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STRUCTURAL, OPTICAL AND PHOTOLUMINESCENCE PROPERTIES OF SPRAY DEPOSITED ZNS, ZNS:PB AND ZNS:CD THIN FILMS

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ABSTRACT Undoped, Pb-doped and Cd-doped ZnS thin films have been deposited on glass substrates by spray pyrolysis technique. The films were characterized by XRD, SEM, UV-vis-NIR and PL. Structural studies confirm that all the films exhibit cubic crystal structure. Crystallite size values were 38, 35 and 29 nm, respectively for the undoped, Pb-doped and Cd-doped ZnS thin films. Both the doped films exhibit better transparency than the undoped film. Optical band gap of pure ZnS got shifted towards lower energy side with Pb and Cd doping.

KEYWORDS : Spray Pyrolysis; Pyrolytic Decomposition; Optical Band Gap; Sulfur Vacancy

1. INTRODUCTION

Zinc sulfide (ZnS) is a II-VI metal sulfide semiconductor which exhibits zinc blende structure with cubic phase and wurtzite structure with hexagonal phase [1]. It exhibits a wide band gap of 3.54 eV in cubic phase and 3.91 eV hexagonal phases [2]. Due to its outstanding luminescent properties, ZnS finds applications in lasers, solar cells, electroluminescent devices, etc. [3]. ZnS thin films are used as buffer layers in solar cells due to superior optical properties such as good transparency and high exciton binding energy [4]. However, ZnS exhibits poor optical absorbency under visible light which limits its optical and luminescent properties. The absorbance and luminescent properties of ZnS could be improved by doping with various transition metal ions. By doping ZnS with Cu^{2+}, Ag^{+} and Au^{+} deep levels between the valence and conduction band are created which resulted in the green, blue and blue-green emissions, respectively [5]. Mn substitution in the host resulted in orange-yellow emission peak at about 585 nm [6]. Alteration in band gap and red shift in the PL peaks with Cu doping has been reported by Lee et al. [7]. Blue shift of the fundamental absorption edges has been reported for ZnS with Fe doping [8]. On motivation with these results, in this work Pb and Cd doping has been performed on ZnS thin films to improve its optical and luminescent properties. ZnS Pb-doped ZnS (ZnS:Pb) and Cd-doped ZnS (ZnS:Cd) thin films were prepared by spray pyrolysis technique and characterized by XRD, SEM, FTIR, UV-vis-NIR and PL spectra.

2. EXPERIMENTAL DETAILS

Spray pyrolysis technique is adopted to coat undoped, Pb-doped and Cd-doped ZnS thin films. Micro glass slides are used as substrates to deposite the films undoped ZnS thin films were prepared by spraying 50 mL aqueous solution containing 0.1 M $ZnCl_2.6H_2O$ and $SC(NH_2)_2$ over the substrates maintained at 400°C. The spray rate and deposition time were respectively 2mL/min and 45 min. In between every spray a time gap of 10S was maintained to keep the temperature constant at 400°C. By adding 5 wt.% each of lead nitrate and cadmium acetate to the above solution, Pb and Cd dopings are achieved. The films were characterized by XRD, SEM, UV-Vis-NIR and PL using the instruments whose model are summarized in Table 1.

Table 1 Models of the instrument used to characterize the undoped, Pb-doped and Cd-doped ZnS thin films.

Characterization Technique	Instrument
XRD	X-pert PRO analytical PW340/60 diffractometer
TEM	200 kV Tecnai-20 G2 transmission electron microscope
Optical	LAMBDA-35 UV-Vis-NIR double beam spectrophotometer
PL	Varian Cary Eclipse Fluorescence spectrophotometer

3. RESULTS AND DISCUSSION

3.1 XRD STUDIES

The XRD patterns of ZnS, ZnS:Pb and ZnS:Cd thin films are shown in Fig. 1. Diffraction peaks corresponding to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes were observed for all the films which corresponds to cubic zinc blende ZnS (JCPDS card NO. 05-0566). A strong (1 1 1) preferential growth is observed.

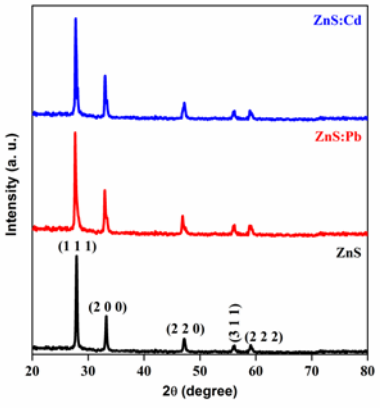

Fig. 1 XRD patterns of ZnS, ZnS:Pb and ZnS:Cd thin films

The effect of Pb and Cd doping is evident from the shift of the (1 1 1) peak position towards smaller diffraction angle, as the ionic radii of Pb^{2+} (1.19 Å) and Cd^{2+} (0.97Å) are larger than that of Zn^{2+} (0.74Å). Due to this angle shift the lattice parameter values of both the ZnS:Pb and ZnS:Cd films exhibit lattice expansion than that of the pure ZnS. No diffraction peaks corresponding to Pb and Cd were detected in the XRD patterns of the ZnS:Pb and ZnS:Cd thin films, confirming the fact that the dopants are homogeneously dispersed into the Zns lattice [9]. The crystallite size (D) values of the ZnS, ZnS:Pb and ZnS:Cd thin films calculated using the Scherrer formula, $D = \frac{0.9\lambda}{\beta cos\theta}$ were found to be 38, 35 and 29, respectively.

3.2 TEM ANALYSIS

Fig. 2 shows the TEM images of ZnS, ZnS:Pb and ZnS:Cd thin films.

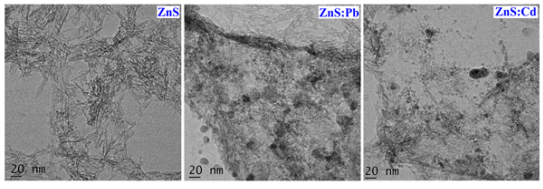

Fig. 2 TEM images of ZnS, ZnS:Pb and ZnS:Cd thin films

Elongated needles are visualized for pure ZnS. Spherical shaped grains were found embedded in the surface of pure ZnS for the ZnS:Pb thin

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films. Nanosized spherical grains were found for the ZnS:Cd thin films. Thus, the surface of pure ZnS got modified with Pb and Cd doping.

3.3 OPTICAL STUDIES

The transmittance spectra of ZnS, ZnS:Pb and ZnS:Cd thin films are shown in Fig. 3 which confirmed a shift of the absorption edges of the doped films towards higher wavelength side and increased transparency. Increased transparency observed for the doped films results from less scattering effects and structural homogeneity [10]. The optical band gap energy (Eg) values of the films were determined from the relation:

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

where A is an energy independent constant, hν is the photon energy and α is the absorption coefficient.

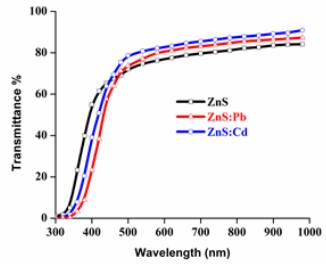

Fig. 3 Transmittance spectra of ZnS, ZnS:Pb and ZnS:Cd thin films

The plots of $(\alpha h\nu)^2$ Vs hν of the films are shown in Fig.4. The band gap values of the ZnS, ZnS:Pb and ZnS:Cd thin films estimated after extrapolating the linear portion of the plots to the energy axis at α=0 were found to be 3.95, 3.75 and 3.85 eV, respectively.

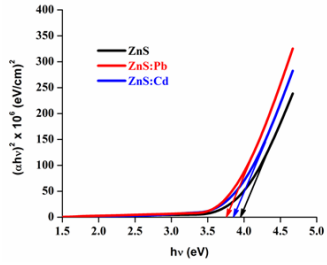

Fig. 4 Plots of $(\alpha h\nu)^2$ vs. hν of the ZnS, ZnS:Pb and ZnS:Cd thin films.

The decreased band gap values observed for the doped films might be due to the existence of Pb and Cd impurities in to ZnS lattice which induce the formation of new recombination centres with lower emission energies [11].

3.4 PL STUDIES

The PL spectra of ZnS, ZnS:Pb and ZnS:Cd thin films recorded at room temperature with the excitation wavelength λ=350 nm are displayed in Fig.5. The emission peaks observed at 361 and 377 nm for all the films are due to S-vacancy states [12].

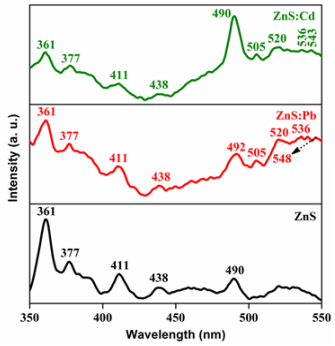

Fig. 5 PL spectra of ZnS, ZnS:Pb and ZnS:Cd thin films

The recombination between the valence band and sulfur vacancy related donor might be responsibile for the emission peak at 411 nm for all the films [13]. The emission peaks observed at 438 nm for all the films might be due to the transitions of electrons to holes trapped at surface states located within the band gap energy from the conduction band [14].

The recombination of impurity bound excitons might be responsible for the emission peaks at 490 nm for pure ZnS, ZnS:Cd and at 492 nm for the ZnS:Pb thin films [15]. Band- to-band transition might have resulted in the emission of peaks at 505 and 520 nm for the ZnS:Pb and ZnS:Cd thin films [16]. The presence of sulfur species on the surface of the ZnS:Pb and ZnS:Cd thin films might be responsible for the peaks at 536 nm and at 548 for ZnS:Pb and at 543 nm for the ZnS:Cd films respectively [17]. Defects density related green emission bands are observed respectively at 582 nm for the ZnS:Pb and at 574 nm for the ZnS:Cd thin films [18]. The yellow bands emission peaks due to the de-excitation of electron via the surface/defect states is observed at 594 nm for the ZnS:Pb and ZnS:Cd thin films [19].

4. CONCLUSION

Spray pyrolysis technique was used to deposit ZnS, ZnS:Pb and ZnS:Cd thin films. XRD studies revealed the cubic belnde structure for all the films. Increased lattice parameter value was observed for the ZnS:Pb and ZnS:Cd thin films. Increased transparency and decreased band gap values was observed for the doped films. The results obtained confirmed that Pb^{2+} and Cd^{2+} ions strongly influenced the structural, optical and luminescent properties of ZnS thin films.

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