

Optical and photoconductivity properties of Mn doped nanocrystalline PbS thin films deposited by chemical bath deposition method

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Mn doped nanocrystalline PbS thin films were deposited onto glass substrates by chemical bath deposition (CBD) method. All the deposited thin films were found to be crystalline having cubic phase structure. The optical properties of the Mn doped nanocrystalline PbS thin films have been studied. They have high absorbance in the UV-visible region. The linear nature of $(\alpha h\nu)^2$ vs $(h\nu)$ plots of PbS thin films confirmed that the transition is direct and the optical band gap energy of PbS films is found to increase from 1.90 eV to 2.28 eV with decreasing crystallite size from 21 nm to 11 nm and the optical band gap values are higher than the bulk value (0.40 eV). The optical band gap of Mn doped PbS films are found to increase with increase in dopant concentrations. The Photoconductive rise time and decay time determined from the prepared films are found to decrease with increase in doping concentrations.

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1. Introduction

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures.[1] The study of optical properties of nanocrystalline solids have become the topic of great interest from the theoretical and experimental research point of view [2]. As a consequence of quantum confinement, the continuum of states in the conduction and valance band are broken down into discrete states with an energy spacing relative to the band edge, which is approximately inversely proportional to the square of the particle radius [3], resulting in widening of the band gap as compared to the bulk. This is normally observed by a blue shift in the optical absorption spectra. The absorption edge of lead sulphide (PbS) exhibits a large blue shift when the size of the crystallite size is reduced to nanometer scale [4-7]. In this paper, the structural and optical properties of chemical bath deposited undoped and Mn doped PbS nanostructured thin films are reported. This study will enhance the knowledge of practical applications in electronic devices such as photovoltaic cells, light emitting devices, light detector etc.

2. Experimental details

Nanocrystalline undoped PbS thin films were deposited onto chemically cleaned glass substrates by Chemical Bath Deposition (CBD) method using lead acetate and thiourea as Pb^{+2} and S^{-2} sources respectively while Mn doped PbS thin films were deposited by the same method using Manganese acetate, lead acetate and thiourea as Mn^{+2} , Pb^{+2} and S^{-2} sources respectively as reported earlier [8]. For preparation of Mn doped PbS thin films at three different Mn dopant concentrations, pH values of three sets of freshly prepared 0.2 M solution of lead acetate premixed with 1 wt. %, 1.5 wt. % and 2 wt. % Manganese acetate respectively are maintained at 11 by drop wise addition

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of NH_3 solution into each set of solution. Another equal amount of 0.2 M solution of thiourea was added to each set of lead acetate and Mn acetate solution mixture and the final solution mixture was stirred well. Then proceeding in the same way of depositing undoped PbS thin films, Mn doped PbS thin films at different doping concentrations (1 wt%, 1.5 wt % and 2 wt %) of Mn Acetate are deposited onto glass substrates at constant molarity 0.2 M, pH value 11 and deposition temperature 313 K to study their effects on structural, morphological and optical properties of the films. The structure of the film was studied with X-ray diffraction (XRD) XPERT-PRO Philips diffractometer. The optical properties of the samples were studied using UV-visible spectrophotometer CARRY 300.

3. Results and discussion

3.1. Structural properties

Fig.1 shows the XRD pattern of Undoped and Mn doped PbS thin films deposited at deposition temperature 313K, pH value 11 and concentration 0.2M at different dopant concentrations (1 wt%, 1.5 wt% and 2 wt%). In the case of undoped PbS films, we observe sharp peaks at $2\theta = 25.825^\circ$, 29.75° , 42.975° and 50.875° which correspond to (111), (200), (220) and (311) planes respectively with preferred growth orientation along (200) plane. The observed peak positions are consistent with the fcc cubic phase structure of PbS [9,10]. With the addition of different dopant concentrations (Mn^{+2} source), the peak intensities decrease considerably. This can be attributed to doping induced structural disorder in the films [11].

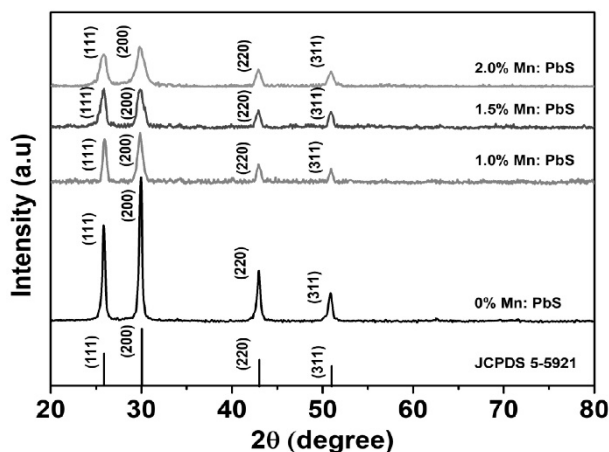


Fig. 1. XRD spectra of undoped and Mn doped PbS thin films prepared at different weight percent doping of Mn^{+2} source at constant reactant concentration 0.2 M, pH value 11 and deposition temperature 313K.

The observed peaks are broaden due to two main possible causes, the first is the increase in heterogeneity of the films due to the occupation of Mn into the host lattice and the second is due to decrease in the particle size (D). When Mn^{+2} occupies more and more sites of Pb^{+2} in the host lattice, internal strain would arise and the crystal structure of Mn doped PbS solid solution becomes unstable. In order to stabilize the crystal structure, there would be a spontaneous size reduction of the particles which might release the strain. As the Mn concentration is increased, the diffraction peaks become broader due to a reduction in the size [12-13]. The crystalline sizes of the films are calculated from the XRD spectra using the Scherer's relation [14] are found to be 21 nm, 17 nm, 14nm and 11 nm for undoped PbS film, 1 wt %, 1.5 wt % and 4 wt.% Mn doped PbS films respectively. The calculated crystallites size decreases with increase in dopant concentrations. The decrease in crystallite size of Mn doped PbS may be due to the replacement of some the larger size lead ions (Atomic radius = 119 pm) by smaller radius Mn ions (80 pm). Similar results are reported earlier [15, 16].

3.2. Elemental analysis

The quantitative and qualitative compositional analysis of the as-deposited undoped and Mn-doped PbS films is carried out by EDAX technique as reported earlier [17]. Fig. (2-5) show EDAX spectra of undoped PbS, 1 wt.%, 1.5 wt.% and 2 wt.% Mn-doped PbS thin films respectively. The spectrum of undoped thin film confirms the average atomic percentage of Pb and S as 52.62 and 47.38 respectively showing that the film is Pb rich whereas, other spectra indicate that Mn atoms are incorporated with the PbS film.

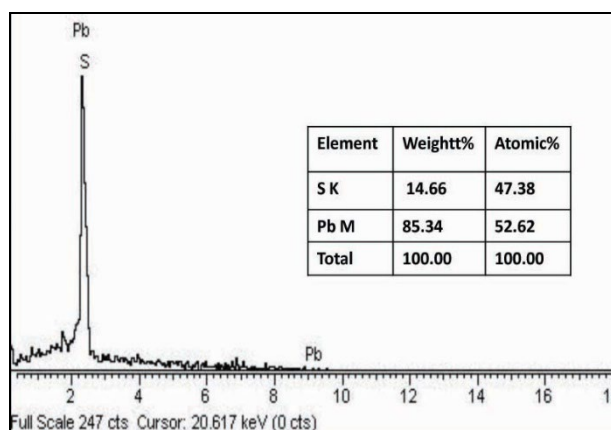


Fig. 2. EDAX Spectra of undoped PbS thin film prepared at concentration 0.2 M, pH value 11 and deposition temperature 313K.

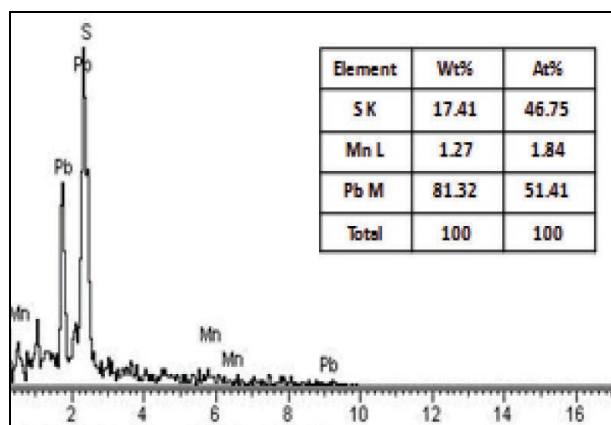


Fig. 3. EDAX Spectra of 1 wt.% of Mn doped PbS thin film prepared at concentration 0.2 M, pH value 11 and deposition temperature 313K.

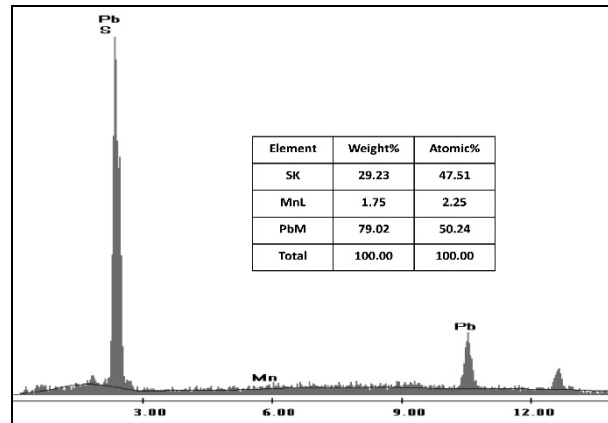


Fig. 4. EDAX Spectra of 1.5 wt% of Mn doped PbS thin film prepared at concentration 0.2 M, pH value 11 and deposition temperature 313K.

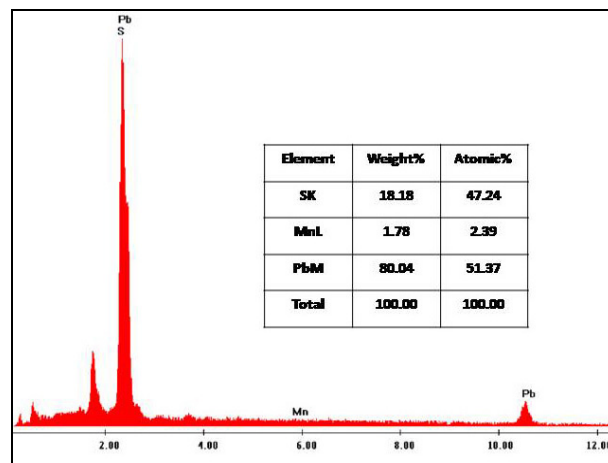


Fig. 5. EDAX Spectra of 2 wt. % of Mn doped PbS thin film prepared at 0.2 M, pH 11 and deposition temperature 313K.

The atomic percentage of Mn atom increases with increase in dopant concentration. The extra peaks observed in the EDAX spectra correspond to some impurity elements like Mg, Si, Na, Ca which are due to glass substrate or the substrate holder used in the EDAX instrument [18]. These might also be due to presence of C and O due to exposure of the film to the atmosphere [19]. There is no source of these elements in the chemicals used for the Mn doped and undoped PbS films synthesis.

3.3. Optical Properties of Mn doped nanocrystalline PbS thin films

Fig. 6 shows absorption spectra of undoped and Mn doped PbS thin films. It is evident from the figure that the absorbance decreases with increase in Mn doping concentration. Fig. 7 shows the $(ah\nu)^2$ vs $(h\nu)$ plots for undoped and Mn doped PbS thin films respectively corresponding to different doping concentrations.

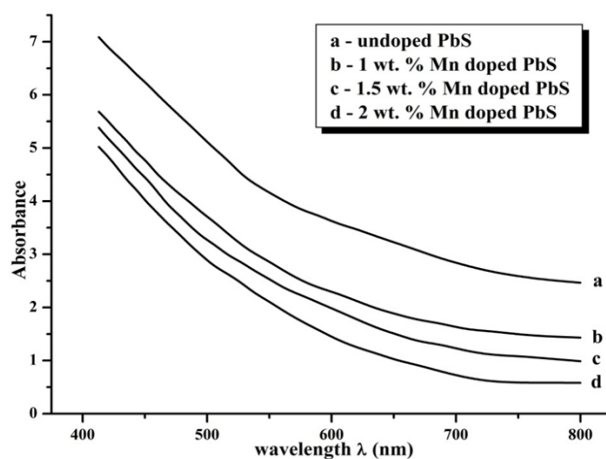


Fig. 6. Absorption spectra of undoped and Mn-doped PbS thin films prepared at three different wt. % of Mn^{+2} source keeping constant concentration 0.2 M, pH value 11 and deposition temperature 313K.

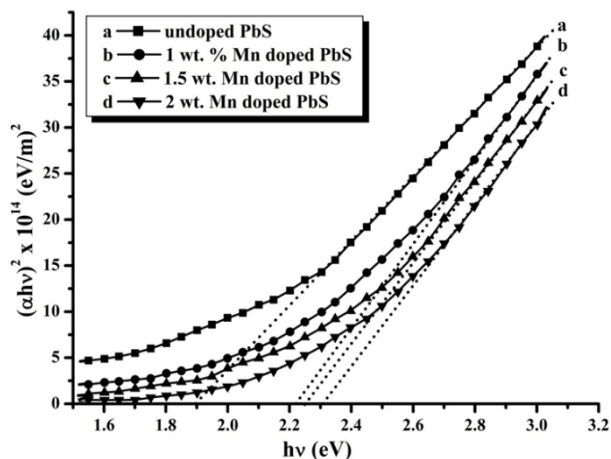


Fig. 7. Plot of $(\alpha h\nu)^2$ vs $h\nu$ of PbS thin films of undoped PbS and Mn-doped PbS thin films prepared at three different wt. % of Mn^{+2} source keeping constant concentration 0.2 M, pH value 11 and deposition temperature 313K.

Extrapolation of the linear portions of the plots to the energy axis yield the direct band gap values for the Mn doped PbS thin films (Table 1). It is observed that band gap increases with increase in Mn doping concentration. Incorporation of Mn to PbS creates some structural changes and the optical band gap is strongly dependent on fractional concentration of Mn atoms. This may be due to the tendency of Mn atoms to introduce high degree of disorder and hence higher densities of localized states in the forbidden gap [20-23].

Table 1. Calculated values of crystallites size and optical band gap of PbS thin films prepared at different doping concentrations keeping fixed deposition parameters.

Deposition parameters	Sample of nanocrystalline PbS thin film with doping percentage of	Thickness (nm)	Crystallite Size (nm)	Optical band gap (eV)
Concentration = 0.2M pH value = 11 temperature = 313 K	0 wt% Mn (Undoped)	262	21	1.90
	1 wt% Mn	220	17	2.15
	1.5 wt% Mn	216	14	2.20
	2 wt% Mn	212	11	2.28

3.4. Photoconductive rise and decay studies of Mn doped nanocrystalline PbS thin film

From Fig. 8, it is observed that for all the Mn doped PbS films at three different concentrations the photocurrent rises very quickly on switching on the light source and then reaches a steady state. Fast rise time response may be attributed to the dominant fast process of photo generation of electron-hole pairs. The current reaches a steady value when the rate of recombination becomes equal to the rate of generation of new carriers and concentration of carriers reaches a steady value. When the light is switched off, electron-hole pair recombination process dominates, so the photocurrent decays slowly. The photoconductive rise time (τ_r) and decay time (τ_d) are determined from tangents drawn to the photoconductive rise and decay curves. The values are found to decrease with increase in doping concentrations and the estimated values of τ_r and τ_d are tabulated in Table 2. The value of decay constant is determined from the slopes of $\ln I_t$ versus $\ln t$ curves shown in Fig. 9 by using the given relation:

$$I_t = I_o(1 + at)^{-b} = I_o t^{-b} \quad (13)$$

where I_o is the initial photocurrent at $t=t_{\text{off}}$ and I_t is the photocurrent after time t from t_{off} and b is the decay constant.

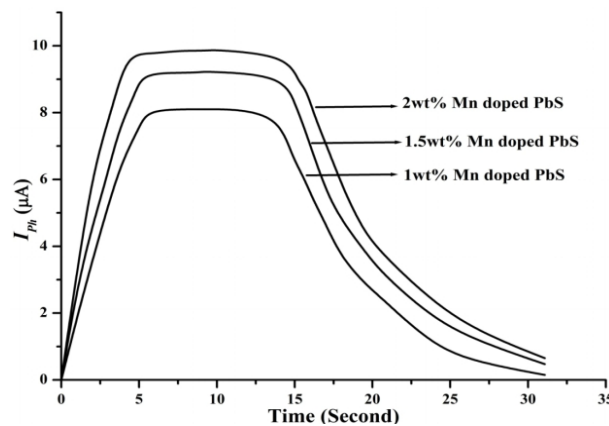


Fig. 8. Rise and decay of photocurrent with time of Mn doped nanocrystalline PbS thin films under illumination of 1700 Lux.

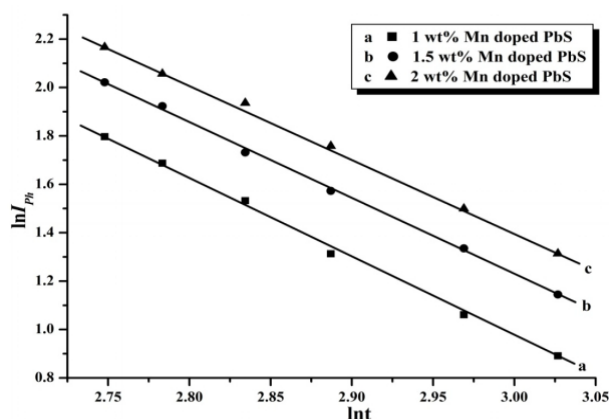


Fig. 9. $\ln I_t$ vs $\ln t$ plots for photoconductive decay of Mn doped nanocrystalline PbS thin films.

Table 2. Various parameters calculated from rise and decay characteristics of Mn doped PbS films under illumination of 1700 Lux.

PbS film	Rise time (τ_r) sec	Decay time (τ_d) sec	Decay constant (b)
1.5wt% Mn doped	4.43	8.41	3.04
2wt% Mn doped	4.16	7.48	3.14
2.5wt% Mn doped	3.63	6.40	3.19

4. Conclusion

The chemically prepared undoped and Mn doped nanocrystalline PbS thin films have high absorbance in the UV-visible region. The linear nature of $(\alpha h\nu)^2$ vs $(h\nu)$ plots of PbS thin films confirmed that the transition is direct and the optical band gap energy of PbS films is found to increase from 1.90 eV to 2.28 eV with decreasing crystallite size from 21 nm to 11 nm and these obtained band gap values are higher than the bulk value (0.40 eV). The increase in optical band gap supports the quantum confinement effect in the PbS thin films prepared by CBD technique. The optical band gap of Mn doped PbS films are found to increase with increase in dopant concentration and the photoconductive rise time and decay time are found to decrease with increase in doping concentrations.

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