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Structural characterization of lead sulfide thin films by means of X-ray line profile analysis

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Abstract. **X-ray diffraction patterns of chemically deposited lead sulphide thin films have been recorded and X-ray line profile analysis studies have been carried out. The lattice parameter, crystallite size, average internal stress and microstrain in the film are calculated and correlated with molarities of the solutions. Both size and strain are found to contribute towards the broadening of X-ray diffraction line. The values of the crystallite size are found to be within the range from 22–33 nm and the values of strain to be within the range from $1{\cdot}0 \times 10^{-3}$–$2{\cdot}5 \times 10^{-3}$.**

Keywords. **PbS thin films; X-ray diffraction; average internal stress; microstrain.**

1. Introduction

Lead sulfide (PbS) is a semiconducting chalcogenide with a direct bandgap of 0·41 eV and has a cubic structure. Owing to their suitable bandgaps, PbS thin films are widely used in IR detectors. PbS is suitable for the detection of the radiation between wavelengths 1 and 3 μm. This detector can operate at any temperature between 77 and 300 K (Johnson 1984). The possibility of using very thin (20–60 nm) chemically deposited PbS films as solar control coatings have been discussed by many workers (Nair *et al* 1989). Analyses of the mechanism of photoconductivity in PbS thin films are also widely reported (Espevik *et al* 1971). Chemical bath deposition (CBD) is one of the standard methods used for preparing PbS films (Choudhuri *et al* 1981; Gadave *et al* 1994; Popa *et al* 2006; Ubale *et al* 2007). This method is less expensive, easy to handle, allowing deposition of films on a large area and on various substrates (Dhumure and Lokhande 1993; Devi *et al* 2007). Although many investigations on PbS thin films deposited by CBD method have been done so far it is found that not much results are reported on structural attributes of the films and their correlation to other deposition properties. Keeping in view all these aspects, an experimental study on the structural characterization of chemically deposited PbS films has been undertaken. A correlation between molarity and different structural parameters has been highlighted in the present work.

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2. Experimental

In the present work, glass slides of dimension, 35 × 20 × 1·35 mm, were used as substrates. They were suitably cleaned in detergent, chromic acid and distilled water. Solutions of lead acetate of four different concentrations (0·25 M, 0·50 M, 0·75 M and 1·00 M) were prepared and NH_4OH solution was then added slowly to maintain pH of the solution at around 11. Then the equimolar solution of thiourea was added to the solution. The substrates were introduced vertically into the solution with the help of a suitably designed substrate holder. The glass substrates were kept in the solution for 24 h at room temperature for deposition of films. After deposition, the substrates were taken out and thoroughly washed and rinsed with doubly distilled water and dried in air. Structural characterizations of the films were determined by X-ray diffraction method using Philips X-pert Pro diffractometer (PW 1830) at room temperature with CuKα radiation.

3. Determination of structural parameters

3.1 *Lattice constant*

The chemical bath deposited PbS thin films possess face-centred cubic structure. It is confirmed by comparing the peak positions (2θ) of the XRD patterns of the films with the standard X-ray powder diffraction data file (card no. 5-0592). The lattice constant 'a' for the cubic phase structure is determined by the relation

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

The corrected values of lattice constants are estimated from the Nelson–Riley plots. The Nelson–Riley curve is plotted between the calculated 'a' for different planes and the error function (Nelson and Riley 1945)

$$f(\theta) = 1/2(\cos^2\theta/\sin\theta + \cos^2\theta/\theta), \quad (2)$$

and extrapolating the plot to $\theta = 90°$.

A typical Nelson–Riley plot for a PbS thin film is shown in figure 2.

3.2 *Crystallite size*

The crystallite sizes of the nanocrystalline PbS film is estimated using Scherrer's formula

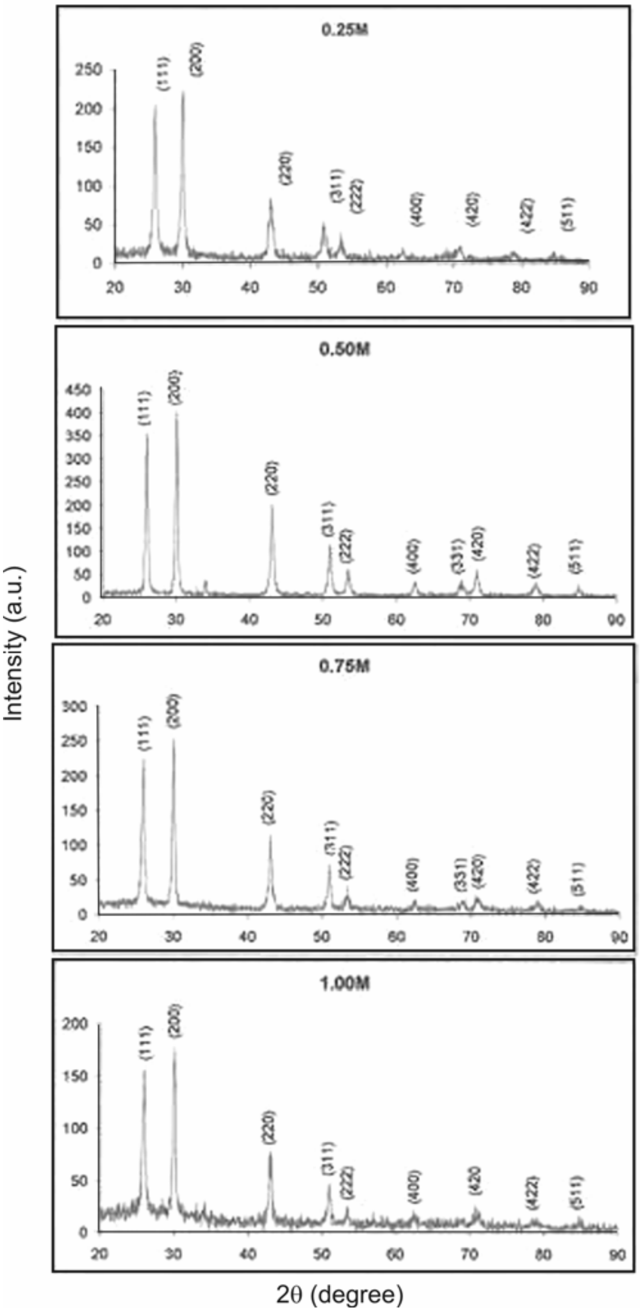

Figure 1. X-ray diffraction patterns of PbS films for different molarities.

$$D = K\lambda/\beta_{2\theta}\cos\theta, \quad (3)$$

where the constant K is taken to be 0·94, λ the wavelength of X-ray used which is CuKα radiation (λ = 1·54 Å), and $\beta_{2\theta}$ the full width at half maximum of the diffraction peak corresponding to [111] plane.

3.3 *Average internal stress and microstrain*

It is found that lattice constant 'a' of the film deviates from its bulk value 'a_0' which is 5·936 Å. This shows that films are under strain. Apart from smallness of the crystallite size, presence of strains also contributes towards broadening of the diffraction line. The built-in average stresses developed in the film is determined by the relation (De and Misra 1997)

$$S = \{(a_0 - a)/a_0\}Y/2\sigma, \quad (4)$$

where a and a_0 are the lattice parameters of the thin film samples and bulk samples, respectively and the value $\varepsilon[= (a_0 - a)/a_0]$ is obtained from W–H plot, Y and σ are the Young's modulus and Poisson's ratio of the bulk sample, respectively. For PbS, the value of Y is 70·2 GPa and σ is 0·28 (Weber 2003).

The total stress in the films is due to (i) differences in the thermal expansion coefficient of the films and substrate material and (ii) lattice mismatch between the material and the substrate and other crystallographic defects that may be present in the film. If the size and strain broadening is present simultaneously then the crystallite size and strain may be obtained from Williamson–Hall plot (Sengupta and Chatterjee 2002). In figure 4, W–H plot for the films are shown.

The slope of the plot represents average strain in the film whereas the intercept on β^* axis gives the crystallite size according to the relation (Ungar and Borbely 1996)

$$\beta\cos\theta/\lambda = 1/D + 4\varepsilon\sin\theta/\lambda, \quad (5)$$

where β is the full width at half maximum (FWHM), D the average crystallite size and ε the average strain.

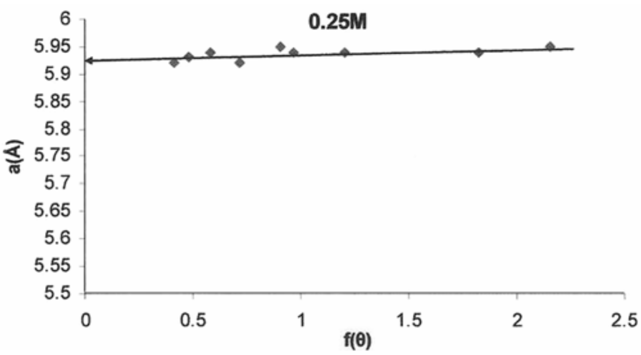

Figure 2. Nelson–Riley plot for a PbS thin film.

Table 1. Structural parameters of PbS thin films deposited at room temperature (time of deposition, 24 h).

Sl. no.	Molarities of solutions	2θ (degrees)	d(Å)	a calculated (Å)	a corrected (Å)	$S \times 10^9$ (N/m^2)	$\varepsilon \times 10^{-3}$
1	0·25	25·93	3·44	5·95			
		30·11	2·97	5·94			
		43·02	2·10	5·94			
		50·95	1·79	5·94			
		53·40	1·72	5·95	5·92	0·16	1·25
		62·51	1·48	5·92			
		–	–	–			
		71·03	1·33	5·94			
		78·85	1·21	5·93			
		84·90	1·14	5·92			
2	0·50	25·94	3·44	5·95			
		30·08	2·97	5·94			
		43·03	2·10	5·94			
		50·99	1·79	5·94			
		53·41	1·72	5·95	5·93	0·19	1·50
		62·59	1·48	5·92			
		68·89	1·36	5·93			
		71·00	1·33	5·94			
		78·99	1·21	5·93			
		84·94	1·14	5·93			
3	0·75	25·98	3·43	5·93			
		30·10	2·97	5·94			
		42·98	2·10	5·94			
		51·01	1·79	5·94			
		53·41	1·72	5·95	5·94	0·31	2·50
		62·51	1·48	5·92			
		68·98	1·36	5·93			
		70·89	1·33	5·94			
		78·86	1·21	5·93			
		84·83	1·14	5·93			
4	1·00	26·02	3·42	5·92			
		30·16	2·96	5·92			
		43·06	2·10	5·94			
		51·02	1·79	5·94			
		53·42	1·72	5·95	5·93	0·13	1·00
		62·53	1·48	5·92			
		–	–	–			
		71·08	1·32	5·90			
		79·17	1·21	5·93			
		84·92	1·14	5·93			

4. Results and discussion

X-ray diffraction pattern of the PbS film for four different molarities of the solutions are shown in figure 1. The PbS films are found to be polycrystalline in nature having *fcc* structure. Well defined peaks of (111), (200), (220), (311), (222), (400), (331), (420), (422) and (511) reflections are observed in XRD pattern. The strong and sharp peaks suggest that the films deposited on glass substrates with different molarities are well crystallized (Cheng *et al* 2006).

The various structural parameters, e.g. corrected values of lattice constant (a), average internal stress (S) and microstrain (ε) for PbS thin films deposited with different molarities are calculated and systematically represented in table 1. The values of lattice constant, crystallite size, average internal stress and microstrain are correlated with molarities of the solutions and are shown in figure 3. The lattice constant 'a' is found to increase gradually with the solutions up to a molarity of 0·75. Beyond 0·75 M (molarity), there is a slight fall in the lattice constant (figure 3i). The change in lattice constant for the deposited thin

Table 2. Comparison of '*D*' values for PbS thin films deposited at room temperature.

		Crystallite size [*D* (nm)]	
Sl. no.	Molarities of solutions	From Scherrer's formula	From W–H plot
1	0·25 M	22	22
2	0·50 M	25	25
3	0·75 M	29	33
4	1·00 M	19	23

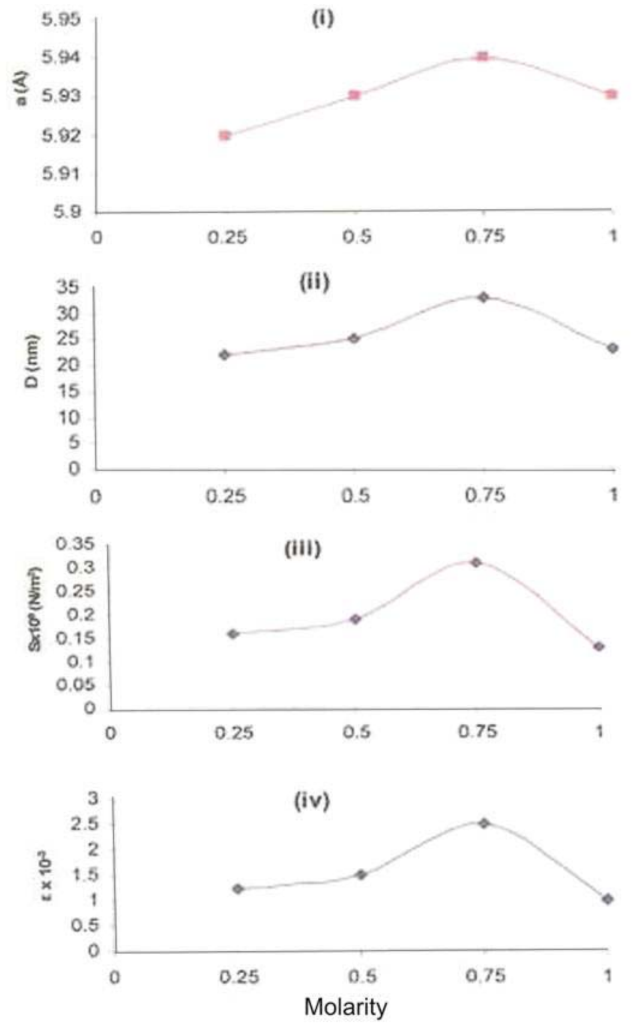

Figure 3. Variation of (i) lattice constant, (ii) crystallite size, (iii) average internal stress and (iv) microstrain with molarities in PbS films.

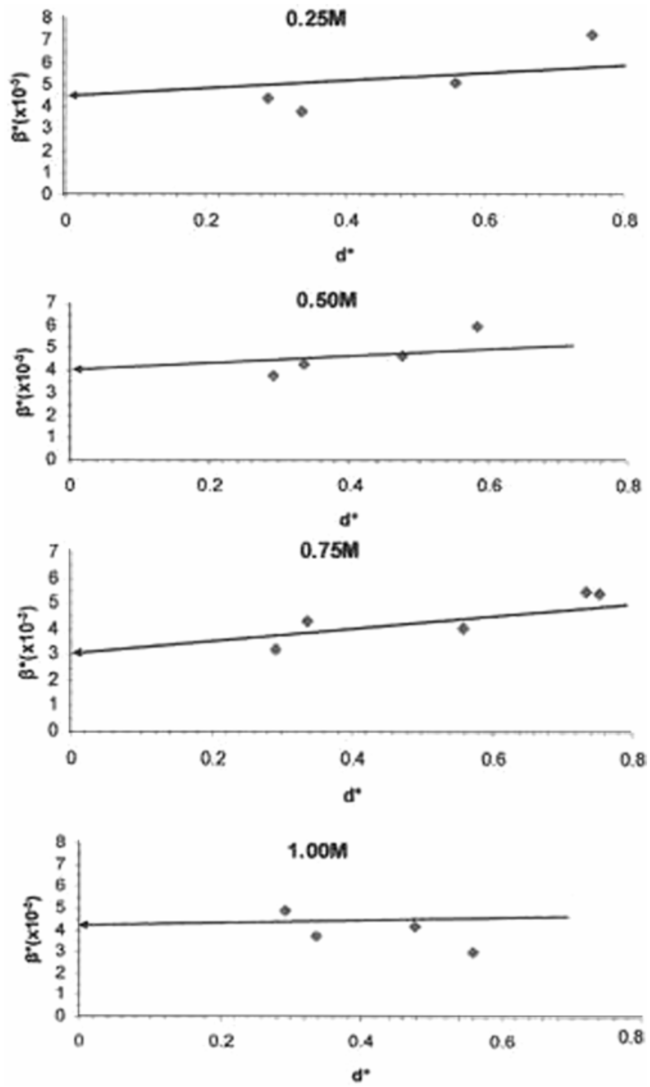

Figure 4. Williamson–Hall plots of PbS films for different molarities where $\beta^* = (\beta \cos\theta)/\lambda$ and $d^* = (2\sin\theta)/\lambda$.

film over the bulk clearly suggests that the film grains are strained (Reichelt and Jiang 1990).

It is observed that with the increase in the molarities of the solutions there is a gradual increase in the crystallite size up to a molarity of 0·75. Beyond 0·75 M (molarity) there is a slight fall in the crystallite size. Similar results are also reported earlier by us (Choudhury and Sarma 2008). The values of the average internal stress in the PbS films are determined by using relation (4). In figure 3 (iii), it is observed that at 0·75 M, the stress is maximum.

From the W–H plots of the films (figure 4), it has been confirmed that the X-ray line broadening in polycrystalline thin films of PbS is due to the presence of size effect as well as strain effect. The slopes of the W–H plot represent average internal strain in the film while the inverse of the intercept at β^* axis gives the crystallite size according to the relation (5). The values of the average crystallite size as determined from W–H plot are shown in table 2.

The values of the microstrain in the PbS films determined from slope of the W–H plot are shown in table 1. In figure 3 (iv), it is observed that at 0·75 M, the microstrain is maximum.

5. Conclusions

The structural parameters like lattice constant, crystallite size, internal stress and strain of PbS thin films deposited by CBD technique using equimolar but with different individual molarities of the solutions are determined and are found to be affected by the molarities of the solutions. The lattice constant, crystallite size, internal stress and strain in the films are found to be maximum for solution with molarity 0·75. Both size and strain effects on broadening of X-ray diffraction line are found to be present in the films.

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