Original Article

Cationic concentration and pH effect on the structural, morphological and optical band gap of chemically synthesized lead sulfide thin films

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ABSTRACT

Lead sulfide (PbS) thin films were deposited by chemical bath deposition method from two baths to study the effects of bath pH and lead ion concentration. The X-ray diffraction analyses revealed that all the films synthesized from the two baths were polycrystalline in nature. The XRD results also verified that the crystalline size decreased from 40 nm to 25 nm while lead ion concentration increased from 0.1 M to 0.3 M. Moreover, the XRD analyses confirmed that the highest strain was found from bath-A at a pH of 10.5. The elemental analyses were performed by EDX and it was confirmed that a better stoichiometric ratio was found for higher pH value. The optical absorption study revealed that the optical band gap of the PbS thin films found from bath-B decreased from 1.15 eV to 0.81 eV while the lead ion concentration decreased from 0.3 M to 0.1 M. Whereas, a higher optical band gap of 1.57 eV was found for pH = 10.5 from bath-A. Photoluminescence study revealed that the PbS thin film exhibited a broadband emission spectra from 410 nm to 625 nm with well defined twin peaks around 451 nm and 465 nm in the visible region. The PL emission spectra confirmed that emission intensity decreased gradually as the lead ion concentration decreased from 0.3 M to 0.1 M.

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1. Introduction

In recent years there has been an increasing interest in the synthesis of nanocrystalline materials due to their outstanding physical and chemical properties and their prospective applications [1]. Lead sulfide (PbS) nanocrystals among group IV–VI compound semiconductors have a face centered cubic crystal structure [2]. Since discovered early 19th, it attracted considerable attention due to their especially small direct band gap (0.41 eV, excitation edge of 3200 nm at 25 °C) and large exciton Bohr radius (∼18 nm) [3]. PbS exhibits strong quantum size effects below excitonic Bohr radius and hence the energy band gap of its nanocrystals can be tuned to anywhere between 0.41 eV and 5.2 eV [4]. Quantum sized PbS can be useful in many applications, particularly in electroluminescent devices such as light emitting diodes and high speed switching and IR detectors. PbS has been also recommended

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as an earth abundant sustainable material for affordable photovoltaic devices [5]. A wide variety of deposition techniques are used for coating PbS thin films like, successive ionic layer adsorption and reaction [6], hydrothermal process [7], spray pyrolysis [8], chemical vapor deposition [9] and chemical bath deposition (CBD) [10,11]. Among aforementioned methods, CBD is one of important techniques which attracting considerable attention due to its low temperature compatibility, large area deposition with better homogeneity and good reproducibility. The characteristics of chemically synthesized thin films strongly depend on the growth parameters like deposition time, bath temperature, concentration of reactants, bath pH, etc. [12]. The optimization of these deposition parameters leads to nanoparticles with different size and shapes exhibiting different structural, optical and electrical properties [13]. The physical properties of thin films such as film thickness, crystalline size, optical band gap and surface roughness can be easily controlled by varying the growth parameters for different optoelectronic applications. From the literatures it is noticed that there are several reports available on the synthesis of PbS thin films from low lead ion concentration (<0.15 M) [10,14,15], however, only few reports are found on the deposition of PbS thin films from high lead ion concentration [11,16]. It was also observed that the effect of lead ion concentration on the photoluminescence (PL) properties of PbS thin film is rarely reported. In the present work, the effect of lead ion concentration on the structural, morphological, optical band gap and PL properties of lead sulfide thin films were systematically investigated. Furthermore, effort had been made to optimize the deposition condition for relatively high lead ion concentration by varying the bath pH.

2. Synthesis of PbS thin films and characterization techniques

PbS thin films were deposited on silica glass substrate. In the present study, two baths with different chemical compositions were prepared to deposit PbS thin films in a 100 ml beaker. The first bath (bath-A) contained an aqueous solution of 5 ml lead acetate trihydrate, (7 ml) 0.25 M thiourea, sodium hydroxide and ammonia. Sodium hydroxide and ammonia were used as complexing agents and to get favorable pH. PbS thin films deposited at three different pH (10.5, 11.5 and 12.0) by changing the volume of ammonia. The total volume of the chemical bath was maintained 65 ml by adding enough amount of distilled water. The second bath (bath-B) was prepared by mixing 5 ml lead acetate trihydrate and 10 ml sodium hydroxide (0.25 M). Then about 5 ml ammonia (28%) added drop wise to use as a secondary complexing agent and to adjust the pH of the bath around 12 (optimal value obtained from bath-A). Thiourea (0.25 M) and 7 ml with some distilled water were added to obtain a final volume of 65 ml. Five different PbS thin films were synthesized by varying the concentration of lead acetate trihydrate from 0.1 M to 0.3 M per step of 0.05 M. In both deposition conditions the bath temperature was maintained at 70 °C. Chemically cleaned substrates were immersed vertically into the above prepared solutions and the reaction mixtures were maintained at a continuously magnetic stirring till the end of the deposition. After 30 min the samples were removed from the solution, rinsed ultrasonically with distilled water and dried under ambient conditions before film characterization. The crystallographic structure of PbS thin films was characterized by Bruker D8 advance diffractometer with CuKα (1.5406 Å) radiation and the machine was operated at 40 mA and 40 kV. The elemental composition and surface morphology of the samples were studied using energy dispersive X-ray analysis (EDX) equipped with a high resolution JEOL JSM-7800F field-emission scanning electron microscope (FESEM). High resolution transmission electron microscopy (HRTEM) model TECNAI F30 S/TEM used to investigate shapes and crystallographic nature of PbS thin films. The absorption spectrum was examined by Perkin Elmer Lambda 950 UV–Vis–NIR Spectrophotometer within the wavelength range of 250–2000 nm. Room temperature photoluminescence spectroscopy (PL) measurements were carried out by use of F-7000 FL Spectrophotometer. The excitation source was a Xenon lamp coupled to a monochromator interfaced with computer in front-face configuration. The PL spectra were measured in luminescence mode with canning speed 240 nm/min.

3. Results and discussion

3.1. X-ray diffraction analyses

Fig. 1 shows the XRD patterns of PbS thin films for Bath-A (Fig. 1a) and Bath-B (Fig. 1b). The diffraction patterns were well matched with the standard JCPDS data file reference code: 005-0592 Galena for face centered cubic crystal structure. The XRD result (see Fig. 1a) revealed that the PbS thin film deposited at a pH of 10.50 had very weak diffraction peak along the (200) plane. As the bath pH increased the intensity along the (111) plane increased significantly, moreover, new diffraction peaks were emerged. This phenomena is an evidence of enhancement of the crystallinity nature of the prepared material [17]. For the pH less than 10.5 it was noticed a non-uniform and non-adherent thin film which peeled off easily. The films deposited from Bath-B (Fig. 1b) exhibited very sharp diffraction peaks corresponding to reflections from the (111), (200), (220), (311), (222), (400), (420) and (422) planes. This suggests that, PbS phase is stable and its formation is independent on the lead acetate concentration. However, as the lead ion concentration increased from 0.1 M to 0.3 M, the intensity of the diffraction peaks decreased. This may be attributed to the degradation of crystalline size because of a gradual precipitation of PbS due to excess of Pb^{2+} ions in the chemical bath solution. The XRD studies verified that varying pH and the lead ions concentration had a significant effect on the preferred orientations of the crystallites. The films deposited at lower pH ≈ 10.5, had a preferred orientation along the (200) plane but it was changed to the (100) plane when the chemical bath pH to the JM: Correction made in Fig. 1 caption is inappropriate. Kindly advise.

H increased to 12. Similarly, for the films deposited at 0.1 M, 0.2 M and 0.25 M, the crystallites had a preferred orientation along the (111) plane, whilst for 0.15 M and 0.3 M, the crystallites had grown along the (200) plane. This indicates that the orientation of the grains growth along different diffraction planes depending on the lead ions concentration. On the basis of the thermodynamics principle the basic reason for
variation of preferred orientation is the change of the total system free energy during the film growth [18]. This behavior of such preferred orientation changing was observed in many other works [10]. The average crystallite size (D) was calculated from the FWHM found from X-ray diffraction pattern, using the Debye–Scherrer formula [10]. The crystallite size calculated from bath-A and bath-B was in the range of 12–25 nm and 40–25 nm, respectively (see Table 1). The result suggested that the crystallite size increased while the pH of the chemical bath increased. This may likely alter the involved reactions in the bath to produce films with larger grain size when the pH increased in the chemical bath. Similar observation was reported by [19].

In the contrary, the crystallite size calculated for the PbS thin films from bath-B was decreased as the concentration of lead acetate increased (see Table 1). This inverse relationship between crystallite size and lead ion concentration are rarely reported. When the Pb$^{2+}$ ions concentration increased in the chemical bath, rapid precipitation of PbS may occurred, hence only fewer ions were available for film formation, so thinner films formed, resulting in the formation of small grain sizes. The average thickness of the thin films was measured by weight difference method and found in the range of 125–342 nm and 285–627 nm for bath-A and bath-B, respectively. It was noticed that as pH > 12.5 and the concentration of lead acetate increased further (>0.3 M), a lot of dark precipitation, non-uniform and very thin film was found. Lattice constant (a$_{hk0}$) for the cubic structure was calculated using Eq. (1) and the results are presented in Table 1.

\[
a_{hk0} = d_{hk0} \sqrt{h^2 + k^2 + l^2}
\]  

(1)

The calculated value of the lattice constant ‘a$_{hk0}$’ of the films show a slight deviation from its standard value of 5.936 Å (see Table 1). The deviation of the calculated lattice constant from the bulk sample value shows that the crystallites may be under some strain [20], due to the lattice mismatch between material and substrate and other crystallographic defects that may be present in the thin film [21]. The microstrain value (\(\varepsilon\)) of the as-deposited PbS thin films were calculated from the mathematical relation in Ref. [12]. The origin of strain may be related either to lattice ‘misfit’ with the grown substrate or depends upon the growing conditions of the films [22]. The other structural parameter calculated was the dislocation density (\(\eta\)), which is a measure of the defects in the film [20], and this was calculated using Williamson and Smallman’s formula [23]. Strain and dislocation density were calculated from the (200) plane for bath-A and the (111) plane for bath-B and the results are tabulated in Table 1. The values of strain calculated in this study are in good agreement with previously reported works [11]. Relatively large dislocation density was observed

![X-ray diffraction patterns of PbS thin films](image_url)

**Table 1 – Crystallographic parameters of PbS thin films deposited from bath-A and bath-B.**

<table>
<thead>
<tr>
<th>Deps. conditions</th>
<th>Bath-A</th>
<th>Bath-B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH = 10.5</td>
<td>pH = 11.5</td>
</tr>
<tr>
<td>Crystallite size (nm)</td>
<td>12.52</td>
<td>18.02</td>
</tr>
<tr>
<td>Lattice constant (nm)</td>
<td>5.951</td>
<td>5.942</td>
</tr>
<tr>
<td>Strain ((\times 10^{-5})) lines$^{-2}$ m$^{-4}$</td>
<td>25.847</td>
<td>14.302</td>
</tr>
<tr>
<td>Dislocation density ((\times 10^{15})) lines/m$^2$</td>
<td>63.796</td>
<td>30.795</td>
</tr>
</tbody>
</table>

NB: The optimized lead concentration in bath-A was 0.25 M and the optimized pH in bath-B was 12.
at pH = 10.5, this showed that the film has comparatively lesser degree of crystallinity [20].

It was observed that the strain and dislocation density were decreased with increasing crystallite size for both baths (see Table 1). This may be due to a decrease in the occurrence of grain boundaries because of an increase in the crystallite size [24].

3.2. Elemental analyses

Fig. 2 shows the representative EDX patterns of PbS thin films from bath-A and bath-B. The EDX spectra of the PbS thin film deposited at a pH of 10.5 (Fig. 2a) displayed several peaks at different energy values, which correspond to the Pb and S elements, but the strong peak is from silicon. This is as a result of the formation of very thin film at this pH. The presence of silicon in the EDX analysis is due to the composition of the silica glass substrate used for the deposition. However, for the higher pH around 12 the EDX pattern of PbS thin film showed strong peaks from Pb and S elements (see Fig. 2b) and the average atomic percentage improved considerably (see Table 2). Similar report was forwarded by [21]. In the present study, the EDX results verified that varying the chemical bath pH had a vital role on stoichiometric ratio of chemically deposited PbS thin films (see Table 2). However, no such significant variation was noticed as the lead acetate concentration changed from 0.1 M to 0.3 M. The EDX study further established that irrespective of the deposition conditions all the deposited PbS thin films were lead rich. As a consequence, some defects like S vacancies or Pb interstitial will be inhibited at a certain level, which will facilitate the application of PbS thin film in photovoltaic devices.

3.3. Scanning electron microscopy (SEM) studies

The FESEM images of chemically deposited PbS thin films from bath-A and bath-B are displayed in Fig. 3. The SEM micrograph of PbS thin film deposited at a pH of 10.5 (Fig. 3a) shows very small spherically shaped grains with different sizes and distributed over a smooth homogenous background without visible defects. Moreover, large isolated clusters of spherically shaped grains were observed on some parts of the micrographs indicating irregular growth rate of the grains. The formation of such aggregate grains on the PbS thin film surface is a typical future of the CBD technique. As the chemical bath pH increased (see Fig. 3b), the surface morphology of the PbS thin film becomes more homogenous and covered the substrate very well. Also, the grain sizes were noticed to increase gradually, which is consistent with the XRD results. Furthermore, it was noticed that shape of the grains changed from spherical to a mixture of cubic and pyramidal shape as the pH was changed from 10.5 to 12.0.

The different growth rates on the (200) and (111) plans may lead to the formation of the spherical and pyramidal PbS crystals. Similar observation was reported by [25]. The SEM morphology of PbS thin films deposited from bath-B (see Fig. 3c), exhibited densely compact and sharp edges of the grains cover the entire surface without any visible defects, like cracks or pinholes. Increase in grain size favors coalescence between each grains during lateral growth, which in turn explains increase in compactness of the deposited films [26]. Further increased of the lead acetate concentration does not show significant change in surface morphology (see Fig. 3d and b). The grain sizes estimated from SEM images are larger than those obtained by Scherrer formula. This can be attributed to lager clusters deposited on the surface of the film due to an aggregate structure composed of small crystals or grains [27]. Such grain size discrepancy between XRD and SEM were reported by several researchers [28].

3.4. High resolution transmission electron microscope (HRTEM) studies

Fig. 4 shows a high resolution of representative TEM micrographs of the PbS thin films.

The TEM micrographs clearly show the lattice fringes in HRTEM images (Fig. 4a and b) confirm the perfect order of the crystalline lattice of the PbS thin films. The d-spacing of 0.341 nm, 0.296 nm and 0.210 nm corresponds to the (111), (200) and (220) planes of the face center cubic (fcc) crystal structure of PbS respectively (see Fig. 4a). Similarly, the d-spacing of 0.297 nm and 0.211 nm corresponds to the (200) and (220) planes of the fcc PbS respectively (see Fig. 4b). In general, Fig. 4a and b plainly shows that the grains are grown along different planes which confirm a typical polycrystalline nature of the deposited PbS thin films from both baths. These observations are consistent with the XRD results.

3.5. Optical studies

3.5.1. Optical band gap determination

The optical band gap and transition type of nanocrystalline PbS thin films synthesized from the two baths were determined from the Stern relation of near-edge absorption which is given as [12].

\[
(Ahu)^2 = \left[ \frac{k(\hbar \nu - E_g)}{n} \right]^n
\]

(2)

where \( \nu \) is the frequency, \( h \) is the Planck’s constant, \( k \) is a constant, while \( n \) carries either 1 or 4 depending on the optical transition. Since PbS is a direct band gap material [8], and \( n \) was taken as 1. Fig. 4 presents the Stern plot of \((Ah)^2\) versus \((h\nu)\) for the PbS thin films synthesized from bath-A and bath-B. The band gap values of the films were estimated by extrapolating the linear portion of the plots to the energy axis zero. The plot of \((Ah)^2\) versus \((h\nu)\) shown in Fig. 5 is linear at the absorption edge which indicates the presence of direct transition. The optical band gap of the PbS thin films obtained from bath-A and bath-B were estimated in the range of 1.05–1.57 eV and 0.81–1.15 eV, respectively. The results verified that the optical band gap was decreased when the pH was increased, but a direct relationship was observed in the second chemical bath. The observed variation of optical band gap may be attributed to the variation of the average crystallite size, dislocation density and microstrain of the material with bath pH and lead concentration in the respective baths [17]. The optical band gap values of all the PbS thin films found from the two chemical baths are listed in Table 2. In this study the estimated band gap for PbS thin films from both baths shows a significant blue shift from the bulk value of 0.41 eV. For the thin films deposited
Fig. 2 – EDX spectra of PbS thin films: (a) at pH = 10.50 (bath-A), (b) at pH = 12 (bath-A and bath-B).

Table 2 – EDX and optical band gaps of PbS thin films deposited from bath-A and bath-B.

<table>
<thead>
<tr>
<th>Deps. conditions</th>
<th>Bath-A</th>
<th>Bath-B</th>
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<tbody>
<tr>
<td></td>
<td>pH = 10.5</td>
<td>pH = 11.5</td>
</tr>
<tr>
<td>Pb (at. %)</td>
<td>55.79</td>
<td>53.51</td>
</tr>
<tr>
<td>S (at. %)</td>
<td>44.21</td>
<td>46.49</td>
</tr>
<tr>
<td>Eg (eV)</td>
<td>1.57</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Fig. 3 – FESEM images of PbS thin films deposited from bath-A and bath-B.
emission

Fig. 4 – Interplanar distances of PbS thin films: (a) 0.1 M and (b) 0.25 M.

Fig. 5 – A graph of (Aνν)² plotted as a function of the photon energy for PbS thin films deposited from (a) bath-A and (b) bath-B.

from pH = 10.5 and 11.5, this appreciable band gap shift may be due to quantum size effect exhibited by the nanocrystals present in PbS film [28]. But for the rest of the thin films, the quantum confinement effect may not be significant since the crystallite size is greater than 18 nm. The band gap tunability of the films having larger crystallite sizes beyond the quantum confinement regime may have different mechanisms [29]. For instant, defects like vacancies, interstitials, grain boundaries, stacking faults, etc., can act as trap centers and affect the optical absorption. Therefore, an increase in optical band gap can be associated with defect-induced band tailing due to the creation of localized energy states near the band gap [30].

3.5.2. Photoluminescence (PL) studies

PL is a process in which an electron excited by a monochromatic photon beam of certain energy undergoes non-radiative/radiative recombination either at valance band or at traps/surface states. The band edge luminescences in general are weak, whereas efficient luminescence transfer occurs at traps/surface states [4]. The photoluminescence emission spectra of PbS thin films for different cationic precursor concentrations are displayed in Fig. 6a. The measurement was made at an excitation wavelength of 308 nm using a Xenon lamp at room temperature. The PL spectra showed broadband emission in the range of 410–625 nm with well defined twin peaks at 451 nm and 465 nm and a shoulder at 526 nm in the visible region. Such twin peaks emission was reported by [31]. Such broadband PL emission with different emission wavelengths have been reported in previous works from UV to infrared regions under various deposition conditions, which suggest more comprehensive investigation still needed for PbS compound. Kaci et al. [32] observed an intense and broadband emission for PbS thin film at excitation of 230 nm. The broad emission peaks were at 367, 386, 411, 448, 475 and 533 nm. Tohidi et al. [33] also reported a broadband emission for PbS thin film prepared at differ deposition time and they found two emission peaks at 351 nm and 451 nm with an excitation of 320 nm. Bulk PbS semiconductor is narrow direct band gap of 0.41 eV at room temperature, which gives rise emission about 3024 nm. But in this study, all the PL spectra showed a blue-shift similar to the absorption results. The shifting of the emission wavelengths from 3024 nm to 451 nm
can be ascribed to a high level transition in PbS semiconductor crystallites [34]. It has been reported that this kind of band edge luminescence arises from the recombination of excitons and/or sub-band gap surface states [35]. The peak at 465 nm is due to the transitions of trapped electrons to the valence band from donor levels [36]. The green band emission around 526 nm originated from the transition of the increased donors to recombine with S interstitials acceptors in the valence band [36]. According Fig. 6a, as the lead ion concentration increased the peak around 465 nm gradually decreased and disappeared at 0.1 M. It is worth enough to highlight here that, in comparison with colloidal quantum dots, CBD films are generally not deliberately passivated and both the intensity and spectral shape can vary considerably without any obvious reason [33].

The maximum emission peak was observed for 0.3 M lead ion concentration (see Fig. 6a). Several research results verified that the luminescence intensity depends on the surface area of the grains. The materials with smaller crystallites size shows higher luminescence intensity compared to the larger crystallites [37]. Similar trained was observed in the present study (see Fig. 6b). In thin film, the number of ions on the surface quickly increases as the crystalline size decreases (higher surface-to-volume ratio). Furthermore, carrier recombination rate increases as size decreases because of the increase in overlap between the electron and hole wave functions. These two effects may cause PL to increase as particle size decreases [38]. In the present study the PL result verified that the PL emission spectra position of the peaks remain the same for all PbS thin films which infer that they exhibit the same crystal structure irrespective of lead ion concentration which is consistent with XRD results.

4. Conclusion

Lead sulfide thin films were synthesized by chemical bath deposition method from two different baths at a bath temperature of 70 °C. The effect of the lead ions concentration and bath pH on the films structural and optical properties has been well established. The XRD results confirmed that varying the pH and lead ions concentration had a significant effect on the preferred orientations of the crystallites. This indicates that the orientation of the grains growth along different diffraction planes depending on the bath pH and lead ions concentration. The crystallite size calculated using Scherrer formula were in the range of 12–25 nm and 40–25 nm for bath-A and bath-B, respectively. The EDX results verified that varying the bath pH had a vital role on stoichiometric ratio of PbS thin films but there was no significant stoichiometric ratio variation was observed as the lead acetate concentration changed. The optical band gap of the PbS thin films obtained from bath-A and bath-B were estimated in the range of 1.05–1.57 eV and 0.81–1.15 eV, respectively. The PL study revealed that the PbS thin film exhibited a broadband emission spectra from 410 nm to 625 nm with well defined twin peaks at 451 nm and 465 nm and a shoulder at 526 nm in the visible region.

Conflicts of interest

The authors declare no conflicts of interest.

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