Volume 11, Number 2, 2018. pp. 101-105

Jordan Journal of Physics

ARTICLE

Photoluminescence Behavior of $Cu_{2+x}Zn_{1-x}SnS_4$ Thin Films by SILAR Method*

J. Henry[a], **K. Mohanraj**[a] and **G. Sivakumar**[b]

[a] *Department of Physics, Manonmaniam Sundaranar University, Tirunelveli- 627 012, Tamilnadu, India.*

[b] *CISL, Department of Physics, Annamalai University, Annamalai Nagar-608 002, Tamilnadu, India.*

Received on: 22/5/2017; Accepted on: 19/11/2017

Abstract: Cu_2ZnSnS_4 thin films were deposited on a glass substrate by chemical method. The XRD pattern confirms the formation of tetragonal structure CZTS and peak shift is noticed for Cu doping. The absorption coefficient is in the order of $10^4 cm^{-1}$ and the band gap is found to be about 1.9 eV – 1.75 eV. The PL spectra show red shift for higher Cu doping concentrations.

Keywords: Photoluminescence, Cu_2ZnSnS_4 thin films, SILAR Method, XRD.

Introduction

Cu_2ZnSnS_4 (CZTS), a p-type semi-conductor has received significant attention due to its attractive features, such as utilization of abundant metals and high absorbance coefficient of $>10^4$ cm^{-1}[1]. It has a band gap value of about 1.5 eV, which is the optimum value for single-junction solar cell devices [2]. Optical properties of semi-conductor materials can be tuned by doping. The optical properties of doped nanomaterials differ from those of the corresponding host materials, because the dopants create deep trap levels and act as luminescence centers. Discrete energy states can be introduced in the band gap of semi-conducting host by doping with transition metals [3]. Transition metal ion-doped semi-conductors have been investigated intensively, since they can not only retain nearly all intrinsic advantages of semi-conductors, but also possess additional advantages, such as larger Stokes shift to avoid self-absorption/energy transfer, enhanced thermal and chemical stability and longer excited state lifetime [4]. Cu plays an irreplaceable role in modern electronic circuits due to its excellent electrical conductivity [5]. Moreover, optical properties of semi-conductor thin films can be tuned by changing Cu doping concentration.

CZTS thin films have been prepared by physical and chemical methods. There are only few reports available for the preparation of CZTS thin films by low cost Successive Ionic Layer Adsorption and Reaction (SILAR) method. This work aims to study the optical properties of Cu-doped $Cu_{2+x}Zn_{1-x}SnS_4$ (x = 0, 0.02, 0.04, 0.06, 0.08 and 1) thin films.

Experimental Methods

In this work, A.R.- grade copper chloride ($CuCl_2$), zinc chloride ($ZnCl_2$), tin chloride ($SnCl_2$), sodium sulfide (Na_2S) and double distilled water were used. Thin films of the $Cu_{2+x}Zn_{1-x}SnS_4$ (x = 0, 0.02, 0.04, 0.06, 0.08 and 1) system were deposited on precleaned microscopic glass slides by SILAR method at room temperature. The SILAR method includes

---

Corresponding Author: K. Mohanraj **Email**: kmohanraj.msu@gmail.com; mohanraj@msuniv.ac.in

*"6th National Seminar on Advances in Materials Science NSAMS-2017, held on March 2, 3-2017 at the Department of Physics, Manonmaniam Sundaranar University, Tirunelveli-627 012, Tamilnadu, India".

precursor concentration, dipping time and number of cycles. In this work, we have enriched the Cu ion concentration while reducing the Zn ions into the Cu_2ZnSnS_4 system.

For synthesis of Cu_2ZnSnS_4 film, a mixture of cationic precursors (0.1 M $CuCl_2$, 0.05 M $ZnCl_2$ and 0.05 M $SnCl_2$) was dissolved in distilled water. The anionic precursor solution was prepared by dissolving 0.2 M Na_2S in distilled water. First, the precleaned substrates were immersed in the composite cationic solution for 30 s to adsorb Cu^{2+}, Zn^{2+} and Sn^{2+} ions. Then, the substrate was rinsed in distilled water for 10 s to remove the loosely adsorbed ions, if any. After that, the substrate was immersed in the anion solution (S^{2-}) for 30 s, where the chemical reaction takes place between anions and cations to form CZTS. The substrate is again rinsed in distilled water for 10 s to remove the powdery precipitate, if any. The above four steps form one SILAR cycle, which was optimized. Similarly, 70 cycles were employed to obtain homogeneous CZTS films. The same procedure was adopted to enrich Cu concentrations (2.02; 2.04; 2.06; 2.08 and 2.10) into the CZTS system. The deposited films were annealed at 200°C for 2h in air atmosphere.

The prepared CZTS films were characterized by using XRD, UV-Vis. and PL techniques. Powder X-ray diffraction (XRD) patterns were performed using a PANalytical X‘ PERT- PRO diffractometer using Cu Kα radiation (λ= 1.5460Å). The diffraction patterns were collected in the range 2θ=10°-80°. Optical spectra and PL spectra were recorded using UV-2400PC series, UV-Visible spectrometer and LS-45 Perkin Elmer photoluminescence spectrometer, respectively.

Results and Discussion

Thickness of the $Cu_{2+x}Zn_{1-x}SnS_4$ (x = 0, 0.02, 0.04, 0.06, 0.08 and 1) films were determined using optical method [2] given in Table 1. Fig. 1 shows the XRD patterns of CZTS thin films deposited on glass substrates at various x values. The peaks observed at 2θ = 28.5°, 32.9° and 46.39° belong to the (112), (200) and (220) plane, respectively, of tetragonal CZTS phase (JCPDS Card No. 260575). The broad hump is observed around 20 to 30° due to the amorphous glass substrate. The intensity of the (220) plane increases with increase in Cu doping. The prepared CZTS film is polycrystalline in nature. Hence, a large number of grains with various relative positions and orientations cause variations in the phase difference between the wave scattered by one grain and that by the others. The total intensity scattered by all grains is the sum of individual intensities scattered by each grain [6].

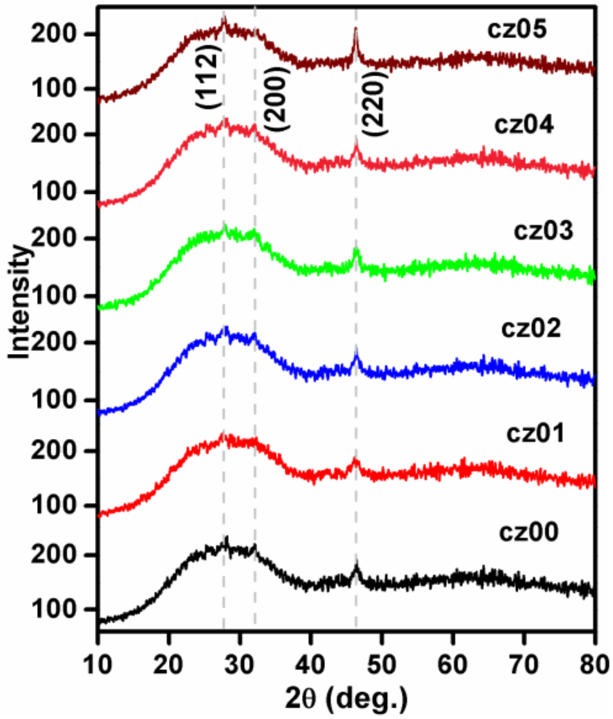

FIG. 1. XRD pattern of CZTS thin film.

The crystalline size was estimated by using Scherrer formula [7]:

$$D = \frac{0.9\,\lambda}{\beta \cos \theta} \qquad (1)$$

where β is full width at half maximum (FWHM), λ is the wavelength of X-ray source and θ is the Bragg's angle.

Table 1 shows the thickness and crystalline size of the CZTS thin films deposited at different Cu concentrations. From the table, it is noticed that the crystalline size was found to be increased with increase in cz05. This increase in crystalline size with increase in copper concentration shows the improvement of the CZTS crystallites under Cu-rich conditions [8]. The film thickness is found to be decreased with increase in Cu doping.

TABLE 1. Thickness and crystalline properties of $Cu_{2+x}Zn_{1-x}SnS_4$ thin films.

S. No.	Cu:Zn ratio	Name of the compound	Sample code	Thickness of the film (nm)	Crystalline size (nm)
1	2.00:1.00	Cu_2ZnSnS_4	cz00	800	9
2	2.02:0.98	$Cu_{2.02}Zn_{0.98}SnS_4$	cz01	760	9
3	2.04:0.96	$Cu_{2.04}Zn_{0.96}SnS_4$	cz02	722	8
4	2.06:0.94	$Cu_{2.06}Zn_{0.94}SnS_4$	cz03	617	9
5	2.08:0.92	$Cu_{2.08}Zn_{0.92}SnS_4$	cz04	537	9
6	2.10:0.90	$Cu_{2.10}Zn_{0.9}SnS_4$	cz05	523	17

The optical absorption spectra of the CZTS films are shown in Fig. 2. The optical spectra of CZTS showed good absorption in the range of 400-500 nm. A gradual reduction is noticed in the absorption profile between 400 and 600 nm for all the films, which is attributed to d-d transition of Cu^{2+}. The absorption coefficient is found to be about 10^4 cm^{-1}. The band gap plot is shown in Fig. 3 and it is found to be about 1.9-1.75 eV. The band gap is decreased for increased Cu doping. The film cz05 shows lesser bandgap, which may be due to the bigger crystalline size which is confirmed from the XRD analysis.

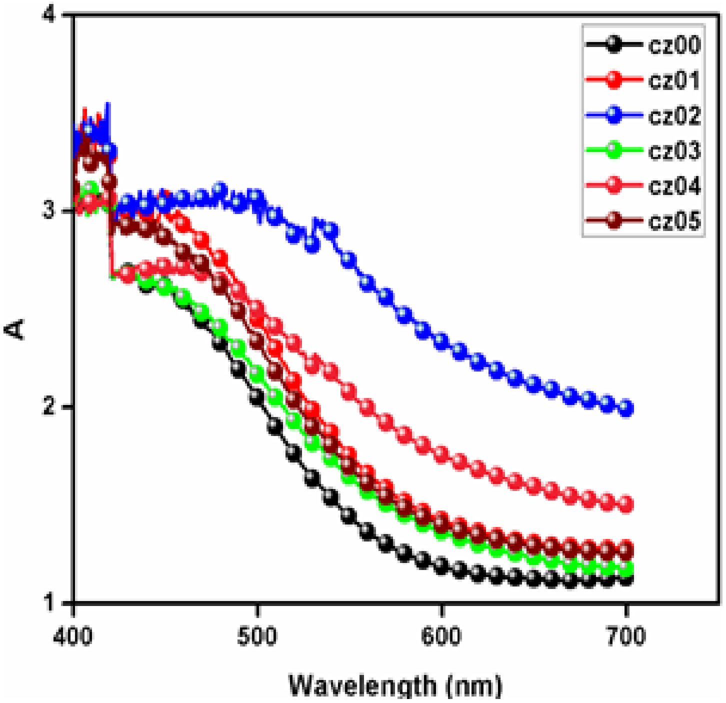

FIG. 2. UV-visible absorption spectra of the CZTS thin films.

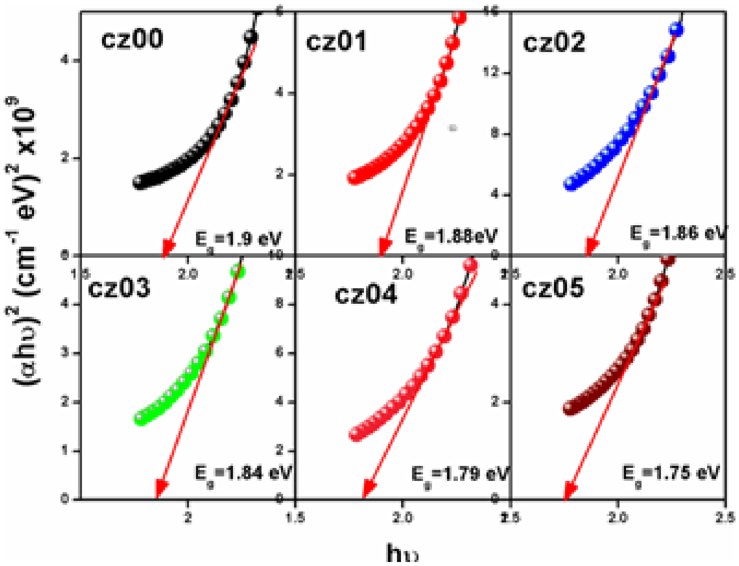

FIG. 3. Optical bandgap of CZTS thin films.

Fig. 4 shows the photoluminescence spectra of $Cu_{2+x}Zn_{1-x}SnS_4$ (x = 0, 0.02, 0.04, 0.06, 0.08 and 1) thin films in the wavelength range of 300 to 600 nm. It can be seen from the emission spectra that the emission band appears in the visible region around 502 nm for all the deposited films. The result is due to the recombination between the sulphur-vacancy-related donor and the valence band. The small shift of the PL peak may be due to the indirect recombination of free electrons moving from trap level formed by Cu atoms to the holes in the valence band. These trap levels are in the energy gap and shift toward the valence band on doping [9].

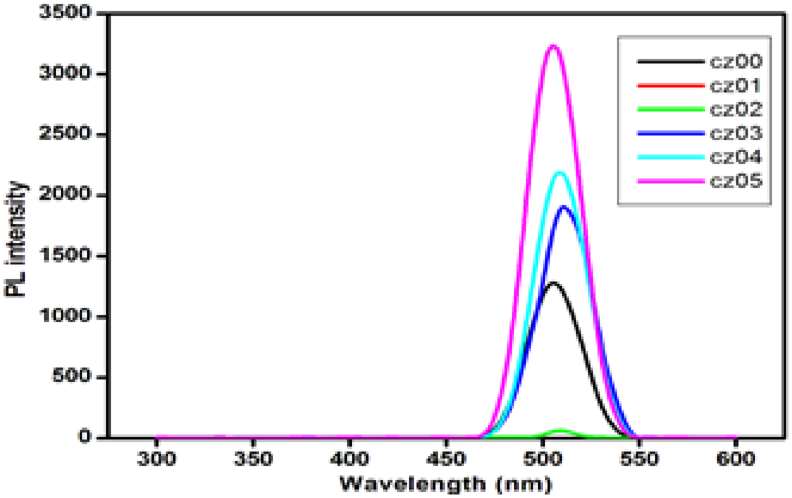

FIG. 4. Photoluminescence spectra of CZTS thin films.

Conclusion

$Cu_{2+x}Zn_{1-x}SnS_4$ (x = 0, 0.02, 0.04, 0.06, 0.08 and 1) thin films were deposited by SILAR method and their optical properties were studied. The XRD pattern confirms the formation of tetragonal structure Cu_2ZnSnS_4 and the crystalline size is found to be higher for $Cu_{20.1}Zn_{0.9}SnS_4$ thin films. The crystallinity is found to be increased with Cu doping. The deposited CZTS thin films show higher absorption in the visible region and the absorption coefficient is in the order of 10^4cm^{-1}, whereas the band gap is found to be decreased with increase in Cu doping. The PL spectra show the red shift for higher Cu doping concentrations. Also, the PL intensity increases with increase in Cu doping.

Acknowledgement

The author J. Henry forwards his thanks to University Grants Commission (UGC), New Delhi for providing financial support through UGC Basic Scientific Research (UGC-BSR) fellowship. The authors are thankful to the DST-FIST and UGC-SAP, New Delhi for providing financial support to the Department of Physics, Manonmaniam Sundaranar University.

References

[1] Sarswat, P.K. and Free, M.L. Journal of Crystal Growth, 372 (2013) 87.

[2] Ge, J., Jiang, J., Yang, P., Peng, C., Huang, Z., Zuo, S., Yang, L. and Chu, J., Solar Energy Materials & Solar Cells, 125 (2014) 20.

[3] Chawla, A.K., Singhal, S., Nagar, S., Gupta, H.O. and Chandra, R., Journal of Applied Physics, 108 (2010) 123519.

[4] Han, D., Cao, J., Yang, S., Yang, J., Wang, B., Fan, L., Liu, Q. and Niu, T.W.H., Dalton Trans., 43 (2014) 11019.

[5] Shyamal, S., Hajra, P., Mandal, H., Singh, J.K., Satpati, A.K., Pande, S. and Bhattacharya, C., ACS Appl. Mater. Interfaces, 7 (2015) 18344.

[6] Jeyaprakash, B.G., Kesavan, K., Kumar, R.A., Mohan, S. and Amalarani, A., Bull. Mater. Sci., 34 (2011) 601.

[7] Poormohammadi-Ahandani, Z. and Habibi-Yangjeh, A., Desalination, 271 (2011) 273.

[8] Suryawanshi, M.P., Shin, S.W., Ghorpade, U.V., Gurav, K.V., Hong, C.W., Agawane, G.L., Vanalakar, S.A., Moon, J.H., Yun, J.H., Patil, P.S., Kim, J.H. and Moholkar, A.V., Electrochimica Acta, 150 (2014) 136.

[9] Sambasivam, S., Jeong, J.H., Choi, B.C., Lim, K.T., Kim, S.S. and Song, T.K., J. Mater. Res., 26 (2011) 706.