Synthesis and characterization of chemical bath deposited lead sulfide (pbs) thin films

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ABSTRACT

Nanocrystalline lead sulphide thin films were prepared by a Chemical Bath Deposition (CBD) method at various time durations. The crystalline nature and particle size of the deposited samples were analyzed by X- ray diffraction analysis. Two prominent phases (111) and (200) were observed bearing particle size 17.14 and 17.05 respectively. The formation of lead sulphide nanoparticles were analyzed using FTIR spectroscopy. The optical band gap of the sample is found to be 2.22 eV determined from UV spectrograph. The semiconducting behavior of PbS thin films was confirmed by dc electrical conductivity measurement.

KEYWORDS: Lead sulphide, chemical bath deposition, XRD, optical band gap

INTRODUCTION

In recent years, semiconducting nanomaterials are of great interest due to their unique physical and chemical properties [Koao *et al.,* 2014]. Their optical and electronic properties are different from that of the materials in bulk form. Semiconductor nanoparticles exhibit size –dependent electronic band gap energies, melting temperatures, solid state phase transition temperatures and pressures [Mulik *et al.,* 2010]. Therefore these semiconducting materials have potential applications in solar cells, optoelectronic devices, photoconductors, sensors and infrared detector devices [Mulik *et al.,* 2010; Borhade *et al.,* 2012]. The emphasis has been mainly given on the synthesis of semiconductor particles belonging to IV-VI, II-VI and III-V groups, which show significant quantum confinement effects [Choudhury *et al.,* 2008; Ezekoye *et al.,* 2015]. PbS thin films has direct optical band gap that can be changed from 0.39 up to 5.20 eV [Kumar *et al.,* 2009]. PbS thin films have been deposited through various deposition processes such as electrodeposition, spray pyrolysis, chemical bath deposition, and successive ionic layer adsorption and reaction [Borhade *et al.,* 2012]. We have opted the Chemical Bath Deposition (CBD) method owing to its advantages as a very simple, relatively cost effective, and

convenient for large area scaling and are used in the deposition of good quality thin films with physical and chemical properties comparable to other methods. In the last decade, there has been a renewed interest in this method, mainly associated with its remarkable success in depositing semiconductor layers in thin film photovoltaic cells. By chemical bath deposition (CBD), the crystallites can be varied by controlling deposition parameters [Borhade *et al.*, 2012].

The aim of this paper is to study the structural, optical and electrical properties of PbS thin films synthesized by chemical bath deposition (CBD) method.

EXPERIMENTAL

Reagents used for the deposition include lead sulfate $PbSO_4$ as Pb^{2+} source, ammonia water NH_4OH and thiourea $CS(NH_2)_2$ as S^{2-} source. All reagents are of laboratory grade and used without further purification. The substrates used are glass slides washed using hydrochloric acid and ultrasonically cleaned for 15 minutes and dried well before use.

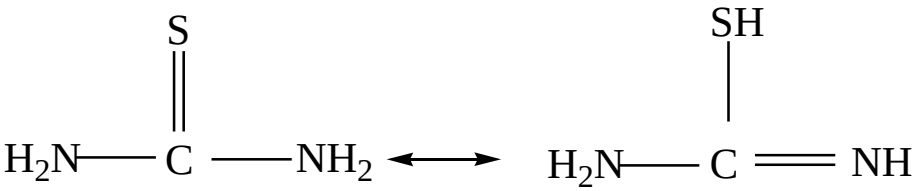
Initially molar concentration of lead sulfate was varied keeping temperature of the reaction bath constant. The attempts were made for 1M, 0.5 M and 0.1M $PbSO_4$ concentrations and keeping reaction bath temperature 60^oC constant. It was found that the films deposited with 1M and 0.5 M $PbSO_4$ concentrations are powdery in nature and less adherent to the substrates. The powder clusters were found on the deposited films, showing poor quality of the film. However the films deposited with 0.1 M $PbSO_4$ concentration are adherent, homogeneous and blackish-grey in color without any powdered precipitation.

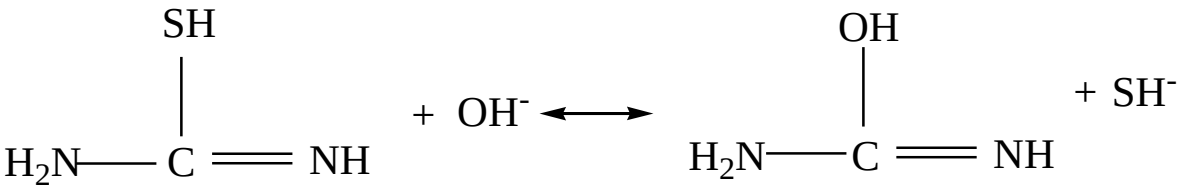
The typical procedure for the film growth is described as follows. In a 100 ml beaker containing 25 ml of 0.1 M $PbSO_4$ solution 25% NH_4OH is added drop by drop until the initially formed white precipitate is completely dissolved. The pH of the solution was maintained ~11. The clean substrates are mounted vertically in the bath beaker in such a way that an approximately 10 mm distance is maintained between the substrates and the wall of the bath. 25 ml of 1M $CS(NH_2)_2$ then is poured into the mixtures. Finally, the distilled water is gradually added to make the volume up to 100 ml. The deposition is made at 60°C under magnetic stirring for all samples. The substrates were subsequently retired from the beaker at different times: 70, 80, 90, 100, and 110 min. After deposition the films were washed by distilled water and then dried at room temperature.

The predicted reaction mechanism for deposition of lead sulfide films is as follows:

$$PbSO_4 + 2NH_4OH \longrightarrow Pb(OH)_2 + (NH_4)_2SO_4$$

$$Pb(OH)_2 + 4NH_4OH \longleftrightarrow Pb(NH_3)_4^{2+} + 2OH^- + 4H_2O$$





$$Pb(NH_3)_4^{2+} + SH^- = PbS\downarrow + NH_4^+ + 3NH_3$$

RESULTS AND DISCUSSION

THICKNESS MEASUREMENT

The thin film thickness for each deposition time is calculated using weight difference method. It is found that the film thickness varied from 250 to 450 nm as shown in Fig. 1. The films deposited for 90 min are smooth, homogeneous, well adherent to the substrate with dark surface like mirror bearing thickness equal to 400 nm.

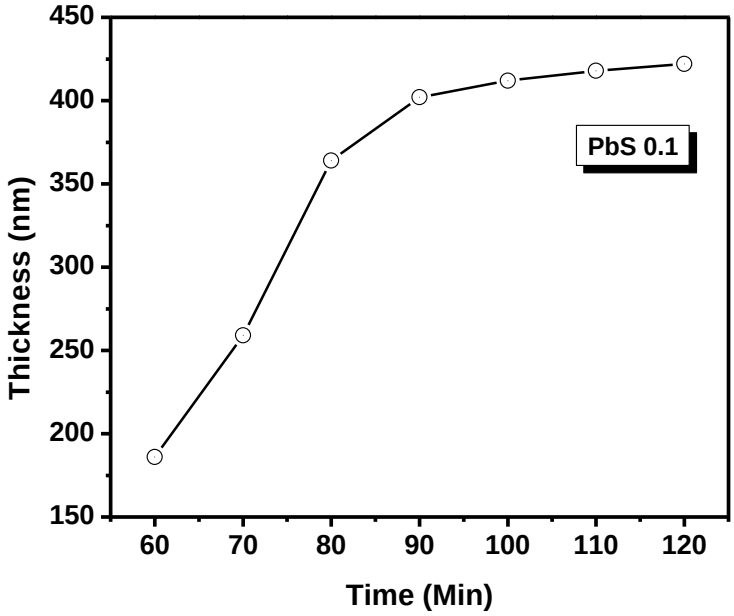


Fig 1: Variation of thickness with deposition time of PbS thin films

Fig 2 shows photograph of PbS thin film deposited on glass substrates.

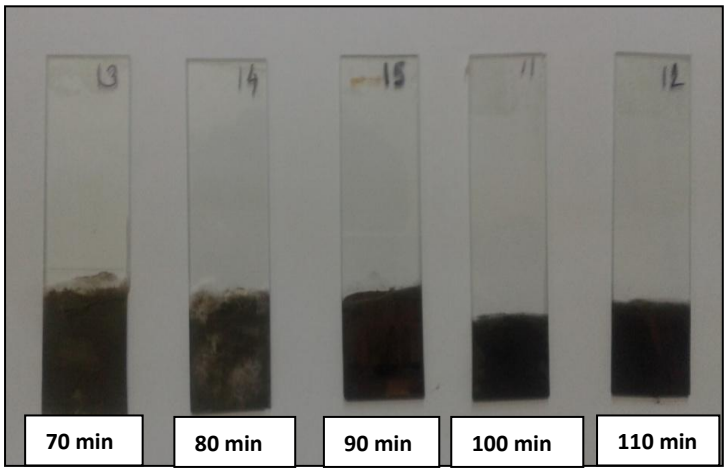


Fig 2: PbS thin film deposited on glass substrates

XRD ANALYSIS

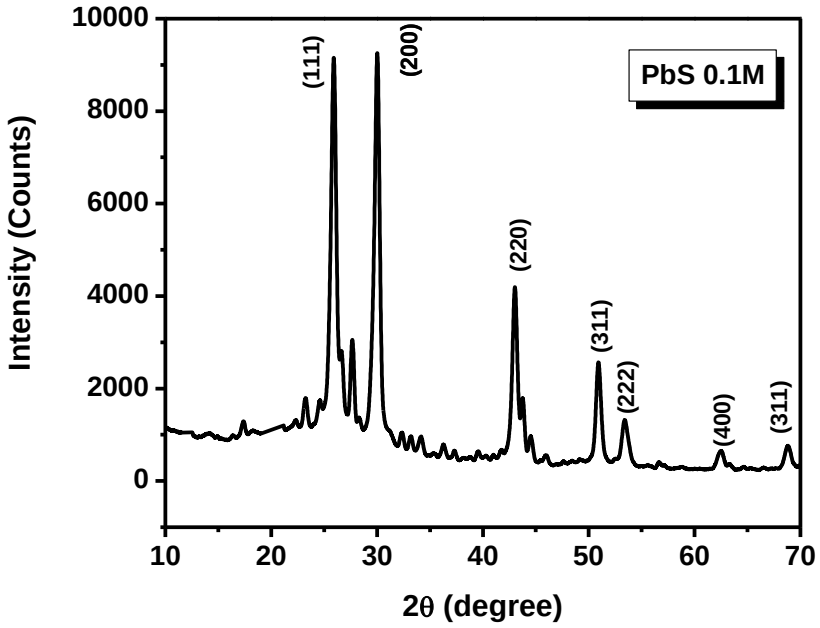


Fig 3: XRD spectra of PbS thin film

Figure 3 shows the X-ray diffraction patterns for PbS thin films. The structural properties of PbS thin film was studiedin 2Θ range of 10^{o} –70^{o} using X-ray diffraction (XRD) (Rikagu Altima-IV) using filtered CuKα radiation (λ=1.5406 Å). The diffraction peaks of PbS thin films were found at (111), (200), (220), (311), (222), (400) and (311). The PbS thin films exhibit face centered cubic structure as confirmed by JCPDS card no. 78-1901. The preferred films have (100) and (200) orientations with lattice constant a = 5.931 Å. The lattice parameter (a) for PbS thin film was calculated using relation

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

Where *h*, *k* and *l* are miller indices and d is the interplanar spacing.

The average nanocrystallite size (D) was determined from full width at half maximum (FWHM) of major diffraction peak using Scherer's formula

$$D = \frac{K.\lambda}{\beta.\cos\theta}$$

Where λ is the X-ray wavelength (1.5406 Å), β is FWHM and θ is the diffraction angle. The average crystallite size was calculated for (111) and (200) planes and were found 17.14 nm and 17.05 nm respectively.

FTIR ANALYSIS

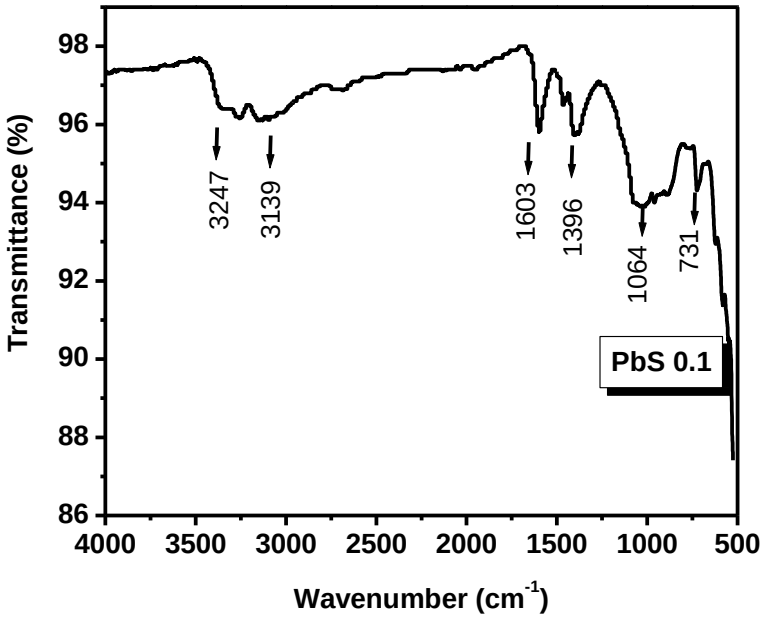


Fig 4: FTIR spectra of PbS thin film

The FTIR spectra of PbS thin film was recorded in the frequency range 500 to 4000 cm^{-1} range using Nicolate i18 spectrophotometer and shown in Figure 4. From the spectrum, the broad band at 3500 to 1700 cm^{-1} is assigned to O-H bending vibration of the sample. This proves the moisture absorbing capacity of the sample. The frequencies due to hetero polar diatomic molecules of lead sulphide are confirmed by the peak at 731, 1064, 1396 and 1603 cm^{-1}[Borhade *et al.*, 2012].

UV-VIS ANALYSIS

Optical absorption spectra of PbS thin film deposited using chemical bath deposition method is studied using UV-vis spectrophotometer (Shimadzu) in the wavelength range 200 to 800 nm.

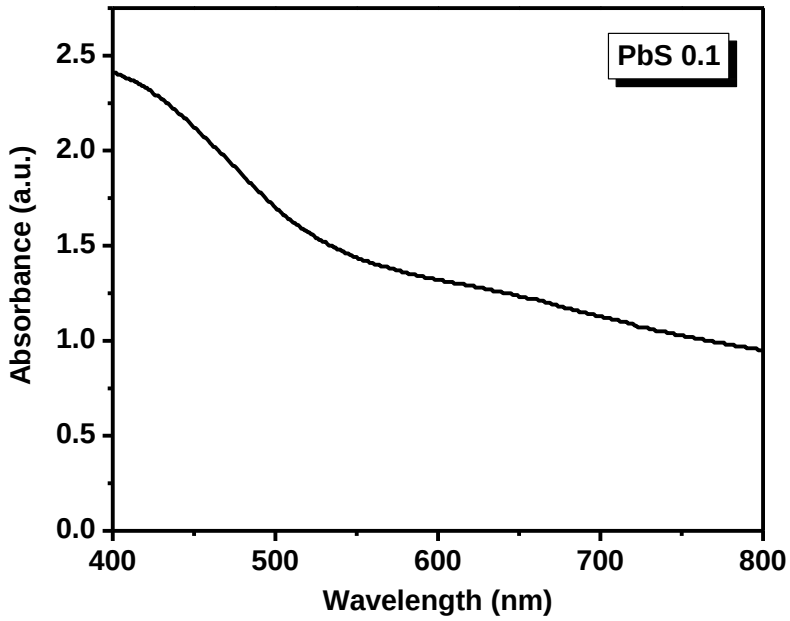


Fig 5: Absorbance spectra of PbS thin film

It is clearly seen from the Fig. 5 that the absorption edge is at about 550 nm.

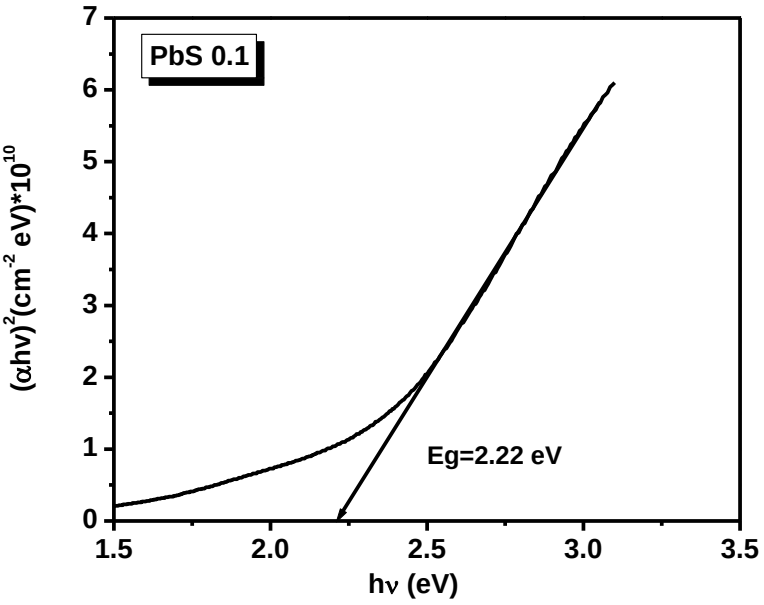


Fig 6: Plot of $(\alpha h\upsilon)^2$ versus hυ of PbS thin film

In semiconductors, the relation connecting the absorption coefficient α, the incident photon energy hν and optical band gap Eg takes the form

$$\alpha = \frac{A(Eg - h\nu)^n}{h\nu}$$

Where A is a constant related to the effective masses associated with the bands and n = 1/2 for a direct-gap material, and n= 3/2 for an indirect-gap material [Sakthivel *et al.,* 2015]. The energy band gap is determined from the plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ as shown in Figure 6 and the intercept of the extrapolated straight line on $h\upsilon$ axis give the value of Eg of the material. The band gap for PbS thin film was found equal to 2.22 eV.

ELECTRICAL ANALYSIS

The electrical resistance of CBD derived PbS thin film was measured in the temperature range 373 K to 473 K using two probe method. In a typical method two silver contacts were made on PbS thin film sample of area 1 Sq cm and variation of resistance with temperature is recorded. The PbS thin films are highly resistive in nature at room temperature. Figure 7 shows the variation of resistivity with temperature. It is clear from figure that the resistivity decreases with increasing temperature exhibiting semiconducting nature. The resistivity of thin film is measured using

$$\rho = \frac{Rbt}{l}$$

Where R is resistivity, t is thickness, b is breadth and l is length of thin film sample [Borhade *et al.*, 2012].

The resistivity of PbS thin film was calculated 4.92 Ω.cm at 473 K.

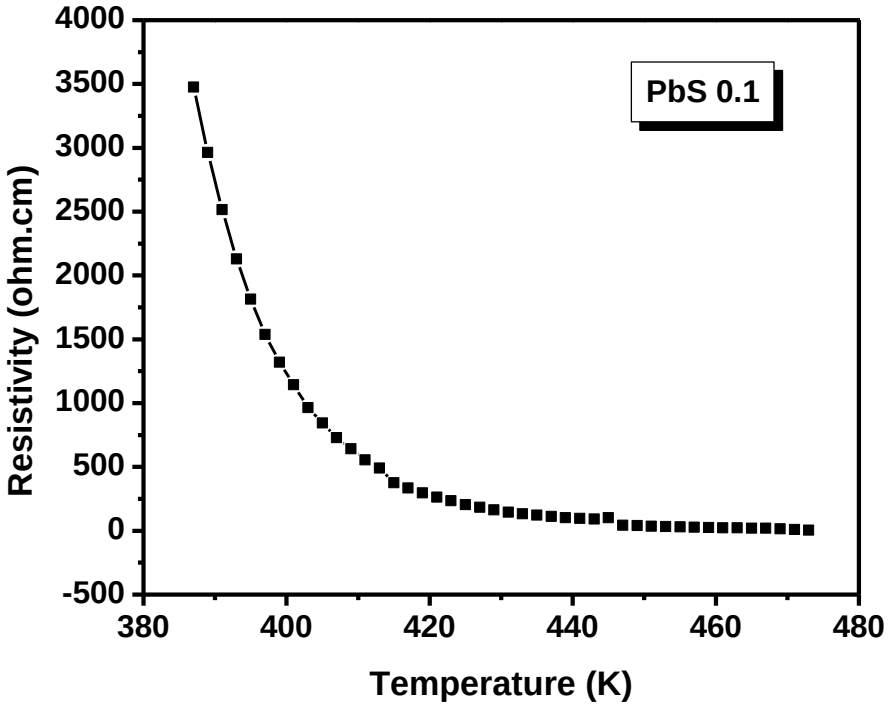


Fig 7: Resistivity versus Temperature of PbS thin film

CONCLUSIONS

A convenient, low cost and large area deposition technique viz. Chemical Bath Deposition (CBD) technique/method is used for deposition of PbS thin films. The deposition carried out for various concentration of lead sulfate at 60^{o}C. The 0.1 M concentration PbS films deposited for 90 minutes were good, adherent, homogeneous and blackish-grey in colour without any powdered precipitation. The thickness of the film deposited was about 400 nm. The obtained PbS thin films were characterized for structural, optical and electrical characterization using XRD, FTIR, UV-vis and Two probe resistivity measurement technique. XRD spectra revealed that PbS thin films exhibit face centered cubic structure with lattice constant a = 5.931 Å. The average crystallite size was calculated for (111) and (200) planes and was found 17.14 nm and 17.05 nm respectively. The FTIR spectra confirmed formation of diatomic molecules of lead sulphide. The energy band gap was estimated from UV-vis analysis equal to 2.22 eV. The semiconducting behavior of PbS thin films was confirmed from plot of resistivity against temperature. The resistivity of PbS thin film was 4.92 Ω.cm at 473 K.

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