

Study of influence of the dopants on growth mechanism of ZnS thin films

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ABSTRACT

In this paper, the effect of dopant indium and cadmium on the growth mechanism of ZnS thin films prepared by spray pyrolysis, containing zinc chloride, thiourea, indium sulphate and cadmium acetate aqueous solutions has been studied in the temperature 450°C. Characterization techniques such as XRD, SEM with EDAX, UV-VIS spectrophotometer and thickness measurements utilized to investigate the effect of doping indium and cadmium. These ZnS thin films possess a polycrystalline structure, have good adherence to the glass substrates and exhibit cubic phase with a preferential orientation along the (111) direction. The use of additive indium is to improve the sensing performance of ZnS thin films for the detection of harmful highly toxic dioxide nitrogen(NO₂). Due to Cd doping, the polycrystalline nature of the films increases and the orientation of grains is found to be deteriorated. Also the surface morphology of the film shows the changes with a decrease in the grain size. Optical measurements showed that the band gap decreases from 3.94 to 3.6eV. With increasing Cd concentration, there is further decrease in bandgap. Therefore, we suggest that ionized impurity and/or neutral impurity effect are the dominant in growth mechanisms of these films.

Key words: Zinc sulfide, Spray pyrolysis, photoelectrochemical response, gas sensor, doping, chemical sensor.

INTRODUCTION

Zinc sulphide is one of II-VI group semiconductors, and it has remarkable optical properties, thermal stability and diverse applications such as Field-emission, FET, UV-light sensor, gas sensor, and chemical sensor. We can improve the properties of these facilities with doping different elements: Mg,Cu,Ga,Ni, etc.,[1]. There is rare research on In-doped ZnS, so we focus on this topic. It is well known that the physical properties of the ZnS thin films depend on the doping, and then a study of the doping effect on the physical characteristics is always

interesting. The primary motivation for doping of ZnS is wavelength tunability for optoelectronic applications, although doping also results in marked improvement in the photoelectrochemical properties of ZnS as demonstrated in this work. Cadmium and zinc sulphide are wide band gap compounds. Their uses include: as collectors and/or window materials in heterojunction solar cells [2], light emitting diodes [3] and ultrasonic transducer applications[4]. Sulphide thin films find extensive use in the fabrication of a number of solid state devices such as photoconductive and solar cells, thin film transistors and electroluminescent cells. A large variety of deposition techniques, which include vacuum evaporation, spray pyrolysis, sputtering, molecular beam epitaxy, vapour phase epitaxy, chemical vapour deposition, solution growth, screen printing and electrophoresis have been used for the preparation of these films. In recent years, a large amount of effort has been put into developing sample and low-cost methods for the deposition of these films suitable for device applications [5]. Therefore, in this paper, the effects of In and Cd content on structural and optical properties of In-doped and Cd doped ZnS thin films prepared by spray pyrolysis method were studied. Finally, the photoelectrochemical response of Cd- and In-doped ZnS samples is shown to be superior to the undoped material.

EXPERIMENTAL DETAILS

Zinc chloride (99%), thiourea (99.95%), indium sulphate (99%), and cadmium nitrate (99%) were used without further purification. All other chemicals were from commercial sources and were of the highest purity available and were used without further purification. Thiourea was used as the fuel (reducing agent) in this study. The experimental arrangement of the computerized spray pyrolysis by which the ZnS thin films were coated is fully controlled by computer and microcontrollers. Deposition of ZnS and In and Cd doped ZnS thin films on glass substrates was carried out from 0.2 M zinc chloride(ZnCl_2), 0.2 M thiourea($\text{CH}_4\text{N}_2\text{S}$) and dopants 5wt%, 7wt% & 10wt% of Indium sulphate(InSO_4), 3wt%, 6wt% & 9wt% of Cadmium nitrate(CdNO_3). The spray solution was prepared by mixing the appropriate amount of precursors dissolved in a mixture of deionized water. In order to obtain a homogeneous clear transparent solution, the mixture was mechanically stirred for 2h. Thus prepared solution was loaded into the dispenser unit of the spray pyrolysis unit. Then it was drained into the spray unit. Compressed air was used as the carrier gas. Before real sample preparations, several initial trials were made to optimize the deposition conditions. Under the optimized conditions, during deposition, the solution flow rate and carrier gas flow rate were maintained constant at 5ml min^{-1} and 20l min^{-1} respectively. The spray nozzle to substrate distance was maintained at 15cm. The substrate temperature was maintained at 450°C . In order to avoid the fast cooling of the substrate due to continuous spraying of the solutions, the solution was sprayed on the substrates for few spraying cycles of 1minute, followed by an interval of no spray for 1m. All the films were sprayed with the above said systematic steps, which enabled us to have films of thickness approximately few nanometers. For each dopant concentration, several films were prepared on glass substrates and confirmed that the thickness of the films are reproducible.

The crystalline properties of the films were studied by the x-ray diffraction (XRD) method employing a X-PERT x-ray Diffractometer with Cu K_α radiation. Typical XRD patterns were recorded for the 2θ values ranging from 20° to 80° . The experimental peak positions were compared with the standard JCPDS files and the Miller indices were indexed to the peaks. The elemental analysis of the films were performed by an energy dispersive x-ray

spectrometer (EDAX) attached to a JEOL JSM 6390 scanning electron microscope (SEM). The surface morphology of the film has been studied using the SEM method. In order to understand the optical properties of the films, transmittance and absorption spectra were recorded for the wavelengths ranging from 1100 to 200 nm using PERKIN ELMER LAMDA35 UV SPECTROMETER. The bandgap value and the other related parameters such as Reflectance, Absorption co-efficient, Exinction co-efficient, Refractive index, Optical conductivity of the films has been calculated from the absorption edge of the transmittance and absorption spectrum. The luminescent properties of the films have been studied by photoluminescence (PL) measurements and were performed using KIMON SPEC 1401K, Japan employing a He-Cd light source with an excitation wavelength of 325 nm.

RESULTS AND DISCUSSION

1. X-ray diffraction.

The crystalline structure of In:ZnS, Cd:ZnS films were analyzed by the XRD method. Typical x-ray diffractograms recorded are depicted in fig. They showed a decrease in the intensity of the (111) peak along with additional new peaks due to Cd doping and In doping. It has also been observed that the Intensity of the (111) peak decreased with the simultaneous increase in the FWHM value and indicates the constant decrease in the grain size values. Apart from ZnS characteristic peaks, no peaks that correspond to either cadmium, zinc or their complex sulphides could be detected, which are normally expected to appear upon mixing these sulphides. This observation suggests that the films do not have any plane segregation or secondary phase formation. As said in the experimental section, the experimental peak positions were compared with the theoretical JCPDS files and the Miller indices were indexed. The lattice parameter a slightly increases with the indium dopant percentage. The increase in the lattice parameter must be caused by interstitial incorporation of indium ions into the lattice. It is reported that indium atom takes interstitial site rather than replacing zinc sites thereby deforming the lattice.

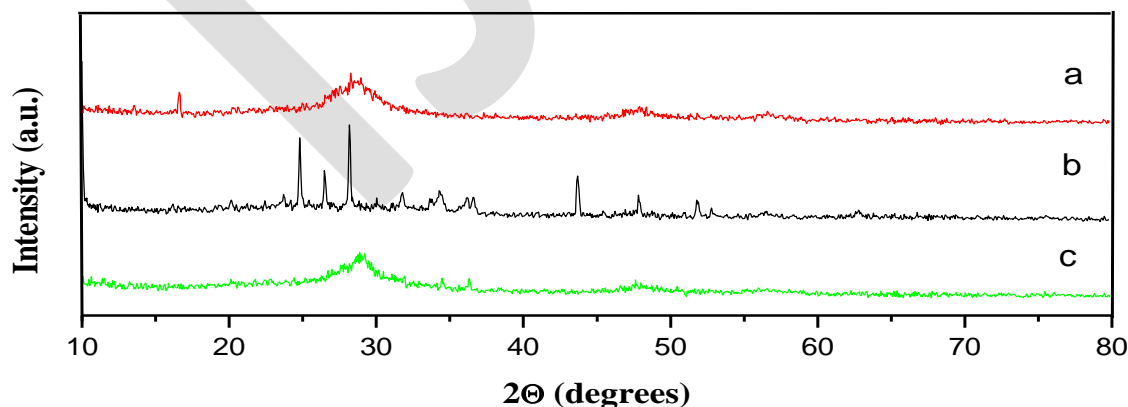


Figure 1(a – c) XRD patterns of pure, In and Cd doped ZnS thinfilms

Parameters	Un doped ZnS	In doped ZnS	Cd doped ZnS
Grain size	8nm	8nm	77nm
Dislocation density	$1.5625 \times 10^{16} \text{ Kg/m}^3$	$1.5625 \times 10^{16} \text{ Kg/m}^3$	$1.6866 \times 10^{16} \text{ Kg/m}^3$
Strain	4.2356×10^{-3}	4.2356×10^{-3}	4.6665×10^{-3}
Inter Planar spacing	3.0753×10^{-10}	3.0753×10^{-10}	3.1499×10^{-10}

Table 1 : Structural parameters of pure and In- and Cd- doped ZnS thin films

2. EDAX elemental analysis

The elemental analysis of In:ZnS, Cd:ZnS films deposited on glass substrates with different In & Cd doping concentrations has been investigated using EDAX instrument attached with SEM instrument and is shown in fig 2(a-c). The EDAX analysis confirmed the presence of Zn, S, In and Cd elements in the deposited films. It has been observed that upon increasing the In and Cd concentration in the starting solution, the amount of In and Cd in the solid films was also found to be increased.

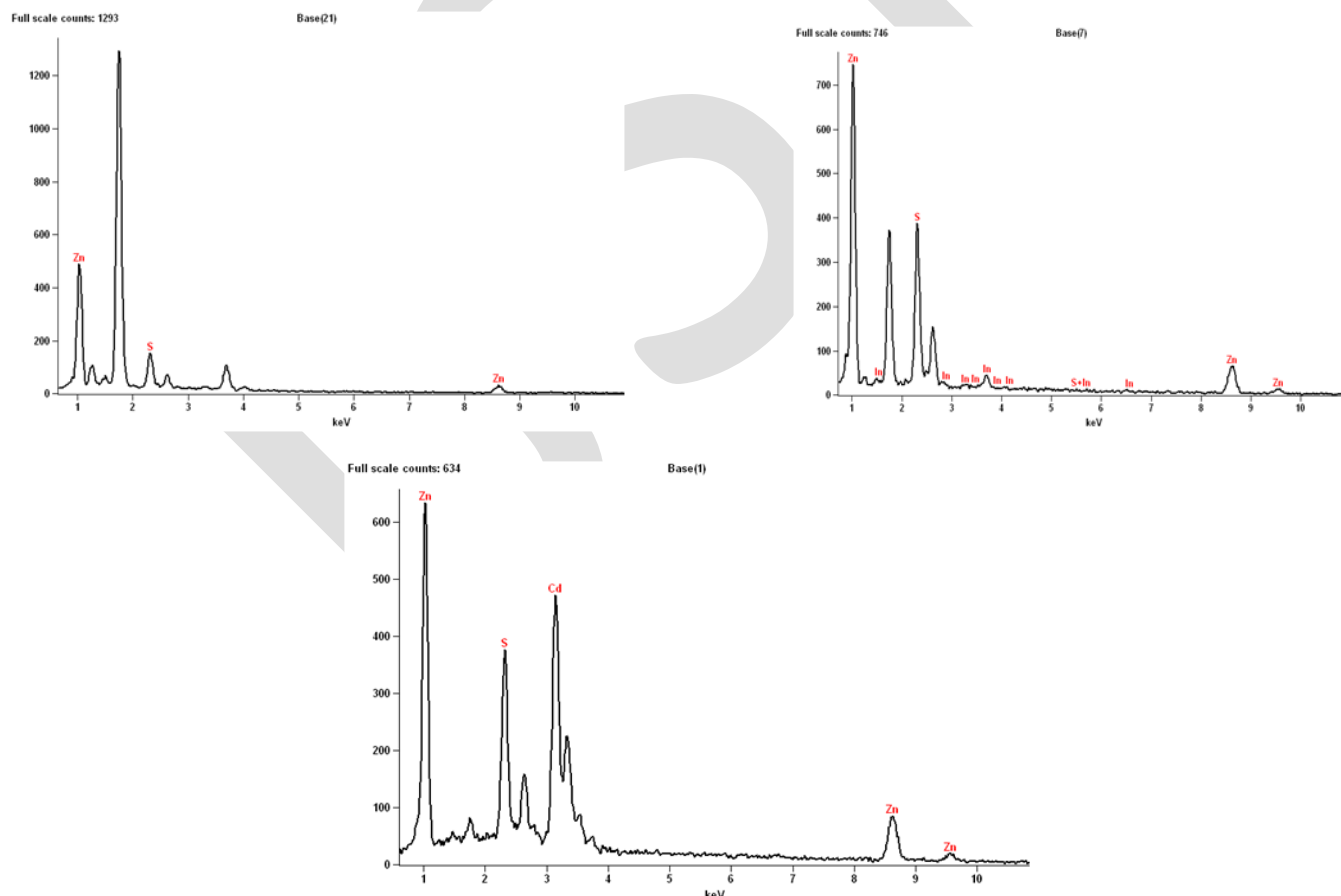


Figure 2(a – c) EDAX spectra of pure, In and Cd doped ZnS thinfilms

Film	Zn	S	Cd	In	Total
Undoped ZnS	64.90	35.10			100.00
Cd doped ZnS	63.86	33.34	2.80		100.00
In doped ZnS	68.89	29.79		1.32	100.00

Table 2 : Compositional analysis of pure and In- and Cd- doped ZnS thin films

It is also interesting to note that the intensity of the In and Zn characteristic peaks observed at higher energies decreases upon increasing the In and Cd concentration. This clearly indicates the substitution of In and Cd into ZnS. It is clear that the intensity of the In and Cd peak increases upon increasing the In and Cd concentration in the starting solution.

3. Surface morphology of the films

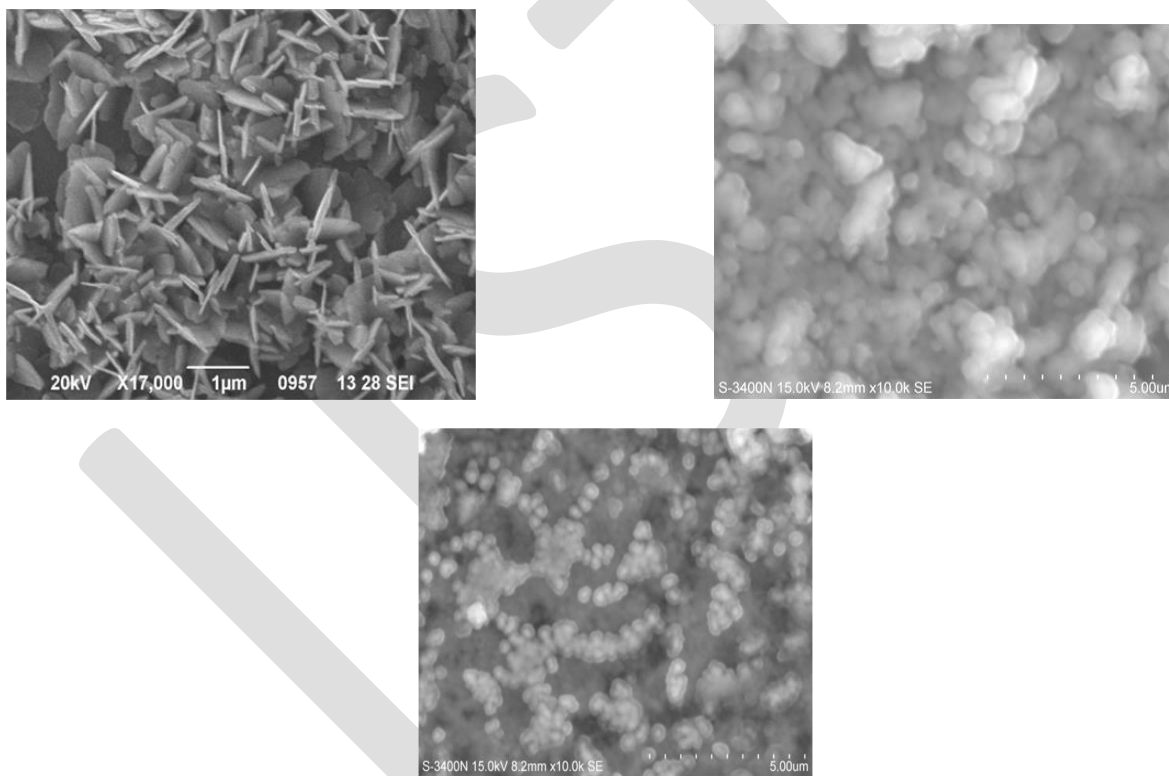


Figure 3(a – c) SEM images of pure, In and Cd doped ZnS thinfilms

Figures 3(a-c) shows the SEM images of pure ZnS, In:ZnS & Cd:ZnS with different In & Cd concentrations deposited onto the glass substrates at 450⁰C. It is observed that pure ZnS films posses larger grains. The images consists of rods and sticks like structures. However, upon increasing the Cd concentration, the grain size of Cd:ZnS films was found to be decreased simultaneously. The decrease in grain size upon increasing the Cd concentration can be attributed to the polycrystallization of the films which has also been confirmed by XRD analysis. Interestingly, the grains grow distinctly as the percentage of indium increased. On further doping

of In, the grain size have increased with grains having irregular size and shape, Although the x-ray diffraction patterns indicate that with increase in indium concentration, clusters of various sizes are formed, themselves are aggregate of grains. The boundaries can't seen in the distinguished manner. Increase in the grain size observed in the SEM images may be attributed to the agglomeration of the smaller particles which could not be resolved due to the limitations of SEM instrument.

4. Optical studies

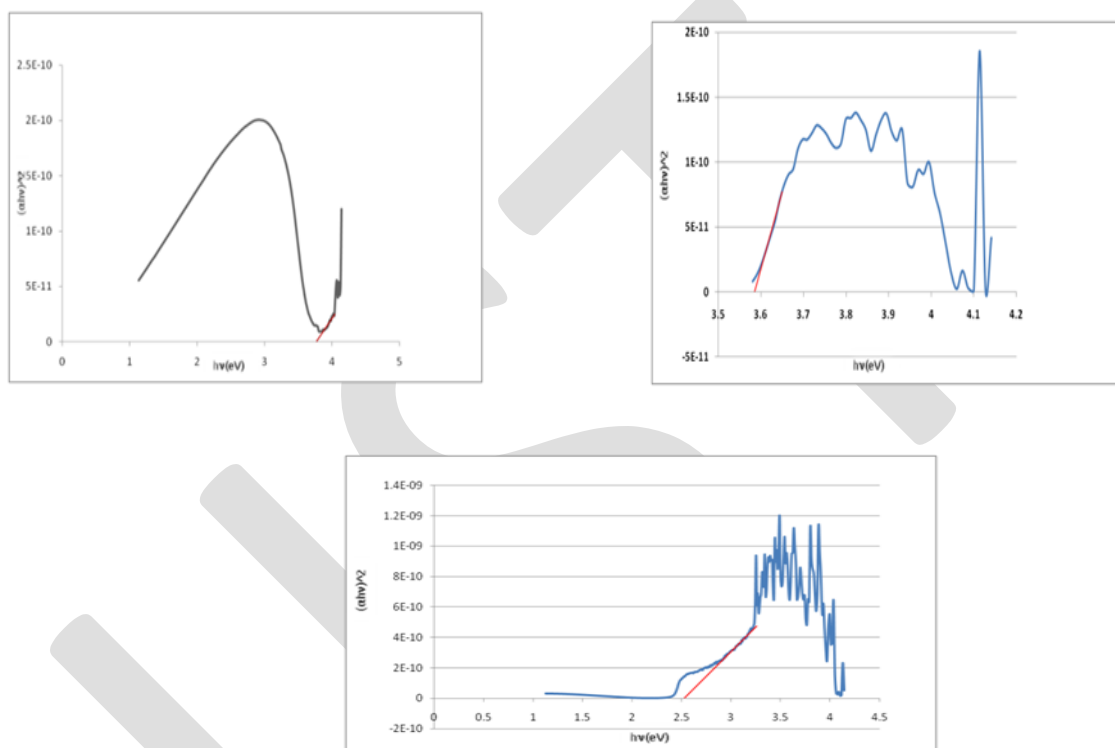


Figure 4(a – c) Bandgap of pure, In and Cd doped ZnS thinfilms

Parameters	Un doped	Cd doped	In doped
Band gap	3.94ev	3.96ev	3.6ev
Reflectance	96.6811	96.742	96.4731
Absorption co-efficient	-469856	-6429222.516	12336987
Exinction co-efficient	-2.4E +07	0-3.3E+08	6.86E+08
Refractive index	8948.166	8959.696	2.67
Optical conductivity	-1E+17	-1.4E+18	2.63E+18

Table 3 : Results of Optical studies of pure and In- and Cd- doped ZnS thin films

From the absorbance and transmission spectra of undoped and Indium and Cadmium doped ZnS films, it is clear that there was no optical absorption in the visible region. Beyond the absorption edge, figure was not symmetric for the undoped and lightly indium doped film. This could be related to the sulphide and metal charge transfer. The energy at which charge transfer occurs between sulphides and metals depend on the cations and the symmetry of its coordinate site (Girjesh. et al 2010). As the indium doping increases, the figure was found to be more symmetric. Thus we can say that for lightly doped film, there is less charge transfer, while at higher doping, better charge transfer is seen between sulphide and zinc. Symmetry of the absorption spectrum could be related to the transfer of electron to the conduction band and hence to the variation in resistivity. Optical transmittance spectra of Indium doped ZnS films show excellent transmittance (>80%). It is clear from the transmittance spectra that increment in doping percentage slightly affects the transmittance of the film. This might be due to the formation of grainy surface leading to large scattering loss. The transmittance measurements of the Cd doping reveals that the films are highly transparent in the visible region. Depending on the Cd concentration in the starting solution, the transmittance values varies between 75% and 85%. The increase in the Cd concentration in the starting solution, up to 6wt% in the starting solution, did not show any remarkable change in the transmittance value. Above this dopant concentration level, we observed coloration (transparent to pale yellowish color) in the films with a decrease in the transmittance values. The average transmittance of these films decreased for higher Cd concentrations. It has also been observed that the absorption edge showed a red shift for higher Cd concentrations, which indicates that the decrease in the E_g values is due to Cd doping. The optical bandgap (E_g) of the thin films could be obtained by plotting $(\alpha h\nu)^2$ vs $h\nu$ curve (is the absorption coefficient and $h\nu$ the photon energy) and extrapolating the straight line portion of this plot to the energy axis as shown in fig. The absorption coefficient ' α ' has been calculated using Lambert's law for directly allowed transition for simple parabolic scheme as a function of incident photon energy as (Ables 1992);

$$\alpha h\nu = (h\nu - E_g)^{1/2},$$

where E_g is the optical band. The values of optical bandgap along with the other parameters calculated using the corresponding formulas are listed in table. Initially for lower In doping, E_g value increases drastically and then at higher doping, it remains nearly constant. The large shift in optical bandgap is mainly due to Burstein effect, which starts that in semiconductor as we increase the doping concentration, the lowest state in the conduction band is blocked which is responsible for the widening in the optical bandgap. This shift is caused by a charge carrier density increase, which is presumably the reason for the measured resistivity decrease with doping concentration. At higher doping small widening in E_g value might be due to low crystallinity.

5 . Luminescent properties

The PL spectra of pure, In and Cd doped ZnS thin films deposited at 450⁰ C on glass substrates have been measured at low temperatures, and shown in the figure 5(a-c). The PL spectrum for intentionally undoped ZnS showed a broad band peaking at 340 nm at room temperature. It is clear that pure ZnS films show two emission peaks: a narrow UV emission peak centered approximately at 345 nm, which corresponds to the near band edge (NBE)

emission of ZnS due to direct band-to-band electronic transitions [6]. However, compared with the NBE emission, the intensity of the defect related peaks observed at 350 nm is very weak, indicating that deposited ZnS films have only a few defects and satisfactory luminescent properties. Upon increasing the Cd concentration in the spray solution, the NBE emission showed a red shift that indicates the narrowing of the band gap due to Cd incorporation. Due to incorporation of Cd, the width of this NBE emission peaks tends to increase greatly with a simultaneous decrease in the intensity of the peak. Furthermore, no NBE peak is detected for films prepared from the spray solution containing more wt% of Cd concentration.

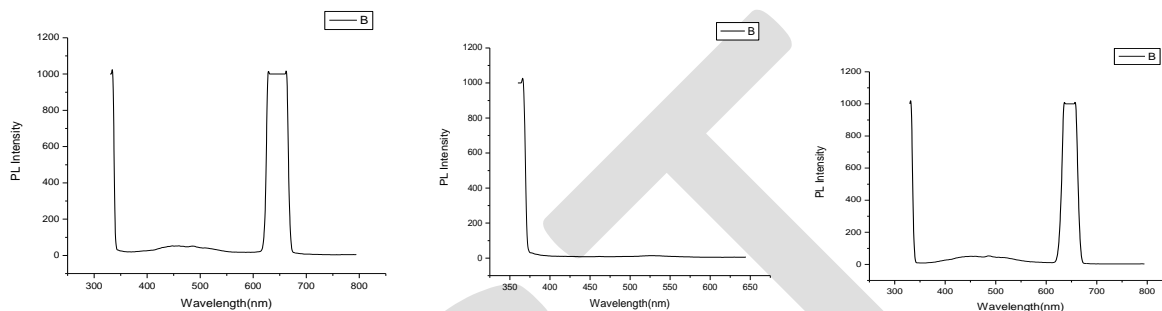


Figure 5(a – c) PL Spectra of pure, In and Cd doped ZnS thinfilms

This implies the degradation of the grains as well as the crystalline quality with increasing Cd concentration. The most remarkable difference of In doped ZnS as compared to the undoped one is the appearance of a very strong PL band peaking at a longer wavelength than 350 nm at room temperature. The peak wavelength of this new band decreased as the indium concentration was increased. The PL intensity of In doped ZnS was stronger than that of the undoped one, but it was insensitive to the indium concentration in the range measured.

CONCLUSIONS

Thin films of undoped, In and Cd doped ZnS were deposited on glass substrates by the computerized spray pyrolysis method at 450⁰ C. The effects of In doping and Cd doping on the structural, morphological, composition and optical properties of ZnS thin films were investigated. All the deposited films are polycrystalline in nature. The SEM images of the thin films showed that the surface morphology is affected by the indium and Cadmium content. It confirms the formation of uniform grains for all samples. x-ray diffraction studies show that ZnS thin films grown on glass preferentially orientation along the (111) direction. The composition analysis confirms the presence of In/Cd, Zn and S. The grain size is found to be 8nm and 77nm for undoped and Cd doped thin films and remain unchanged on doping with In, from x-ray diffraction analysis. The bandgap is found to be 3.94eV, 3.96eV and 3.60eV for undoped, Cd and In doped thin films respectively as calculated from UV studies. Due to Cd doping, the polycrystalline nature of the films increases and the orientation of grains is found to be deteriorated. Also the surface morphology of the film changes with a change in the grain size. Therefore, we suggest that ionized impurity and/or neutral impurity effect are the dominant in growth mechanisms of these films.

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