Studies on Structural and Optical Characterization of In-Zn-S Ternary Thin Films Prepared by Spray Pyrolysis

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Abstract— Thin films of indium doped zinc sulfide (ZnS) for different indium (In) concentrations (x=0.0 - 0.8) were deposited onto glass substrate by spray pyrolysis method at 523K temperature. Aqueous solution of zinc acetate, indium chloride and thiorea were used to deposit the In-Zn-S film. The deposited thin films were characterized by Energy dispersive X-ray (EDX), Scanning electron microscopy (SEM), X-ray diffraction (XRD), and by UV-visible spectroscopy. The XRD spectra of In-Zn-S revealed both the amorphous and polycrystalline property for different In concentration. The EDX showed a well stoichiometric result of different compositions of In in ZnS thin films. The granularity of irregular shape is observed in In doped ZnS thin films surface by scanning electron microscope. From the absorbance and transmittance data it is observed that the band gap energy is decreased from 3.75eV to 3.1eV with the increase of In concentration in ZnS.

KEYWORDS: Spray pyrolysis, In-Zn-S, Thin films, EDX, SEM, Optical properties, Band gap.

I. INTRODUCTION

Zinc sulfide (ZnS) thin films are very promising II-VI semiconductor material for electroluminescent devices and photovoltaic heterojunction solar cells for its wide band gap energy and n-type conductivity [1, 2]. ZnS have two different crystal structures (cubic zinc blende and hexagonal wurtzite), both of which have the same direct transition band gap energy (3.68 eV). Due to high transmittance of all the wavelengths of solar spectrum, ZnS thin films are very much suitable for solar cell window material, data storage, data transfers, etc. [3]. Due to high refractive index and low optical absorption in the visible and infrared ranges it can be used as reflectors and dielectric filters. It also can be used in blue light emitting diodes, electro optic modulator, optical coating and photoconductors [4].

Semiconductor nanoparticles have drawn much interest as they change their properties due to quantum confinement [5]. Cadmium Sulfide (CdS) is an important material for CdS/CdTe and CdS/$CuInSe_2$ solar cells. In order to decrease optical absorption losses and to enhance response in the short wavelength region, more transparent buffer layer is needed. In this respect, ternary $Zn_xCd_{1-x}S$ thin film is a promising material as buffer layer for solar cells [6]. But Cd is a toxic material and growth of this layer in solar cells causes a serious environmental problem [7-11]. For this reason, much attention is given on the development of alternative buffer layer with appropriate properties in the solar cell heterostructure. From this point of view, ZnS is a good one. However to enhance the efficiency of light conversion, it is most important to develop semiconductor materials with suitable band gap to work under visible light range [12]. Thus to tune the band gap

energy for buffer layer of solar cell, In is doped with ZnS. A very few work has been done on In-Zn-S ternary thin film material. Chemical vapor transport method, solvent method, chemical bath method and spray pyrolysis is the methods by which thin film has been deposited [8-12].

Recently more attention has been given on the development of cost effective thin films deposition techniques for alternative absorber and buffer layer over large areas in order to economize the technology. Spray pyrolysis is a continuous, controllable and low-cost process for the preparation of nanoparticles [13]. From this point of view, a simple and low cost spray pyrolysis deposition technique is used for the preparation of In doped ZnS film in the present investigation. In this paper, we studied the surface morphology, structural and optical properties of In doped ZnS thin films prepared by spray pyrolysis technique.

II. EXPERIMENTS

The deposition method involves the decomposition of an aqueous solution of zinc acetate $Zn(CH_3COO)_2.2H_2O$ and thiourea $[CS(NH_2)_2]$ for pure ZnS. To achieve indium doping, indium chloride ($InCl_3.4H_2O$) was added to the solution. $In_xZn_{1-x}S$ films were deposited on glass substrates with different In (at %) concentrations (for x = 0, 0.4, 0.6, 0.8, etc.) using spray pyrolysis technique. Here x represents the In concentration in the spraying solution. Aqueous solutions of 0.1M ($InCl_3.4H_2O$), 0.1 M, $Zn(CH_3COO)_2.2H_2O$ and 0.2M $CS(NH_2)_2$ were used as sources for In, Zn and S, respectively. Distilled water was used as a solvent. The normal microscopic plane glass slides were used as the substrate of area 5 x 2.5 cm^2 with a suitable mask (in which open area 2 x 1.5 cm^2) which was put on the hot plate. The glass substrates were cleaned first using soap solution and then boiled in water and then dipped in acetone, and then dry to use as the substrate. Compressed air was used as the carrier gas and the gas pressure was fixed at 0.5bar. The total volume of the solution sprayed was 100 mL and the flow-rate of spray was kept constant at 4 mL/min throughout the whole deposition process of the thin film. The deposition time was fixed at 10 minutes. An optimized temperature of 523 K was maintained for film deposition and the nozzle to the substrate distance was 25 cm.

The optical transmission and absorption spectra of the films with respect to glass substrate were taken for wavelength range 250 to 1100 nm using a double beam UV-VIS spectrophotometer (UV-1601 Shimadzu, Japan). The film thicknesses of $In_xZn_{1-x}S$ thin films were measured by the Fizeau fringes method. Surface morphology of $In_xZn_{1-x}S$ thin films was observed using a scanning electron microscope (SEM) (S-3400N HITACHI, JAPAN). A Philips X'Pert PRO XRD PW 3040 was used to characterize the materials and to determine the structural parameters using a nickel CuK_α radiation whose primary beam power was 60 kV and 55mA. The value of 2θ was swapped between 10º-60º.

III. RESULTS AND DISCUSSION

A. *Energy Dispersive X-ray Analysis*

The composition of In doped ZnS films was estimated by energy dispersive X-ray (EDX) spectroscopy. Figures (a-c) shows the EDX spectra of (x=0.4, 0.6 and 0.8) In doped ZnS thin films. Two different peaks corresponding to zinc (Zn) and sulfur (S) in the spectrum confirms the pure ZnS thin film. Sulfur deficiency was observed in all the films and the peak height of sulfur is decreased with the increase of In concentration in ZnS. This may be due to the fact that sulfur has great affinity towards oxygen, so it might have converted to SO_2 and then evaporated.

Table 1 Elemental composition of as deposited $In_xZn_{1-x}S$ thin films.

Compositions	Zn atomic%	In atomic%	S atomic%
$In_{0.4}Zn_{0.6}S$	28.72	19.22	52.06
$In_{0.6}Zn_{0.4}S$	18.05	34.07	48.88
$In_{0.8}Zn_{0.2}S$	15.42	38.07	46.51

Oxygen has the tendency to diffuse as it has the high electronegativity and since air has been used as a carrier so it is possible to get

oxygen into the film. A peak corresponds to silicon (Si) is observed which is due to the glass substrate. EDX result reveals that the deposited films are very close to the nominal composition. Table1 shows the composition of elements in the films of the sprayed solution.

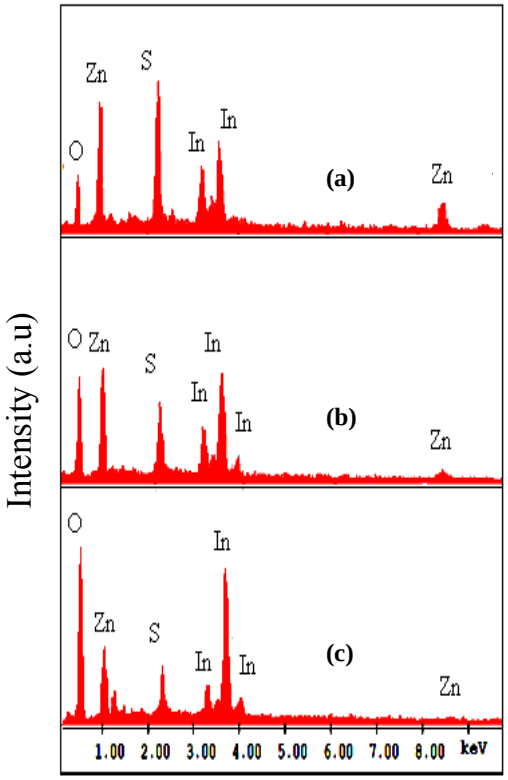

Fig. 1 The EDX spectra of (a) x= 0.4, (b) x= 0.6, and (c) x= 0.8 of $In_xZn_{1-x}S$ thin films

B. *Scanning Electron Microscopy*

The surface morphological studies of as-deposited In doped ZnS films were carried out using a scanning electron microscope (SEM) and the SEM pictures of the films deposited at different concentrations of In in the ZnS are shown in Figs. 2(a–c). It is observed that all the films have continuous grains without any voids or cracks on the film surface. In the In-Zn-S film when x=0.4, the surface is full of small grains with very small pinholes. But when the In concentration is increased then the grains are diffused uniformly in irregular shape and size. The surface of the as-deposited $In_{0.6}Zn_{0.4}S$ and $In_{0.8}Zn_{0.2}S$ films showed a nonuniform granular structure with increased porosity. The grains have an irregular fibrous shape and size. Furthermore the grain boundaries are not well defined.

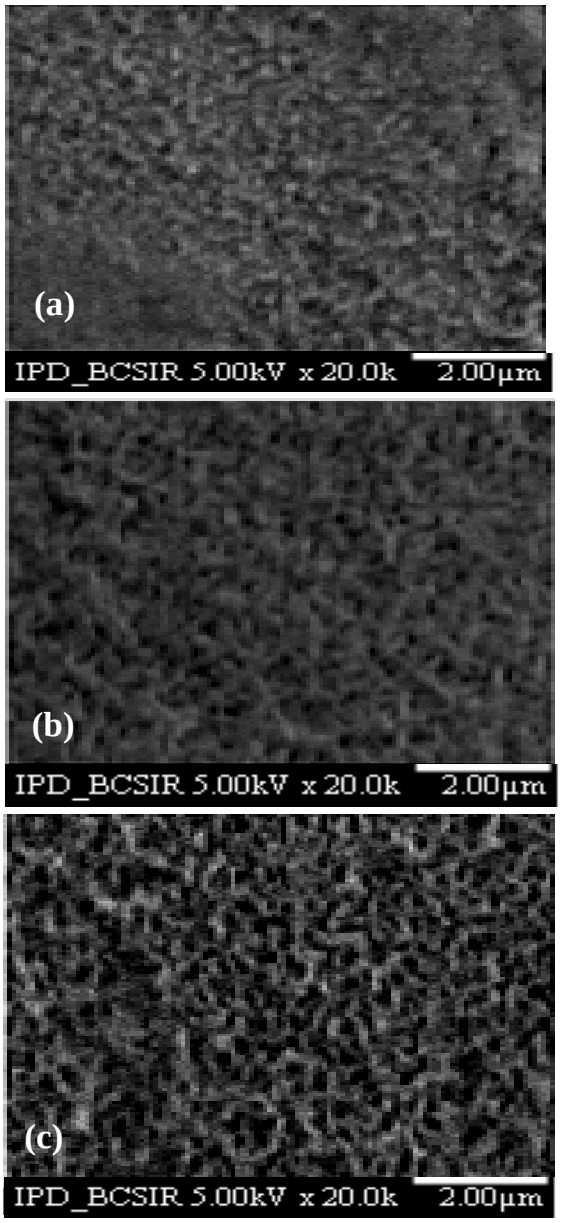

Fig. 2 SEM images under 10000 magnification for Indium concentration of (a) x= 0.4, (b) x= 0.6, and (c) x= 0.8 of $In_xZn_{1-x}S$ thin films.

C. *X-ray Diffraction*

Figure 3 shows the X-ray diffraction pattern of In doped ZnS films with different In concentrations. The XRD of In doped ZnS ($In_xZn_{1-x}S$) with x=0.2, 0.4 have shown the amorphous broadening due to poor crystalline nature of the film. The film nature has been changed to polycrystalline for $x \geq 0.6$. Three

diffraction peaks corresponding to (220), (400) and (440) are observed when concentration of In is x=0.6 in $In_xZn_{1-x}S$ film. There are some significant changes observed as the concentration of In is increased to x=0.8. The peak intensity corresponding to (400) and (440) plane is increased and new peaks of (111), (311) and (511) are appeared. Moreover the diffraction plane of (220) disappeared. The predominant (111), (311), (400), (511), and (440) peaks confirmed the improved crystalline character of In-Zn-S film [12]. The plane (400) at 2θ = 34° has shown the 100% relative intensity. Thus we can say (400) shows the major orientation. This result is similar to that of previous data [14].

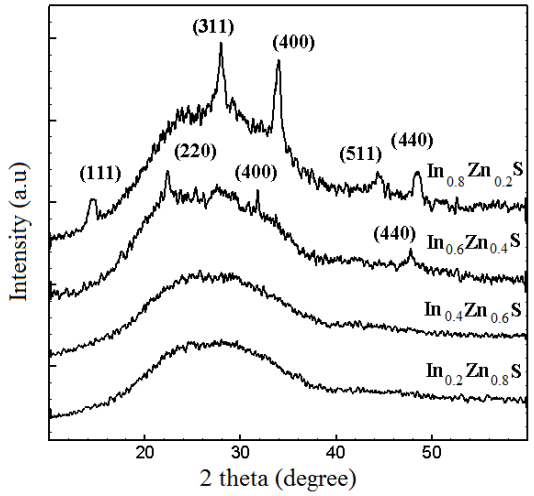

Fig. 3 XRD spectra of deposited $In_xZn_{1-x}S$ thin films.

Table 2 The X-ray diffraction data of the In doped ZnS thin film

Position (2θ)	FWHM (2θ)	d- spacing (Å)	Rel. Int. (%)	(hkl)
14.56	0.6298	6.081	26.97	(111)
27.99	0.4723	3.187	71.08	(311)
34.00	0.2952	2.636	100.00	(400)
44.34	0.9446	2.042	17.94	(511)
48.52	0.7680	1.874	35.05	(440)

The colour of the deposited films is found as yellowish and has showed good adhesion to the substrate surface. The grain sizes of $In_{0.8}Zn_{0.2}S$ are found in the range of 9 to 28 nm. The grain size of crystallites was calculated quantitatively using the well-known Scherrer's formula [7]:

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

where D is the grain size of crystallite, λ=1.5405 Å is the wavelength of X-rays used, β is the broadening of diffraction line measured at half its maximum intensity in radians and θ the angle of diffraction.

D. *Optical Properties*

The optical transmission spectra of ZnS films deposited at 523K substrate temperature for different In concentrations are shown in fig.4. These spectra reveal that the transmittance is high in the visible/near infrared region from 400-1100 nm. The high transmittance of the films is a direct consequence of the wide band gap. The transmittance is found to decrease with the increase of In concentration in ZnS sulfide. The decrease in transmittance at higher doping concentration may be caused from the increased scattering of photons by crystal defects created due to doping [15]. However, the absorbance is high in the ultraviolet region and the figure shows that absorption edge shifted to longer wavelength region with the increase in In incorporation with ZnS.

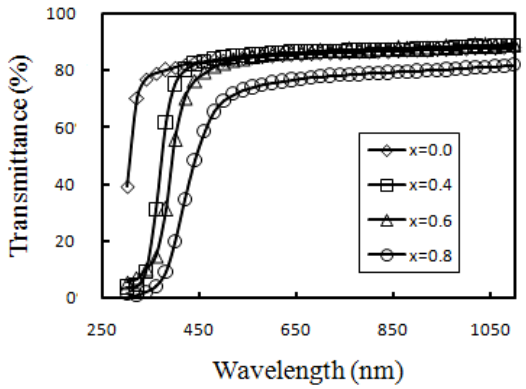

Fig. 4 Variations of transmittances' spectra of $In_xZn_{1-x}S$ films with different concentrations.

The higher transmittance indicates a fairly smooth surface and relatively good homogeneity of the film. The transmittance decreases up to 70% when concentration of In incorporation increased further. The decrease of transmittance at higher doping concentrations may also be due to the

increased scattering of photons by crystal defects created by doping. When In incorporation increased the scattering of the light is increased, the coherence between the primary light beam and the beam reflected between the film boundaries is lost and results in the disappearance of the interference which in turn decrease the transmittance of the film. Thus the free carrier absorption of photons contributes to the reduction in optical transmittance.

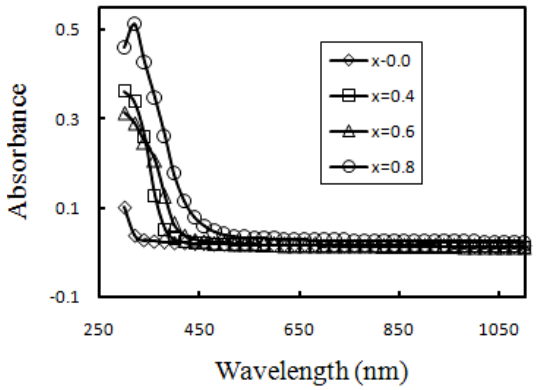

Fig. 5 Variations of absorbances' spectra of $In_xZn_{1-x}S$ films with different concentrations.

The absorption coefficient α, is calculated from the observed absorbance data using Beer Lambert's formula [5]:

$$\alpha = \frac{2.303A}{t} \tag{2}$$

where A is the absorbance and t the thickness of the film. The optical band gap (E_g) of In doped ZnS sulfide was determined from the variation of α as a function of photon energy, $h\nu$. The optical band gap of the films was determined using the relation [9]:

$$\alpha h\nu = C\left(h\nu - E_g\right)^{\frac{1}{2}} \tag{3}$$

where C is the constant that depends on the material. The $(\alpha h\nu)^2$ vs. $h\nu$ graphs for In doped ZnS films are plotted in Fig. 6.

The direct band gap energy of the films has been obtained from X-intercept of the straight line section of $(\alpha h\nu)^2$ vs. $h\nu$. The E_g of the films varied between 3.75 eV to 3.1 eV. It is observed that small amount of indium present in the film greatly affects the E_g. It has been observed that the fundamental absorption edges shift towards the longer wavelength with increasing In incorporation. This suggests the decrease in the E_g with the increasing In incorporation. The overall absorbance has been increased with the increasing In incorporation. There are some absorption peaks upper the fundamental edge. These absorption peaks are an indication that some states have been created in the region between the conduction and valance band. These states may be due to some structural defects in the films.

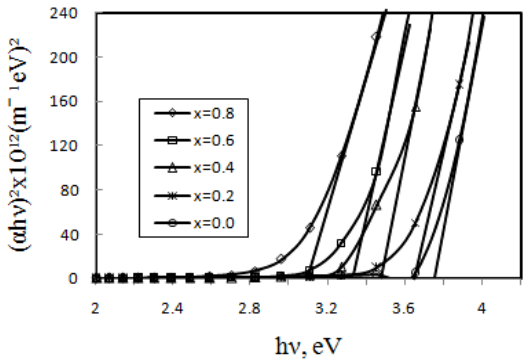

Fig. 6 Variations of band gap of $In_xZn_{1-x}S$ thin films with different compositions vs. $h\nu$.

The extinction coefficient (k), refractive index (n) and dielectric constant of the In doped ZnS thin films have been calculated. The extinction coefficient, k is calculated from the equation [9]:

$$k = \frac{\alpha\lambda}{4\pi} \tag{4}$$

The complex optical refractive index of the films is described by the following relation:

$$n = n + ik \tag{5}$$

where n is the real part and k is the imaginary part (the amount of absorption loss when the electromagnetic wave propagates through the material) of complex refractive index. The

refractive index of the film was determined by the following relation,

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\left(\frac{4R}{(1-R)^2} - k^2\right)} \qquad (6)$$

where R is the reflectance and it is calculated from the equation $R=1-(A+T)$.

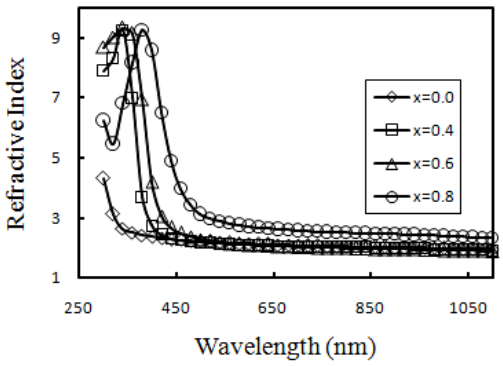

Fig. 7 Variations of refractive index (n) spectra of $In_xZn_{1-x}S$ films with different concentrations.

IV. CONCLUSION

Undoped and In doped ZnS films were deposited by spray pyrolysis method on clean glass substrate at 523K temperature. The effect of In doping on structural and optical properties was investigated by EDX, SEM, XRD and UV-Visible spectroscopy.

(a) EDX spectrum confirms the presence of In, Zn and S in the deposited films. The atomic wt% changes with the change in concentration of In in ZnS thin film.

(b) SEM reveals that the In incorporation changes the surface morphology of the deposited films.

(c) X-ray diffraction shows that the film is polycrystalline when the concentration of In is $x \geq 0.6$ and 0.8 other than the films are amorphous in nature.

(d) The transmittance is decreased to almost 70% when the In incorporation increased to x=0.8 in ZnS. For pure ZnS it is almost 85%.

Finally it can be stated that these deposited films could be a suitable ternary alloy compound as absorber layer for solar cells and other optoelectronic applications.

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