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Structural, Optical and Magnetic studies of Mn doped PbS Thin Films by SILAR method

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ABSTRACT

Undoped and Mn doped lead sulfide (PbS) thin films were grown on glass substrate by Successive Ionic Layer Adsorption and Reaction deposition method. Mn content in aqueous solution was varied by adding 0.1, 0.25 and 0.5 mol of manganese chloride. The structural, surface morphological, optical properties and magnetic properties of the films were studied by X-ray diffraction, scanning electron microscopy, UV-Vis spectroscopy, Atomic force microscopy and Vibrating Sample Magnetometer respectively. The X – Ray diffraction studies reveal that the Mn doped PbS thin films were polycrystalline in nature with preferential orientation along (2 0 0) plane. The scanning electron microscopy results indicate that the films were uniform. The bandgap energy of PbS and Mn doped PbS thin films are 2.4 eV and 3.1 eV. The Atomic Force Microscope results indicate that the films are uniform and adherent to the substrate. The VSM studies reveal that the thin film exhibit multi domain behavior.

Introduction

Lead sulphide belongs to IV – VI compound semiconductor material. The colour of the film is grayish – black[1]. PbS is an important direct band semiconductor material with cubic structure [2] and has been widely used in fields such as optical fiber communication, humidity and temperature sensors, LASERs, IR detectors and photodetectors[3,4]. In addition, PbS has been utilized as photoresistance, diode lasers, decorative and solar control coatings[5,6]. Many research groups have shown a great interest in the development and study of this material by various deposition processes such as electrodeposition [7], spray pyrolysis[8], chemical bath deposition[9] and SILAR method [10,11].

In the present work, Mn doped PbS thin films were obtained by SILAR method by changing the molarity of Manganese in PbS thin films. The fundamental feature of SILAR is that it is convenient, simple, inexpensive and eco friendly method[12,13]. Using SILAR method, the thickneness of the layer can be controlled and crystalline materials can be deposited at room temperature. The aim of this work is to investigate the influence of Manganese in Lead Sulphide for different molarities of Manganese on structural, optical and magnetic properties. The characterization of the films was done using X – Ray Diffractometer, Scanning Electron Microscope, Atomic Force Microscope, UV – Vis – NIR spectrophotometer and VSM. The crystalling nature of the grown thin film, grain size, optical band gap have been highlighted.

Experiment

Synthesis of lead sulphide and manganese doped lead sulphide thin films

Mn doped PbS thin films were grown on ordinary glass substrate by SILAR method at room temperature. Prior to the deposition of films on glass slides, the glass slides were first cleaned with distilled water and then dipped in acetone and finally dried in air. The adsorption, reaction and rinsing times were optimized to get homogeneous thin films.

All the reagents used were of analytical grade. Lead nitrate is used as cationic precursor, yellow ammonium sulphide solution is used as anionic precursor and manganese chloride is used for doping Mn in PbS material.

The chemical reaction for forming lead sulphide film is

$$Pb(NO_3)_2 + (NH_4)_2S \longrightarrow PbS + 2\,NH_4NO_3$$

Manganese (0.1 M, 0.25 M. 0.5 M) is doped in the above PbS thin film. Four samples were prepared(undoped PbS, 0.1 M Mn in PbS, 0.25 M Mn in PbS and 0.5 M Mn in PbS). The cycles of operation were continued to 50 cycles for the preparation of all samples.

Results and Discussion

X – Ray Diffraction

Fig. (1) shows XRD of PbS thin films and Mn doped PbS thin films. The peaks with 2 θ values of 26.02º, 30.18º, 43.03 º, and 51.11º correspond to the crystal planes of (1 1 1), (2 0 0), (2 2 0) and (3 1 1) of crystalline PbS respectively. The peak centered at 34º strongly confirms the incorporation of manganese into PbS thin films. The plots indicate that the prepared samples are crystalline and XRD peaks match with face centered cubic structure of PbS(JCPDS No. 65-0692). The main orientation of thin films remains as (2 0 0) direction. The lattice constant of PbS thin films is 5.940 Å.

The grain sizes, dislocation density, Number of Crystallites per unit area are determined using Debye-Scherrer formula. The size of the crystallites (D)[19] and dislocation density (**δ**)[20], defined as the length of dislocation lines per unit volume are calculated using the Scherrer formula

$$D = \frac{K\lambda}{\beta\cos\theta} \quad \text{and} \quad \delta = \frac{1}{D^2}$$

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where K is a constant (0.94) and λ is the wavelength of the X-ray used (1.5406Å), β is the full-width at half-maximum (FWHM) of the peak which has maximum intensity, θ is the Bragg angle.

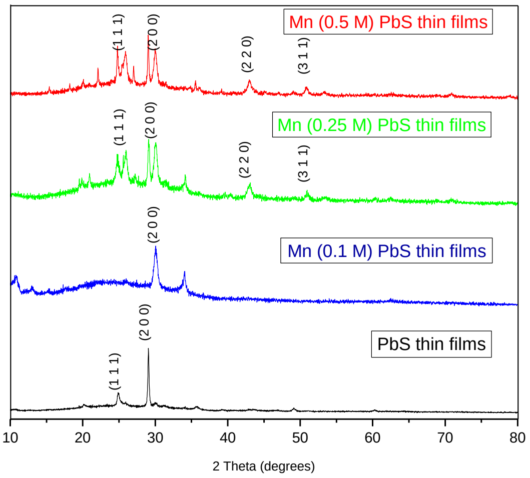


Fig 1. XRD graph of PbS and Mn doped PbS thin films

Since **δ** is the measure of the amount of defects in a crystal, the small values of D obtained in the present study confirmed the good crystalline of the PbS films deposited using the perfume atomizer.

The number of crystallites per unit area (N) of the films is estimated using the relation

$$N = \frac{t}{D^3} \quad / \, unit \; area$$

where 't' is the thickness of the grown thin film.

The thickness of the grown thin film was calculated using surface profilometer and determined as 36 nm, 62.5 nm, 133 nm, 41.3 nm for PbS thin film and Mn doped PbS (0.1 M, 0.25 M, 0.5 M) respectively.

The calculated values of FWHM, Crystallite size, Dislocation density and Number of crystallites per unit area are shown in Table 1.

Table 1

Micro Structural Parameters	**PbS**	**Mn doped PbS (0.1 M)**	**Mn doped PbS (0.25 M)**	**Mn doped PbS (0.5 M)**
FWHM	0.22507	0.42	0.3939	0.197
Crystallite Size (Å)	6.643	3.568	3.7965	7.591
Dislocation density (10^{18} lines/m^2)	2.267	7.855	6.938	1.735
No. of Crystallites/unit area N(per unit area)	$1.288*10^{20}$	$1.376*10^{22}$	$2.43*10^{22}$	$0.9442*10^{20}$

Surface morphological studies

Fig. (2) shows the SEM micrographs of the surface of Mn doped PbS prepared with different molarities of manganese.

The SEM micrograph of the Mn doped PbS thin films are shown in Fig. (2). All the prepared thin films have uniform surface morphology over the entire glass substrate and were of good quality. We see from the SEM images of undoped PbS thin film and Mn (0.1 M) doped PbS thin film, that the particle size decreases which is also confirmed from the XRD results (Table 1).

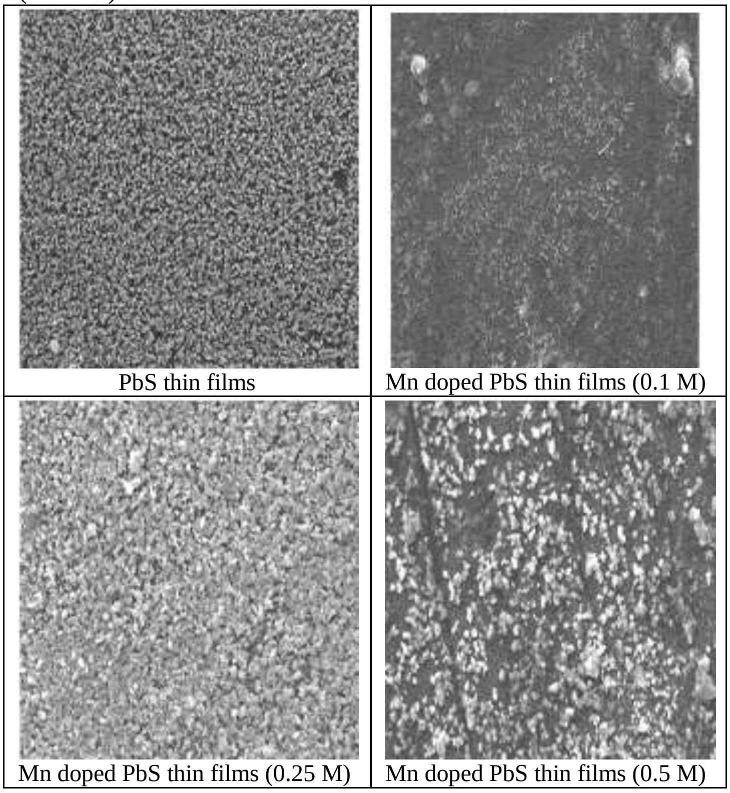


Fig 2. SEM images of Mn doped PbS thin films

Images reveal that the particle size increases with increasing the molarity of manganese which is further confirmed from increasing full width half maximum values shown in first row in Table 1 thus conforming XRD results.

Optical properties:

Fig. (3) shows the optical tran smission spectra of PbS thin films and Mn doped PbS thin films. The optical transmittance spectra of thin films deposited onto a glass substrate were studied at room temperature in the wavelength range of 300 nm – 2500 nm. The transmittance is very low in the UV region, moderate in visible region and high in the IR region. The transmittance graph reveals that the grown thin film can be used as IR detector. The PbS thin film having very low transmittance in UV region is a suitable material for solar control coatings[14]. The spectra of all the films show a sharp fall in transmission near the fundamental absorption, which is an identification of the good crystallinity of these films.

The thin film deposited with 0.1 M(Mn) shows higher transmittance compared to 0.25 M and 0.5 M(Mn). This property of high transmittance makes the thin film a good material for optical coating[24].

From the absorbance data, the absorption coefficient (α) was calculated using Lambert law [15]:

$$\ln\left(\frac{I_0}{I}\right) = 2.303A = \alpha t$$

Where I_0 and I are the intensities of the incident and transmitted light respectively,

A is the optical absorbance and t is the film thickness.

Mathematical treatment of data obtained from optical absorbance versus wavelength gives the energy band gap and the type of transition. The following equation is used to determine the band gap and the type of transition

$$(\alpha h\nu) = k\,(h\nu - E_g)^n$$

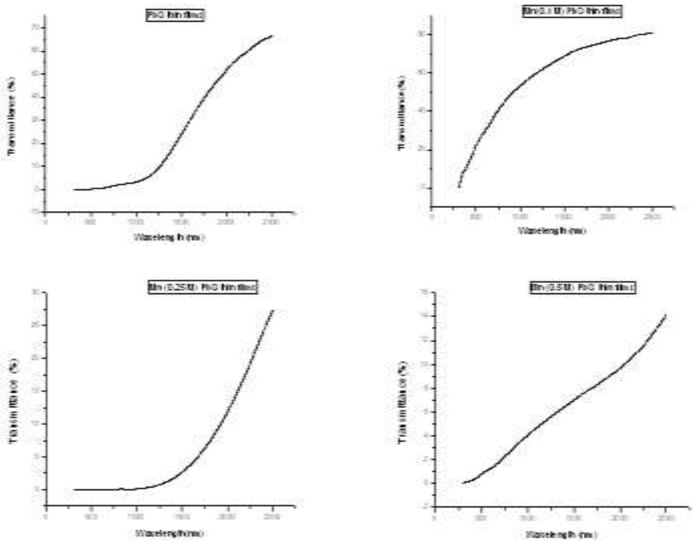
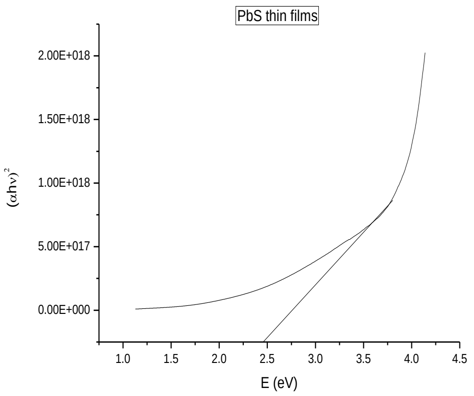


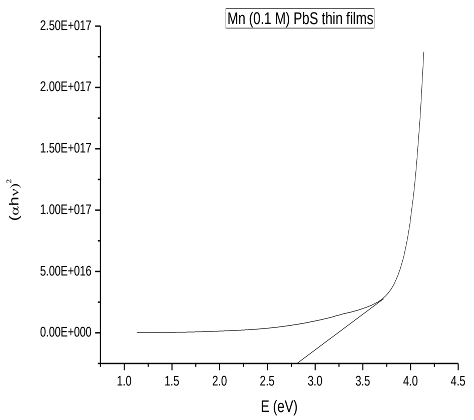
Fig 3. Transmittance spectra of undoped and doped PbS thin films

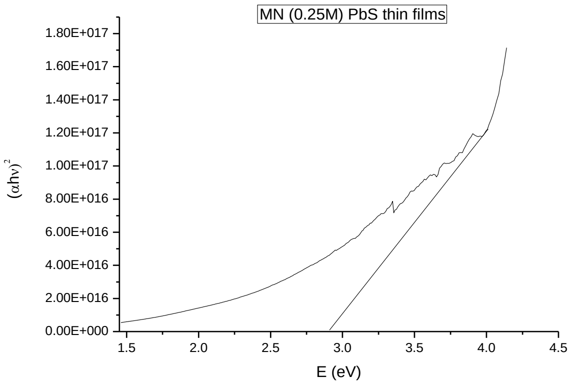
where K is a constant, E_g is the band gap energy, h is Planck's constant.

n carries the value ½ for direct transition and 2 for indirect transition.

Fig. (4) shows the plot of $(\alpha h\nu)^2$ versus hν for PbS thin films for different molarities of Mn. The linear nature of the plot indicates the existence of direct transitions. The band gap energy is obtained by extrapolating the linear portion of the graph to the energy axis at α = 0 which are found to be equal 2.45 eV, 2.8 eV, 2.9 eV and 3.1 eV for PbS films, 0.1 M Mn, 0.25 M Mn, 0.5 M Mn doped PbS thin films.







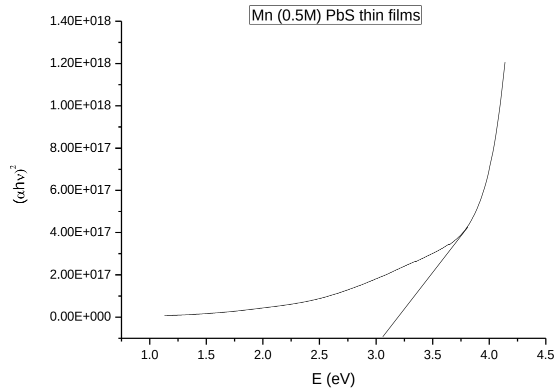


Fig 4. Variation of $(\alpha h\nu)^2$ Vs hν of undoped and doped PbS thin films

From the energy band gap values, cut off wavelength is calculated using the formula $\lambda = {hc}/{E_g}$ and tabulated in Table 2. The cut off wavelength lies in the visible region which indicates that the grown thin films can be used as solar control coating.

Table 2

Material	Bandgap	Cut-off wavelength
PbS thin films	2.45 eV	506 nm
Mn (0.1 M) PbS thin films	2.8 eV	443 nm
Mn (0.25 M) PbS thin films	2.9 eV	428 nm
Mn (0.5 M) PbS thin films	3.1 eV	401 nm

Atomic Force Microscope:

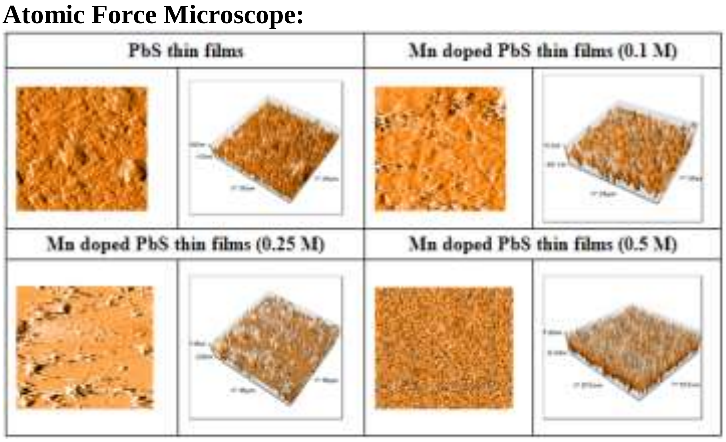


Fig 5. 2d and 3d representation of undoped and doped PbS thin films using AFM

The PbS thin films and Mn doped PbS thin films were characterized using Atomic Force Microscope (AFM) technique. Fig. (5) shows the undoped and doped PbS thin film samples. Fig. (5) represents that the preferred orientation of the film is c axis. The substrate surface is well covered with grains that are uniformly and regularly distributed over the surface, indicating more nucleation sites has been formed. The surface roughness is unavoidable since the particles are grown in different sizes.

Magnetic properties:

The magnetic properties of the grown thin film were studied by Vibrating Sample Magnetometer.

Magnetization of the PbS thin films and Mn doped PbS thin films was measured at room temperature as a function of the applied magnetic field as shown in fig. (6). The magnetization curves show the grown thin films exhibit hysteresis nature which suggests the existence of ferromagnetic ordering at room temperature in the given sample.

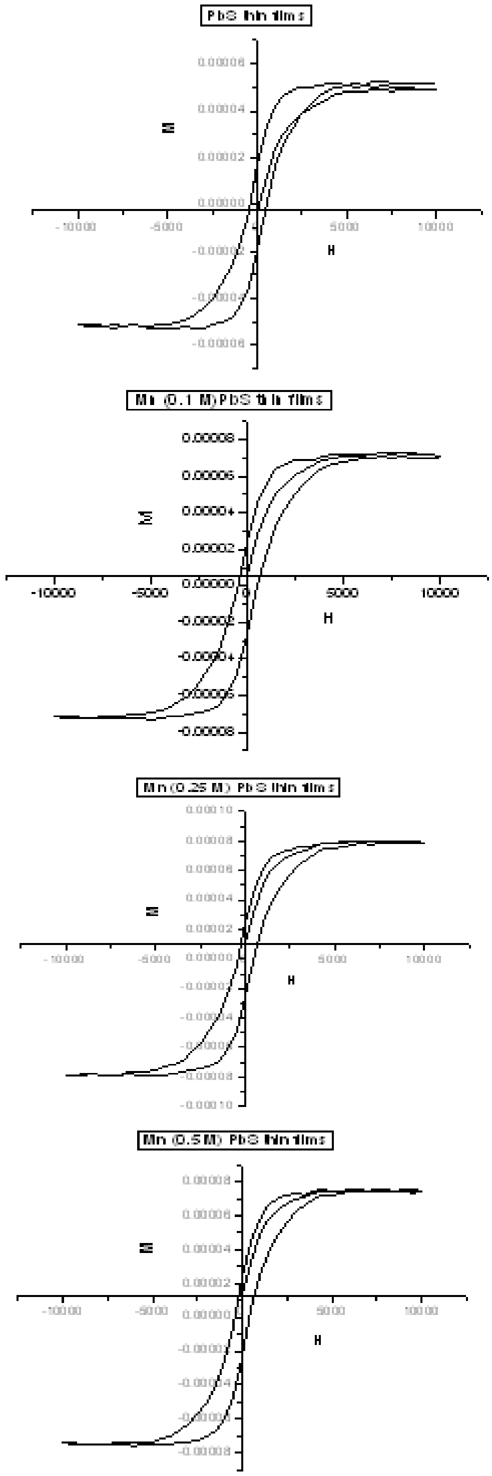


Fig 6. Field dependence of undoped and doped PbS thin films

The remanences, coercivities, saturation magnetization and squareness values of PbS thin films and Mn doped PbS thin films are shown in Table 3.

It is observed that coercivities and squareness as obtained from the hysteresis loops are very low when the manganese content is increased. This decrease can be attributed to an increase in grain size. Larger values of Coercivity *Hc* and retentivity indicates single domain (SD) behavior of the material whereas the lower values of retentivity Mr and the corecivity Hc indicates multi domain (MD) behavior of the material. As magnetization/ demagnetization due to domain wall movement requires lower field energy compared to that required for domain rotation (SD) *Mr* and *Hc* values in multi domain samples are lower than the values observed for single domain samples[18].

From the values shown in Table 3 we confirm that the grown material has low retentivity and low coercivity which indicates the multi-domain behavior of the material and strongly confirms that the material behaves as a soft magnetic material.

Table 3

Material	**Retentivity(M_r)**	**Coercivity G**	**Saturation Magnetisation(M_s)**	**Squareness (M_r/M_s)**
PbS	18.461×10^{-6}	449.1	52.576×10^{-6}	0.351
Mn (0.1 M) PbS	25.232×10^{-6}	468.9	72.847×10^{-6}	0.346
Mn (0.25 M) PbS	24.91×10^{-6}	428.45	79.91×10^{-6}	0.311
Mn (0.5 M) PbS	23.405×10^{-6}	412.62	75.591×10^{-6}	0.310

Conclusion

The structural, morphological, optical and magnetic properties of Mn doped PbS thin films grown by SILAR method were studied. The structural study indicates the crystalline nature with the cubic structure. It revealed that the grain size of the grown films increases with increasing the manganese content, dislocation density decreases with increasing the manganese content. The SEM micrograph shows that the film is uniform and is well adhered to the substrate. The optical absorption studies reveal that the grown thin films have allowed direct transitions. The optical band gap energy varies from 2.8 eV to 3.1 eV with manganese. The VSM studies reveal that the grown thin film exhibits multi-domain behavior and the grown thin films behave as a soft magnetic material.

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