Effect Of Antimony Concentration On The Properties Of Spray Pyrolysed Cusbs$_2$ Thin Film Absorbing Layer For Photovoltaic Application

S. Thiruvenkadam, A. Leo Rajesh

Abstract: Thin films of $CuSbS_2$, a potential candidate for absorber layer in thin film solar cells, were successfully deposited on soda lime glass substrates by using spray pyrolysis and the effect of variation of antimony concentration on the structural, morphological and optical properties were investigated. An aqueous solution of precursor containing cupric chloride, antimony acetate and thiourea was used to deposit $CuSbS_2$ thin films onto heated glass substrates kept at 573K. The deposited thin films were characterized by GIXRD, Micro-Raman, AFM and UV-Visible Spectroscopy. The GIXRD pattern showed that all the $CuSbS_2$ thin films exhibited chalcopyrite structure with preferential orientation along the (006) direction. The optical band gap was found to be increased from 1.40 eV to 1.60 eV due to increasing the antimony amount in $CuSbS_2$ thin films, which is close to the ideal band gap for solar cell applications.

Keywords: Antimony Composition ,$CuSbS_2$, Optical Properties, Solar Cells, Spray Pyrolysis, Structural Properties, Thin films.

1 INTRODUCTION

The absorber $CuInS_2$ chalcopyrite semiconductors have proved to be successful candidates for photovoltaic applications. But it contains expensive and scarce elements like indium, which affect large scale production. In order to achieve the goal of cost-effective photovoltaic cell, $CuSbS_2$ obtained by replacing the indium with abundant antimony for several reasons. First, the ionic radii of indium and antimony are almost equal. Second, their property matches with the requirement of photovoltaic applications [1],[2]. The $CuSbS_2$ semiconductor thin film is one of the most promising material for absorption layer in thin film solar cells. It has suitable band-gap energy of 1.52 eV, large absorption coefficient (more than 10^4 cm^{-1}) showing potential applications in various optoelectronic devices [3],[4],[5]. $CuSbS_2$ thin films could be deposited using several deposition techniques such as thermal evaporation [4],[6], chemical vapor deposition [7], thermal diffusion [8], chemical bath deposition [9], electro-deposition [10] and spray pyrolysis [11],[12]. Chemical Spray pyrolysis is proved to be a versatile and economical method, which is widely used to deposit large-area chalcogenide, selenide, sulfide and oxide semiconductor thin films.

- *Research Scholar, Department of Physics, St. Joseph's College, Tiruchirappalli-620002, Tamil Nadu, India, Mobile: 09894801047, E-mail: stmthiru@gmail.com*
- *Corresponding Author: Assistant Professor, Department of Physics, St. Joseph's College, Tiruchirappalli-620002, Tamil Nadu, India, Mobile: 09444122070, E-mail: aleorajesh@gmail.com*

Monalache and Duta investigated the effect of deposition parameters of $CuSbS_2$ thin films and they reported the best photovoltaic properties which was obtained from the sample deposited at 240ºC, 25 cm and 60s, E_g = 1.13 eV [11]. The effect of antimony concentrations on the structural, morphological and optical properties of spray pyrolysed $CuSbS_2$ thin films were investigated to obtain suitable photovoltaic properties. The results of these investigations are presented in this paper.

2 EXPERIMENTAL DETAILS

2.1 Deposition of thin films

$CuSbS_2$ thin films were deposited by the Spray Pyrolysis method starting an aqueous solution containing the precursors such as cupric chloride (0.001M), antimony acetate (0.003-0.03M), and thiourea (0.006M). Concentration of thiourea was three times larger than that of its required quantity to maintain stoichiometry and compensate the loss of sulfur during pyrolysis. Small amount of acetic acid was added to increase the solubility of antimony acetate. In order to optimize the antimony amount on the formation of $CuSbS_2$ films, concentration of antimony acetate in the precursor solution were varied from 0.003M to 0.03M insteps of 0.006M. The aqueous solution was sprayed at a rate of 5 ml/min on to ultrasonically cleaned soda lime glass substrates kept at 573K with an accuracy of ±5K by using compressed air as a carrier gas.

2.2 Characterization

The Glancing Incidence X-Ray Diffraction (GIXRD) pattern of $CuSbS_2$ thin films was recorded using Bruker D8 discover glancing incidence X-ray diffractometer with a copper source. The room temperature Raman spectra were performed using Jobin-Yvon Horiba (LABRAM HR-800) Micro-Raman spectrometer. The grain size and the roughness of $CuSbS_2$ thin films were observed using Nano scoped E model Atomic Force Microscope (AFM) with contact mode. The optical analysis of $CuSbS_2$ thin films was carried out by recording the transmission and absorption spectra of the samples using Perkin-Elmer Lambda 35, double beam UV-Visible spectrophotometer.

3 RESULTS AND DISCUSSION

3.1 XRD Characterization

The GIXRD pattern of $CuSbS_2$ thin films deposited at various antimony concentrations are shown in Fig.1. According to JCPDS Card No: 88-0822, the formation of orthorhombic system was identified in all the deposited films with representative peaks located at 28.34°, 36.56°, 42.79° and 47.05° corresponding to the reflections form (111), (006), (213) and (116) planes respectively. Moreover, the crystallinity was improved with increase of antimony amount in $CuSbS_2$ thin films. The lattice parameters of the $CuSbS_2$ thin films were found to be a=0.6016 nm and b= 0.3796 nm and c=1.4499 nm. The crystallite grain size of all the samples were calculated using the Debye Scherer's formula, for the (006) peak at $2\theta = 36.56^{\circ}$

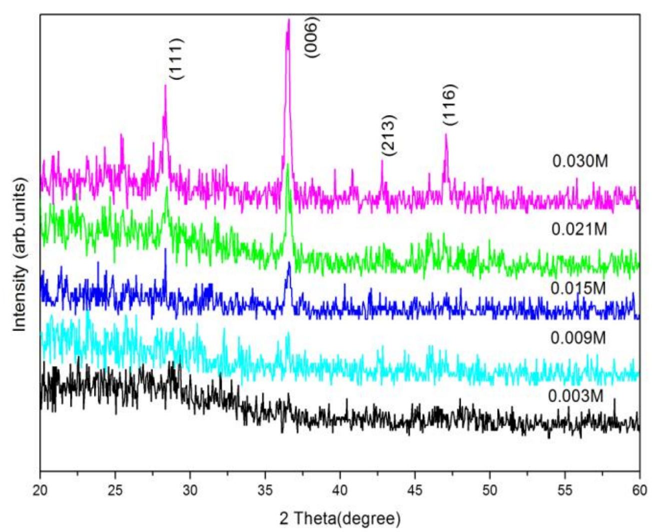

Fig. 1. GIXRD pattern of $CuSbS_2$ thin films deposited using precursor solutions with different antimony concentrations

$$D = (0.94\lambda / \beta \cos\theta)$$

Where, D is the mean diameter of the crystallites, λ is the wavelength of the X-ray source (1.5406 Å), β is the full width of the dominant peak in radians at half its intensity and θ is the Bragg's angle. The size of the crystallites for the spray deposited $CuSbS_2$ thin films were found to be increased from 15 nm to 25 nm with increase of antimony amount in $CuSbS_2$ thin films.

3.2 Micro-Raman Analysis

In order to support the XRD results, the room temperature Raman measurements were performed in the range 200–1200 cm^{-1} by Micro-Raman spectra using Ar+ laser (488 nm wavelength, 10 mW power) as excitation source. Fig.2. shows the Raman spectra of the $CuSbS_2$ thin films deposited at various substrate temperatures. The spectral peak at 1102 cm^{-1} confirms the characteristic of $CuSbS_2$ thin films and the secondary peak at 471 cm^{-1} corresponds to the $Cu_{2-x}S$ impurity phase indicated a small amount of excessive copper in these samples.

3.3 AFM Characterization

Two dimensional and three dimensional micrographs of $CuSbS_2$ thin films deposited from solutions with different antimony concentrations were performed using AFM and the results were shown in Fig.3. The micrographs evidently showed that the entire thin films surface was occupied with spherical shaped nanoparticles and the superstructures of clusters with sizes roughly of 100-700 nm were observed. The size of sub-grains in clusters was in the range of several tens of nanometers identical to the crystallite size calculated from XRD pattern. Based on the AFM analysis, the average surface roughness surface of $CuSbS_2$ thin films observed to be rough but the vertical height between the highest feature (brightest) and lowest (darkest) is in the range 60 nm to 207 nm indicating that the surface is relatively flat. Based on the AFM micrographs, the average roughness values of the $CuSbS_2$ films were found to 16 nm, 20 nm, 28 nm, 55 nm and 62 nm for decreasing the antimony amount in the films.

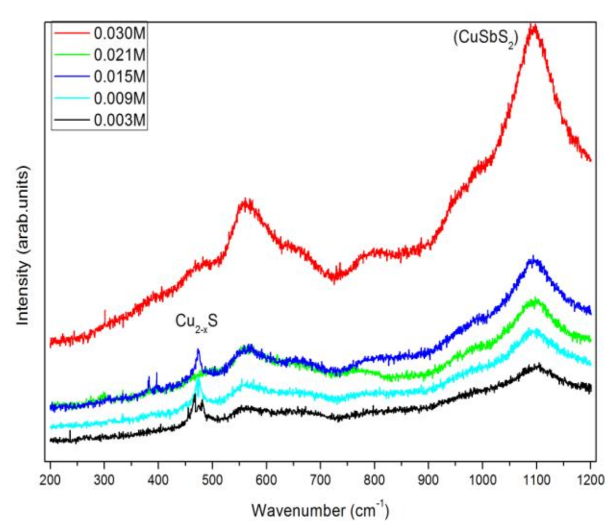

Fig. 2. Micro-Raman spectra of $CuSbS_2$ thin films deposited using precursor solutions with different antimony concentrations

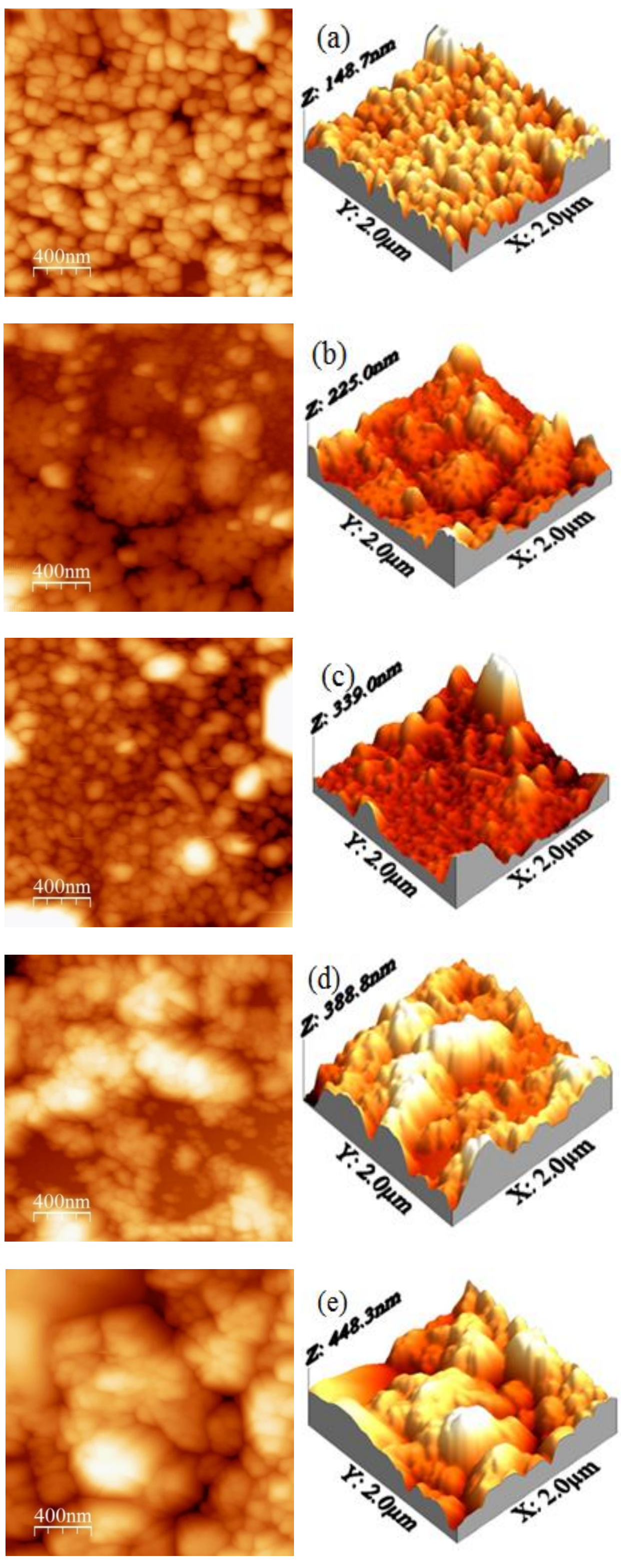

Fig. 3. 2D and 3D AFM micrographs of $CuSbS_2$ thin films deposited using precursor solution with different antimony concentrations: (a) 0.003M, (b)0.009M, (c)0.015M, (d)0.021M, (e)0.03M

3.4 Optical Properties

The $CuSbS_2$ thin films were characterized by the optical absorption and transmission spectra in the wavelength range 300-1100 nm using UV-Vis spectrophotometer. The variation of optical density with wavelength is analyzed to find out the nature of transition involved and the optical band gap. The nature of the transition is determined using classical relation,

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

Where, α is the absorption coefficient, A is a constant, h is the Plank's constant, ν is the frequency of the incident beam and E_g is the optical band gap. The value of absorption coefficient in all the deposited thin films was in the order of $10^6 cm^{-1}$, which supports direct band gap nature of the material. A plot of $(\alpha h\nu)^2$ versus $h\nu$ for $CuSbS_2$ thin films deposited at various substrate temperatures were shown in Fig. 4. Based on the allowed direct inter band transition, the band gap is determined by extrapolating straight line of $(\alpha h\nu)^2$ versus $h\nu$ curve to the intercept on horizontal photon energy axis. The direct optical band gap values are increased from 1.40 eV to 1.60 eV with respect to antimony amount. The difference in band gap values owing to the variation of antimony amount in $CuSbS_2$ thin films. The band gap values are quite close to the optimum band gap for a solar cell indicates that $CuSbS_2$ thin films are promising absorber material for solar cell applications.

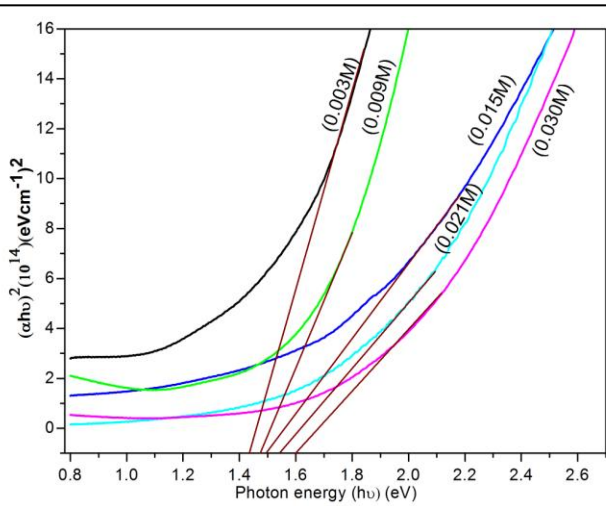

Fig. 4. $(\alpha h\nu)^2$ versus $h\nu$ of $CuSbS_2$ thin films deposited using precursor solution with different antimony concentrations

4 Conclusions

The $CuSbS_2$ thin films were successfully deposited by Chemical spray pyrolysis method onto soda lime glass substrates kept at 573K. The effect of antimony concentration on the properties of sprayed $CuSbS_2$ thin film was investigated. GIXRD pattern showed that the crystallinity of deposited thin films was improved with increasing the antimony concentration. The size of the crystallites increased with increases in the amount of antimony in $CuSbS_2$ thin films. Micro-Raman spectra were revealed the characteristics of $CuSbS_2$ thin films with a peak located at 1102 cm^{-1}. AFM micrographs elucidate that the average roughness decreased with increases of antimony amount in $CuSbS_2$ thin films. The direct optical band gap of $CuSbS_2$ thin films was found between 1.40 eV and 1.60eV, with an optical absorption coefficient over $10^6 cm^{-1}$. These characteristics reported in this paper offered perspective for $CuSbS_2$ thin films as suitable absorber material for solar cell applications.

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REFERENCES

[1] Y.R. Lazcano, M.T.S. Nair, P.K. Nair, “$CuSbS_2$ thin film formed through annealing chemically deposited Sb_2S_3–CuS thin films”, *J. Cryst. Growth*, vol.223, pp.399-406, 2001.

[2] J. Nelson, *The Physics of Solar Cells*, Imperial College Press, pp.265-272, 2003.

[3] J.Zhou, G.Bian, Q.Zhu, Y.Zhang, C.Li, J.Dai, “Solvothermal crystal growth of $CuSbQ_2$ (Q=S, Se) and the correlation between macroscopic morphology and microscopic structure”, *J. Solid State Chem.*, vol.182 (2) , pp.259–264, 2009.

[4] A.Rabhi, M.Kanzari, B.Rezig, “Growth and vacuum post-annealing effect on the properties of the new absorber $CuSbS_2$ thin films”, *Mater. Lett*, vol.62 (20), pp.3576–3578, 2008.

[5] A.Rabhi, M.Kanzari, B.Rezig, “Optical and structural properties of $CuSbS_2$ thin films grown by thermal evaporation method”, *Thin Solid Films,* vol.517 (7), pp.2477–2480, 2009.

[6] A.Rabhi, M.Kanzari, “Effect of air annealing on $CuSbS_2$ thin film grown by vacuum thermal evaporation”, *Chalcogenide Letters*, vol.8, pp.255 – 262, 2011.

[7] V.Estrella, M.T.S.Nair, P.K.Nair, “Semiconducting Cu_3BiS_3 thin films formed by the solid-state reaction of CuS and bismuth thin films”, *Semicond. Sci. Technol.,* vol.18, pp.190-194, 2003.

[8] C.Garza, S.Shaji, A.Arato, E.Perez Tijerina, G.Alan Castillo, T.K.Das Roy, B.Krishnan, “p- type $CuSbS_2$ thin films by thermal diffusion of copper into Sb_2S_3”, *Sol. Energy Mater. Sol. Cells*, vol.95, pp.2001–2005, 2011.

[9] S.C.Ezugwu, F.I.Eze ma, P.U.Asogwa, “Synthesis and characterization of ternary $CuSbS_2$ thin films: effect of deposition time”, *Chalcogenide Letters*, vol. 7, pp.341-348, 2010.

[10] Jeroh, M.Diemiruaye, “A study on the structural, optical and electrical properties of $CuSbS_2$ thin films and possible applications”, *Int. J. Thin Film Sci. Tec.,* vol. 2, pp.43-52, 2013.

[11] S.A.Manolache, A.Duta, “The influence of the spray deposition parameters in the photovoltaic response of the three-dimensional (3D) solar cell: TCO/ dense TiO_2/ $CuSbS_2$/ graphite”, *J. Optoelectron. Adv. Mater.,* vol.9, pp.3219–3222, 2007.

[12] S.A.Manolache, L.Andronic, A.Duta, A.Enesca, “The influence of the deposition condition on crystal growth and on the band gap of $CuSbS_2$ thin film absorber used for solid state solar cells (SSSC)”, *J.Optoelectron. Adv. Mater.,* vol.9, pp.1269–1272, 2007.