu_xS reported earlier in literature is in the range 1.7-2.16 eV, depending on the value of 'x' [12].

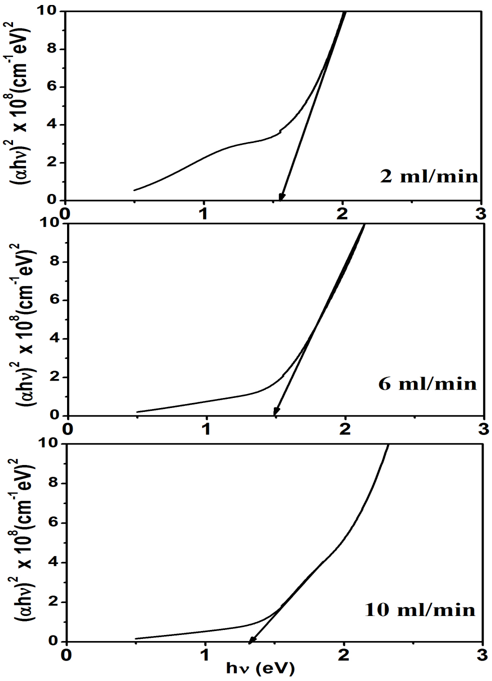

FIGURE 2. Absorption Spectra Of Sprayed CZTS Thin films Prepared At Different Spray Rates.

Electrical Studies

Resistivity of the films was calculated from the values of sheet resistance and thickness. Thickness of the samples increased from 650 nm to 880 nm when the spray rate is varied from 2 ml/min to 10 ml/min. Resistivity values increased steadily up to 6 ml/min and then slightly decreases (table 1). Roughness of the films also increased with spray rate, which is a common observation in spray deposited films [10].

TABLE 1. Thickness and Resistivity Of the Samples Prepared For Different Tin Precursors.

Sample name	Thickness	Resistivity (Ω.cm)
C2	650	4.6×10^{-3}
C4	690	4.4×10^{-3}
C6	775	1.8×10^{-2}
C8	820	2.2×10^{-2}

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C10	880	4.6×10^{-2}

CONCLUSIONS

Effect of spray rate on the opto-electronic properties of spray pyrolysed CZTS thin films was investigated. Single phase CZTS films with kesterite structure could be obtained at a spray rate of 6 ml/min. For spray rates below and above 6 ml/min, secondary phases were observed. For the optimized film we obtained a band gap of 1.5 eV, which is the ideal band gap value for efficient photo converters. All the films are found to be p- type and have absorption coefficient larger than 10^4 cm^{-1} in the visible region. Conductivity of the samples decreased with increase in spray rate up to 6 ml/min and then increased.

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REFERENCES

1. K. Ito and T. Nakazawa, *Jpn. J. Appl. Phys*. **27**, 2094-2097 (1988).
2. J. Seol, S. Lee, J. Lee, H. Nam and K. Kim, *Sol. Energy mater. Sol. Cells* **75**, 155-162 (2003).
3. T. Tanaka, T. Nagatomo, D. Kawasaki, M. Nishio, Q. Guo, A. Wakahara, A. Yoshida and H. Ogawa, *J. Phys. Chem. Solids* **66**, 1978-1981 (2005).
4. K. Moriya, J. Watabe, K. Tanaka and H. Uchiki, *Phys. Status Solidi (c)* **3**, 2848-2852 (2006).
5. K. Oishi, G. Saito, K. Ebina, M. Nagahashi, K. Jimbo, W. S. Maw, H. Katagiri, M. Yamazaki, H. Araki and A. Takeuchi, *Thin Solid Films* **517**, 1449-1452 (2008).
6. J. J. Scragg, P. J. Dale, L. M. Peter, G. Zoppi and I. Forbes, *Phys. Status Solidi (b)* **245**, 1772-1778 (2008).
7. L. Sun, J. He, H. Kong, F. Yue, P. Yang and J. Chu, *Sol. Energy Mater. Sol. Cells* **95**, 2907-2913 (2011)
8. V.G. Rajeshmon, C. Sudha Kartha, K. P. Vijayakumar, C. Sanjeeviraja, T. Abe and Y. Kazhiwaba, *Solar Energy* **85**, 249-255 (2011).
9. H. Katagiri, N. Sasaguchi, S. Hando, S. Hoshino, J. Ohashi and T. Yokota, *Sol. Energy Mater. Sol. Cells* **49**, 407-414 (1997).
10. T. Sebastian, R. Jayakrishnan, C. Sudha Kartha and K. P. Vijayakumar, *The Open Surface Science Journal* **1**,1-6 (2009).
11. T. Kobayashi, K. Jimbo, K. Tsuchida, S. Shinoda, T. Oyanagi and H. Katagiri, *Jpn. J. Appl. Phys*. **44**, 783-787 (2005)
12. A. C. Rastogi and S. Salkalachen, *Thin Solid Films* **97**, 191-199 (1982).

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