Available Online http://www.ijncse.com

ISSN Online: 2395-7018
2(5) (2015) 392-400

INTERNATIONAL JOURNAL OF NANO CORROSION SCIENCE AND ENGINEERING

Nebulized spray pyrolysised Indium sulfide thin film and characterization

J.Raj Mohamed [a] and L.Amalraj [b]

[a]PG & Research Department of Physics, V.H.N.S.N College, Viruthunagar 626001, India

[b] PG & Research Department of Physics, H.H.The Rajah's College, Pudukkottai 622001, India

corresponding Author : Email: amalraj.raj1973@gmail.com, Mobile:+91 9443192168.

ABSTRACT

Nebulized spray pyrolysis is a novel and easy technique to grow thin films. Indium sulfide (In_2S_3) thin films have been prepared on a glass substrate by this technique using precursor solution of $InCl_3$ and CS $(NH_2)_2$ at a substrate temperature of 300° C. The as prepared film was characterized by x-ray diffraction analysis (XRD), optical transmission studies (UV-VIS-NIR double beam spectrophotometer) and electrical conductivity studies by Hall Effect measurement system. The as deposited film exhibited good crystallinity with cubic structure and preferential orientation along (111) plane. The direct and indirect band gap values of In_2S_3 thin films have been determined from the transmission spectra in the visible range and found to be 2.73 and 2.14 eV respectively. The electrical resistivity of the film was 9.84 Ω cm for as prepared film. Carrier concentration and mobility of the same sample were found to be 4.32 x 10^{18} cm^{-3} and 86.2 cm^2/Vs. The results of optical and electrical properties confirm that the nebulized spray pyrolysised In_2S_3 films may be suitable for solar cell applications.

Key words: Nebulized spray pyrolysis; band gap; In_2S_3;

INTRODUCTION

Indium sulfide (In_2S_3) is a grievous material for optoelectronic and photovoltaic application [1] due to its wider band gap (2.0-2.8eV), stability and higher transmittance. In_2S_3 thin films are also used as promising buffer layer in the CIGS solar cells due to its non-toxic in nature than CdS. In_2S_3 compound exists in three different phases such that yellow α-In_2S_3 has a defect cubic structure, red β -In_2S_3 has a defect spinel tetragonal structure and γ - In_2S_3 has a layered structure. Besides In_2S_3 is an n type semiconductor material belonging to III-VI compound which involves numerous applications in picture tube manufacture [2], catalysis [3] and photovoltaic solar cells [4]. In_2S_3 thin films were synthesized by many techniques such as chemical bath deposition (CBD) [5-8], physical vapour deposition [9], spin coating [10], SILAR method [11] and spray pyrolysis technique [12-15]. An ultrasonic nebulized spray pyrolysis technique was used earlier to form In_2S_3 thin films [16, 17]. However, Nebulized spray pyrolysis is a simple, time saving and cheaper for the growth of thin films. In this work, In_2S_3 thin film was deposited on micro glass substrate at the substrate temperature of 300^{o}C. The structural, optical and electrical properties have been discussed.

EXPERIMENTAL

Nebulized spray pyrolysis unit consists of a nebulized unit, temperature control unit and a compressor unit. A nebulizer unit, which is actually utilized to spray the medicine through mouth to provide comfort to the asthma patients, was used in the present study to spray mist like particles of precursor solution to the preheated substrates. A temperature controller maintains the substrate temperature at T_s-300 ^{o}C. The size of the micro glass substrate used was 7.5x 2.5x0.25 cm^3. Compressed air (oxygen) was taken as a carrier gas. The amount of solution taken was 10 ml per substrate. The precursor solution (In_2S_3 & CS $(NH_2)_2$)) containing In and S sources was coated on the substrate with 2:3 molar concentration ratio. When the compressed air was passed through the nebulized unit, the precursor solution travelled through a tube in order to spray fine particles on the glass substrate.

The structural properties were analyzed by XPERT-PRO x- ray diffractometer (CuKα – λ = 1.5405 Å) in which x-ray diffraction patterns were scanned and recorded in 2θ interval from 10 to 70^{o}C with the step of 0.05^{o}C at room temperature. UV-VIS-NIR double beam spectrophotometer (Hitachi U3410 Model) was used to observe the transmission spectra of the films measured in the wavelength range 300 to 1100nm. The thickness of all the samples was taken by MITUTOYO SJ300 profile meter. The electrical conducting properties were analyzed by Hall Effect measurement system (ECOPIA-HMS 5000).

RESULT AND DISCUSSION

Structural analysis

The x-ray diffraction profile of In_2S_3 thin film by nebulized spray pyrolysis technique is shown in Fig.1. The diffraction of the film found at 2θ = 14.23, 28.67, 43.61 and 59.37° corresponding to the reflection from (111), (222), (511) and (444) planes conforming that the polycrystalline nature of the film. All the diffraction peaks were in good agreement with original JCPDS data [18]. The compared result of d-spacing values with the JCPDS data was tabulated in Table-1. (111) plane was identified as preferable orientation phase. Lina Zhang et al [19] and M.Kraini et al [20] had obtained the cubic structured In_2S_3 thin film using facile hydrothermal and spray pyrolysis technique respectively. M.Kraini et al [20] had reported the same preferred orientation (111) peak as in the present study. The d-spacing corresponding to all the peaks are determined and tabulated. The lattice constant (a) in the present case was 10.77A° whereas the reported value is 10.7A°.

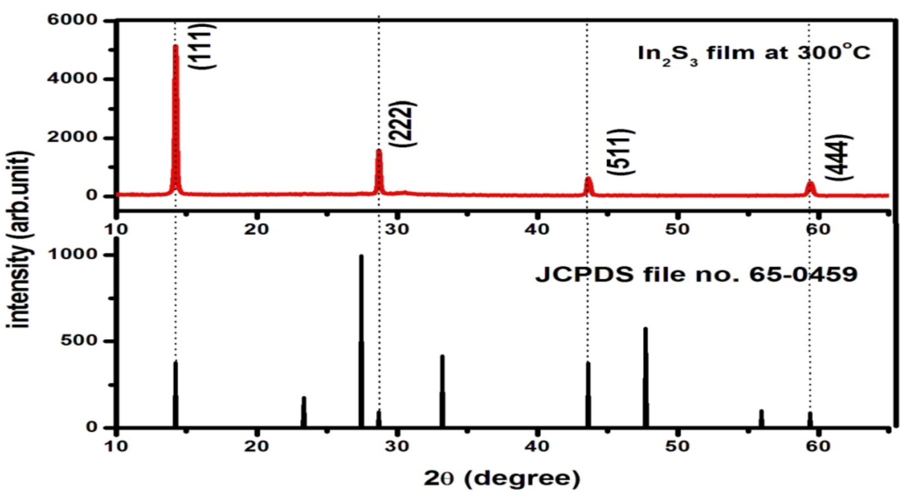

Fig.1. X-ray diffraction pattern of In_2S_3 film deposited at T_s-300°C.

The structural parameters of In_2S_3 thin films deposited at substrate temperature of 300 °C was calculated and analyzed. The grain size (D) of the films was calculated of all the diffraction peaks for all the film samples with different substrate temperature using Debye Scherrer formula

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

Where λ is the wavelength of x-ray (1.5406Å), β is the full width at half-maximum value (FWHM) and θ is the Bragg's angle.

Table. 1. Comparison of d values and relative intensities with literature

Observed		In_2S_3(JCPDS file -65-0459)	
d values(A°)	**I/I_0**	**d values(A°)**	**(hkl)**
6.2183	100	6.2203	111
3.1105	-	3.1101	222
2.0737	-	2.0734	511
1.5553	-	1.5550	444

The number of crystallites per unit area (N) of the samples found using the relation

$$N = t / D^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where D is the grain size and t is the thickness of the film. The thickness for the sample was obtained in the micro metre range (~1µm) by using profile meter. The strain (ε) of all the films was determined using the formula

$$\varepsilon = \beta\cos\theta/4 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The dislocation density (δ) of all the films was determined using the equation

$$\delta = 1/D^2 \text{ lines / unit area} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Since the amount of defects in a crystal could be found by measuring δ value and the results confirmed that In_2S_3 thin film having good crystallinity with less amount of defects.

The average crystalline size of In_2S_3 thin film was found to be 44.52 nm. The crystallization levels of the film were good due to their small dislocation density (δ) and lower strain (ε) values, which represent the amount of defect in the film. The average dislocation density of the film was calculated as 9×10^{13} lines/ m^2. The strain of the film was found to be 7×10^{-4}. The number of crystalline formed by the same sample was calculated to be 2.1×10^{15} m^2.

Optical analysis

Fig. 2 shows the optical transmittance curve as function of the wavelength. High transmittance (above 70%) in the visible wavelength range was presented in the film sample prepared at Ts-300°C. The transmittance curve showed multiple interference patterns which might be due to the stoichiometric deviations in the film. The absorption edge was observed between the wavelength ranges of 410 to 550 nm.

The absorption coefficient (α) is determined using the given equation

$$\alpha = -(1/t) \times \ln(1/T)$$

Where T is the transmittance and t is film thickness. The optical band gap (E_g) can be determined by the absorption coefficient (α) and photon energy (hν) by the equation (αhν) = A $(h\nu - E_g)^p$ where A is constant, h is plank's constant and p has ½ (or) 2 for direct and indirect transition.

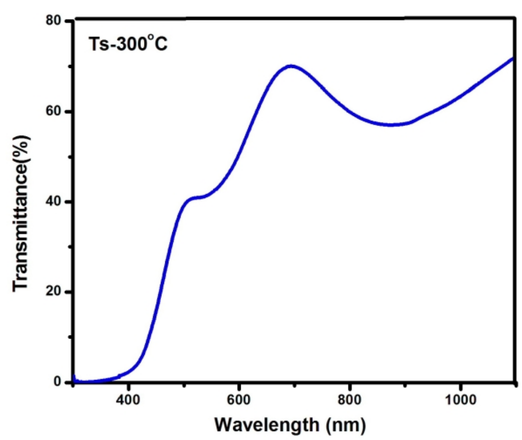

Fig. 2. Transmittance spectra of In_2S_3 thin film

Fig. 3(a) and 3(b) show that $(\alpha h\nu)^2$ vs (hν) and $(\alpha h\nu)^{1/2}$ vs (hν) plots in order to find direct and indirect band gap values and that were determined from the spectra by extrapolation of the linear part of the curve. Eg = 2.73 and 2.14 eV were found as direct and indirect transition. M.G. Sandoval-Paz et al [21] had reported similar observation (E_g = 2.65 & 2.12 eV) for direct and indirect band gaps by annealing the In_2S_3 films using chemical bath deposition.

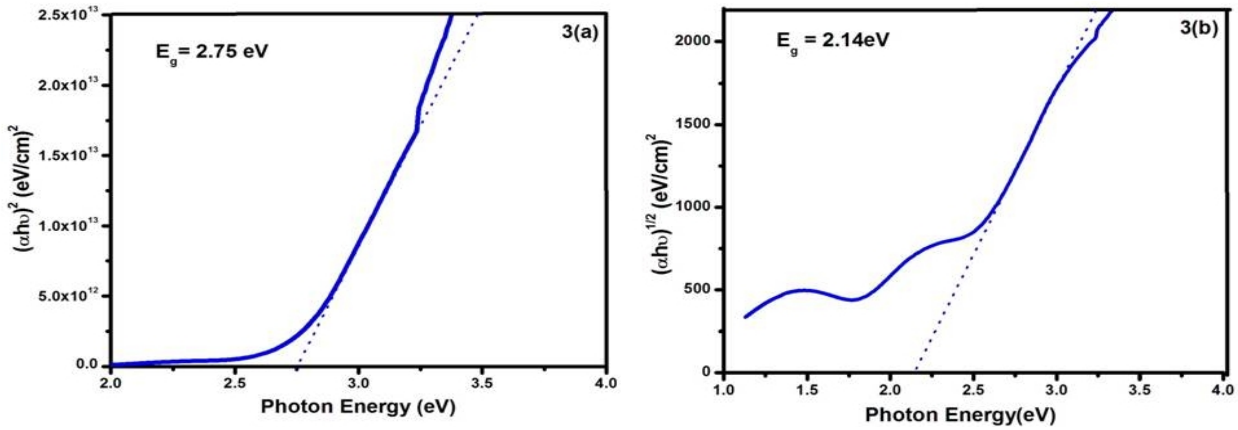

Fig.3. (a) $(\alpha h\nu)^2$ vs. (hv) and (b) $(\alpha h\nu)^{1/2}$ vs (hv) spectra for In_2S_3 films.

Morphological and elemental analysis

The scanning electron microscope is one of the versatile tool to study morphology of the surface of the film. The surface morphology of as prepared In_2S_3 thin film was analysed by SEM photograph shown in the Fig. 4a. It is observed that large number of nano sized spherical and flakes covered on the surface of the film kes. The film has no voids and cracks. The average size of the crystallites was 30 – 55nm. The recorded EDAX spectrum for the In2S3 film grown at 300 oC in the binding energy region of 1.0-7.0 eV is shown in Fig 4b.it is revealed that the presence of Indium and sulfur is confirmed. The atomic percentage of indium and sulfur elements were observed as 43.58 and 56.42% and S/In ratio is calculated as 1.29.

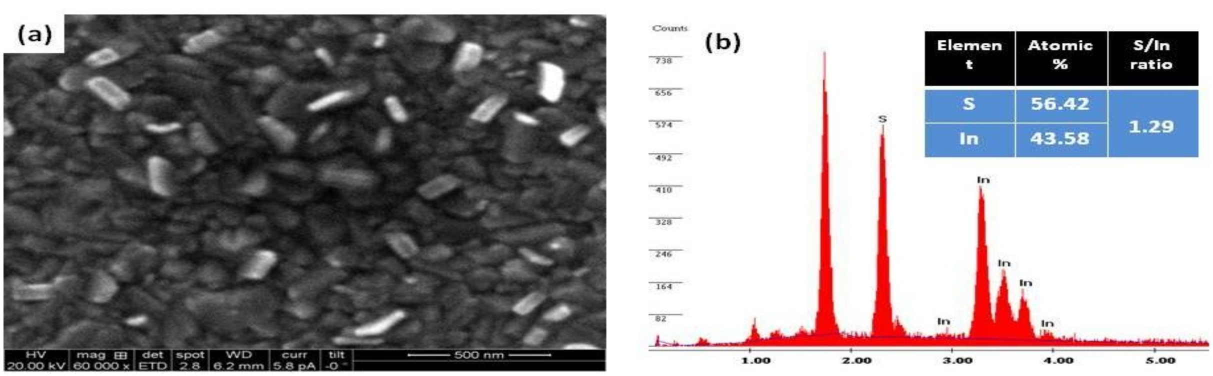

Fig. 4 (a) SEM photograph and (b) EDAX spectrum of In_2S_3 thin film

Electrical characterization

The conductivity, resistivity, hall coefficient and carrier concentration values of In_2S_3 thin film prepared at Ts-300^{o}C was found using hall instrument. The carrier concentration of as prepared thin film was calculated from the relation n = (1/e R_H) [20], where R_H is the hall coefficient and e is the charge of electron. The mobility (μ) was found using the formula μ = (1/ enρ) where ρ is the resistivity of the film. Using hall coefficient results, it confirmed that the In_2S_3 film sample belongs to n type semi conducting nature. The carrier concentration and mobility of the film were found to be 4.32 x 10^{18} cm^{-3} and 86.2 cm^2/Vs. The resistivity of the film sample was shown to be 9.84 Ωcm and corresponding conductivity of the film was calculated as 1.02 x 10^{-3}(Ω $cm)^{-1}$. S.Lugo-Loredo et al [22] had reported the closer value of conductivity such as 2.8 x 10^{-3} (Ω $cm)^{-1}$ after thermal annealing the In_2S_3 sample at 400^{o}C by CBD method.

CONCLUSION

Indium sulfide (In_2S_3) thin film was prepared on micro glass substrate at Ts-300^{o}C by nebulized spray pyrolysis technique. The x-ray diffraction patterns revealed that the as prepared film had cubic crystal structure with preferable orientation along (111) plane. The structural parameters had been found using x-ray diffraction studies. The optical transparency increased up to 70% in the visible region. The direct and indirect band gap values were found using transmittance curve by UV-VIS spectrophotometer. The resistivity, conductivity, carrier concentration and mobility of the film were also determined. All the results confirmed that the film deposited at the substrate temperature of 300^{o}C could be used in any one of the application of solar cells.

REFERENCES

[1] N.Barreau, Indium Sulfide and relatives in the world of Photovoltaics, Sol. Energy 83(2009)363-371.

[2] S.Yu, L.Shu, Y.Qian, Y.Xie, J.Yang, L.Yang, Hydrothermal Preparation and Characterization of Nanocrystalline Powder of β-Indium Sulfide, Mater. Bull. 33 (1998) 717-721.

[3] Y.He, D.Li, G.Xiao, W.Chen, Y.Cen, M.Sun, H.Huang, X.Fu, A New Application of Nanocrystal In_2S_3 in Efficient Degradation of Organic Pollutants under Visible Light Irradiation, J.Phy.Chem. C 113 (2009) 5254 – 5262.

[4] A.Belaidi, T.Dittrich, D.Kieven, J.Tornow, K.Schwarzbug, M.Kunst, N.Allsop, M.C Lux-Steiner, S.Gavrilov, ZnO-nanorod arrays for solar cells with extremely thin sulfidic absorber, Sol. Energy Mater. & Sol. Cells 93 (2009) 1033-1036.

[5] N.Barreau, R.Bayon, J.C.Bernede, L.Assmann, 203rd meeting of the Electro Chemical Society, Paris, France, April 27- May2, 2003.

[6] X. Meng, Y. Lu, X. Zhang, B. Yang, G. Yi, J. Jia, Fabrication and characterization of indium sulfide thin films deposited on SAMs modified substrates surfaces by chemical bath deposition, Appl. Surf. Sci. 258 (2011) 649 – 656

[7] B.Yahmadi, N.Kamoun, C.Guasch, R.Bennaceur, Synthesis and characterization of nanocrystallized In_2S_3 thin films via CBD technique, Mater. Chem. Phys. 127 (2011) 239-247

[8] Zhihus Gao, Jingbing Liu, HaoWang, Investigation on growth of In**2**S_3 thin films by chemical bath deposition, Mater. Sci. in Semicond. Processing 15 (2012) 187 -193.

[9] D.Abou-Ras, G.Kostroz, A.Strohm, H.M. Schock, A.N. Tiwari, Interfacial layer formations between Cu(In,Ga)Se_2 and In_xS_y layers, J. Appl. Phys. 98 (2005) 123512-1-7.

[10] Y.Yasaki, N.Sonoyama, T.Sakata, Semiconductor sensitization of colloidal In_2S_3 on wide gap semiconductors, J. Electroanal. Chem. 469 (1999) 116-122

[11] M.Kundakci, A.Ates, A.Astam, M.Yildirim, Structural, optical and electrical properties of CdS, $Cd_{0.5}In_{0.5}S$ and In_2S_3 thin films grown by SILAR method, Physica E 40 (2008) 600-605

[12] M.Calixto-Rodriguez, A.Tiburcio-Silver, A.Ortiz, A.Sanchez-Juarez, Optoelectronical properties of indium sulfide thin films prepared by spray pyrolysis for photovoltaic applications, Thin Solid Films 480-481 (2005) 133-137

[13]S.Buecheler, D.Corica, D.Guettler, A.Chirila, R.Verma, U.Muller, T.P.Niesan, J.Palm, A.N.Tiwari, Ultrasonically sprayed indium sulfide buffer layers for Cu(In,Ga)$(S,Se)_2$ thin film solar cells, Thin Solid Films, 517 (2009) 2312 – 2315

.[14]A.S.Cherian, M.Mathew, C.Sudha Kartha, K.P.Vijayakumar, Role of chlorine on the opto-electronic properties of β-In_2S_3 thin films, Thin Solid Films, 518 (2010) 1779 – 1783

[15] K.Otto, A.Katerski, O.Volobujeva, A.Mere, M.Krunks, Indium sulfide thin films deposited by chemical spray of aqueous and alcoholic solutions, Energ. Procedia 3 (2011) 63-69

[16] C.S.Huang, C.S.Tao, C.H.Lee, Nebulized Spray Deposition of Pb(Zr,Ti)O Thin films, J. Electrochem. Soc. 144 (1997) 3556-3561

[16]S.P.S. Arya, H.E.Hintermann, Growth of Y-Ca-Ba-O superconducting thin films by ultrasonic nebulized spray pyrolysis, Thin solid film 193/194 (1990) 841-846

[17] JCPDS diffraction data, file No. 65-0459.

[18]L. Zhang, W.Zhang, H.Yang, W. Zhao, W.Fu, H. Zhao, J.Ma, Growth studies and characterization of In_2S_3 films prepared by hydrothermal method and their conversion to In_2O_3 films, Mater. Chem. Phys. 130 (2011) 932-936

[19] M.Kraini, N.Bouguila, I.Halidou, A.Timoumi, S.Alaya, Properties of In_2O_3 films obtained by thermal oxidation of sprayed In_2S_3, Mat. Sci. in Semicond. Processing 16(2013) 1388-1396.

[20] M.G.Sandoval-Paz, M.Sotelo-Lerma, J.J.Valenzuela-Jauregui, M.Flores-Acosta, R.Ramirez-Bon, Structural and optical studies on thermal-annealed In_2S_3 films prepared by the chemical bath deposition technique, Thin Solid Films. 472 (2005) 5-10

[21] S.Lugo-Loredo, Y.Pena-Mendez, M.Calixto-Rodriguez, S.Messina-Fernandez, Indium sulfide thin films as window layer in chemically deposited solar cells, Thin Solid Films, 550 (2014) 110-113.

Received: 1-12-2015

Accepted: 7-12-2015