International Journal of Advanced Research in Physical Science (IJARPS)
Volume 2, Issue 11, November 2015, PP 21-28
ISSN 2349-7874 (Print) & ISSN 2349-7882 (Online)
www.arcjournals.org

Synthesis and Characterization of Cu_2SnS_3 Films Grown by Two-Stage Process

G. Phaneendra Reddy, K. Saritha and K. T. Ramakrishna Reddy

Department Of Physics, Sri Venkateswara University, Tirupati-517502, A.P. India
phaneendra369@gmail.com, sarayuphysics@gmail.com ktrkreddy@gmail.com

Abstract: *Cu_2SnS_3 (CTS) thin films have been synthesized by a two stage process using sulfurization of sputtered Cu-Sn precursors. The effect of sulfurization temperature on the properties of CTS films was investigated. The Cu-Sn layers were deposited by Co-sputtering onto soda-lime glass substrates and annealed at different temperatures 350°C, 400°C and 450°C. The films were analyzed by their elemental composition, structural, morphological and optical properties. CTS thin films exhibiting tetragonal structure with (200) as preferred orientation were obtained. The lattice parameters were found to be a=0.541 nm and c=1.082 nm. The crystallanity and the grain size increased with increase of sulfurization temperature. The grain size of the films was found vary in the range 45 - 123 nm. The direct optical band gap of these films was found to be between 1.55 eV and 1.65 eV, which depend on the sulfurization temperature.*

Keywords: *Sulfurization, co-sputtering, Cu2SnS3 (CTS) films and SIMS.*

1. Introduction

Semiconductors of Kesterite family, Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) with direct optical band gaps (1.0-1.5 eV), high optical absorption coefficient ($\alpha > 10^4$ cm^{-1}) and p-type electrical conductivity are emerging as potential solar cell absorber layers to the currently existing $Cu(In,Ga)Se_2$ films. These quaternary films contain complex crystal structure and difficult to control the growth mechanism. Therefore, a binary or ternary compound involving some of these elements and showing optimum material properties would be more useful. In this work, a ternary system Cu-Sn-S is taken for investigation.

CTS thin films were prepared by various physical methods like sulfurization of sputtered [1-3] and electron beam evaporate [4] Cu and Sn precursors, chemical approaches like spray pyrolysis [5], electro deposition technique [6], chemical bath deposition [7] and SILAR methods [8]. In sulfurization of precursors, the reported sulfurization duration is varied from 30 min. to 120 min. [1,2]. In this method, the ramp rate, sulfurization time and cooling period of the sulfurization play an important role in achieving good grain growth, morphology and compositional homogeneity of the films. Long sulfurization duration was reported to result in loss of Sn from the film.

This paper deals with a slightly different growth of CTS films by sulfurization of Cu-Sn co-sputtered metallic precursors at different temperatures and the effect of sulfurization temperature on the compositional, structural, morphological and optical properties was investigated and discussed.

2. Experimental Details

2.1. Sample Preparation

In this work, CTS films were formed by a two stage process. The Cu and Sn precursors used to grow CTS layers were prepared by co-sputtering process using DC magnetron sputtering followed by sulfurization of the precursors. In the first stage, the metallic precursors were deposited by DC magnetron sputtering (Model No: VRSU04D) onto ultrasonically cleaned soda-lime glass substrates. High purity (99.95%) Cu and Sn targets (2" diameter x 0.125" thickness) were used for sputtering the precursor layers 99.99% pure argon was used as sputter gas. The sputter power was maintained as 55W for Cu and 25W for Sn. The co-sputter deposition of Cu-Sn metallic precursors was carried out for 20 minutes. The base pressure of the vacuum chamber was 3 $\times 10^{-5}$ mbar and the working pressure during deposition was 14 $\times 10^{-3}$ mbar. The substrate holder was rotated using a rotary drive mechanism for uniform deposition of the precursor layers.

In the second stage, the precursors were sulfurized at 350°C, 400°C and 450°C in a two-zone tabular furnace (Fig.1). The sample was kept in zone-I and high purity sulfur pellets (99.99%) in zone-II. The temperature of zone-II was maintained constant at 130°C for generation of sulfur vapours and that of zone-II was varied. The temperature of each zone could be controlled by PID controllers. Rotary pump was used to evacuate the quartz tube. Nitrogen gas was used as the carrier gas and desired pressure in the tube was maintained by using the needle valve at gas inlet and control valve connected to the rotary pump. The N_2+S_2 vapour pressure was maintained constant at 300 Pa.

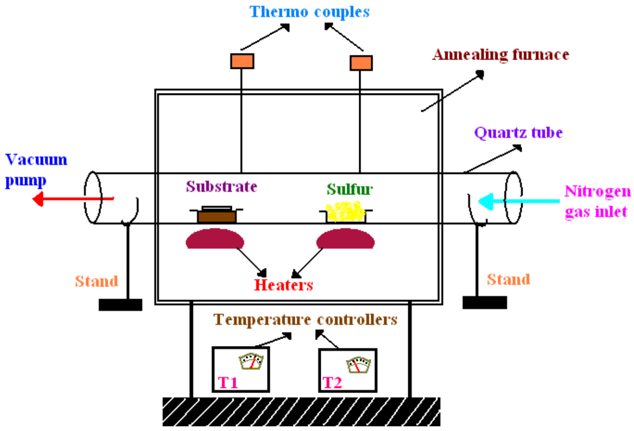


Fig1. *Schematic diagram of two zone furnace*

The sample temperature was increased at the rate of 20°C/min up to 200°C and then rate of 10°C/min upto the required annealing temperature in order to allow sulfurization to take place as shown in Fig. 2. The substrates were held at the three sulfurization temperatures for 60 min. The ramp rate of sulfur source continues till the temperature reaches to 300°C to minimize Sn loss. After the sulfurization process, the samples were allowed to cool naturally to room temperature.

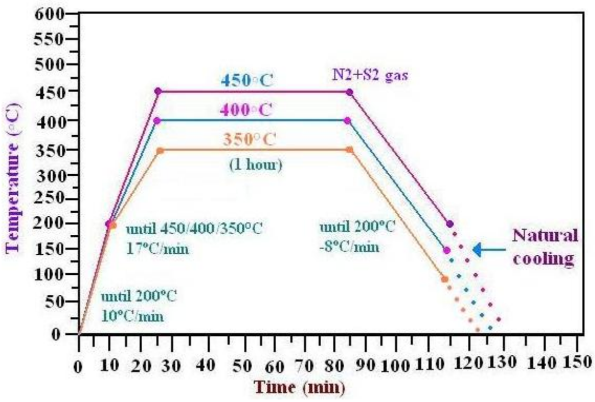


Fig2. *Schematic diagram of temperature profiles for the change in sulfurization process.*

2.2. Sample characterization

The as-grown samples were analysed to evaluate the physical behaviour. The structural properties of CTS films were characterized by using X-ray diffractometer (XRD) with Cu Kα radiation (λ=1.054Å) and micro structure using Raman Spectrometer. The film composition was obtained using energy-dispersive X-ray analysis (EDAX) and secondary ion mass spectroscopy (SIMS). The surface morphologies were evaluated by using scanning electron microscope (SEM). The optical properties were measured by UV-Vis-NIR spectrophotometer in the wavelength range 300-1100 nm.

3. Results and Discussions

The as-grown CTS films were homogeneous, uniform and strongly adherent to the substrate surface.

3.1. Compositional analysis

3.1.1. EDAX analysis

Figure 3 shows the EDAX spectra of Cu_2SnS_3 thin film grown at 450 °C. The EDAX compositional analysis of the films showed peaks corresponding to Cu, Sn and S without the presence of any impurity elements. The uncertainty in the determination of elemental composition by EDS is ±5 at. %. Through EDS studies, it was deduced that the atomic percentages of Cu, Sn and S were consistent with S/metal ratio (table 1). The relative variation in the Cu/Sn and S/metal ion ratio is from 1.78 to 2.14 and 0.47 to 0.32 respectively with the increase of sulfurization temperature. The deviation in Cu/Sn ratio is greater than the targeted value of 1.07, due to higher Sn loss. The concentration of Sn was decreased because of its re-evaporation owing to the high vapour pressure of Sn at high temperatures. The S/metal ratio is close to the targeted value of 0.39 which indicate that sulfurization process was successfully completed [14].

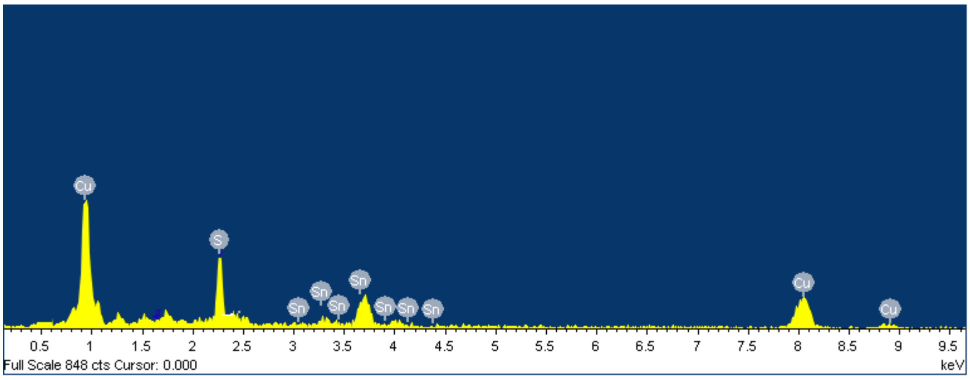


Fig3. *EDAX spectrum of CTS film obtained on sulfurization temperature at 450 °C.*

Table 1: EDAX composition data of CTS films

T_s (°C)	**Cu** (at.%)	**Sn** (at.%)	**S** (at.%)	**Cu/Sn**	**Cu/metal ion ratio**
350	43.47	24.42	32.11	1.78	0.47
400	45.11	23.4	27.4	1.92	0.4
450	52.36	23.21	24.43	2.14	0.32

3.1.2. SIMS analysis

The surface elemental distribution of CTS films deposited on soda lime glass substrates were performed using Secondary Ion Mass Spectrometry (SIMS). Figure 4 represents the SIMS profiles of CTS films indicating the variation of Cu, Sn and S in the layers obtained at various sulfurization temperatures. Initially the films formed at low temperatures showed excess Cu and the composition approached near stoichiometry as the sulfurization temperature is increased. The SIMS spectra revealed the presence of Cu, Sn and S which were uniformly distributed across the bulk of the film. No other impurity elements were noticed in the data. The intensity of copper is very high as compared with Sn and S elements at the initial stage that decreases with increase of T_S. This might be due to the re-evaporation of Sn at high temperatures. This type of data has been reported for the first time on CTS films that closely maps onto other measurements.

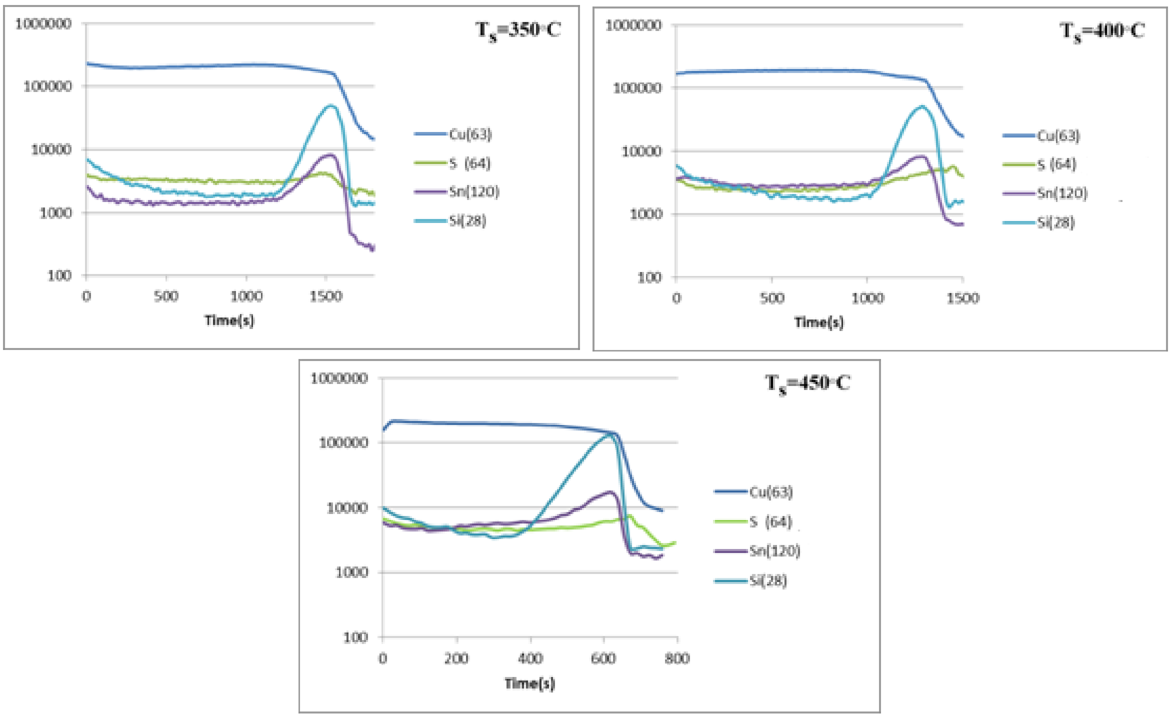
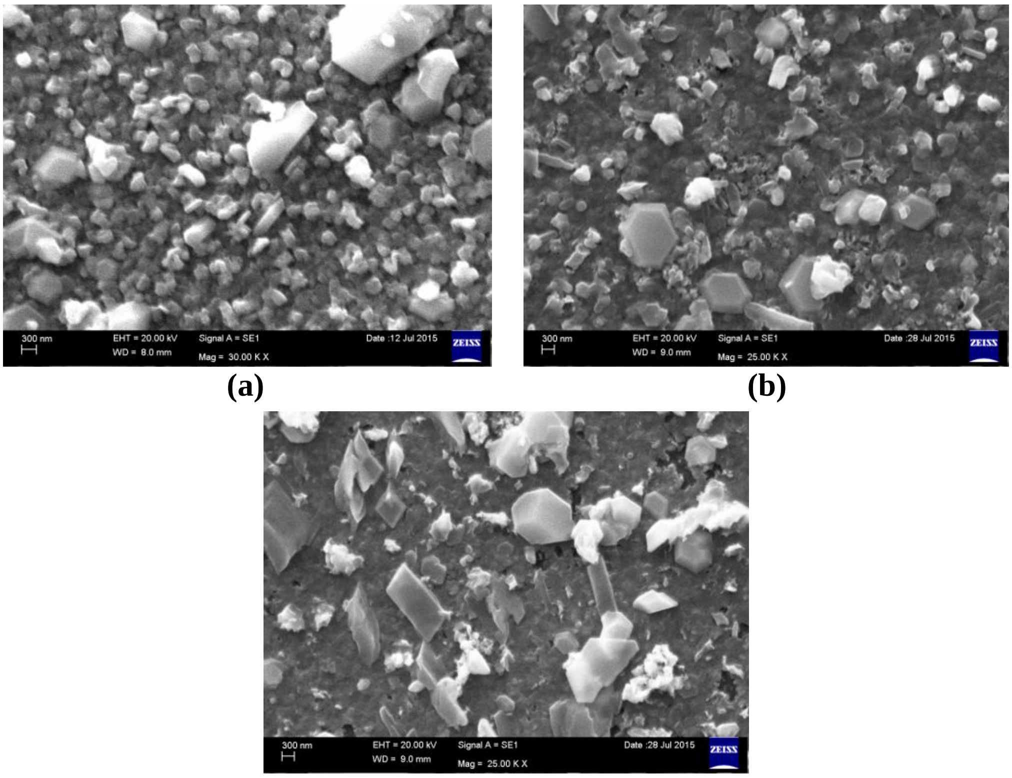


Fig. 4: SIMS profiles of CTS films obtained at various Sulfurization temperatures.

3.2. Surface morphology

The sulfurization temperature has a great influence on the surface morphology of the CTS films, as the grown layers were lightly sensitive to this temperature [3]. The SEM micrographs of CTS films grown at different sulfurization temperatures were shown in Fig. 5. The pictures showed pinhole free and irregular shaped grains without any micro cracks. A clear change in the crystallanity of the films was observed and the grain size was increased with increase of sulfurization temperature.



(c)

Fig5. *SEM images of CTS films obtained at (a)T_s= 350 °C (b) T_s= 400°C (c) T_s= 450 °C.*

3.3. Structural analysis

3.3.1. X-ray diffraction analysis

Fig. 6 shows the XRD patterns of CTS films obtained on sulfurization of metallic precursors at 350°C, 400°C and 450 °C. The observed diffraction peaks matched well with the standard JCPDS data file No. 89-4714 related to Cu_2SnS_3. In figure 6, the intense peaks clearly exhibit Cu_2SnS_3 phase which has (200) plane as the preferred orientation. The evaluated crystal structure was found to be tetragonal and the lattice parameters were found to be a=0.541 nm and c=1.082 nm. At lower temperatures some other smaller peaks were also observed with the appearance of (112) and (220) planes, which were related to Cu_2SnS_3 phase. S. Kahraman et al. [27] also reported similar planes for CTS films grown by sol-gel spin coating method, which exhibited tetragonal structure. A few secondary peaks corresponding to Sn_2S_3 and Cu_2S were also observed. The figure shows a significant improvement in the intensity of (200) peak with slight reduction in the FWHM, which reveals an improvement in crystallanity with increase of sulfurization temperature. The crystallite size (D) was calculated using Scherrer's formula,

$$D = \frac{c\lambda}{\beta \cos\theta} \quad \text{(nm)} \tag{1}$$

where 'β' is the full width at half maximum in radians, 'θ' is diffracting angle and 'λ' is the wavelength of X-rays and 'c' is the correction factor, which is taken as 0.94. The evaluated crystallite size of the layers varied in the range of 45 nm to 123 nm with increase of sulfurization temperatures.

The dislocation density (δ) in the grown Cu_2SnS_3 layers was also calculated using Williamson and Smallman's formula given below

$$\delta = \frac{1}{D^2} \quad (\text{Lines/m}^2) \tag{2}$$

The dislocation density decreased from 4.8×10^{-14} lines/m^2 to 5.6 x10^{-15} lines/m^2 with the rise of sulfurization temperature. This is mainly attributed to the improvement in crystallinity as revealed by the XRD studies.

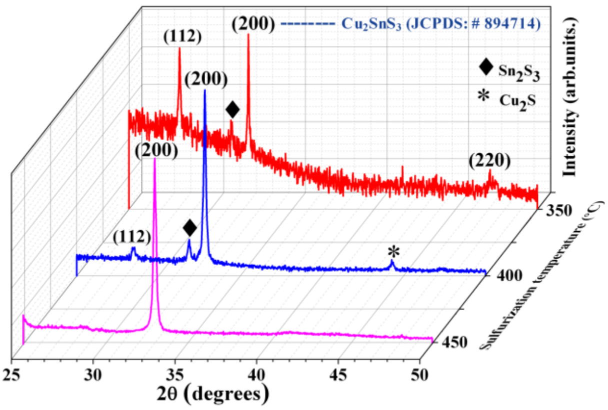


Fig6. *XRD pattern of CTS films synthesized at different sulfurization temperatures*

3.3.2. Raman Analysis

Raman spectroscopy is a standard characterization technique to reveal the exact phases of ternary semiconductor compound thin films. Figure 7 shows the Raman spectra of CTS film deposited at T_s=400°C, recorded in the wavelength range 250-550 cm^{-1} with Gaussian fitting. The micro Raman spectra contains Raman modes present at 290 cm^{-1}, 307 cm^{-1}, 332 cm^{-1}, 351 cm^{-1} and 472 cm^{-1}.Among these modes the peaks present at 290 cm^{-1}, 332 cm^{-1}, 351 cm^{-1} are the characteristic vibration symmetry modes of the tetragonal Cu_2SnS_3 phase [3,13]. The high intense mode at 332 cm^{-1} is attributed to the tetragonal phase Cu_2SnS_3, which is in close agreement with reported Raman data by T.S. Reddy et al. [15]. The ternary (Cu_2SnS_3) and binary phases (Cu_2S and Sn_2S_3) present in the film grown at T_s=400°C were also supported by XRD data. The Raman mode appeared at 472 cm^{-1} was characteristic of the binary phase of Cu_2S [15] and the mode at 307 cm^{-1} was attributed to the binary phase of Sn_2S_3 as reported in literature [17].

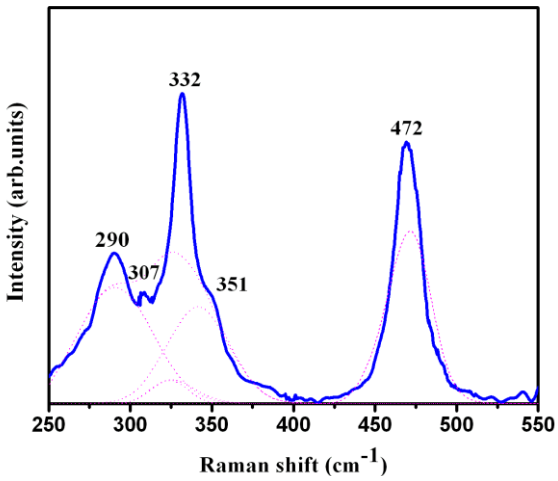


Fig7. *Raman spectra of CTS films obtained at sulfurization temperature of 400 °C.*

3.4. Optical analysis

The optical absorption of the CTS films grown at different sulfurization temperature was studied in the wavelength range 300-1100 nm using UV-Vis-NIR spectrometer. Figure 8 shows the variation of absorption coefficient of CTS films with wavelength. From the figure 8, it can be noted that the material exhibit sharp absorption edge and it absorbs entire visible region. The energy absorbed by the sample for direct/indirect optical transition from the incident photon energy (hν) is calculated using the following relation.

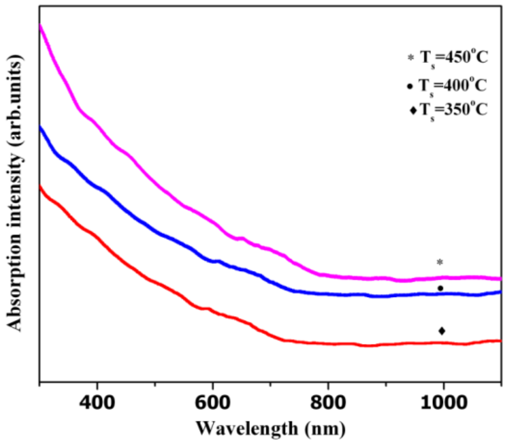


Fig8. *Absorption spectra of CTS films obtained at various sulfurization temperatures*

$$\alpha h\nu = A\,(h\nu - E_g)^n \tag{3}$$

where ‘A’ is a constant, ‘E_g’ is the energy band gap, hν is the incident photon energy and ‘n’ is the nature of the optical transition involved between the parabolic bands in the material. Here n = 1/2 indicates direct allowed transition; n = 3/2 reveals direct forbidden transition, n = 2 shows indirect allowed transition and n = 3 refers indirect forbidden transition. In this study, the data followed the above relation with n = 1/2, indicating the presence of direct allowed transition in the layers.

The characteristic plot of the variation in $(\alpha h\upsilon)^2$ with photon energy hυ of the films sulfurized at 350°C, 400°C and 450°C was shown in figure 9. The direct optical band gap values were found to be 1.66 eV, 1.62 eV and 1.55 eV respectively for films synthesized using T_S= 350°C, 400°C and 450°C. The optical band gap of CTS films was decreased with increasing sulfurization temperature because of the decrement of secondary phases and improvement in crystallanity. The band gap of the CTS film grown at T_s=450°C was ~1.55 eV and was in agreement with the reported value [15]. This value is closure to the optimum value suitable for photovoltaic applications [10-12].

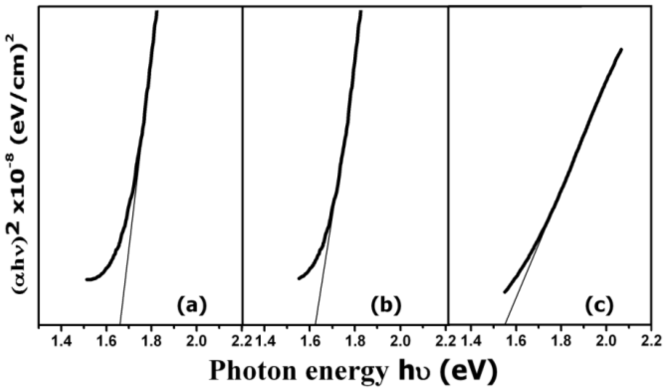


Fig9. *$(\alpha h\upsilon)^2$ versus hυ plots of CTS films obtained at various sulfurization temperatures (a)350 °C (b) 400°C (c) 450°C*

4. Conclusions

In this work Cu_2SnS_3 thin films were grown by a two-stage process, sulfurization of co-sputtered Cu, Sn metallic precursors and the effect of sulfurization temperature on the growth and properties of the layers was investigated. The EDAX analysis revealed the presence of only Cu, Sn and S. while the SIMS data revealed the uniform distribution of these elements across the layer thickness. The SEM micrographs revealed an increase of grain size with sulfurization temperature. The XRD studies of the film formed at T_S=450 °C indicated the existence of CTS films with an intense (200) plane as preferred orientation and exhibited tetragonal crystal structure. The Raman analysis of these films also supported the XRD observations. However the films synthesized at lower temperatures had shown secondary phases related to Cu_2S and Sn_2S_3. The band gap of these single phase CTS films was found to be 1.55 eV. Since Cu_2SnS_3 consists of wide absorbance in the visible region with a band gap close to the optimum value of 1.5 eV, it can be used as an absorber layer in the development of hetero junction solar cell.

REFERENCES

[1] Naoya Aihara, Hideaki Araki, Akiko Takeuchi, Kazuo Jimbo and Hironori Katagiri, Fabrication of Cu_2SnS_3 thin films by sulfurization of evaporated Cu-Sn precursors for solar cells, Phys. Status Solidi C 10, No. 7-8, 1086-1092 (2013).

[2] Pengyi Zhao and Shuying Cheng, Influence of Sulfurization Temperature on Photovoltaic Properties Cu_2SnS_3 Thin Films Deposited by Magnetron Sputtering, Advances in Materials Science and Engineering, Article ID 726080, (2013).

[3] P.A. Fernandes, P.M.P. Salome and A.F. da Cunha, Cu_xSnS_{x+1} (x=2,3) thin films grown by sulfurization of metallic precursors deposited by dc magnetron sputtering, Phys. Status solidi C7, 3-4,901-904 (2010).

[4] Kotaro Chino, Junpei Koike, Shinya Eguchi, Hideaki Araki, Royata Nakamura, Kazuo Jimbo and Hironori Katagiri, Preparation of Thin Films by Sulfurization of Cu/Sn Stacked Precursors, Japanese Journal of Applied Physics 51, (2012).

[5] M. Bouaziz, M. Amlouk, S. Belgacem, Structural and optical properties of Cu_2SnS_3 sprayed thin films, Thin Solid Films 517, 2527-2530, (2009).

[6] Francesco Di Benedetto, IIaria Bencista, Stefano Caporali, Serena Cinotti, Antonio De luca, Alessandro Lavacchi, Francesco Vizza, Maurizio Muniz Miranda, Maria Luisa Foresti and Massimo Innocenti, Electrodeposition of ternary $Cu_xSn_yS_z$ thin films for photovoltaic applications, Prog. Photovolt: Res. Appl. (2013).

[7] Jianmin Li, Cong Xue, Yaguang Wang, Guoshun Jiang, Weifeng Liu, Changfei Zhu, Cu_2SnS_3 solar cells fabricated by chemical bath deposition-annealing of SnS/Cu stacked layers, Solar Energy Materials & Solar Cells, 144 , 281- 288 (2016).

[8] Zhenghua Su, Kaiwen Sun, Zili Han, Fangyang Liu, Yanqing Lai, Jie Li and Yexiang Liu, Fabrication of ternary Cu-Sn-S sulfides by a modified successive ionic layer adsorption and reaction (SILAR) method, Journal of Materials Chemistry, 22, 16346, (2012).

[9] Mehdi Adelifard, Mohamad Mehdi Bagheri, Mohagheghi and Hosein Eshghi, Preparation and characterization of Cu_2SnS_3 ternary semiconductor nanostructures via spray pyrolysis technique for photovoltaic applications, Phys.Scr. 85, 035603 (6pp) (2012).

[10] Dominik M. Berg, Rabie Djemour, Levent Gutay, Guillaume Zoppi, Susanne Siebentritt, Philip J. Dale, Thin film solar cells based on the ternary compound Cu_2SnS_3, Thin Solid Films, 529, 6291-6294 (2012).

[11] Jun Xu, Xia Yang, Tai-Lun Wong and Chun-Sing Lee, Large-scale synthesis of Cu_2SnS_3 and $Cu_{1.8}S$ hierarchical microspheres as efficient counter electrode materials for quantum dot sensitized solar cells, The Royal Society of Chemistry, 4, 6537- 6542, (2012).

[12] Naoya Aihara, Ayaka Kanai, Kazuki Kimura, Manami Yamada, Kotoba Toyonaga, Hideaki Araki, Akiko Takeuchi and Hironori Katagiri, Sulfurization temperature depends of photovoltaic properties in Cu_2SnS_3-based solar cells, Japanese Journal of Applied Physics 53, 05FW13 (2014).

[13] Devendra Tiwari, Tapas K, Chaudhuri, T. Shripathi, U. Deshpande and V.G. Sathe, Microwave-assisted rapid synthesis of tetragonal Cu_2SnS_3 nanoparticles for solar photovoltaics, Appl. Phys. A, 117, 1139–1146, (2014).

[14] S. Kahraman, S. Çetinkaya, S. Yaşar and I. Bilican, Polyethylene glycol-assisted growth of Cu_2SnS_3 promising absorbers for thin film solar cell applications, Philosophical Magazine, Vol. 94, No. 27, 3149–3161, (2014).

[15] T. Srinivasa Reddy, R. Amiruddin, M.C. Santosh Kumar, Deposition and characterization of Cu_2SnS_3 thin films by co-evaporation for photovoltaic application, Solar Energy Materials & solar Cells, 143, 128-134, (2015).

[16] P.A. Fernandes, P.M.P. Salome and A.F.D. Cunha, A study of ternary Cu_2SnS_3 and Cu_3SnS_4 thin films prepared by sulfurizing stacked metal precursors, Journal of Physics D, vol. 43, no. 21, Article ID 215403,(2010).

[17] Louise S. Price, Ivan P. Parkin, Amanda M. E. Hardy, and Robin J. H. Clark, Atmospheric Pressure Chemical Vapor Deposition of Tin Sulfides (SnS, Sn2S3, and SnS2) on Glass, Chem. Mater, 11, 1792-1799 (1999).

AUTHORS' BIOGRAPHY

G. Phaneendra Reddy, he was born in 1989 at Kadapa, India. He did his B.Sc. with Maths, Physics and Computer Science as his subjects in 2010. He completed his M.Sc. in Physics at Sri Venkateswara University, Tirupati in 2012. He was qualified CSIR NET (LS) in December-2012 with 88th rank. Now he is doing Ph.D. under the guidance of **Prof. K.T. Ramakrishna Reddy**, Solar Photovoltaic Laboratory, Department of Physics, S.V. University, Tirupati. His research interest is 'Application of Thin film Technology for the betterment of Solar photovoltaics'.

K. Saritha, she was born in 1990 at Tirupati, India. She did her B.Sc. with Maths, Physics and Computer Science as her subjects in 2010. She completed her M.Sc. in Physics at Sri Venkateswara University, Tirupati in 2012. She did her B.Ed. course in 2013 at Sri Padmavathi Mahila Visvavidhyalayam, Tirupati. She recently submitted her M.Phil. Dissertation under the supervision of **Prof. K.T. Ramakrishna Reddy**, Department of Physics, S.V. University, Tirupati in 2015. Now, she is doing Ph.D. under the guidance of Prof. K.T.R.K. Reddy, whose subject of research specialization is 'Thin film Solar cells'.

Professor K. T. Ramakrishna Reddy, is an esteemed teacher and active researcher at the Department of Physics, Sri Venkateswara University, Tirupati, India. He has supervised 17 PhD students and guided many projects. Prof. Reddy has contributed more than 150 research publications in well reputed international journals, including four book chapters on photovoltaic research and two UK patents. He has widely travelled to work in various international Laboratories / Universities / Institutes of repute in photovoltaics devices, including the Northumbrian Photovoltaic Applications Centre, University of Stuttgart, University of Science and Technology of Hefei, China, Weizmann Institute of Science, Israel and Tokyo University of Science, Japan. He was awarded with many coveted foreign fellowships like the Marie Curie, EPSRC, DAAD, Commonwealth, JSPS and BOYSCAST to work abroad apart from those like INSA, SERC, CSIR, DST, MNES and UGC fellowships / associateships to work within India. He was also a Visiting Professor to Northumbria University (2006-2009) and Tokyo University of Science (2009-2011). Dr. Reddy is on the Editorial Board of the International journal of Optoelectronic Engineering and a member of various scientific bolides in India and abroad. He is a Fellow of the AP Academy of Scienecs and currently awarded with the "Best Teacher Award" by the Governemnt of Andhra Pradesh. He has completed more than 10 research projects awarded by both the Indian and foreign funding agencies.