Chapter III

Structural studies of nanocrystalline PbS
3.1 Introduction

Scientific research on the structure of matters has been of keen interest in chemistry and physics for many years. The primary cause of such interest is that important structural features of the thin films play a major role in determining the properties of the films. Hence analysis of the deposited nanocrystalline films for these features is very important.

The important structural parameters which influence the mechanical, optical and other optoelectronic properties of a thin film are (i) crystallinity, (ii) crystal phase, (iii) lattice constant, (iv) grain size, (v) average stress and strain, (vi) lattice faults, (vii) surface or bulk chemical impurity etc. Structure and structure sensitive properties of nanocrystalline PbS are likely to vary with deposition conditions and growth parameters of chemically deposited films.

The various structural characterization methods that are most widely used in characterizing nanomaterials and nanostructures are X-ray diffraction (XRD), various electron microscopy (EM) including scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM) and scanning probe microscopy (SPM).

X-ray diffraction techniques like powder diffraction is employed to probe crystallinity, crystal structure, lattice constants, grain size, stress of crystalline materials in the microlevel and also in nano-levels. Like X-ray diffraction electron microscopy has also become important tool in analyzing microstructure of materials in the form of thin films, nanowires and nanoparticles. Due to small wavelength of the electrons and the dependence of electron wavelength on the accelerating potential
given to the electrons, resolution of measurement increases. The two different configurations in which electron microscopy are generally used are scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The X-ray powder profile analysis is now a most powerful and versatile method to reveal microstructure parameters of crystalline solid in a qualitative as well as quantitative manner. A good correspondence with other methods like electron microscopy (TEM and SEM) makes it more useful with increased confidence in the measurement. Our works have been concentrated mainly on structural characterization of films by XRD technique supported by some other characterization using SEM and TEM.

The mechanical stability of thin film is one of the major factors for designing various electronic devices. Therefore considerable interests have been shown for studying the behaviour of thermal and intrinsic stress and strain in thin films. Several workers studied the structural characterization of IV-VI compound thin films\textsuperscript{7-9} and their correlation with other properties. Microstructure of thin film is also strongly affected by deposition rate, nature of substrate and growth parameters. However, the studies on the correlation between microstructural parameters with different growth parameters have not received much attention.

There are two major approaches for the measurement of the crystallite size and lattice strain in nanocrystalline materials\textsuperscript{10}. One is the direct imaging by transmission electron-microscopy (TEM) and scanning electron microscopy (SEM) and the other is indirect measurement by X-ray diffraction (XRD). Though the direct imaging by TEM and SEM are capable of giving the entire distribution of the crystallite size in the sample, but it requires time-consuming sample preparation (thinning) and image
analyzing. Moreover, there is a risk that change may occur in the nanostructured material during the thinning process or during the interaction with the electron beam. Again, the volume that can be examined in the microscope is always very small in comparison with the entire sample, leading to further uncertainty. On the other hand, XRD average over a much larger fraction of the sample, and the essentials in sample preparation are minimal. Therefore, X-ray diffraction line profile analysis has been widely used to characterize the crystallite size and lattice distortions in nanostructured materials.

In this chapter, detail structural analysis by XRD technique supported by SEM observations of chemically deposited PbS films are described. An attempt has been made to correlate different structural and microstructural parameters with growth conditions such as molarity of the reactants, bath temperatures, deposition time, and different substrate materials in freshly prepared and annealed PbS films.

3.2 Experimental details

For studying the effect of growth parameters on crystalline parameters, the films were deposited on five substrates at a time in the same bath so that all the films employed for optical and structural studies have same deposition parameters. The X-ray diffractograms of all the samples were taken using X-ray diffractometer (Philips X-pert Pro PW 1830). The line profile was recorded at a scanning rate (0.01)° s⁻¹ with a Phillips automatic recorder. XRD patterns of the samples under different conditions were analysed using Philips X’pert software. The spectrum of the powder sample was used as a standard to make the comparison with the thin film sample.
3.3 Theoretical consideration of X-ray diffraction technique

Epoch making Laue experiment (1992), first demonstrated the phenomenon of X-ray diffraction by a crystalline material\textsuperscript{11}. Generally X-ray diffraction became a convenient powerful tool to study the structural parameters of crystalline materials. It is based upon the principle of Bragg's law of X-ray diffraction. When a monochromatic parallel beam of X-ray impinges on a crystal, the constituent atoms which are arranged in a regular manner can diffract the beam to form the interference pattern. The diffracted beam make constructive interference provided they satisfy Bragg's condition

\[ 2d_{hkl} \sin \theta = n\lambda \]  

(1)

and thereby show sharp maxima in certain directions in scattered radiations. Here $d_{hkl}$ is the inter planer spacing of a set of lattice plane $(h, k, l)$, $\theta$ is Bragg angle (glancing angle of incidence of X-ray), $\lambda$ is the wavelength, and $n$ is any integer corresponding to spectral orders. Since in a polycrystalline sample large number of crystallites is randomly assembled, the X-ray beam is incident on large number of sets of crystal planes denoted by $(h_1, k_1, l_1)$, $(h_2, k_2, l_2)$, $(h_3, k_3, l_3)$ ...etc. at different Bragg angles $\theta_1$, $\theta_2$, $\theta_3$ ......etc. and as a result different beam of X-rays are diffracted at different angles by different sets of planes having precise of values of "d" to satisfy Bragg's equation. These diffracted beams are recorded by the diffractometer and the resultant diffractogram is obtained, where we get different intensities as a function of $2\theta$.

In general, thin films of most materials assume similar crystal structure as that of the material in bulk. Depending on various growth techniques and various growth parameters, the structural order of atomicity (number of atoms contained in a
molecule of an element) deposited films can be varied from a highly disordered (amorphous) to polycrystalline (nanocrystalline) and well-ordered state (epitaxial growth) on a single-crystal substrate.

3.4 Determination of Structural parameters

3.4.1 Lattice constant

The chemical bath deposited PbS thin films are found to possess face-centered cubic structure. In the present study the phase structure of chemically deposited PbS films are determined by comparing the peak positions (2θ) of the XRD patterns of the films and powder samples with the standard JCPDS (Joint Committee on Powder Diffraction Standards) X-ray powder file data of the material. The lattice constant ‘a’ for the cubic phase structure for each plane [h, k, l] is determined by the relation

\[ a = d_{hkl} \left( h^2 + k^2 + l^2 \right)^{\frac{1}{2}} \]  

(2)

The corrected values of lattice constants are estimated from the Nelson-Riley plots. The Nelson-Riley curve is plotted between the calculated lattice constant ‘a’ for different planes and the error function

\[ f(\theta) = \frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\sin^2 \theta}{\theta} \right) \]  

(3)

The resulting straight line is then extrapolated the plot to \( \theta = 90^\circ \), and its intercept on the Y-axis is taken to be accurate value of “a”.

3.4.2 Crystallite Size

It is well known that decreasing crystallite size leads to broadening of X-ray
diffraction line profile. This is the principle of the determination of size of the crystallites by X-ray diffraction. The quantitative relationship is given by the well known Scherrer’s formula\textsuperscript{14}

\[ D_{hkl} = \frac{K \lambda}{\beta_{2\theta} \cos \theta}, \quad (4) \]

where \( \theta \) is the Bragg’s angle, \( K \) is the proportionality constant taken to be 0.94, \( \lambda \) is the wavelength of X-ray used, and \( \beta_{2\theta} \) is the full width at half maximum (FWHM) of the diffraction peak corresponding to a particular set of crystal planes. This equation enables us to determine the size of the crystal in a direction normal to the diffracting planes. The relation (4) is derived for cubic crystal, but it is often used to the non-cubic materials also. However, correction for instrumental broadening \((\beta_{2\theta})\) arising due to slit width, wavelength width of \(K\alpha_1\) and \(K\alpha_2\) etc. are to be made for acceptable value of \(D_{hkl}\). To obtain the diffraction broadening only due to the grain, \(\beta_g\), we applied Warren’s rule\textsuperscript{12}

\[ \beta_g^2 = \beta_{2\theta}^2 - B^2, \quad (5) \]

where \( B \) is the half maximum intensity breadth of a line obtained under similar geometrical conditions for a material with a crystallite size well in excess of 1000 Å (Silicon in our case).

\textbf{3.4.3 Average internal stress and Strain}

Basically, stresses in thin films consist of two components — the thermal stress arising during variation of temperature due to the difference in the thermal expansion coefficient of the film and the substrate, and the intrinsic one, which depends on
number of factors like lattice constant, grain size, orientations etc. The stress is also considered to be related to film deposition conditions and compositions and the structures of the thin films. It is difficult to avoid thermal stress for films deposited at higher solution temperatures of the bath. The average strain ($\varepsilon$) is given by \(^{15}\)

$$\varepsilon = \frac{a_0 - a}{a_0}$$ \hspace{1cm} (6)\

The built-in average stresses developed in the film is determined by the relation \(^{16}\)

$$S = \left( \frac{a_0 - a}{a_0} \right) \frac{Y}{2\sigma}$$ \hspace{1cm} (7)\

where $a$ and $a_0$ are the lattice parameters of the thin film samples and bulk samples respectively. $Y$ and $\sigma$ 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 $\sigma$ is 0.28 \(^{17}\). The origin of the strain is related to lattice misfit, which in turn depends on the growing conditions. The microstrain ($\varepsilon$) developed in the thin film along different preferred orientations can be calculated from the relation \(^{16}\),

$$\varepsilon_{hkl} = \frac{\beta_{2\theta} \cot \theta}{4}$$ \hspace{1cm} (8)\

### 3.4.4 Determination of particle size and strain from X-ray line profile analysis

Scherrer's formula applies when small crystal size is the only cause of line broadening. Generally two kinds of structural broadening can be present simultaneously. These two kinds are — crystallite size broadening caused by small
sizes of the crystallites in the specimen diffracting coherently and the strain broadening due to varying displacement of the atoms from its reference positions\textsuperscript{18}. Assuming both size and strain broadened profile is of similar nature, Williamson and Hall (W-H) used the following equation to determine crystallite size and strain\textsuperscript{19}.

\[ \delta(2\theta)\cos\theta = \frac{0.9\lambda}{D_{WH}} + 4\varepsilon\sin\theta \]  \hspace{1cm} (9)

Here \( D_{WH} \) is the average crystallite size, \( \delta(2\theta) \) is the FWHM measured in radians, \( \theta \) is the Bragg angle of a reflection, \( \lambda \) is the wavelength of X-ray used [Cu-K\textsubscript{a} radiation, \( \lambda=0.154056 \text{ nm} \)] and \( \varepsilon \) is the strain. All PbS reflections are used to construct a linear plot of \( \delta(2\theta)\cos\theta \) versus \( \sin\theta \). The plot is a straight line with an intercept on the \( \delta(2\theta)\cos\theta \) axis. The crystallite size is then obtained from this intercept and strain from the slope of the straight line.

Williamson and Hall (W-H) plot is a typical linear fit of the data in Eq. (9). But the experimental data do not fit exactly in a straight line which may be because of the existence of anisotropic variation in the residual strain. This makes accurate determination of crystallite size and strain from W-H plot difficult. Unger et al. suggested that the introduction of a dislocation contrast factor in Eq. (9) might result in better fit to the data\textsuperscript{20,21}.

If the dislocations are the main contributors to the strain, then the modified form of Eq. (9) can be expressed as\textsuperscript{22}

\[ (\Delta K)^2 = \left( \frac{0.9\lambda}{D_{WH}} \right)^2 + \left( \frac{\pi b^2 \rho}{2B} \right) K^2 C_{hkl} \]  \hspace{1cm} (10)
where $\Delta K = \frac{(2 \cos \theta_B \Delta \theta_B}{\lambda}$, $\Delta \theta_B$ is FWHM (in radians) of the Bragg reflections, $\lambda$ is wavelength of the X-rays, $D_{MWH}$ is average crystallite size, $K = 2 \sin \frac{\theta_B}{\lambda}$, $\varepsilon$ is strain and $C_{hkl}$ is the dislocation contrast factor, $b = (\sqrt{3}/2)a$ is modulus of the Burgers vector of dislocations, $\rho$ is the average dislocation density and $B$ is a constant that can be taken as 10 for a wide range of dislocation distributions$^{22}$. Equation (10) is called the modified Williamson-Hall (MWH) plot.

The contrast factor for Bragg reflection $(hkl)$, $C_{hkl}$, can be calculated from the contrast factor for Bragg reflection $(h00)$, $C_{h00}$, according to the relation$^{20}$,

$$C_{hkl} = C_{h00}(1 - qH^2) \quad (11)$$

where $H^2 = \frac{(h^2k^2 + k^2l^2 + l^2h^2)}{(h^2 + k^2 + l^2)^2}$ for a cubic system and $q$ is a constant which is deduced by fitting the data as explained below.

Inserting equation (11) in equation (10) yields,

$$\frac{(\Delta K)^2 - \alpha}{K^2} = \left(\frac{\pi b^2 \rho}{2B}\right)C_{h00}(1 - qH^2) \quad (12)$$

where $\alpha = \left(\frac{0.9 \lambda}{D}\right)^2$. From the linear regression of the left hand side of equation (12), the parameter $q$ can be determined experimentally.

### 3.5 Results of Structural Characterization

#### 3.5.1 X-ray diffractogram of bulk PbS sample

The fine powder of PbS was analyzed by X-ray diffraction technique to identify
the structural phase. The diffraction lines of the PbS powder as shown in Fig. 3.1 were in good agreement for 'd' values with the standard data for pure cubic phase.

3.5.2 Calibration of XRD instrument

To test the validity of performance the Philips automated powder X-ray diffractometer (X'PERT PRO) system were calibrated from time to time. Standard Silicon sample with peak positions of three major peaks at 2θ values 28.44, 47.30 and 56.12 were used for calibration. Fig. 3.2 shows the typical X-ray diffraction pattern of the standard Si sample.

3.5.3 Effect of variation of PVA concentration on nature of films

As mentioned in chapter II, several bath solutions were prepared having 1%, 2%, 3% and 4% PVA concentrations with same molarity of the reagents. Fig. 3.3 shows the XRD patterns of various representative films prepared by variation of concentration of PVA, the matrix solution in the chemical bath, from 1% to 4%, which was prepared by mixing different amount of PVA powder by weight in 100 ml water. It has been clearly seen from the diffractogram that crystalline nature of the films improves as PVA concentration of solution increases from 1% to 2% and 3%. Further increase of PVA percentage in the solution deteriorates the film quality and crystallinity. Keeping temperature and pH constant at 30°C and 10.5 respectively, it was found that the films deposited with 2% PVA is of good quality and of smaller crystallite sizes. That's why, we have opted for 2% PVA concentration for bath solution to deposit all the PbS samples.
Figure 3.1. X-ray diffractogram of bulk PbS sample

Figure 3.2. X-ray diffractogram of standard Silicon sample
Fig. 3.3 XRD pattern of PbS films deposited at room temperature, pH value at 11, for various PVA concentrations.
3.5.4 *PbS films prepared with different molarities of the bath solutions*

As mentioned in chapter II, PbS films were deposited on glass substrates at room temperature with 2% PVA concentration, keeping pH value at 10.5 for various molarities. It is seen from the X-ray diffraction patterns that the PbS films deposited with lower molarities with thickness of about 210 nm are of amorphous nature having single or small peaks, while films prepared with higher molarities were found to be polycrystalline in nature. XRD show that the films grown with molarity higher than 0.25M posses good crystallinity whereas beyond 1M it is found to be amorphous again. Fig. 3.4 shows the XRD patterns of five PbS films having different molarities deposited at 300 K. The diffraction peaks can be indexed to a face-centered-cubic (fcc) rock-salt structure of PbS. From the XRD pattern it is seen that two broad peaks corresponding to [111] and [200] planes appear around angles 25.85° and 29.95° for films with molarities 0.25M and 0.50M. For molarities 0.75M and 1M, diffraction peaks are observed at 2θ values around 25.80°, 29.90°, 42.85° and 50.85° corresponding to [111], [200], [220] and [311] planes. Thus, it has been observed from XRD patterns that the number of peaks is more in case of films deposited with higher molarities (0.75M and 1M). Similar results in CdS films have been reported by R. Devi\(^\text{23}\). All the observed peak positions corresponding to different planes have fcc structure of PbS as confirmed by JCPDS (Joint Committee on Powder Diffraction Standards) card no. 5-0592. The broadening of the diffraction lines indicates that the films are nanocrystalline in nature. The various structural parameters such as the diffraction peak positions (2θ) and their corresponding planes \([hkl]\), interplaner spacings (\(d\)), the calculated values of lattice constants (\(a\)), average stress (\(S\)) and...
microstrain (\(\varepsilon\)) and grain sizes (D) for PbS films deposited with different molarities are calculated and systematically represented in Table 3.1. The lattice parameter 'a' is calculated using relation (2) and the corrected values are estimated from the Nelson-Riley plots, as shown in Fig. 3.5. The values of lattice constant, average grain size and microstrain are correlated with molarities of the solutions and are shown in Fig. 3.6. The lattice constant 'a' is found to increase gradually with the solutions up to a molarity of 0.75M. Beyond 0.75M (molarity), there is slight fall in the lattice constant (Fig. 3.6a). These results are reported by N. Choudhury et al\(^{24}\). The change in lattice constant for the deposited film over the bulk clearly suggests that the film grains are strained\(^{25}\).

The average grain size \(D_{111}\) was calculated by using relation (4) & (5). In equation (5), taking \(B = 0.07456\) for Silicon sample of grain size 110 nm, the values of diffraction broadening \(\beta_g\) are obtained for calculation of grain size. From the diffractograms, the values of \(\beta_{2\theta}\) were calculated by using the computer software (Origin 8). The average grain sizes for all the films are estimated to be within the range 13-18 nm. 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 0.75M (molarity), there is a slight fall in the crystallite size, which was reported by us\(^ {24}\).

The values of the average internal stress (S) and microstrain (\(\varepsilon\)) are calculated by using the formula (7) & (8) respectively. The average stresses of the deposited films are found to be of compressional in nature. Compressive stress is likely due to the grain boundary effect which is prominent in polycrystalline film.
3.5.5 Effect of variation of pH on nature of films

XRD studies show that the pH variation of the solution in the chemical bath plays an important role in determining the crystalline nature of the film. Fig. 3.7 shows the XRD pattern of various representative films prepared by variation of pH value from 9 to 11.5. It has been clearly seen from the diffractogram that the crystalline nature of the films improves as pH of solution increases. Below pH value 9, no peaks were observed probably due to poor adhesion and small thickness. At pH value 9, a small peak appears at $2\theta = 25.97^\circ$ corresponding to (111) plane. Crystalline nature of the film increases when pH value increases to 10, which is evident from peak height. When pH value increases to 10.5, the peak corresponding to (111), (200) and (220) planes also become prominent. Further increase in pH value to 11, all the peaks corresponding to (111), (200), (220) and (311) planes become prominent showing polycrystalline growth of the films. Further increase in pH value to 11.5, crystallinity of the films deteriorates gradually. The effect of pH variation on film structure for solution grown PbS nanoparticle films was also reported earlier by Joshi et al\textsuperscript{26}. The pH variation of the solution is caused by varying ammonia concentration in the chemical bath. Our present study on the effect of varying pH of the solution by adding ammonia shows that a pH value 11 is found to be suitable for the growth of good quality nanocrystalline films. The peak positions are also in good agreement with the standard JCPDS data file (card no. 5-0592) of PbS.
Fig. 3.4  XRD pattern of PbS films deposited at room temperature with various molarities (0.25 to 1.25M).
Table 3.1: Structural parameters of PbS films deposited at room temperature
30 °C for different molarities (Bulk value of lattice constant, $a_0=5.936$ Å).

<table>
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<tr>
<th>Molarities of solutions</th>
<th>Bragg angle 2θ (degree)</th>
<th>Observed d (Å) from XRD</th>
<th>Reflecton plane [hkl]</th>
<th>Lattice constant calculated a (Å)</th>
<th>Lattice constant corrected a (Å)</th>
<th>Grain size D (nm)</th>
<th>Internal stress $S \times 10^9$ N/m²</th>
<th>Internal strain $\varepsilon \times 10^{-3}$</th>
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Fig. 3.5  Nelson-Riley plots for PbS films deposited at room temperature for various molarities.
Fig. 3.6 Variation of (a) lattice constant, (b) average grain size and (c) average strain with different molarities of solution.
Fig. 3.7  XRD pattern of PbS films deposited at room temperature with various pH values.
3.5.6 XRD of films deposited at different solution temperatures for various deposition time for molarity 0.5M

XRD pattern of PbS films deposited at bath temperature 60 °C for 0.5M concentration at three deposition time 10, 15 and 20 minutes are shown in Fig. 3.8(a). Similar XRD of another set of three PbS films having bath temperature 70 °C, for the same molarity and the same deposition time are also represented in Fig. 3.8(b). All PbS films have fcc structure as confirmed by JCPDS data file (card no. 5-0592). The lattice parameter ‘a’ is calculated using relation (2) and the grain size D is calculated by using relation (4) & (5). The average grain size for all the films is estimated to be within the range 7-15 nm. All structural parameters are systematically represented in Table 3.2. It is observed that all the lattice constants ‘a’ are slightly less than the standard value (5.936 Å). This indicates that the as-deposited films are under a compressive strain. The grain size decreases with increasing deposition time for the higher solution temperature of the bath for molarity 0.5M. Fig. 3.8(a) shows that at bath temperature 60 °C and at deposition time 20 min, all the peaks corresponding to (111), (200), (220), (311) and (222) planes of PbS become prominent showing polycrystalline growth of the films. Variation of average grain size with different deposition time at bath temperature 60 °C and 70 °C for molarity 0.5M is shown in Fig. 3.9. It is seen from the XRD lines and from the calculated values that good quality nanocrystalline films can be deposited with higher deposition time (20 min) and bath temperature (60 °C). At bath temperature 60 °C and at deposition time 20 min or higher than that, the precipitation of PbS is rapid and does not adhere to the substrate fully.
Fig. 3.8(a) XRD pattern of PbS films deposited at bath temperature 60°C for various deposition time (10, 15 and 20 min) for bath molarity 0.5M.
Fig. 3.8(b) XRD pattern of PbS films deposited at bath temperature 70°C for various deposition time (10, 15 and 20 min) for bath molarity 0.5M.
Table 3.2: Estimated values of grain sizes of PbS films deposited at bath temperatures 60 and 70 °C for various deposition time for bath molarity 0.5M (Bulk value of lattice constant, $a_0=5.936$ Å).

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<th>Deposition time (minute)</th>
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<th>Lattice constant calculated a (Å)</th>
<th>Lattice constant corrected a (Å)</th>
<th>Grain size D (nm)</th>
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<td>2.1120</td>
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<td>50.70</td>
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<tr>
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<td>3.4232</td>
<td>[111]</td>
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<td>5.9203</td>
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<td>[200]</td>
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<td>42.99</td>
<td>2.1021</td>
<td>[220]</td>
<td>5.946</td>
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</tr>
<tr>
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<td>15</td>
<td>26.05</td>
<td>3.41771</td>
<td>[111]</td>
<td>5.920</td>
<td>5.9313</td>
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<td></td>
<td>29.98</td>
<td>2.9781</td>
<td>[200]</td>
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<td></td>
<td></td>
<td>42.97</td>
<td>2.1032</td>
<td>[220]</td>
<td>5.949</td>
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<td>26.00</td>
<td>3.4234</td>
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<td>5.9330</td>
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<td>30.04</td>
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<td>[200]</td>
<td>5.945</td>
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<td></td>
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<td>43.09</td>
<td>2.0974</td>
<td>[220]</td>
<td>5.932</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 3.9 Variation of average grain size with different deposition time at bath temperature 60 and 70 °C for molarity 0.5M.
3.5.7 Determination of particle size and strain from the X-ray line profile analysis

X-ray line profile analysis (XLPA) is a powerful tool for characterizing the microstructure of crystalline materials in terms of size and strain\textsuperscript{27-45}. Published works on determination of microstructural parameters by using X-ray line profile analysis are mostly about application of the analysis to bulk solids, cold worked alloys and thin films\textsuperscript{46-49}. Further, most of the works on X-ray line profile analysis of nanocrystalline materials are limited to determination of sizes of the crystallites from broadening of X-ray powder line profile ignoring possible contribution from strain to the broadening.

It is found that value of the lattice constant ‘a’ of the film deviates from its bulk value 5.936 Å. This shows that the crystallites may be under some strain and in that case, the broadening of X-ray diffraction line profile is not entirely due to crystallite sizes and presence of non-uniform strain in the sample also have some contribution to broadening, however small may be. This means that the sizes of the crystallites as obtained by using Scherrer’s formula will be slightly more than actual sizes of the crystallites. If the size and strain broadening is present simultaneously then the crystallite size and strain may be obtained from Williamson-Hall (W-H) plot. Assuming both size and strain broadened profile is of similar nature; we use relation (9) to determine the average grain size and strain of PbS films.

W-H plots of PbS films deposited at room temperature (30 °C) for different molarities (0.25M, 0.5M and 0.75M) are shown in Fig. 3.10. From the W-H plot of the samples it has been confirmed that the X-ray line broadening in nanocrystalline
PbS is due to the presence of both size effect and strain effect. The average grain sizes and strains in samples as obtained from W-H plot are shown in Table 3.3. The variation of average grain size and strain with different molarities of solution determined from W-H plots is shown in Fig. 3.11. It is seen that the crystallite sizes are found to increase with molarities of the solutions. With the increase of molarities of the solutions larger number of Pb$^{2+}$ and S$^{2-}$ ions are reacting to form the deposit resulting in the increase of crystallite sizes$^{50}$.

Modified Williamson-Hall (MWH) plots of PbS films deposited at room temperature (30 °C) for different molarities (0.25M, 0.5M and 0.75M) are shown in Fig. 3.12. A comparison of the fit of the same data using W-H plot shows that much better fit is obtained using MWH plot. This again implies presence of high strain anisotropy in the films. From the slope and intercept of the MWH plot (Fig. 3.12), the average crystallite size and average dislocation density in nanocrystalline PbS films deposited using different molarities of the solutions are calculated (Table 3.4). The variation of average grain size and dislocation density with different molarities of solution determined from MWH plot is shown in Fig. 3.13. The dislocation densities are found to increase with molarities of the solutions. With the increase of molarities of the solution larger number of ions participates, in a given time, in the formation of crystallites. This means reaction become faster and deposition quicker which cause increase of dislocation density$^{50}$.

3.5.8 XRD of annealed films deposited on glass substrates

PbS films as deposited under various growth conditions on glass substrates were annealed at 200 °C for 2 hours in an oven at air atmosphere and after that XRD of the
Fig. 3.10 W-H plots of PbS films deposited at room temperature 30°C for different molarities.
Table 3.3: Estimated values of average grain size and strain from W-H plots for PbS films deposited at room temperature 30 °C for different molarities.

<table>
<thead>
<tr>
<th>Molarities of solutions</th>
<th>Average grain size, D (nm)</th>
<th>Strain (ε x10⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>15</td>
<td>2.86</td>
</tr>
<tr>
<td>0.50</td>
<td>17</td>
<td>2.00</td>
</tr>
<tr>
<td>0.75</td>
<td>19</td>
<td>1.66</td>
</tr>
</tbody>
</table>

Table 3.4: Estimated values of average grain size and dislocation density from MWH plots for PbS films deposited at room temperature 30 °C for different molarities.

<table>
<thead>
<tr>
<th>Molarities of solutions</th>
<th>Average grain size, D (nm)</th>
<th>Dislocation density (ρ x10¹⁷) m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>12</td>
<td>1.19</td>
</tr>
<tr>
<td>0.50</td>
<td>12.5</td>
<td>3.28</td>
</tr>
<tr>
<td>0.75</td>
<td>13</td>
<td>7.25</td>
</tr>
</tbody>
</table>
Fig. 3.11 Variation of (a) average grain size and (b) average strain with different molarities of solution determined from W-H plot.
Fig. 3.12 MWH plots of PbS films deposited at room temperature 30 °C for different molarities.
Fig. 3.13 Variation of (a) average grain size and (b) dislocation density with different molarities of solution determined from MWH plot.
films were taken. Only three representative XRD pattern for three different deposition times are shown in Fig. 3.14. After annealing, the crystalline nature of the film is much improved and is indicated by the observed peak at 2θ values around 25.93°, 30.07°, 43.13°, 50.84° and 53.63° corresponding to [111], [200], [220], [311] and [222] planes. The peak positions and peak intensities are in good agreement with the standard JCPDS data file (card no. 5-0592). Grain sizes (D) are measured from [111] and [200] peaks and the values are represented in Table 3.5. From the Table 3.5, it is clearly seen that after annealing crystallite size increases. In the annealed samples, the diffraction peaks are sharp with high intensity compared to the as-deposited ones, indicating increase in crystallite size. The increase in crystallite size shows the improvement in crystallinity that decreases the grain boundary discontinuities.

3.5.9 XRD of films deposited on different substrates

Materials other than glass, like Over Head Projector (OHP) sheets, mica sheets are also used as substrate to study the difference in formation of PbS films due to different substrate materials.

Substrates of glass, OHP sheet and mica sheet are dipped in the four chemical baths at room temperature 30 °C having different molarities (0.25M, 0.5M, 0.75M and 1M) and pH 11. All the substrates of different materials are dipped simultaneously in the bath with solutions having a certain molarity and XRD of all films are taken. XRD pattern of PbS films deposited in glass and OHP sheets at room temperature 30 °C with various molarities (0.25M, 0.5M, 0.75M and 1M) are shown in Fig. 3.15 and Fig. 3.16 respectively. From the XRD pattern it is seen that a
prominent broad diffraction peak are observed at 2θ values around 25.96° corresponding to [111] plane of PbS for OHP sheets. All PbS films deposited on OHP sheets show a preferential orientation in the [111] plane parallel to the substrate (Fig. 3.16). XRD pattern of PbS films deposited in different substrates (glass, mica and OHP sheet) at room temperature 30 °C with molarity 0.75M is shown in Fig. 3.17. The structural parameters of all the values are tabulated in Table 3.6.

3.5.10 XRD of PbS precipitates

As mentioned in Chapter II, PbS precipitates deposited on zeolite (ZSM-5) at room temperature 30 °C, pH 10.5 and molarities of the solution (0.25M and 0.125M) are taken and shown in Fig. 3.18. The sample is crystallized in f.c.c. rock-salt structure of PbS having diffraction peaks corresponding to (111), (200), (220), (311), (222), (400), (331), (420) and (422) planes. The X-ray diffraction peak positions (2θ = 25.9°, 29.9°, 43.0°, 50.8°, 53.4°, 62.1°, 68.7°, 70.8° and 78.6°) has remained fixed for all PbS samples. This is consistent with the standard JCPDS data (card no. 5-0592). The broadened nature of XRD peaks implies that the particles are of the nanoscale dimensions. The average crystallite sizes of the PbS nanoparticles are estimated by measuring the full width at half maximum of the (111), (200) and (220) peaks using relation (4). The calculated average crystallite sizes are 8 nm for PbS with molarity of the solution 0.25M and 6 nm for PbS with molarity of the solution 0.125M. The crystallinity of the as-synthesised sample, which was crystallized with molarity of the solutions 0.25, showed the better crystallinity. The peaks at 2θ values around 20.7°, 23.0°, 23.9°, 24.4° and 26.9° corresponds to ZSM-5 zeolite51.
Fig. 3.14 XRD of annealed films deposited at bath temperature 60 °C for various deposition time (10, 15 and 20 min) for bath molarity 0.5M.
Table 3.5: Calculated values of grain sizes of ‘as-deposited’ and ‘annealed’ PbS films, for different deposition parameters for bath molarity 0.5M.

<table>
<thead>
<tr>
<th>Bath Temperature (°C)</th>
<th>Deposition time (minute)</th>
<th>Grain size, D (nm)</th>
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</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td>As-deposited</td>
<td>Annealed (473 K)</td>
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</tr>
<tr>
<td>60</td>
<td>10</td>
<td>13</td>
<td>31</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>7</td>
<td>17</td>
<td></td>
</tr>
<tr>
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<td>10</td>
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<td>34</td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>20</td>
<td>10</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 3.15  XRD pattern of PbS films deposited in glass substrates at room temperature with various molarities.
Fig. 3.16 XRD pattern of PbS films deposited in OHP substrates at room temperature with various molarities.
Fig. 3.17  XRD pattern of PbS films deposited in different substrates at room temperature with molarity 0.75M.
Table 3.6: Calculated values of grain sizes of PbS films deposited at room temperature 30 °C on various substrates for different molarities of the solution.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Molarities of solutions</th>
<th>Bragg angle 2θ (degree)</th>
<th>Reflecting plane [hkl]</th>
<th>Observed d (Å) from XRD</th>
<th>Grain size D (nm)</th>
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<tr>
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<td></td>
<td>0.75</td>
<td>25.77</td>
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<td>3.4517</td>
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<td>1.00</td>
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<td>3.4669</td>
<td>10</td>
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<tr>
<td>OHP sheet</td>
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<td>[111]</td>
<td>3.4657</td>
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<tr>
<td></td>
<td>0.50</td>
<td>26.02</td>
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<td>3.4239</td>
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<tr>
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<td>25.62</td>
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<td>1.00</td>
<td>26.01</td>
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<td>Mica</td>
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<td>3.4464</td>
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<tr>
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<td>25.68</td>
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<td>1.00</td>
<td>26.00</td>
<td></td>
<td>3.4239</td>
<td>12</td>
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</tbody>
</table>
Fig. 3.18 XRD pattern of PbS powder samples deposited on zeolite (ZSM-5) at room temperature with molarities (0.25M and 0.125M).
3.6 Morphological study of PbS films by Scanning Electron Microscope (SEM)

Scanning electron microscope is a convenient technique to study the microstructure of thin films. The study of surface morphology of PbS films were done using scanning electron microscope (SEM) operating with an accelerating voltage of 15 to 20 kV. Fig. 3.19 shows the surface morphology of PbS films, deposited at room temperature using solutions of four different molarities (0.25M, 0.50M, 0.75M and 1M), as observed by SEM. The micrographs were taken at nearly equal magnifications (10.00 KX, 11.99 KX, 11.35 KX and 10.24 KX). The scale bar length for all the micrographs are 1μm. The morphology study shows that the PbS films obtained with molarities 0.25M and 0.50M are not compact and does not have good coverage of the glass substrates. The uniformity of PbS film was increased with the molarity of 0.75M in the bath, and reached the maximum value at 0.75M. At molarity 0.75M, the quality of the film is significantly improved. Highly uniform and adherent PbS film is obtained. It is observed that the film is smooth, homogeneous, fine-grained and excellently covered to the substrate. But at molarity 1M, the film is not uniform and does not cover the substrate. From the micrographs it is observed that the grain sizes are not of much uniformity and therefore average grain sizes are estimated from different grains within the film and found to be about 40 nm. It is clear from the results that the average grain size estimated by SEM is quite larger than measured by XRD.
Fig. 3.20 shows the scanning electron micrographs of PbS films deposited at bath temperature 60 °C for various deposition time (10 min, 15 min and 20 min) for bath molarity 0.5M. Three representative films with magnifications (7.32 KX, 7.98 KX and 10.48 KX) observe nanocrystalline growth of the films. The micrograph observation also support XRD observation as was shown in Fig. 3.8(a). From these SEM images, it can be seen that the grain sizes of the films are not of much uniformity and therefore average grain sizes were estimated from different grains within the film and found to be 31 nm. It is clear from the results that the average grain size estimated by SEM is comparatively larger than measured by XRD.

PbS films as deposited under various growth conditions on glass substrates were annealed at 200 °C for 2 hours in an oven at air atmosphere and after that SEM of the films were taken. The scanning electron micrographs of annealed PbS films deposited at bath temperature 60 °C for various deposition time (10 min, 15 min and 20 min) for bath molarity 0.5M is shown in Fig. 3.21. Three representative films with magnifications (2.30 KX, 5.43 KX and 5.73 KX) indicate better crystalline growth of the films with larger grain size. From the micrograph, it is observed that the films are smooth, homogeneous, fine grained and well covered to the substrate. The average grain sizes were estimated from different grains within the film and found to be larger. From SEM microstructure, it is observed that, due to annealing a number of grains and crystals diffused or united together to effectively form larger grains. This was confirmed from XRD analysis also. SEM micrographs of PbS films deposited in different substrates (glass, mica and OHP sheet) at room temperature with molarities
Fig. 3.19  SEM micrographs of PbS films deposited at room temperature with various molarities (0.25 to 1M).
Fig. 3.20 SEM micrographs of PbS films deposited at bath temperature 60 °C for various deposition time for bath molarity 0.5M.

Fig. 3.21 SEM micrographs of annealed PbS films deposited at bath temperature 60 °C for various deposition time for bath molarity 0.5M.
Fig. 3.22 SEM micrographs of PbS films deposited in different substrates at room temperature with molarity 0.5M.

Fig. 3.23 SEM micrographs of PbS films deposited in different substrates at room temperature with molarity 0.75M.
0.5M and 0.75M are shown in Fig. 3.22 and Fig. 3.23 respectively. Representative films indicate nanocrystalline growth of the films. From SEM images, it can be seen that the grain sizes of the films are not uniform and average grain sizes were estimated from different grains within the film and found to be 27 nm.

Nanocrystalline growth of PbS films are indicated by scanning electron micrographs under similar optimized growth conditions and bath parameters shown by XRD studies. Films grown under optimized conditions are seen to be free from pinholes and cracks and cover the substrates well, making them suitable for device applications. From the micrographs it is also observed that annealing improves the crystallinity of the films and the grain size increases due to annealing. However, crystallite sizes revealed from SEM images are seen to be higher than measured from XRD peaks. This larger value of grain size may be due to agglomeration of grains. In higher magnifications the inner and smaller particles are observed. In case of low magnifications the particles of larger sizes are observed.

3.7 TEM analysis

Transmission electron microscopy (TEM) is the primary method used to determine crystal size and its distribution, although the specimen preparation is nontrivial and destructive. The nanostructures of the films, prepared by CBD on carbon coated copper grids, were studied at room temperature with TEM. Fig. 24(a) shows the TEM images of PbS films deposited at room temperature 30 °C for bath molarity 0.75M. From the TEM
Fig. 3.24 (a) TEM image of PbS films deposited at room temperature 30 °C for bath molarity 0.5 M and (b) corresponding SAED pattern.

Fig. 3.25 (a) TEM image of PbS films deposited at bath temperature 60 °C for deposition time 20 min for bath molarity 0.75 M and (b) corresponding SAED pattern.
Fig. 5.2 SEM photographs of pristine and 100 MeV Ni$^{8+}$ ion irradiated nanocrystalline PbS.

SEM photographs of pristine and 100 MeV Ni$^{8+}$ ion irradiated nanocrystalline PbS.
images it is seen that the average crystallite size is 11 nm. The corresponding selected area electron diffraction (SAED) pattern of the PbS film shown in Fig. 24(b) can be indexed to (111), (200), (220) and (311) reflections from fcc rock-salt PbS structure, and the highly symmetrical dotted lattice in electron diffraction (ED) pattern reveals the crystalline nature of the PbS nanoparticles. From the diameter of the rings we calculate the interplanar spacing of d values, which correspond to reflection from (111), (200) and (220) planes. The diffused nature of the diffraction implies that PbS films are nanocrystalline. The observation of streaks in place of spots on the (111) reflected ring is attributed to the presence of high microstress in the material52. Our XRD results have already shown that such microstrains are indeed present.

TEM studies along similar lines of investigation were also performed on the nanocrystalline PbS films prepared by increasing the deposition time of the bath solution at 60 °C. The information derived from Fig. 3.25 is similar to that from Fig. 3.24. TEM image of nanocrystalline PbS films deposited at bath temperature 60 °C for deposition time 20 min for bath molarity 0.75M is shown in Fig. 3.25(a). Fig. 3.25(b) shows an ED pattern of the film consists of a central halo and concentric rings, indicating crystalline structure of the films. The average crystallite size is 9 nm. The majority of the particles in both the Fig. 3.24 and Fig. 3.25 are found to be nearly spherical.

3.8 Conclusions

(1) XRD observations of the CBD grown PbS films have shown that under optimized growth conditions, PbS films deposited at room temperature (28 to 30°C) for different concentrations have fcc rock-salt structure.
(2) The lattice constant ‘a’ is found to increase gradually with the solutions up to a molarity of 0.75M. Beyond 0.75M (molarity), there is slight fall in the lattice constant. The change in lattice constant for the deposited film over the bulk clearly suggests that the film grains are strained.

(3) The average grain size of the films lies between 13 to 18 nm.

(4) From the W-H plot of the samples it has been confirmed that the X-ray line broadening in nanocrystalline PbS is due to the presence of both size effect and strain effect.

(5) The values of the strain are also found to be dependent on growth parameters.

(6) The dislocation density in nanocrystalline PbS films are found to increase with molarities of the solutions. With the increase of molarities of the solutions larger number of ions participates, in a given time, in the formation of crystallites. This means reaction becomes faster and deposition quicker which cause increase of dislocation density.

(7) After annealing, the crystalline nature of the film is much improved and the crystallite size is increased.

(8) All PbS films deposited on OHP sheets show a preferential orientation in the [111] plane parallel to the substrate.

(9) From SEM images it is observed that annealing improves the crystallinity of the films and the grain size increases due to annealing.

(10) TEM observations have also shown polycrystalline growth of PbS films.

(11) The larger value of grain sizes determined by SEM may be due to the agglomeration of grains.
3.9 References


