Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Physics Research, 2012, 3 (1):54-59
(http://scholarsresearchlibrary.com/archive.html)

Scholars Research Library
ISSN : 0976-0970
CODEN (USA): APRRC7

EDAX, SEM, Photoluminescence and Electrical properties of Zn-doped polycrystalline $CuInS_2$ Thin films by spray pyrolysis

N. Suriyanarayanan[a] and C. Mahendran[b]

[a]*Department of Physics, Government College of Technology, Coimbatore, Tamil Nadu, India*
[b]*Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts & Science, Coimbatore, Tamil Nadu, India*

ABSTRACT

Copper Indium Disulphide ($CuInS_2$) is an efficient absorber material for photovoltaic and solar cell applications. In this paper Zn (0.02, 0.03M) doped $CuInS_2$ thin films are (Cu/In=1.25) deposited on to glass substrates in the temperature range 300-400^{0}C. The EDAX results confirm the presence of Cu, In, S and Zn in the films. SEM photographs reveal crystalline nature of the films at various temperature ranges. Well defined, broad Blue and Green band emissions are exhibited by Zn-doped $CuInS_2$ thin films which show better crystallinity of the deposited films. All the films present low resistivity (ρ) values and exhibit semiconducting nature. Hence, Zn species can be used as a donor and acceptor impurity in $CuInS_2$ thin films to fabricate efficient solar cells, photovoltaic devices and good IR Transmitters.

Key words:Spray pyrolysis; Thin films; Photoluminescence; Electrical properties; SEM.

INTRODUCTION

Chalcopyrite semiconductors $CuInS_2$ and$CuInSe$ are currently investigated for applications in photovoltaic, solar cells [1] and LED Devices [2]. These applications are based on a p-n junction. Controlled doping of dopants on these materials appears desirable, where the aimed free carrier concentrations are in the range of 10^{16}-10^{18} cm^{-3}.Among the ternary compound semiconductors $CuInS_2$ has the potential for high conversion efficiency due to its direct band gap of 1.5eV [3], which very well match with the solar spectrum and its high absorption coefficient approximately 10^5cm^{-1} [4]. No toxic component is included in this compound semiconductor. For controlling a conduction type and obtaining low resistivity, several impurities doped $CuInS_2$ thin films have been studied.But, the open circuit voltage of solar cell based $CuInS_2$ thin films can be improved by controlled doping of small amounts of Zn [5]. Hence, this paper presents the

elemental compositions, Surface structural, photoluminescence and electrical properties of Zn-doped $CuInS_2$ thin films prepared by spray pyrolysis.

MATERIALS AND METHODS

Zn-doped $CuInS_2$ thin films are deposited by spray pyrolysis on to glass substrates from aqueous solutions of $CuCl_2$, $InCl_3$, $SC(NH_2)_2$ and $ZnCl_2$ using compressed air as the carrier gas. At first, aqueous solutions (0.1M) of the salts are prepared, and then they are mixed with appropriate portions in order to have copper to indium molar ratio (Cu/In = 1.25) and (Cu + In)/S fixed to 1 in the solution. The copper (II) chloride and indium (III) chloride are mixed and then thiourea solution is added. The resulting solution is doped with Zinc chloride ($ZnCl_2$) of (0.01M). The solutions are prepared by dissolving in de-ionized water. Then the solution is sprayed using spray rates of 2ml/min in air on to glass substrates ($2.5\times2.5cm^2$) heated at different temperatures from 300 to 400^0 C. The surface morphology of the film is investigated using a Jeol, JSM-6390, JM-Spot size 35. The compositional analysis is carried out using energy dispersive X-ray spectroscopy (EDAX). Photoluminescence (PL) spectra of the film are recorded using a Cary Eclipse instrument in fluorescence emission scan mode with excitation wavelength of 485nm.The electrical resistivity and conductivity studies are carried out by four probe method.

3. EDAX analysis

EDAX results confirm the presence of Cu, In, S and Zn in the(0.02M and 0.03M) doped $CuInS_2$ films(Fig. 1a,1b).The films are nearly stoichiometric, when oxygen is taken into account in the relative composition.

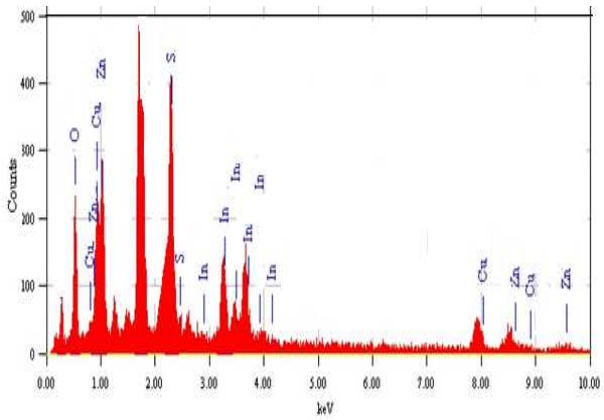

Fig.1a. EDAX spectrum of sprayed Zn-doped $CuInS_2$(0.02M) filmspreparedat350^0C

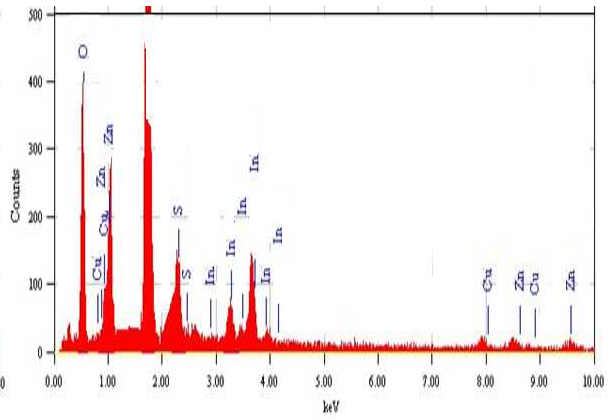

Fig.1b. EDAX spectrum of sprayed Zn-doped $CuInS_2$(0.03M) filmsprepared at350^0C

All the Zn-doped films contain oxygen at all deposition temperatures. There is a slight decrease in the concentrations of Cu, In, S and Zn from the films as the temperature increases from 300 - 400^0C. Oxygen is not only chemisorbed in all the films [6], but oxygen containing phase has been formed during the film growth. InOCl and or ZnOCl could be formed very easily due to the thermal decomposition product of $(NH_4)_2InCl_5\cdot H_2O$ and or $(NH_4)_2ZnCl_5\cdot H_2O$, originally formed in the spray solution [7]. Without any chemical reaction, oxygen probably diffuses along grain boundaries of the films. It does not enter in to crystallites but, bonded at the surface and grain boundaries [8]. Hence, the properties of the films are not altered by oxygen content. The doped

Zn in low concentrations (0.02M and 0.03M) increases the oxygen content as the temperature increases (maximum of 5% is observed) and make the film better stoichiometric with reduced crystallographic defects [9]. Hence better crystallinity of $CuInS_2$ films is obtained.

4. Surface morphology

The SEM photographs of 0.02 and 0.03M Zn-doped $CuInS_2$ thin films grown in the temperature range 350^0C and 400^0C are presented in the Fig 2a,b and 2c,d respectively. Large number of small crystals of size about 200nm is formed at 300^0C. Nearly 60% light is transmitted by the crystals in the UV-visible region and about 70% of transmission is noticed in the IR regions. The crystal size increases from 200-400nm as the temperature of the substrate increases from 325-400^0C (Fig.2a,b), the scattering of light is low and 90% transmission of light occurs in this temperature range.

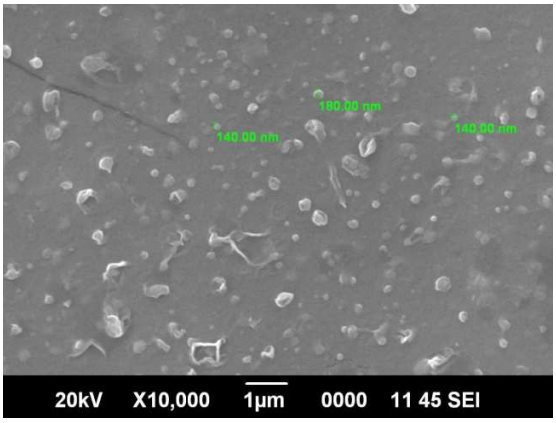

Fig.2a (0.02 M). SEM micrographs of sprayed Zn-doped $CuInS_2$ films prepared at 350^0C

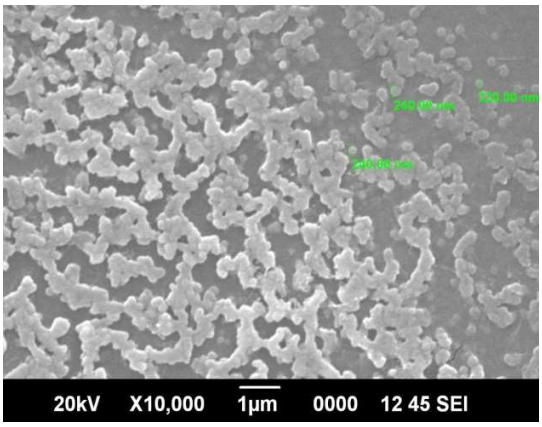

Fig.2b (0.02 M). SEM micrographs of sprayed Zn-doped $CuInS_2$ films prepared at 400^0C

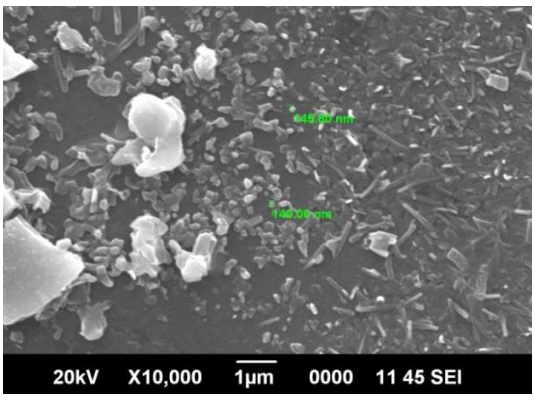

Fig.2c (0.03 M). SEM micrographs of sprayed Zn-doped $CuInS_2$ films prepared at: 350°C

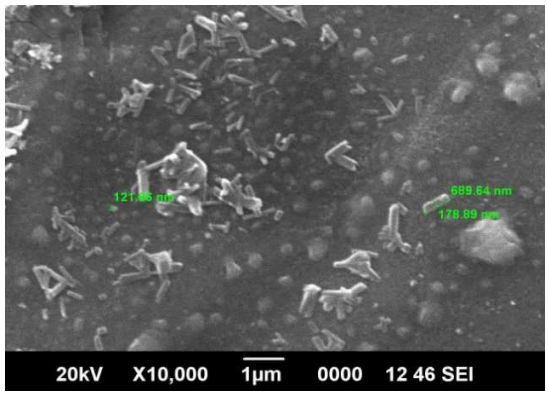

Fig.2d (0.03 M). SEM micrographs of sprayed Zn-doped $CuInS_2$ films prepared at 400^0C

Hence, crystals grown in the temperature range 325-400^0C can be used as an infra-red transmitter.Further the crystal size increases from 400-700nm for 0.03M doped samples in the temperature range 325-400^0C (Fig 2c,d).The undoped $CuInS_2$ samples show crystallites of 100-700nm and about 70% of light transmission is noticed in the temperature 300-400^0C [10].

5. Photoluminescence (PL)

Fig. 3.Shows the emission spectra of (0.03M) Zn-doped $CuInS_2$ thin films grown in the temperature range 300-400^{0}C.Photoluminescence spectra have been recorded at room temperature with an excitation wavelength of 485nm for all the samples.

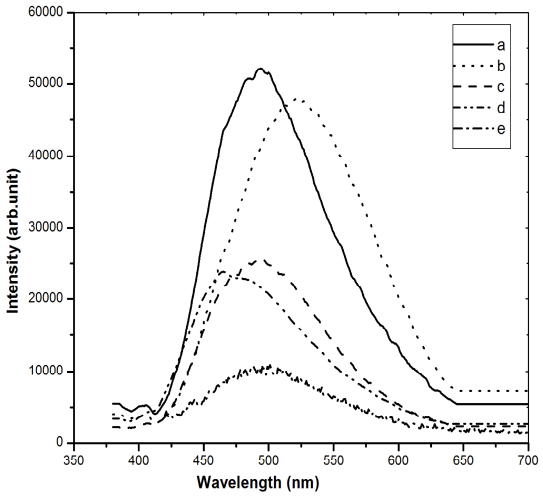

Fig.3.(0.03M)Photoluminescence spectra of sprayed Zn-doped $CuInS_2$ films excited by 485nm at various substrate temperatures: (a) 300°C (b) 325°C (c) 350°C (d) 375°C (e) 400°C.

A strong and broad emission peak is observed in the wavelength range 400-600nm (Blue and Green Band emission) centred at 500nm (maximum emission) when the substrate temperature at 300^{0}C. This feature correspond to Donor-acceptor pair transition (DAP) between a sulphur vacancy and an Indium vacancy (or) Cu (or) Zn on an Indium site [11,12, 13, 14] (or) band-band gap luminescence of Zn doped $CuInS_2$ crystals deposited on the substrate [15]. Further increase in temperature from 325 - 400^{0}C, there is a decrease in emission of intensities and the peak at which the maximum emission occurs slightly shifts towards shorter wavelength region. Similar trend is noticed for 0.01M doped samples but higher value of emission peak intensity is noticed than 0.02 doped samples. Better photoluminescence property is obtained by Zn-doped $CuInS_2$ thin films which reveal better crystallinity than undoped films [10]. All emissions are associated with defects emerging during the growth of crystallites and are related to deformation of crystallinity due to dislocations and vacancies [16]. The undoped films present more no of emission peaks in the visible and IR regions, which reveal large no of defect states or secondary phases generated during its growth than doped one[10].

6.Electrical properties

The variation of conductivity (σ) for the Zn-doped (0.02 M and 0.03M) CuInS2thin films grown in the temperature range 300-400^{0}C is shown in the Fig 4. The incorporation of Zn in $CuInS_2$ materials can occur in three different ways, (i) occupying the sulfur site to make an acceptor (ii) occupying the copper site to make a donor and (iii) occupying the interstitial site to make a donor, and the donor Zn_{Cu} and Zn_i would be compensated by the acceptor Zn_S [17]. From the Fig.4, it is observed that for 0.02M doped samples, ρ value increases with significant n-type conductivity. The increase in ρ value may be due to scattering of electrons by thermally generated defects or due to localization of the impurity states and the compensation of Cu

vacancy defects, and interstitials sites by Zn-donor states generated by the Zn-doping [20]. Further, the introduced Zn in low concentrations cannot compensate all the donors by Zn doping.

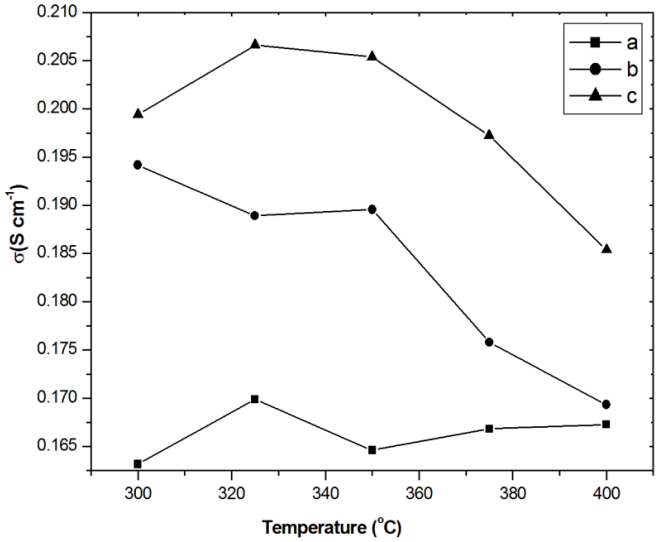

Fig. 4. Variations of the conductivity of Zn-doped $CuInS_2$ thin films with different substrate temperatures: a) 0.01M b) 0.02M c) 0.03M

Hence n-type conductivity is obtained in the temperature range 300-325^{0}C. The value of ρ and hence conductivity (σ) almost remains constant in the temperature range 325-350^{0}C.From 350-400^{0}C, an abrupt increase in ρ is noticed with decreased p-type conductivity. An evolution of n to p type conductivity is observed. It is attributed to the adsorbed and desorbed oxygen by the films during deposition. Oxygen is known to be p-type dopants in chalcogenide semiconductors. In the case of 0.03M doped samples a decrease in ρ value is noticed with p-type conductivity due to Zn atom occupying the sulphur site to make an acceptor which explains the origin of p-type conductivity in temperature range 300-325^{0}C [18, 19].Further increase in temperature from 325-400^{0}C ρ increasesand hence σ decreases due to absorbed and desorbed oxygen. The lowest ρ obtained at 325^{0}C for 0.03M doped sample is 4.9 X10^{-3} Ω-cm. 0.01M doped samples show p-type conductivity to n-type conductivity .Undoped CuInS2 films present high resistivity values.

CONCLUSION

The (112) oriented Zn-doped (0.02M and 0.03M) polycrystalline $CuInS_2$ thin films(at Cu/in=1.25) are deposited on to glass substrates in the temperature range 300-400^{0}C. The increase in temperature and Zn doping affects the structure of the films. The EDAX results confirm the presence of Cu, In, S & Zn in the film. The surface morphology reveals an increase in temperature up to 350^{0}C facilitates the growth of Zn-doped polycrystalline $CuInS_2$ films. The PL spectra exhibit a broad spectral emission centred at 500nm (Blue and Green band) in the visible region.Conductivity studies reveal the semiconducting nature of the films. An evolution of p-type to n-type conductivity is obtained in temperature range 325-350^{0}C which requires further investigations.

REFERENCES

[1] H.W. Schock, A. Shah, in: Stephens Associates (Publ.) Proceedings of the European Conference on Photovoltaic Solar Energy Conversion, Barcelona, Spain,(**1997**), p. 2000.
[2] S. Chichibu, S. Shirakata, A. Isomura, H. Nakanishi, *Jpn. J.Appl. Phys*.(**1997**),36, 1703.
[3] B. Tell, J.L. Shay, H.M. Kasper, *Phys. Rev*., (**1971**), B 4 (8) ,2463.
[4] R. Scheer, K. Diesner, H.-J. Lewerenz, *Thin Solid Films*, (**1995**), 168, 130.
[5] T. Enzenhofer, T. Unold, R. Scheer, H.-H. Schock, in: Material Research Society, **2005** Spring Proc. San Francisco (CA) **2005**, Spring Meeting, MRS, p. F11.3.1.
[6] R.S. Berg, R.D. Nasby, *J. Vac. Sci. Technol*. (**1978**), 15, 359.
[7] M. Krunks, T. Leskela, L. Ninisto, *Jpn. J. Appl. Phys*.(**2000**),39, 181.
[8] R. Scheer, M. Alt, I. Luck, H.J. Lewerenz, *Sol. Energy Mater.Sol Cells*, (**1993**), 9, 423.
[9] S.S. Lin, J.L. Huang, D.F. Lii, *Surf. Coat. Technol*. (**2004**), 176, 173.
[10] C. Mahendran, N. Suriyanarayanan, *Physica B*, (**2010**), 405, 2009–2013.
[11] G.Brandt, A. Ranber, J.Schneider, *Solid State Commun*. (**1983**) ,12 , 481.
[12] J. Van Gheluwe, J. Versluys, D. Poelman, J. Verschraegen, M. Burgelman, P. Clauws, *Thin Solid Films*, (**2006**), 511–512, 304–308.
[13] J. Eberhardt, H. Metzner, R. Goldhahn, F. Hudert, U. Reislohner, C. Hulsen, J. Cieslak, T.H. Hahn, M. Gossla, A. Dietz, G. Gobsch, W. Witthuhn, *Thin Solid Films*, (**2005**), 480–481, 415.
[14] M. Nanu, J. Schoonman, A. Goossens, *Thin Solid Films*,(**2004**), 451–452, 193.
[15] N. Tsujii, Y. Imanaka, T. Takamasu, H. Kitazawa, G. Kido, *J. Alloys Compd*. (**2006**)408–412, 79.
[16] T. Onishi, K. Abe, Y. Miyoshi, K. Wakita, N. Sato, K. Mochizuki, *J. Phys. Chem. Solids*, (**2005**), 66, 1947–1949.
[17] R. Scheer, K. Diesner, H.L. Lewerenz, *Thin Solid Films*,(**1995**), 268, 130.
[18] L.L. Kazmerski, G. A. Sanborn, *J. Appl. Phys*.(**1977**),48, 3178.
[19] P. Migliorato, J. L. Shay, *J. Appl. Phys*. (**1975**)46, 1777.
[20] Tetsuya Yamamoto, Ilka V. Luck, Roland Scheer, *Applied Surface Science*, 159-160,(**2000**), 350-354.