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Electrochemical Growth and Characterization of Lead Sulphide Thin Films

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Abstract: *Growth of lead sulphide thin films has been carried out electrochemically on indium doped tin oxide coated conducting glass substrates from an aqueous acidic bath containing $Pb(CH_3COO)_2$ and $Na_2S_2O_3$. X-ray diffraction pattern showed that the deposited films possess cubic structure with most prominent reflection along (200) plane. The dependency of microstructural parameters such as crystallite size, strain and dislocation density with film thickness has been analyzed. Surface morphology and film composition have been analyzed using scanning electron microscopy and energy dispersive analysis by X-rays. Optical absorption analysis showed that the prepared films possess a direct band gap value of 0.37 eV.*

Keywords: metal chalcogenides, IV-VI semiconductors, surface morphology, PbS, band gap

1. INTRODUCTION

Thin films of metal chalcogenides have received much awareness due to its wide range of applications in manufacturing of large area photodiode arrays, electronic and optoelectronic devices, infrared photography, photothermal converters, solar absorbers, solar control coatings, photoconductors and sensors [1-5]. Chalcogenides of IV-VI group materials are considered as interesting narrow band gap semiconductors with an energy gap value in the range between 0.26 and 0.45 eV which make them interesting for IR detectors [1,3,6]. Among them, lead sulphide (PbS) is found to be an interesting narrow band gap semiconductor with an energy gap value 0.45 eV and continuously increasing absorption coefficient from IR to visible region which make the material suitable for the fabrication of IR detectors from the middle of 1940 [7,8]. Thin films of PbS are found to be crystallized in cubic structure with lattice constant (a=5.9362 Å), small effective mass and high electron mobility [7,9].Numerous methodologies that have been adopted to prepare PbS thin films such as vacuum evaporation [10], chemical bath deposition [11], successive ionic layer deposition [3], spray pyrolysis [12] and photochemical deposition [13]. Preparation of PbS thin films from cationic precursor using SILAR technique and their transport properties are investigated by Preetha et al [3]. Sushil Kumar et al [10] have obtained PbS thin films on ultra clean glass substrates and investigated their properties using X-ray diffraction, optical and electrical measurement techniques,respectively [11].Thangaraju and Kalaianan [12] have prepared PbS thin films on ITO substrates and investigated their properties using structural, morphological, electrical and optical characterization techniques, respectively. Ichimura et al [13] have obtained PbS thin films on Pd-treated glass substrates and investigated their properties using X-ray diffraction, Scanning electron microscope and Fourier transform interferrormetric techniques, respectively. Among the deposition techniques mentioned above, electrodeposition technique is considered to be attractive due to its low cost of synthesize, low temperature processing, no need of vacuum facility, no contamination to the surrounding, convenience for producing large area devices, film thickness and stoichiometry could be easily controlled[1,6,14-17].

In the present study, thin films of PbS have been prepared on ITO substrates using cathodic electrodeposition technique. Thickness of the deposited films could be measured using stylus profilometer. Deposited films are subjected to X-ray diffraction, Scanning electron microscopy, Energy dispersive analysis by X-rays and Optical absorption techniques for the determination of

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structural, morphological, compositional and optical properties. Microstructural parameters such as crystallite size, strain and dislocation density are determined using observed X-ray diffraction data. Effect of deposition time on structural, microstructural, morphological, compositional and optical properties of the films are investigated. The observed results are discussed in detail.

2. EXPERIMENTAL

Thin films of PbS were prepared on ITO substrates from an aqueous electrolytic bath containing 0.1 M $Pb(CH_3COO)_2$, 0.01 M $Na_2S_2O_3$ and 0.05 M EDTA as complexing agent. The chemicals used in the present work were of Analar Grade Reagents. First working solution of $Pb(CH_3COO)_2$ was obtained by dissolving 9.483 g of $Pb(CH_3COO_2)$ in 250 cc of distilled water, the second working solution of $Na_2S_2O_3$ was obtained by dissolving 3.102 g of $Na_2S_2O_3$ in 250 cc distilled water and 0.373 g of EDTA dissolved in 100 cc distilled water was used as complexing agent for all depositions. Electrochemical experiments were carried out using scanning potentiostat/galvanostat (ZAHNER IM6, Germany) with ITO substrate as working electrode, platinum electrode as counter electrode and saturated calomel electrode as reference electrode, respectively. Before used for deposition, ITO substrates were treated for 15 minutes in a bath of isopropanol and then rinsed with acetone. The SCE was introduced into the solution by luggin capillary arrangement whose tip was kept as close as possible to the working electrode. All the experimental potentials are referred with respect to SCE. The deposition potential, bath temperature and solution pH were fixed as -1050 mV versus SCE, 70°C and 3.0 ± 0.1.Time of deposition of the prepared films was found to be vary in the range between 10 and 60 minutes.

Thickness of the deposited films was measured using stylus profilometer(Mitutoyo SJ 301, Japan). X-ray diffraction data of the prepared films was analyzed using an X-ray diffractometer (XPERT PRO PANalytical, Netherland) with CuKα radiation with wavelength (λ= 0.15418 nm). Microstructural parameters such as crystallite size, strain and dislocation density were determined from observed X-ray diffraction data using Williamson Hall plot analysis. Surface morphology and film composition were analyzed using scanning electron microscopy (Philips XL 30) set up attached with energy dispersive analysis by X-rays. Optical properties of the prepared films was determined using an UV-Vis-NIR spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Film thickness

Growth of PbS thin films using electrodeposition technique is controlled by two individual variables such as (i) film thickness and its uniformity (ii) surface morphology [17,18]. The temperature of the electrolytic bath is found to influence the deposition rate by: (i) increase of precursor solubility and (ii) decrease in value of viscosity [17]. Thickness of the deposited films could be controlled by controlling the deposition potential, deposition time and bath temperature. At lower bath temperature such as below 50°C adherence of the deposited film to the substrate is poor. This may be due to the reaction rate is slow. At higher bath temperate such as above 75°C formation of film may be hindered due to the process of hydrogen evolution reaction. Variation of film thickness with deposition time for PbS thin film prepared at bath temperature around 70°C is shown in Figure 1. It is observed that the film thickness increases linearly with deposition time and attained its maximum value at 40 minutes of deposition. Further increasing deposition time above 40 minutes, there is slight decrement in film thickness value is obtained which is noted in Figure 1. Thus, films with higher thickness value is obtained at a deposition time of 40 minutes.

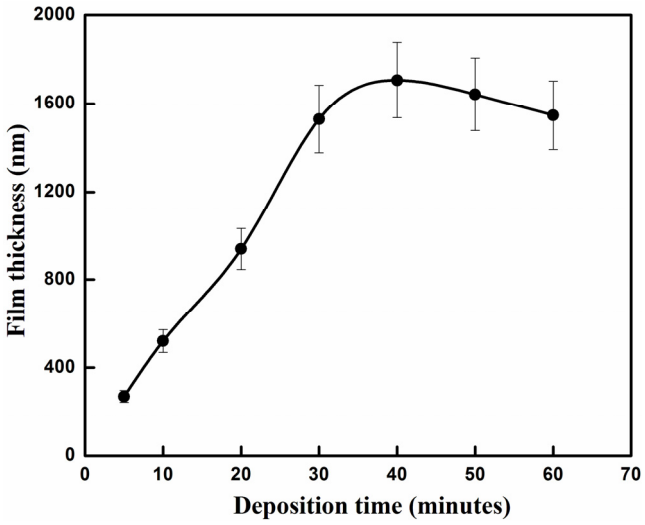

Figure 1. Variation of film thickness with deposition time for PbS thin films.

3.2. Microstructure and surface morphology

X-ray diffraction analysis has been carried out to investigate the crystalline nature and phases of the prepared films. X-ray diffraction pattern recorded for PbS thin films prepared on ITO substrates at various deposition time is shown in Figure 2. XRD pattern showed that the prepared films possess polycrystalline nature with cubic structure with lattice constant (a=5.9362 Å). The diffraction peaks of cubic PbS are found at 2θ values of angles 25.82,30.06,43.02,51.07,53.36,62.57,68.87,71.12,78.77 corresponding to the lattice planes (111), (200), (220), (311), (222), (400), (331), (420) and (422), respectively. Different peaks in the diffractogram are indexed and the corresponding values of interplanar spacing "d" is calculated and compared with standard JCPDS-ICDD file for cubic PbS [19]. It is observed that all the peaks are from PbS and hence no additional peak corresponding to Pb and S could be present. It is also noted that the degree of crystallinity is found to increase while increasing the deposition time upto 40 minutes, thereafter it decreases slightly. The height of (200) peak is found to be higher than all other peaks in the diffractogram indicates that the crystallites are preferentially oriented along (200) plane. The films obtained at a deposition time 40 minutes has sharper peaks with small FWHM data results higher value of crystallite size of the prepared films. The crystallite size of the deposited films is calculated using FWHM data and Debye-Scherrer formula (Eq.1) given below [15-18].

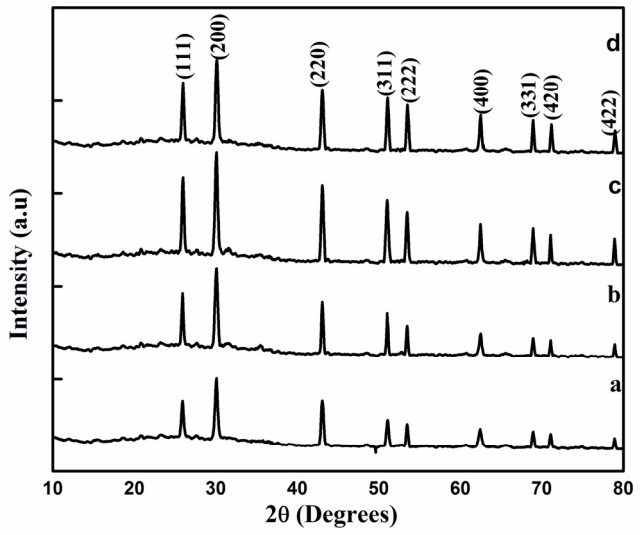

Figure 2. X-ray diffraction pattern of PbS thin films prepared at different deposition time with various film thickness values: (a) 270 (b) 940 (c) 1530 (d) 650 nm

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the wavelength of CuK_α target used, θ is Bragg's diffraction angle at peak position in degree and β is Full Width at Half Maximum of the peak in radian. Strain is defined as the restoring force which can be acts on the surface of the film to restrict the formation of crystallites on its surface [14]. The strain in the deposited films is calculated from the slope of βcosθ versus sinθ plot using the following formula (Eq.2) given below [16,18].

$$\beta = \left(\frac{\lambda}{D \cos\theta} - \varepsilon \tan\theta \right) \tag{2}$$

Dislocation density is defined as the number of dislocation lines per unit volume of the crystal and its value is calculated using the following Eq.(3) [17,18].

$$\delta = \frac{1}{D^2} \tag{3}$$

Figure 3a shows the variation of crystallite size and strain with film thickness for PbS thin films obtained at different deposition time. It is noted that the crystallite size is observed to increase while increasing film thickness value upto 1500 nm. Increase in value of film thickness above this value there is slight decrement in crystallite size value is observed which is indicated in Figure 3a. Due to the removal of defects in the lattice, strain in the deposited film gets released and attained its minimum value at film thickness value around 1530 nm which is obtained at a deposition time 40 minutes. The decrease in value of strain with deposition time thus leads to decrease in value of dislocation density which is calculated

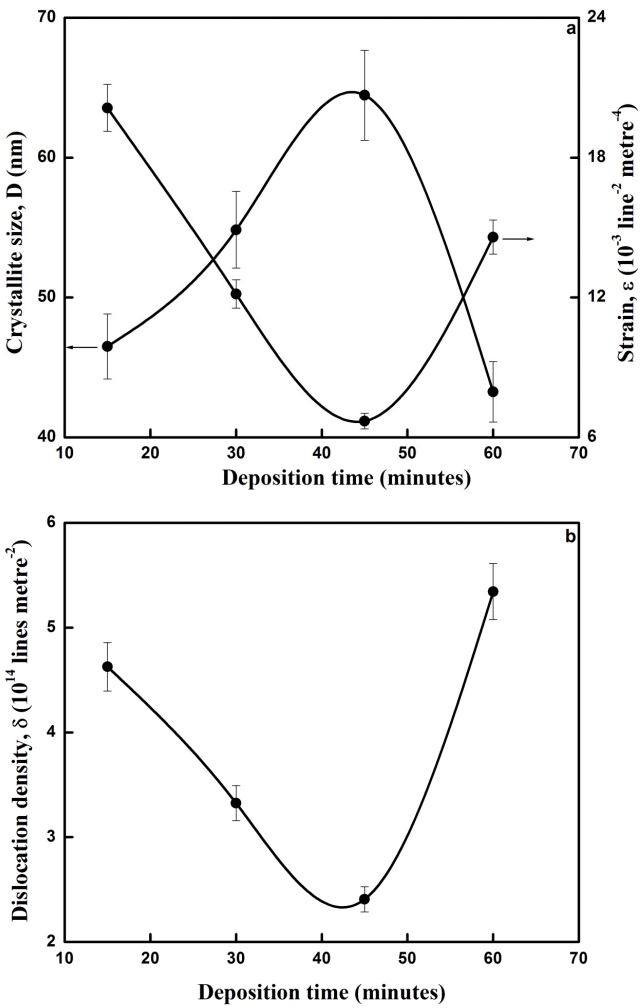

Figure 3. a. Variation of Crystallite size and Strain with film thickness for PbS thin films b. Variation of Dislocation density with film thickness for PbS thin films.

using Eq.(3) and shown in Figure 3b. It is also found that minimum value of strain, dislocation density and maximum value of crystallite size are obtained for films prepared at a deposition time of 40 minutes. This result leads to improvement of stoichiometric nature of the prepared films. Also, improvement in stoichiometric nature of the prepared film causes expansion of volumetry of the prepared films. Similar behaviour of microstructural variation with film thickness have been reported earlier for $FeSe_2$, CdSe thin films [20,21].Surface morphology of PbS thin films has been analyzed using scanning electron microscopy. SEM image of PbS thin films prepared at bath temperature 70°C and at a deposition time of 45 minutes is shown in Figure 4. It is observed that the film surface is observed to be smooth and covered with evenly distributed grains. The shape of the grain is observed to be cube with sizes in the range between 0.25 and 0.50 μm. The average size of the grains is found to be 0.38 μm.

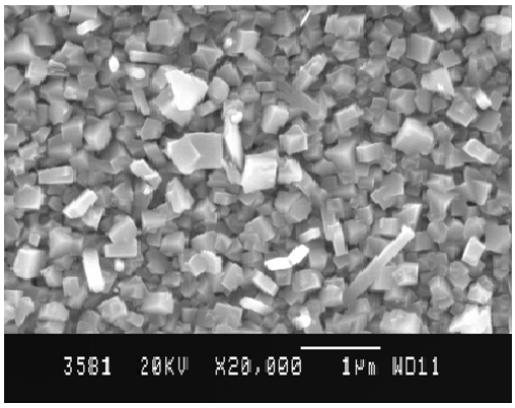

Figure 4. SEM image of PbS thin film prepared at bath temperature 70°C.

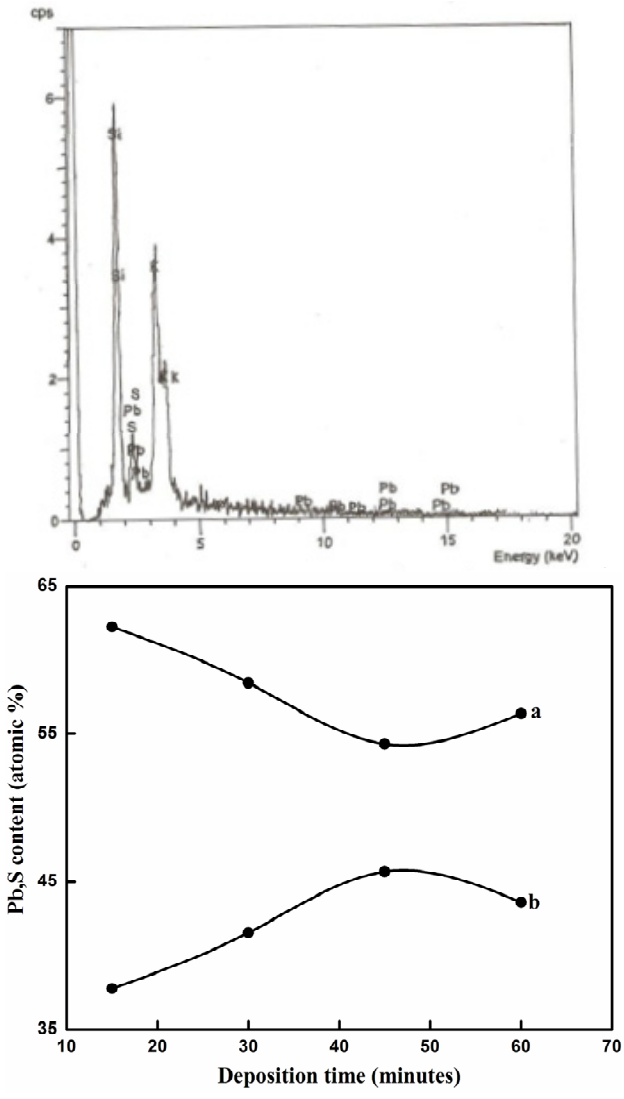

Figure 5. a. Typical EDX spectrum of PbS thin film deposited at bath temperature 70°C b. Variation of Pb and S content with film thickness for PbS thin films: (a) Pb (b) S

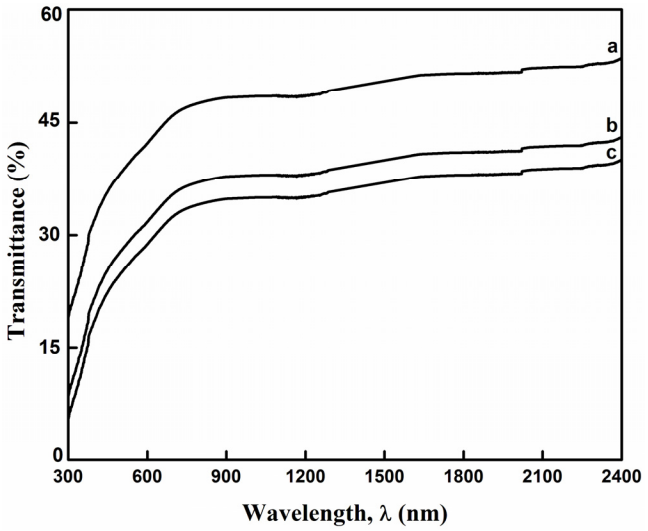

Figure 6. Transmittance spectrum of PbS thin film prepared with different film thickness values: (a) 270 (b) 940 (c) 1530 nm

3.3. Film composition

Film composition has been analyzed using an energy dispersive analysis by X-rays set up attached with scanning electron microscope. A characteristic EDX spectrum of PbS thin film prepared at potential -1050 mV versus SCE, bath temperature 70°C, deposition time 40 minutes is shown in Figure 5a. It is observed that the emission lines Pb and S are present in the investigated energy range indicates the formation of PbS thin films.EDX analysis has been carried out to determine the relationship between film composition and deposition time. Variation of Pb and S content with deposition time for PbS thin film is shown in Figure 5b. It is noted that the content of Pb decreases and the content of S increases while increasing the deposition time from 15 to 45 minutes. If the deposition time is increased above 45 minutes there is slight increment in Pb content is observed which is indicated in Figure 5b. Atomic molar ratio (Pb:S) of PbS thin film prepared at a deposition time 45 minutes is found to be 54.32:45.68 indicating stoichiometric formation of PbS thin films. This result is consistent with X-ray diffraction analysis of the sample with phase corresponds to PbS.

3.4. Optical absorption analysis

Optical parameters such as absorption coefficient, band gap play a vital role in realize the optoelectronic properties of narrow band gap semiconducting materials. Optical transmittance spectrum of PbS thin films prepared with different film thickness value is shown in Figure 6. The parameters such as absorption coefficient and band gap are evaluated from optical transmittance and absorption measurements. The value of strong absorption region of thin film is calculated using the below mentioned Eq.(4) [14,22].

$$\alpha = \frac{1}{t}\ln\left(\frac{A}{T}\right) \tag{4}$$

where α is the absorption coefficient in cm^{-1}, t is the thickness of the film in nm, A is absorbance, T is transmittance. The nature of

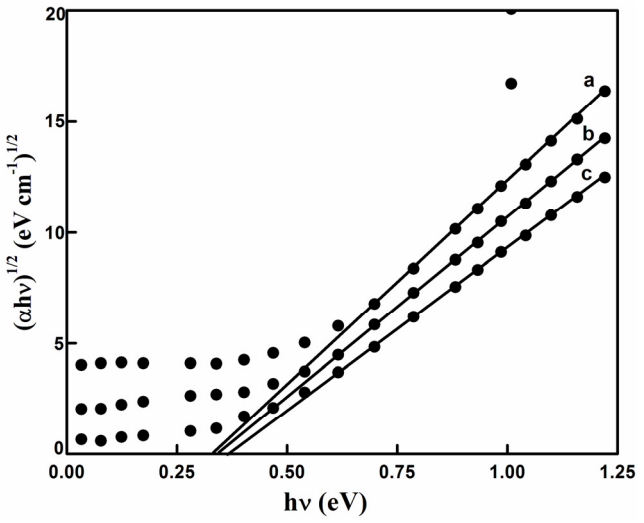

Figure 7. Plot of (hν) versus $(\alpha h\nu)^{1/2}$ for PbS thin film prepared with different film thickness values:(a) 270 (b) 940 (c) 1530 nm

transition is determined using the following Eq.(5) [14,18].

$$\alpha h\nu = K\left(h\nu - E_g\right)^n \quad (5)$$

where K is an energy dependent constant, E_g is the band gap of the material, hυ is photon energy. Optical absorption and transmission spectra of PbS thin films have been recorded as a function of wavelength in the range between 300 and 2300 nm. Substrate absorption if any is corrected by introducing an uncoated ITO substrate in the reference beam. The value of absorption coefficient rises sharply owing to band-to-band transition and levels off latter. From the calculated values of absorption coefficient a plot of hυ versus $(\alpha h\upsilon)^{1/2}$ is drawn for films prepared with different film thickness values (Figure 7). Linear portion of the graph is extrapolated to energy axis hυ gives the band gap value of the material. Band gap value of the material obtained in the present work is found to be in the range between 0.36 and 0.39 eV. The band gap value of the material obtained in the present work is found to in close agreement with the value reported earlier [10].

4. CONCLUSIONS

Polycrystalline PbS thin films were prepared on ITO substrates using potentiostatic cathodic electrodeposition technique. X-ray diffraction results revealed that the formation of films with cubic structure with preferential orientation along (200) plane. Microstructural parameters such as crystallite size, strain and dislocation density are evaluated and its dependency showed that there is monotonic variation with thickness value of the deposited films. Films of smooth surface with cubic shaped grains and well defined stoichiometry were obtained at a deposition time around 40 minutes. Band gap value of the material obtained in the present work is in the range between 0.36 and 0.39 eV.

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