Effect of variation of tin concentration on the properties of Cu2ZnSnS4 thin films deposited using chemical spray pyrolysis

V. G. Rajeshmon, Abin Kuriakose, C. Sudha Kartha, and K. P. Vijayakumar

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Effect of Variation of Tin Concentration on the Properties of Cu_2ZnSnS_4 Thin Films Deposited Using Chemical Spray Pyrolysis

V.G Rajeshmon, Abin Kuriakose, C. Sudha Kartha and K. P. Vijayakumar

Department of Physics, Cochin University of Science and Technology, Cochin-22, Kerala.
Email: kpv@cusat.ac.in

Abstract. Cu_2ZnSnS_4 (CZTS) thin films were prepared using chemical spray pyrolysis technique on soda lime glass (SLG) substrates. The effect of tin concentration on the structural, optical and electrical properties was investigated. We deposited films by varying tin concentration from 0.007 M to 0.013 M in steps of 0.0015 M keeping the concentration of copper, zinc and sulphur at 0.02 M, 0.01 M and 0.12 M respectively. It was found that crystallinity of the film increased up to the tin concentration of 0.01 M and then decreases. Band gap of the films steadily decreased from 1.48 to 1.26 eV with increase in tin concentration. All the samples were observed to be p-type by hot probe method. Resistivity of the films increased with increase in tin concentration. In this work we tuned the optoelectronic properties by varying the tin concentration alone and optimized the concentration of tin which yields samples ideal for photovoltaic applications.

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 promising absorber in thin-film solar cells because of its suitable band gap of ~ 1.5 eV and its large absorption coefficient of over 10^4 cm^{-1} [1]. Elements present in this compound semiconductor are relatively cheap, abundant and non-toxic. CZTS thin films have been prepared by several experimental techniques such as atom beam sputtering, RF magnetron sputtering, hybrid sputtering, thermal evaporation, photochemical deposition, electro deposition, pulsed laser deposition, spray pyrolysis [2] and sulfurization of electron-beam evaporated precursors. Among these, spray pyrolysis is cost effective and scalable technique. In the present work we report preparation and characterization of the spray pyrolysed CZTS thin films with different tin concentration.

EXPERIMENTAL

CZTS films were deposited on cleaned SLG substrates, using indigenously fabricated automated spray machine. Aqueous solution containing cuprous 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 at the rate of 6ml/min onto the substrate kept at 623 K, using compressed air (pressure~1.5 bar) as the carrier gas. Total volume of solution sprayed was 100ml. Effect of tin concentration on the structural, electrical and optical properties of the films was studied by varying concentration of tin from 0.007M to 0.013 M, in steps of 0.0015 M, keeping the concentration of copper, zinc and sulphur at 0.02 M, 0.01 M and 0.12 M respectively. Concentration of thiourea was 3 times larger than that is required to maintain stoichiometry, to compensate for the loss of sulphur during pyrolysis. Crystal structure of the films was analyzed 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

X-Ray diffractograms of the films prepared with different tin concentration is depicted in figure 1. Peaks corresponding to the (112), (220) and (312)

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planes of CZTS could be observed at 2θ values 28.52^0, 47.4^0 and 56.2^0 respectively. These are characteristic of the 'kesterite' structure of CZTS. Preferential orientation was along the (112) direction. Intensity of the peaks increases when tin concentration is increased from 0.007 M to 0.01 M beyond which it decreases. Also for lower concentration of tin, there are peaks corresponding to the binary phase Cu_xS. When tin concentration is low, the possibility of formation of Cu_xS is also high. Grain size (Table 1) also increases for increase in tin concentration up to 0.01M and then decreases.

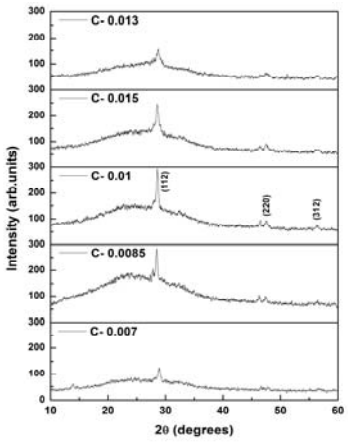

FIGURE 1. X-ray Diffractograms of Cu_2ZnSnS_4 Thin Films Prepared For Different Tin Concentrations

Band gap of the sample was determined from the absorption spectrum of the film. The graph plotted with $(\alpha h\upsilon)^2$ versus hυ when scaled appropriately gave a linear portion which when extrapolated to hυ-axis gives the band gap. As the concentration of tin increases band gap decreases steadily from 1.48 eV to 1.26 eV. The reported band gap of CZTS thin films is in the range 1.4-1.5 eV. As the concentration of Sn increases there is a possibility of formation of Cu_2SnS_3, which has a band gap of 1 eV. This may be the reason for lower bandgap for films with higher concentration of tin. The optimum bandgap of 1.4 eV is obtained for 0.01 M concentration of tin. The absorption coefficient in the visible region was larger than 10^4 cm^{-1}

It is found that thickness increases with increase in tin concentration. This can be attributed to the increased metal incorporation in the film. All the samples were observed to be p-type by hot probe method. Resistivity of the films increased with increase in tin concentration (Table-1).

CONCLUSIONS

Effect of tin concentration on the opto electronic properties of spray pyrolysed CZTS thin films was investigated. Single phase CZTS films with kesterite structure could be obtained with the solution containing 0.02 M copper chloride, 0.01 M zinc acetate, 0.01 M stannic chloride and 0.12 M thiourea. For the optimized film we obtained a band gap of 1.4 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 tin concentration.

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TABLE 1. Grain Size, Band Gap, Resistivity Of the Samples Prepared For Different Tin Precursors

Sample name	Grain Size (nm)	Band Gap (eV)	Thickness (nm)	Resistivity (Ω cm)
C-0.007	21.5	1.48	946	$2x10^{-3}$
C-0.0085	28.1	1.49	1060	$5.8x10^{-3}$
C-0.01	28.6	1.40	1238	$7.5x10^{-3}$
C-0.015	22.6	1.33	1415	$9.8x10^{-3}$
C-0.013	19.1	1.26	1512	$2.4x10^{-2}$

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