International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.5, pp 2257-2264, 2014-2015

X Ray line profile analysis of Mn doped PbS thin films by Successive Ionic Layer Adsorption and Reaction Method

Chidambara Kumar K N[1]*, Khadeer Basha S K[2], Shakil Muhammad G[3]

[1] Department of Physics, Ganadipathy Tulsi's Jain Engineering College, Kaniyambadi, Tamilnadu, India
[2]Department of Physics, Vellore Institute of Technology, Vellore, Tamilnadu, India
[3]Department of Physics, Islamiah College, Vaniyambadi, Tamilnadu, India

Abstract: Manganese doped lead sulphide thin films have been grown on glass substrate by Successive Ionic Layer Adsorption and Reaction Method(SILAR). The structural properties of the grown thin film were studied using X-Ray Diffraction. Lattice constant is determined using Nelson Riley plots. Using X-ray broadening, crystallite sizes, lattice strain and stress were studied by using Williamson – Hall method and Modified Williamson Hall method.
Keywords: PbS, X-Ray Diffraction, Nelson-Riley plot, Williamson Hall method, Microstrain.

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].

Nelson Riley plot has been used by many research groups for calculating the lattice constant of a cubic system[12,13]. Crystallite size, lattice strain and stress have been calculated using Williamson Hall method, Modified Williamson Hall method and Uniform Deformation Energy Density Model[14, 15, 16]. But so far no detailed work has been reported on the influence of manganese on the structural properties of PbS thin film by SILAR method. The aim of this work is to investigate the influence of Manganese on the structural properties of lead sulphide thin film. The characterization of the films was done using X – Ray Diffractometer.

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 is convenient, simple, inexpensive and eco friendly method[17,18]. Using SILAR method, the thickness of the layer can be controlled and crystalline materials can be deposited at room temperature. The crystalline nature of the grown thin film, crystallite size, lattice constant, stress and microstrain have been highlighted.

Experimental

Materials

Lead nitrate (99%), yellow ammonium sulphide(99%) and manganese chloride (99%) from Merck chemicals were used without any further purification.

Synthesis of 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.

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 of different molarities(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 2θ values of 26.02º, 30.18º, 43.03 º, and 51.11º correspond to the crystal planes (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.

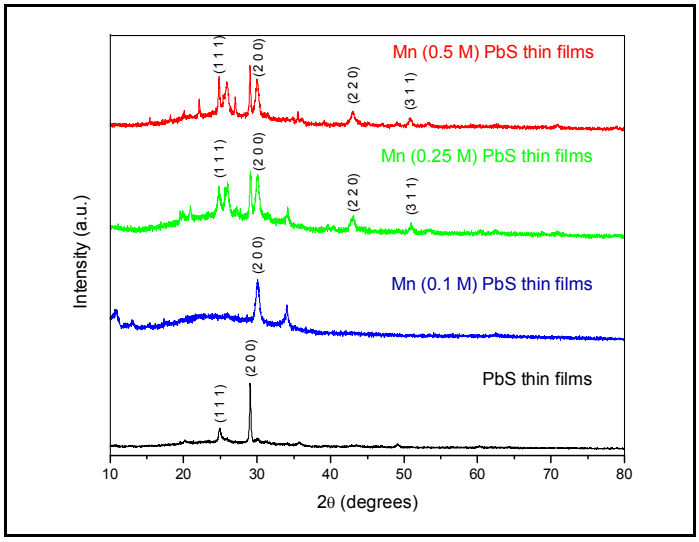

Fig. [1] XRD graph of PbS and Mn doped PbS thin films

Lattice constant:

The lattice constant 'a' for the cubic phase structure is determined by the relation

$$a = d\,(h^2 + k^2 + l^2)^{1/2} \longrightarrow \quad (1)$$

where 'd' is the interplanar spacing of the crystal planes represented by Miller Indices

(h k l)

The corrected values of lattice constants are estimated from the Nelson-Riley plots. The Nelson – Riley curve is a plot between the calculated 'a' for different planes and error function [19]

$$f(\theta)=\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right) \longrightarrow \quad (2)$$ and extrapolation to θ = 90º

A typical Nelson – Riley plot for grown thin films are shown in Fig. 2 and values are shown in Table 1.

The lattice constant 'a' of the film calculated using Nelson-Riley plot (Table 1) deviates from its bulk value 'a_0' which is 5.940 Å. This clearly shows that the grown thin films are under strain. The presence of strains contributes towards broadening of the diffraction peak.

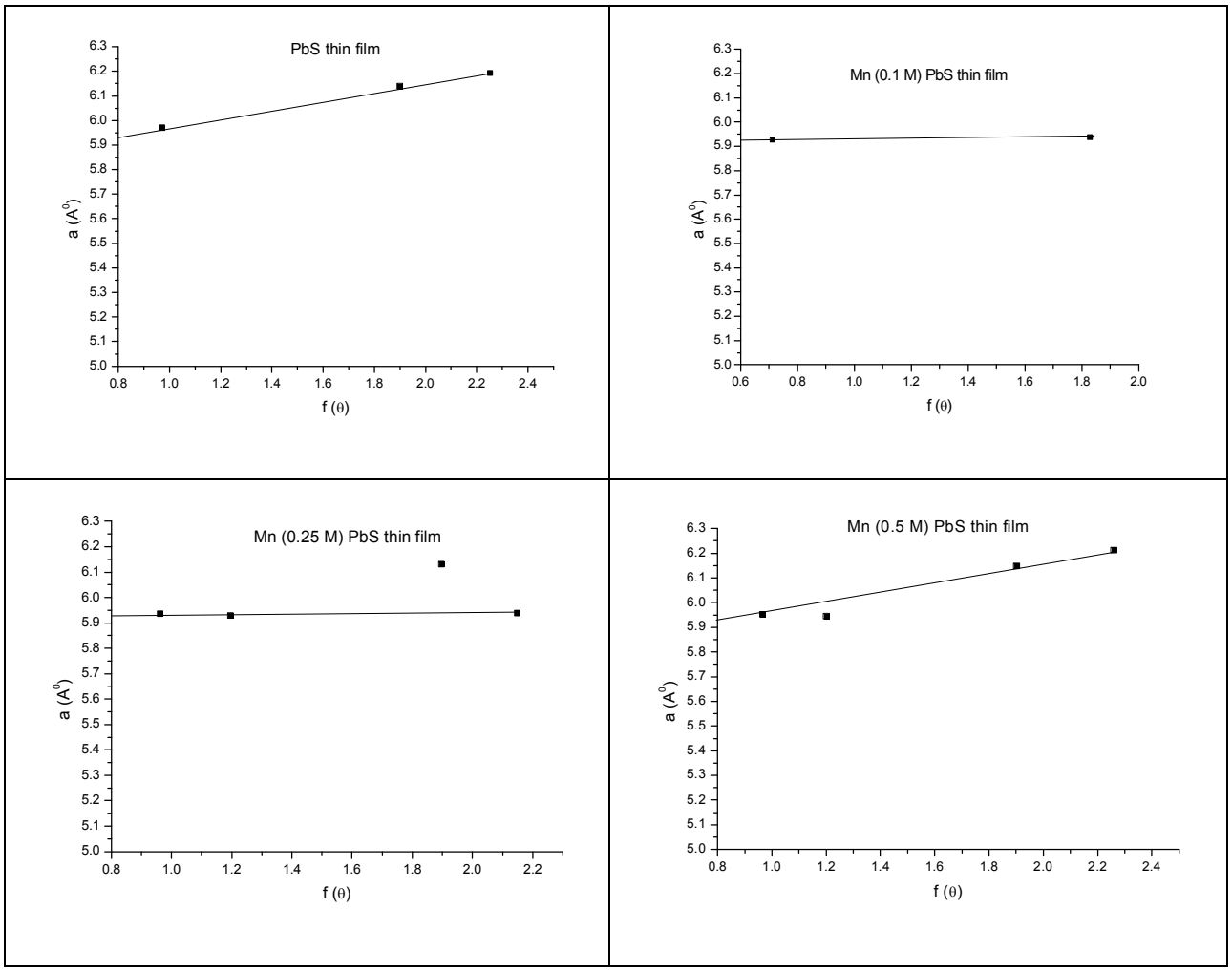

Fig. [2] Nelson – Riley plot for a PbS thin film

Table 1

Thin film	2θ	h k l	d (Å)	'a' calculated (Å)	'a' corrected (Å)	f(θ)
PbS	24.8763	1 1 1	3.575	6.192	5.9369	2.2531
	29.0591	2 0 0	3.069	6.138		1.8997
	50.6633	3 1 1	1.780	5.969		0.9708
	Mean 'a' calculated			6.099		---
Mn (0.1 M) PbS	30.0653	2 0 0	2.969	5.937	5.9259	1.8294
	62.6196	4 0 0	1.482	5.927		0.7138
	Mean 'a' calculated			5.933		---

Mn (0.25 M) PbS	25.9615	1 1 1	3.428	5.937	5.9260	2.1501
	29.0985	2 0 0	3.065	6.130		1.8970
	43.1068	2 2 0	2.095	5.928		1.1973
	50.9593	3 1 1	1.790	5.936		0.9630
	Mean 'a' calculated			5.983		---
Mn (0.5 M) PbS	24.7974	1 1 1	3.586	6.211	5.932	2.260
	29.0196	2 0 0	3.073	6.147		1.9026
	42.9884	2 2 0	2.101	5.944		1.2015
	50.8212	3 1 1	1.794	5.951		0.9668
	Mean 'a' calculated			6.063		---

Crystallite size

Scherrer's formula

The crystallite size of the Manganese doped PbS thin film is estimated from the Scherrer's formula

$$D = \frac{K\lambda}{\beta_{hkl}\cos\theta} \longrightarrow \quad (3)$$

where the constant K is taken as 0.94, λ is the wavelength of the wavelength of X-rays used (λ = 1.5406 Å). β_{hkl} is the full width at half maximum of the diffraction peaks.

Williamson Hall method

In X-Ray Diffraction, peak broadening arises from two sources: instrumental contributions and sample contributions. The Bragg peak breadth is a combination of both instrument and sample dependent defects.

The instrument corrected broadening [20] β_D is calculated from the relation

$$D = \frac{K\lambda}{\beta_D\cos\theta} \text{ or } \beta_D = \frac{K\lambda}{D\cos\theta} \longrightarrow (4)$$

Crystal imperfections and distortion of strain induced peak broadening are related by

$$\varepsilon = \frac{\beta_s}{4\tan\theta} \text{ or } \beta_s = 4\varepsilon\tan\theta \longrightarrow (5)$$

Scherrer equation given by eq. (4) follows a 1/cosθ dependency but not tanθ as Williamson – Hall method. The basic difference was that both microstructural causes small crystallite size and microstrain occur together from the reflection broadening. Depending on different θ positions, the separation of size and strain broadening analysis is done using Williamson and Hall.

According to Williamson and Hall, $\beta_{hkl} = \beta_s + \beta_D$

Substituting eq. (3) and (4) in the above equation we get,

$$\beta_{hkl} = \left(\frac{K\lambda}{D\cos\theta}\right) + 4\varepsilon\tan\theta \text{ or } \beta_{hkl}\cos\theta = \left(\frac{K\lambda}{D}\right) + 4\varepsilon\sin\theta \longrightarrow (6)$$

A graph is drawn with βcosθ along Y – axis and 4 sinθ along X – axis (Fig. [3]). From the graph, strain and crystallite size are calculated from the slope and y intercept of the fitted line respectively and the values are tabulated in Table 2.

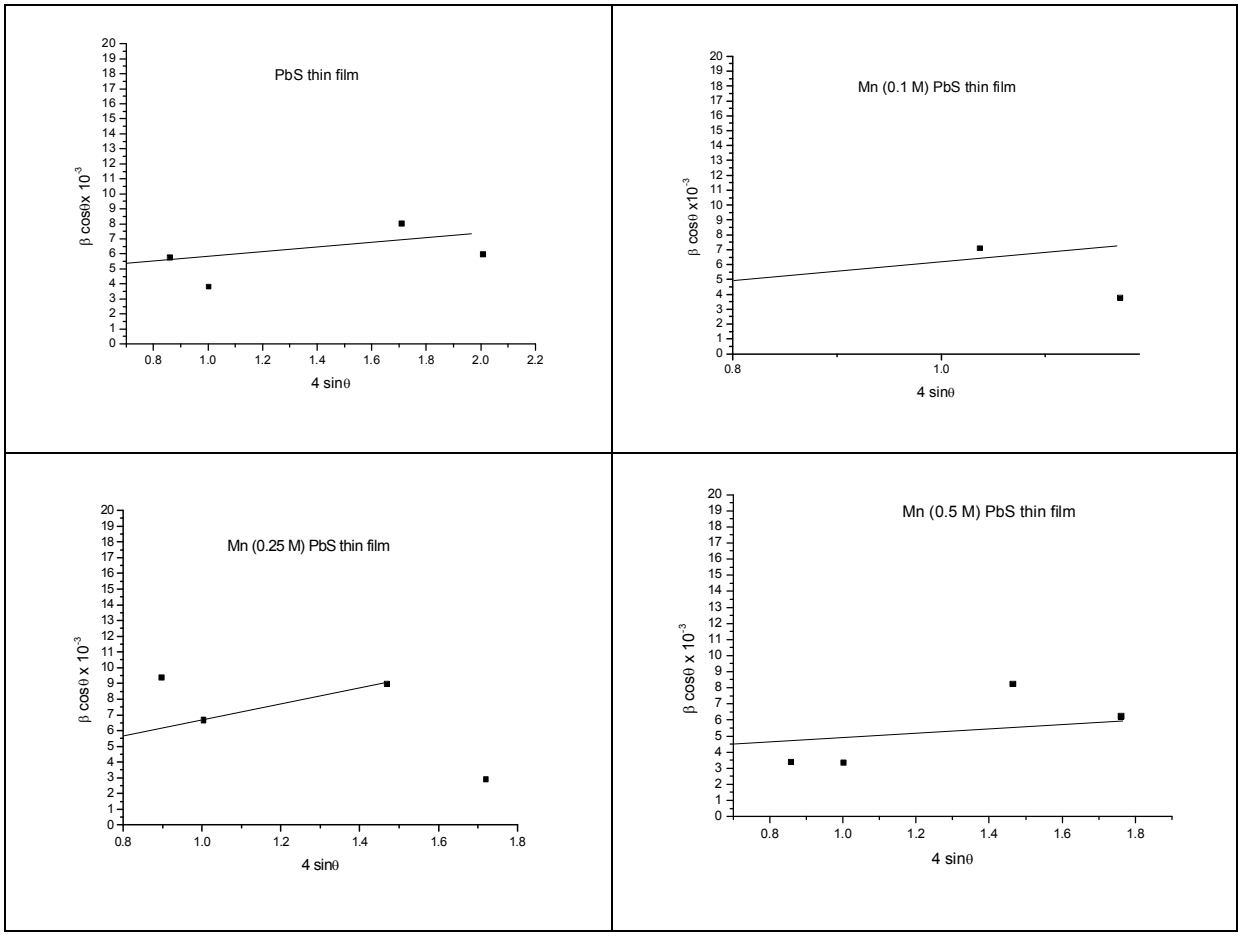

Fig. [3] Williamson Hall plot for PbS thin films

Modified Williamson – Hall method

From Uniform Stress Deformation Model (USDM), strain is calculated from Hooke's law maintaining linear proportionality between stress and strain given by $\xi = E\varepsilon$ where ξ is the stress, ε is the strain and E is the Young's modulus.

Applying Hooke's law approximation to eq. (6), we get

$$\beta_{hkl}\cos\theta = \left(\frac{K\lambda}{D}\right) + \frac{4\xi\sin\theta}{E_{hkl}} \longrightarrow \quad (7).$$

where E_{hkl} for a cubic system in the direction of unit vector li, can be calculated using the following equation:

$$\frac{1}{E_{hkl}} = s_{11} - 2(s_{11} - s_{12} - \frac{1}{2}s_{44})(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2) \longrightarrow \quad (9)$$

where s_{11}, s_{12} and s_{44} are the elastic compliances. The relation connecting elastic compliances and the stiffness c_{ij} are as follows:

$$s_{11} = \frac{(c_{11} + c_{12})}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \longrightarrow \quad (10)$$

$$s_{12} = \frac{-c_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \longrightarrow \quad (11)$$

$$s_{44} = \frac{1}{c_{44}} \longrightarrow \quad (12)$$

For PbS, C_{11} = 124 GPa, C_{12} = 33 GPa and C_{44} = 23 GPa [21]

A graph is plotted between 4 sinθ/E_{hkl} along X – axis and βcosθ along Y – axis(Fig [4]). The stress is calculated from the slope of the graph and crystallite size from the Y intercept and the values are tabulated in Table 2.

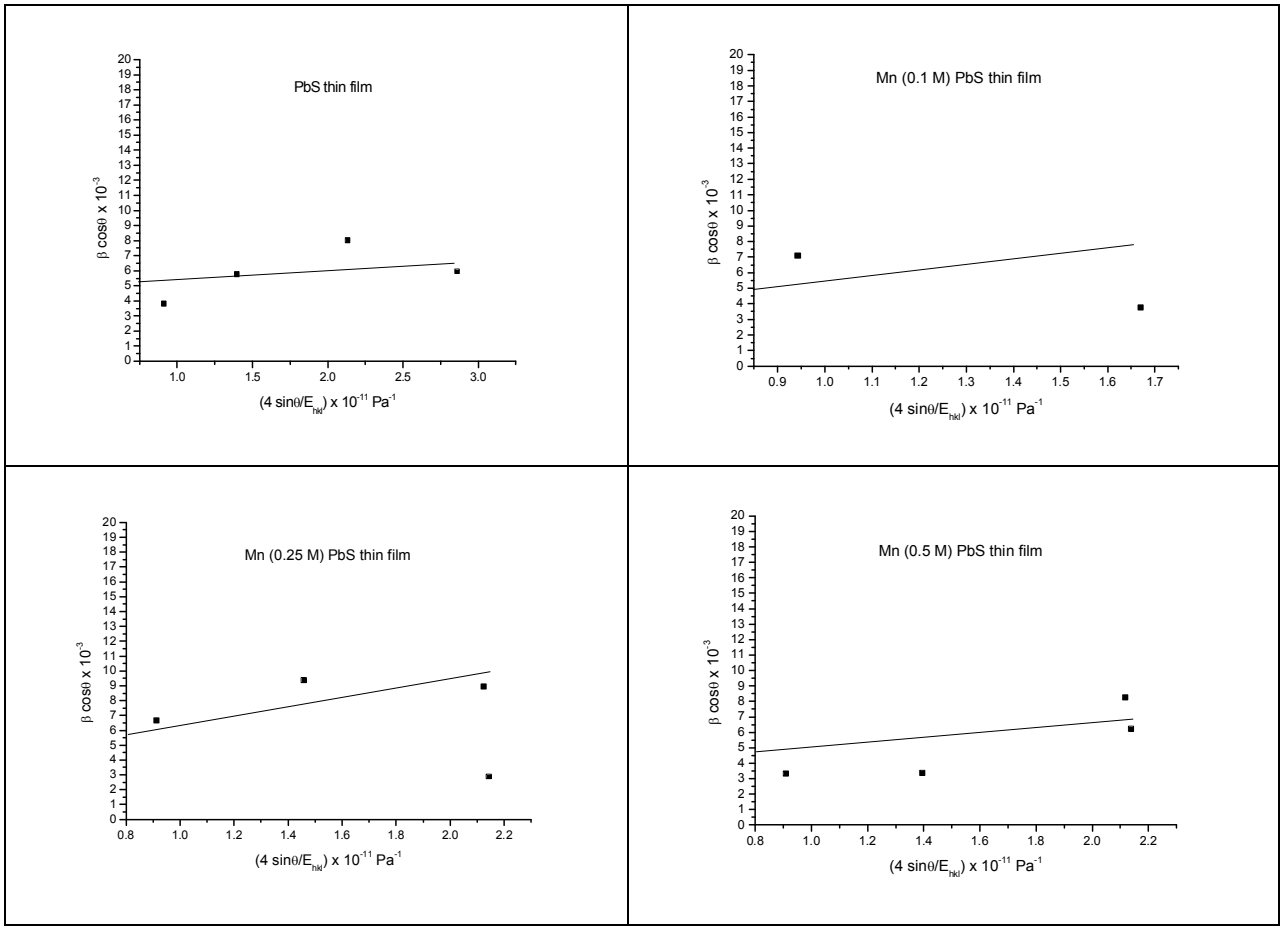

Fig. [4] Modified Williamson Hall plot

The energy density of a crystal was calculated from a model called Uniform Deformation Energy Density Model (UDEDM). The energy density u is calculated from $u = \frac{\varepsilon^2 E}{2}$ using Hooke's law. Hence eq. (6) can be modified according to the energy and strain relation given by

$$\beta_{hkl} \cos\theta = \left(\frac{K\lambda}{D}\right) + 4\sin\theta\left(\frac{2u}{E}\right)^{1/2} \longrightarrow \quad (8)$$

A graph is plotted between 4 sinθ $(2/E_{hkl})^{1/2}$ along X axis and β_{hkl}cosθ along Y axis(Fig. [5]). From the slope of the graph, energy density u is calculated and the crystallite size D is calculated from the Y intercept.

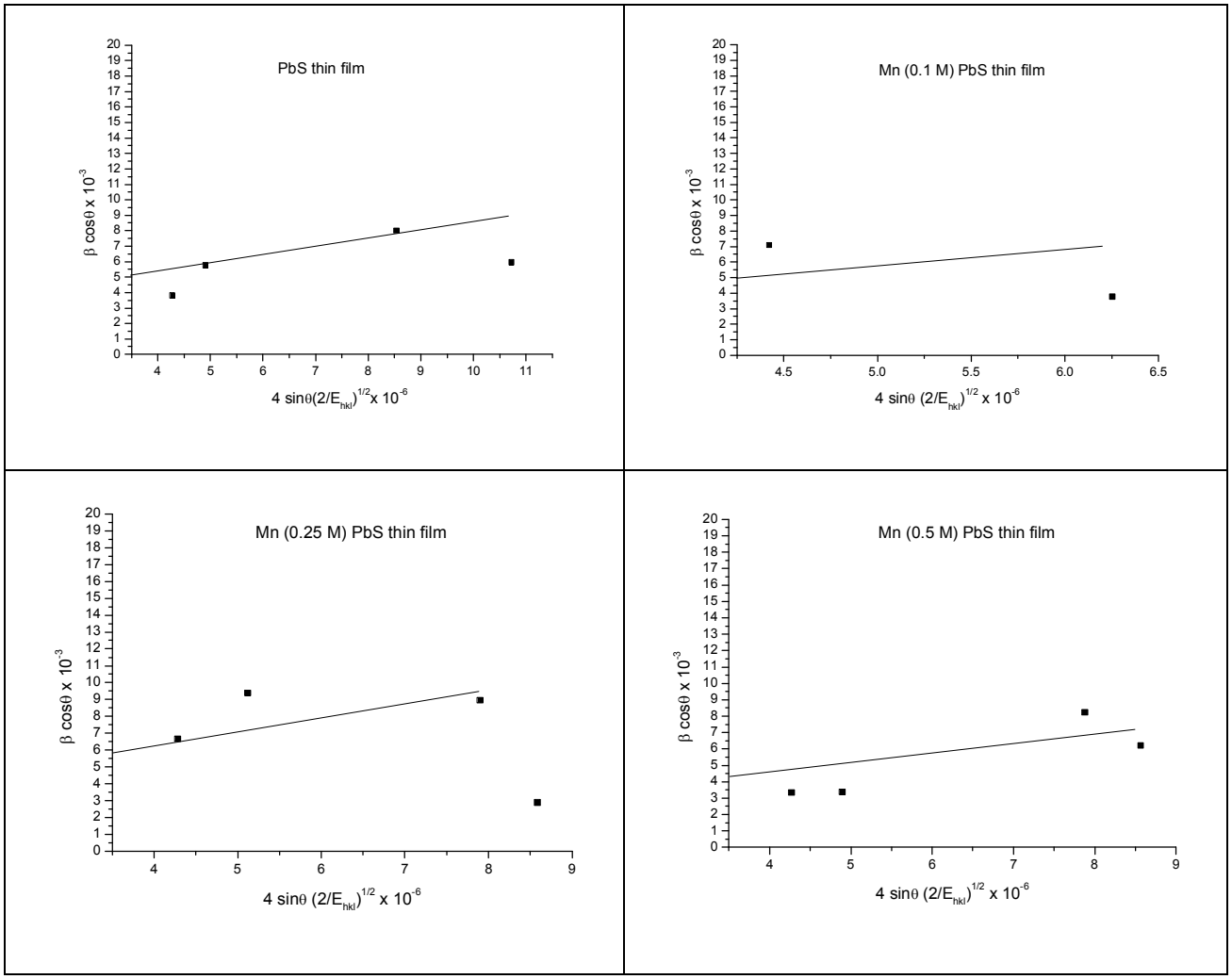

Fig. [5] Uniform Deformation Energy Density Model plot

Table 2

Sample	Crystallite size (Å)				Strain from Williamson Hall method	Stress from modified Williamson Hall method (pascal)
	Scherrer's formula	Williamson Hall method	Modified Williamson Hall method	Uniform Deformation Energy Density Model		
PbS	264.482	271.44	274.79	282.35	0.00103	0.5191×10^8
Mn (0.1 M) PbS	295.17	293.155	294.204	289.694	0.00610	3.418×10^8
Mn (0.25 M) PbS	259.147	258.823	254.79	246.358	0.00521	3.285×10^8
Mn (0.5 M) PbS	318.9125	321.638	311.378	340.789	0.00101	1.665×10^8

Conclusion:

Manganese doped PbS thin films of different molarities of manganese were deposited by SILAR technique and characterized by XRD measurements. Lattice constant of the grown thin films are calculated from Nelson Riley plots. The displacement of diffraction peaks from their corresponding positions indicates

that a stress exists for all manganese doped PbS thin films. The line broadening due to crystallite size was analyzed by Scherrer's formula. The size and strain contributions to line broadening were analyzed by Williamson Hall method and modified Williamson Hall method. The crystallite size obtained from Scherrer's formula, Williamson Hall method, modified Williamson Hall method and Uniform Deformation Energy Density model are in good agreement with each other.

References:

1. H M Pathan, C D Lokhande, "Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction method", Bull. Mater. Sci., 2004, 27(2), 85 – 111.
2. T Sugimoto, Adv. Colloid Interface Sci. 1987, 28, 65 – 108.
3. K Onuma, A Ito, Chem. Mater. 1998, 10, 3346 – 3351.
4. P Gadenne, Y Yagil, G Deutscher, J. Appl. Phys., 1989, 66, 3019
5. T K Chaudhuri, S Chatterjes, Proceedings of the International Conference on Thermoelectronics, 1992, 11, 40.
6. P K Nair, V M Garcia, A B Hernandez, M T S Nair, J. Phys. D: Appl. Phys. 1991, 24, 1466 – 1472.
7. Maheshwar Sharon, K S Ramaiah, Mukul Kumar, M Neumann – Spallart, C Levy-Clement, Electroanal. Chem. 1997, 436, 49 – 52.
8. B Thangaraju, P Kaliannan, Semicond. Sci. Technol. 2000, 15, 849 – 853.
9. J J Valenzuela – Jauregui, R Ramirez – Bon, A Mendoza – Galvan, M. Sotelo – Lerma, Thin Solid Films 2003, 441, 104 – 110.
10. Saloniemi H, Ritala M, Leskela M, Lappalainen R, Cyclid electrodeposition of PbS thin films[J]. Electrochem. Soc, 1999, 146, 2522 – 2525.
11. Kanniainen T, Lindroos S, Ihanus J, Leskela M. Growth of strongly orientated lead sulphide thin films by SILAR technique[J]. Mater. Chem., 1996, 6:161 – 164.
12. Choudhury N and Sarma B K, "Structural characterization of lead sulphide thin films by means of X – ray line profile analysis", Bulletin of Material Science, 2004, 32(1), 43 – 47.
13. Sumbit Chaliha, Borah M N, Sarmah P C and Rahman A, "Effect of Substrate Temperature on Structural Properties of Thermally Evaporated ZnSe thin films of different thickness", Journal of Physics,(2008), 114, 1 – 6.
14. Mote V D, Purushotham Y and Dole B N, "Williamson Hall analysis in estimation of lattice strain in nanometer sized ZnO particles", Journal of Theoretical and Applied Physics (2012), 736, 128 – 134.
15. Prabhu Y T, Rao K V, Kumar V S S and Kumari B S, "X-ray Analysis by Williamson Hall and Size-Strain plots methods of ZnO nanoparticles with Fuel Variation", World Journal of Nano Science and Engineering, (2014), 4, 21-28.
16. Triloki, Garg P, Rai R, Singh B K, "Structural characterization of "as-deposited cesium iodide films studied by X ray Diffraction and transmission electron microscopy techniques", Condensed Matter Material Science, (2013).
17. J. Puis'O, S Tamulevicius, G Laukaitis, S Lindroos, M Leskela, V Snikta, Thin Solid Films 2002, 403, 457.
18. T Kanniainen, S LIndroos, R Resch, M Leskela, G Friedbacher, M Grassrebauer, Mater. Res. Bull. 2000, 35, 1045.
19. J B Nelson, D P Riley, Proc. Phys. Soc. (London) 1945, 57, 160.
20. Rogers K D and Daniels P (2002) An X-Ray Diffraction Study of the Effects of Heat Treatment on Bone Mineral Microstructure, Biomaterials, 23, 2577 – 2585.
21. Abe S, K Masumoto, Journal of Crystal Growth, 217, 25 – 30, (2000).
22. Cullity B D, Stock S R: Elements of X-ray diffraction, 3rd ed. Prentice Hall Publication, India (2001).
23. Suryanarayana C, Grant Norton M: X – ray diffraction: A Practical Approach, Springer, New York (1998).

*****