Effect of Molarity on Structural and Optical Properties of Chemically Deposited Nanocrystalline PbS Thin Film

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Abstract. Thin films of PbS were deposited by chemical bath deposition (CBD) method under various molarities using lead acetate as Pb$^{2+}$ ion source, thiourea as S$^{2-}$ ion source and ammonia as complexing agent at a fixed pH value of 9 under bath temperature of 333 K. Four different molarities of PbS thin films were prepared. The as-prepared films were characterized by using X-ray diffraction (XRD), X-ray fluorescence (XRF), EDX, field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). Parameters like crystallite size, lattice constant, microstrain, dislocation density were calculated. Optical constants such as extinction coefficient, absorption coefficient were measured from absorption spectra. Studies show that average nanocrystallite size increases from 14.2 nm to 18.1 nm as the molarity of the film increases. Optical studies reveal the decrease of band gap from 1.75 eV to 1.44 eV with increasing molarity of the film indicating higher electrical conductivity of the films.

1. Introduction

Studies on crystalline semiconductors materials belong to the II-VI and IV-VI groups are increasing as these are easy to synthesize and are generally prepared in nano particles or thin film forms by various deposition methods. Lead sulphide (PbS) is an important IV-VI narrow direct band gap semiconductor material having approximate band gap of 0.41 eV at 300k and a large exciton Bohr radius of 18 nm [1,2]. These properties make PbS very suitable for infrared detection application [3]. This material has also been used in many fields such as photography [4], Pb$^{2+}$ ionselective sensors [5], optical switches and solar absorption [6]. Thus PbS materials have extremely broad applications. Due to these wide variety of applications many researcher study this material with various deposition techniques such as vacuum evaporation [7], electrodeposition [8], spray pyrolysis [9], molecular beam epitaxy [10], chemical bath deposition (CBD), etc. Among these methods CBD is the suitable for deposition of PbS thin films as it is very simple, inexpensive, convenient for larger area deposition and capable of yielding good quality thin films. Now a days CBD draws more attention in film deposition techniques as it does not require much sophisticated instruments to make a thin film. Chemical solution methods (i.e. hydrothermal, solvothermal, and CBD) generally require lower temperatures to synthesize PbS thin films of good quality [8]. Many researchers synthesized PbS film chemically and studied various properties of PbS. Effect of deposition time on chemically deposited PbS film was studied and obtained multilayered grains of films with band gap values varies from 1.88- 1.55 eV [11]. Well crystallized, with good surface homogeneity and roughness cubic PbS films were prepared and studied by S. Seghayer et al. [12]. Decrease of band gap from 2.65-2.50 eV with increasing deposition time was obtained by F. Gode et al. They also reported that small variations in grain size of PbS nanoparticles can give rise to significant modifications in the optical and electrical properties of PbS thin films [13]. In most of the cases, as the crystals obtained in the chemically deposited thin films are very small, considering the current interest in nanoparticles, CBD is the excellent technique to deposit nanocrystalline thin films.

In this present paper we report the preparation of PbS thin film by CBD method at various molarities and at a fixed pH value and studied the variations on structural, surface, optical properties of the PbS thin films with different molarities. We also calculated some basic parameters...
like dislocation density, internal strain, lattice constant, extinction coefficient, band gap etc and compare their variations with change of molarities.

2. Experimental Details

Lead sulphide thin films were deposited on glass substrate by using lead acetate \{Pb(CH₃COO)₂\} as Pb ion source and thiourea \{SC(NH₂)₂\} as S ion source. Four different molarities (0.05M, 0.1M, 0.15M, and 0.2M) of lead acetate and thiourea solutions were prepared separately. At first 30 ml of lead acetate solution of each molarity was mixed together with the 30 ml of equal molar solutions of thiourea. The reaction bath temperature was increasing gradually and was fixed at 333K finally. pH of the solution was adjusted by drop wise addition of NH₃ which was also act as complexing agent. pH value was fixed at 9. Then the glass substrates were immersed in the glass beaker vertically. Substrate cleaning plays an important role in the thin film deposition in CBD process. Films does not deposit on un-cleaned glass substrates. Rather it precipitates on the reaction beaker. So, prior to the deposition process, the glass substrates to be immersed to the solutions were cleaned with the mixture of isopropyl alcohol and nitric acid solution. Afterward the substrates were rinsed several times with distilled water and finally heated in a muffle furnace at 100 °C for drying. In the deposition process, after few minutes, colour of the solutions in the beakers slowly changed from brownish to dark brown indicating the initiation of chemical reaction and formation of films on glass substrate.

After almost 30 minutes, the solutions turned black and then the solutions were kept at room temperature for further deposition of PbS film. After 24 hours of deposition glass substrate fully covered with PbS layers on both sides of the glass substrates were taken out and washed with distilled water and dried in air. All the deposited films were smooth, reflective, homogeneous, highly adhered to the glass substrate and dark grey in colour. One side layer of the few deposited thin film samples were removed by dilute acid for the optical absorption studies. Remaining films were kept as it were. The as prepared films were characterized for their structural properties, elemental analysis and surface morphology. Thickness of the films was calculated by the gravity method. The value of the films thickness varied from 72 nm- 101 nm.

The structural characterization of PbS thin films were carried out by observing the X-ray diffraction (XRD) patterns obtained using a SEIFERT XRD 3003TT \((\lambda = 1.5406 \text{ Å for Cu Kα radiation, } V=40kV, I=30mA)\) at the department of physics, IIT Guwhati. X-ray fluorescence (XRF) study was done using Axios PANalytical DY 840 for the elemental analysis of the as prepared films at the Department of University Science and Instrumentation Center (USIC), Gauhati University, Guwahati (India). Surface morphology of films was studied using AFM, (Nt-Mdt, Ntegra Prima) and FESEM (ZEISS SIGMA VP) at IASST, Guwahati. Absorbance of the as prepared thin films was recorded using Cary-300 Scan UV-Visible spectrophotometer (Varian, Victoria-3170, Australia) for optical studies.

3. Results and Discussion

3.1. Reaction Mechanism

PbS thin film deposition is mainly based on the slow release of Pb²⁺ and S²⁻ ions in the chemical solutions which then condense on the glass substrate. Deposition of PbS film occurs when ionic product of Pb²⁺ and S²⁻ ions exceeds the solubility product of PbS. The chemical reaction occurs during formation of PbS thin film can be given as follows:

In aqueous solution lead acetate releases Pb²⁺ ion as-

\[ \text{Pb(CH₃COO)₂} \cdot 3\text{H₂O} \rightarrow \text{Pb}^{2+} + 3\text{H₂O} + 2\text{CH₃COO}^- \]

Pb²⁺ ion react with ammonia to give-

\[ \text{Pb}^{2+} + 4\text{NH}_3 \rightarrow \text{Pb(NH}_3)_4^{2+} \]
Thiourea decomposes in the alkaline solution as:

\[
SC(NH_2)_2 + 2OH^- \rightarrow S^2^- + CH_2N_2 + 2H_2O
\]

Finally, the global reaction in PbS formation process can be given as:

\[
Pb(NH_3)_4^{2+} + SC(NH_2)_2 + 2OH^- \rightarrow PbS + 4NH_3 + CH_2N_2 + 2H_2O
\]

3.2. XRD Study

The X-ray diffraction patterns of all prepared samples of different molarities have been shown in the Fig.1. The analysis has been carried out within 2θ = 20-60° with a resolution of 0.05° in 2θ angle. Five well defined peaks have been observed which are the diffraction from the (111), (200), (220), (311) and (222) crystalline planes respectively. Thus, all prepared films are polycrystalline in nature with cubic structure. Films have preferred orientation along the (200) planes as the intensity of the peak in it is highest. This result is in good agreement with the JCPDS data file 5-5921. The narrow peaks represent the good crystallinity of the films. It has also been observed that intensity of the most prominent peaks increase as molarity of the samples increase from 0.05M to 0.2M which indicates the improvement in crystallinity of the prepared films with increase of molarity.

The average crystallite size was calculated from the prominent peaks using the Scherrer’s equation [14]

\[
D = \frac{k\lambda}{\beta cos\theta}
\]  

(1)

where \(k\) is a constant whose value is taken as 0.94, \(\beta\) is the full width at half maximum (FWHM) intensity of the peak in radian, \(\theta\) is the Bragg’s diffraction angle, \(\lambda\) is the wave length of X-ray (1.5406Å). The values of \(D\) are observed to be increase as the molarity increase from 0.05M to 0.2M indicating the reduction of grain boundaries and increase of the electrical conductivity of the films. Variation of \(D\) with molarity is shown in Fig.2.
3.2.1. Average Crystallite Size and Internal Strain from W-H Plot

In the thin film samples, the broadening of X-ray diffraction peaks arises due to the simultaneous contribution of both particle size and internal strain. Therefore using the Williamson and Hall (W-H) method [15] for Cauchy nature of broadened profile, we have the relation, [16]

$$\beta = \frac{\lambda}{D \cos \theta} + 4\epsilon \tan \theta$$

or,

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + 4\epsilon \sin \theta / \lambda$$

(2)

where $\epsilon$ is the average internal strain. For multiple ordered diffraction pattern a plot of $\beta \cos \theta / \lambda$ versus $2 \sin \theta / \lambda$ will give a straight line and inverse of intercept of this plot (W–H plot) will give the average crystallite size $D$ and slope will give the average internal strain $\epsilon$. W-H plot of all prepared PbS films has been shown in Fig.3. The straight lines in these plots have been drawn as best fit regressive lines. $D$ values obtained from W-H plot are larger than that obtained from Scherrer’s equation indicating strain contained in prepared PbS thin films. Values of $D$ and $\epsilon$ obtained from W-H plot have been tabulated in Table1. Variation of $\epsilon$ with molarity of the films has been shown in Fig. 4. It has been observed that $\epsilon$ values decreases with higher molarities films attributing the decrease of lattice defect among the grain boundaries with increasing crystallite size of the films.
3.2.2. Lattice Constant

The lattice constant of all the PbS thin films prepared at different molarities on glass substrates for the cubic structures were determined from the relation

\[ a = d(h^2 + k^2 + l^2)^{1/2} \]  \hspace{1cm} (3)

The values of lattice constants evaluated are slightly different for different orientations of the same film. This is due to the divergence of the X-ray beams, refraction and absorption of X-rays by the specimens, etc. These give a number of systematic errors in the measurement of \( \theta \) and hence in the \( d \) values. Therefore, for corrected value of lattice constant, we have drawn the Nelson-Riley plots [17] by taking the calculated values of lattice constants for different planes and the error function:

\[ f(\theta) = (\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta) / 2 \]  \hspace{1cm} (4)

The corrected values of lattice constants are estimated from the intercept of the plot for error function \( f(\theta)=0 \). Nelson-Riley plot for all prepared PbS films of various molarities has been represented in Fig. 5.

Figure 3. W-H plot for (a) 0.5M (b) 0.1M (c) 0.15M (d) 0.2M PbS films.

Figure 4. Variation of internal strain of PbS films with molarity.
Here also the straight lines have been drawn as best fit regressive lines. The corrected values of lattice constants for all the prepared films have been tabulated in Table 1. Higher value of lattice constant was obtained for the higher molarity film indicating increase of crystallite size. Variation of corrected lattice constant with molarity of the films has been shown in Fig. 6. Again, it has been observed that the corrected lattice constant deviates from its bulk value of lattice constant (5.9362 Å). This deviation indicates that the as prepared films are under strain.
Table 1. Various parameters of as prepared PbS thin films of different molarities.

| Molarity [M] | Average Crystallite size [D] | Average internal Strain [ε × 10^{-3}] | Dislocation density [δ × 10^{15} Lines/m^2] | Calculated lattice constant [Å] | Corrected lattice constant [Å] | Band gap from absorption spectra [eV] |
|--------------|-------------------------------|---------------------------------------|-------------------------------------------|---------------------------------|---------------------------------|-------------------------------------|
| 0.05         | 14.2                          | 18.2                                  | 2.37                                      | 4.97                            | 5.958                           | 5.960 5.961                        |
|              |                               |                                       |                                           |                                 |                                 | 5.911 5.937 5.958               |
| 0.10         | 15.2                          | 19.5                                  | 1.90                                      | 4.31                            | 5.976                           | 5.980 5.981                        |
|              |                               |                                       |                                           |                                 |                                 | 5.968 5.937 5.958               |
| 0.15         | 17.7                          | 22.9                                  | 1.75                                      | 3.21                            | 5.993                           | 5.980 5.981                        |
|              |                               |                                       |                                           |                                 |                                 | 5.996 5.969 5.993               |
| 0.2          | 18.1                          | 23.2                                  | 1.69                                      | 3.05                            | 6.010                           | 6.020 6.003                        |
|              |                               |                                       |                                           |                                 |                                 | 5.996 5.993                      |

3.2.3. Dislocation Density

Dislocations are the mostly encountered lattice defects in thin film phenomena. The dislocation density was determined from the Williamson and Smallman’s formula [18]:

\[ \delta = n/D^2 \]  

(5)

where ‘n’ is a factor which is equal to unity giving minimum dislocation density and ‘D’ is the average crystallite size. It has been observed that the dislocation density decreases as the molarity of the film increases. This is due to the decrease of grain boundary with increasing crystallite size of the films. Thus higher molarity films represent better lattice quality with decreasing dislocation density. The variation of dislocation density with molarity is shown in Fig. 7.

![Figure 7. Variation of dislocation density of PbS films with molarity.](image-url)
3.3. XRF Analysis

For the elemental purpose XRF analysis have been done on a typical as prepared PbS film. The XRF spectra of a 0.05 M PbS thin film is shown in Fig. 8. XRF analysis confirms the presence of Pb and S in the prepared film. Pb exists in Lβ at 2θ value of 40.5° and S exists in Kα at 2θ value of 110.7°.

![XRF spectra of a 0.05M PbS film](image)

Figure 8. XRF spectra of a 0.05M PbS film scanned for (a) Pb and (b) S.

3.4. AFM Study

AFM is actually a promising technique to study the surface topography of thin films as this provides some valuable information regarding the growth mechanism, shape and size of grains and RMS roughness of the film surfaces. Fig.9 shows the 2D and 3D AFM images of 3 prepared PbS thin films (0.05M, 0.1M, 0.15M) in a scanning area of 3×3, 5×5 and 10×10 μm². Grains of different sizes are observed in all the prepared films. In 0.05M PbS film round shaped grains can be observed. Lots of empty spaces are there in this film. As the molarity increases, uniformity of the films also enhance as shown in the other two films images. In 0.1M and 0.15M PbS film, the substrates are completely covered with PbS layer. Some large grains are observed over the valley of small grains in 0.15M film. However all the prepared films are good adherent to their respective substrates. RMS roughness and average grain size of the films have been measured with the reported software (WSxM 4.0 Beta 7.0 version) [19]. RMS roughness of all the films varies from 81.9nm to 28.9nm. Thus with increasing molarity RMS roughness decreases. Average grain sizes are found to be 177nm, 186 nm and 197nm for the three films respectively. Grain sizes are found to be larger in AFM analysis as compared to the average crystallite size measured from the XRD data. This may due to the formation of larger grain by the small crystallites.

3.5. FESEM and EDX Study

Surface morphology of a typical 0.2M PbS film was investigated by FESEM. Fig. 10 shows FESEM image of the film under different magnification. These images reveal the smooth, homogeneous and good crystalline structure of the film with different grain size which is fully covered with the glass substrate and are very well adhesive to the substrate. The EDX pattern is shown in the Fig. 11 which confirms the presents of Pb and S in the particular film along with some extra peaks (Na, Ca, C and O) and are supposed to be arise due to the glass substrate or the substrate holder used in the EDX process [20].
Figure 9. AFM images of (a-f) 0.05M, (g-l) 0.1M (m-r) 0.15M PbS films [(a-c), (g-i), (m-o) are in 2D; (d-f), (j-l), (p-r) are in 3D view under different magnifications].
3.6. Optical Study

Optical absorption of PbS films have been studied in the wave length range 400-850 nm. Optical absorption studies of semiconducting materials give some information relating to band structure. Optical absorption spectra of four different sets of PbS thin film have been shown in Fig.12. At higher wave length i.e. at lower energy side, absorption has been found to decrease towards visible region. However, higher value of absorbance have been observed in high molarity films. This is due to the extra energy states associated with the films that absorbs more photon energy.
The nature of the transition (direct or indirect) is obtained by using the relation
\[ \alpha \hbar \nu = B (\hbar \nu - E_g)^n \] (6)
where \( B \) is constant, \( \alpha \) is absorption coefficient and \( E_g \) is the band gap energy. Fig.13 shows a typical plot of \((\alpha \hbar \nu)^2\) versus \( \hbar \nu \) for all the as prepared PbS films from which extrapolation of data to the \((\alpha \hbar \nu)^2 \rightarrow 0\) axis gives the band gap energy. From this figure it is clear that the band gap energy decreases with increase of molarities. As molarity increases, thickness of the films also increases and hence increase of localized density of states near the band edges decreases the band gap energy of the films. Reduced microstrain, decrease of dislocation density and increase of lattice constant with molarity can also attribute the decrease of band gap. Again, it has been observed that the calculated band gap of as prepared PbS thin films is higher than that of bulk PbS. This is because of the quantum confinement effect due to small grain size of the polycrystalline PbS films. The properties of nanocrystalline materials change from their corresponding bulk properties, because the crystallites sizes become comparable to the Bohr excitonic radius. The variation of band gap at crystallite diameters around 40 nm arising from quantum confinement of excitons in PbS is well documented and solar cells have been developed based on this behavior [22].

Value of absorption coefficient \( \alpha \) is calculated from the relation [23]
\[ \alpha = 2.303 \frac{A}{t} \] (7)
where \( A, t \) are the absorbance and thickness of the films respectively.

From the knowledge of \( \alpha \), the extinction coefficient or imaginary part of refractive index \( k \) was calculated from:
\[ k = \frac{\alpha \lambda}{4\pi} \] (8)
Figure 13. Plots of \((\alpha h\nu)^2\) versus \(h\nu\) for (a) 0.5M (b) 0.1M (c) 0.15M (d) 0.2M PbS films.

Variations of \(k\) with wavelength have been shown in Fig. 14.

From this plot it has been observed that, in the 0.05 M film the \(k\) values show interesting result; which increases up to the wavelength 580 nm and then decreases rapidly towards the IR region. However, in the 0.1M, 0.15M and 0.2M film, \(k\) value has been observed to be almost steady towards the IR region after the wavelength of 610 nm.
4. Conclusions

PbS thin films were deposited on glass substrate by simple CBD method and the effect of molarities on structural properties of the films has been studied. XRD results show the polycrystalline nature of the films with increasing crystallite size with the molarity. Various structural parameters like dislocation density, internal strain etc. were calculated and observed to be decreased with molarity. Higher value of lattice constant was obtained for the higher molarity of a typical film where the corrected lattice constant was deviated from its bulk value indicating that the as-prepared films were under strain. Decreasing dislocation density and internal strain with increasing molarity indicates improvement of lattice quality of the as prepared films. AFM studies reveals the covered and rough surface of the as-prepared films with increasing grain size with molarity. FESEM images shows dense, uniformly distributed film with different grain size. XRF and EDX analysis confirms the presence of Pb and S in the prepared films. Optical studies show the direct band gap nature of PbS films and also the higher value of absorbance, extinction coefficient and decrease of band gap was observed with increasing molarity. k values were observed to be almost steady towards the IR region after the wavelength of 610 nm for 0.1M, 0.15M, 0.2M and above attributing uniform transparency and conductivity.

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