REVIEW

Structural, morphological, optical, and photoluminescence properties of nanocrystalline PbS thin films grown by chemical bath deposition

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Received 21 July 2014; accepted 24 November 2014

KEYWORDS
Lead sulfide films; CBD; XRD; Optical properties; SEM

Abstract  The transparent and nanocrystalline lead sulfide (PbS) thin films were prepared by the chemical bath deposition (CBD) technique onto glass substrates deposited at 80 °C using aqueous solution of lead acetate and thiourea. The X-ray diffraction pattern proves the crystallinity of deposited films that crystallize in the orthorhombic structure and preferred orientation. The energy band-gap and refractive index were estimated using UV–visible absorption spectra. The variation in band-gap with grain size showed blue-shift typical of electron quantum confinement. The effect of crystal ordering on refractive index was also evident by the linear increase of the refractive index with grain size. The PbS thin films were characterized by XRD, optical and SEM analysis.

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Peer review under responsibility of King Saud University.
1. Introduction

In the recent years, a variety of binary semiconductor thin films especially from the IV–VI groups of periodic table have been studied due to their small energy gap and potential use in solar cells and sensors. In this view, lead sulfide (PbS) is an important direct narrow gap binary semiconductor material with relatively large excitation Bohr radius of 18 nm (Machol et al., 1993). This is the very important property for the applications of infrared detection (Gadenne et al., 1989). This PbS is also used in various applications such as ion-selective sensors, solar absorption, solar control coatings and diode lasers (Nair et al., 1992, 1991; Hirata and Higashiyama, 1971; Chaudhuri and Chatterjes, 1992; Pop et al., 1997; Obaid et al., 2012a,b, 2013; Carrillo-Castillo et al., 2012, 2014).

The energy band gap of bulk crystals and polycrystalline coarse – grained PbS thin films are approximately 0.37–0.4 eV at room temperature (Bube, 1992). So the optical constants such as refractive index, extinction coefficient of thin films are very important for optical sensor applications. Recently the size varied PbS nanoparticles (grain) are prepared that decreasing the size it generates the band gap of the PbS films increases. This gives the quantum confinement in PbS nanoparticles (Sadovnikov and Gusev, 2013). These properties make the quantum confinement effects more notable in PbS compared to other lead chalcogenides, even for relatively larger particle sizes. In this viewpoint, PbS has been grown in various forms by different techniques such as electro deposition (Sharan et al., 1997; Takahashi et al., 1993), spray pyrolysis (Thangaraju and Kaliannan, 2000; Agarwal and Pillai, 1982), photoaccelerated chemical deposition (Nair et al., 1991), vacuum evaporation (Kumar et al., 2003), solid vapor deposition (Obaid et al., 2012a,b), microwave heating (Ding and Zhu, 2003), SILAR (Kanniainen et al., 1996; Puis’o et al., 2003) and chemical bath deposition (Enriquez and Mathew, 2003; Popa et al., 2006; Seghaier et al., 2006; Abbas et al., 2011; Obaid et al., 2012a,b).

In general, the preparation of thin films has been used many methods such as dc magnetron sputtering (Li et al., 2009), pulse electro-deposition method (Cheng et al., 2007), thermal evaporation method (Shah et al., 2009), rf magnetron sputtering (Elanchezhiyan et al., 2009), spray pyrolysis method (Koteeswara Reddy and Ramakrishna Reddy, 2005) and chemical bath deposition method (CBD) (Mnari et al., 2009). When CBD is compared with the above methods, it is relatively easier, more rapid and inexpensive. Moreover, by using this method, a film can be deposited on large substrates irrespective of the shape and morphology of substrates nearly at room temperature. Due to this CBD method provides, it is found highly attractive by researchers aiming to obtain thin films (Pathan et al., 2002; Cortes et al., 2004; Gode and Gumus, 2009; Seghaier et al., 2006; Slonopas et al., 2015).

CBD technique is a thin film depositing method on a substrate from a solution, it comprises of a source of metal, hydroxide and sulfide or selenide ions (Nair et al., 1998). CBD has become an attractive method based on many reasons, including ease of manufacturing, low cost, suitability for large scale deposition areas and the ability to deposit thin films on different substrates and ease of controlling thin film properties by controlling the deposition parameters. The main advantage of this method is, during the growth of a film on a substrate, it is possible to ensure that the reaction occurring in the deposition bath takes place sufficiently slowly (Hodes, 2003). The film deposited by this technique has possible applications in solar absorbers and solar control coatings window glazing applications in warm climates, etc. (Pentia et al., 2001). So we are very much interested to prepare the PbS thin films using chemical bath deposition technique.

In the present work, a systematic investigation was carried out on lead sulfide thin films growth from chemical bath deposition technique. The films were characterized by X-ray diffraction (XRD), optical and scanning electron microscopy. From the optical study the optical constants such as refractive index, extinction coefficient and real and imaginary parts of the dielectric constant are evaluated for the prepared films.

2. Experimental details

The PbS thin films were grown on ordinary glass slide substrates. The deposition was done in a reactive solution prepared in a 100 ml beaker containing lead acetate \( \text{[Pb(C_2H_3O_2)_2\cdot3H_2O]} \), which concentration range 0.1 M. This reactive was mixed in alkaline aqueous solution with thiourea \([\text{CS(NH}_2)_2]\) at concentration 0.1 M. The alkalinity is set using sodium hydroxide [\( \text{NaOH} \)] at concentration 0.5 M. The pH of the solution was adjusted by adding a small amount of triethanolamine (TEA) was used as a complexing agent. The distilled water was added to the solution to achieve a total volume of 100 ml.

PbS thin films were deposited on properly cleaned glass substrates by chemical bath deposition (CBD) technique. This method is inexpensive and does not require sophisticated vacuum equipments. Before, the immersion of the glass substrates into the growth solution, they were mechanically cleaned with detergent and rinsed in bi-distilled water. Cleaned substrates was vertically immersed in water heating bath circulated placed on heating magnetic agitator was maintained at 80 °C and time taken 3 h. Then, they were glass substrates supported vertically and immersed into a deposition bath containing aqueous solutions. The reaction process can be considered as follows (Palomino Merino et al., 2013).
Properties of nanocrystalline PbS thin films

\[ \text{Pb(CH}_2\text{COO)}_2 \cdot \text{3H}_2\text{O + 2NaOH} \rightarrow \text{Pb(OH)}_2 \cdot \text{2CH}_3\text{COONa} \]

\[ \text{Pb(OH)}_2 \rightarrow \text{Pb}^{2+} + 2\text{OH}^- \]

\[ \text{CS(NH}_3)_2 + 3(\text{OH}^-) \rightarrow \text{CO}_3^{2-} + \text{S}^{2-} + 7\text{H} \]

\[ \text{Pb}^{2+} + \text{S}^{2-} \rightarrow \text{PbS} \]

After deposition, obtain good quality thin films deposition time, temperature and speed of rotation (60 rpm) were optimized. The films were cleaned by rinsing with tripped distilled water and then dried at room temperature. The deposition films were smooth, homogeneous, well adherent to the substrate with darker surface like mirror.

The crystallite structure and crystallography orientation of the films were characterized by X-ray diffraction technique using Bruker AXS D8 advance with CuKα line (\( \lambda = 1.5406 \text{ Å} \)). Morphology and microstructure of the films were examined by scanning electron microscopy (SEM) taken by JEOL model JSM 6490. Optical measurements were conducted at room temperature using Shimadzu UV–vis NIR ranging from 300 to 1100 nm.

3. Results and discussion

3.1. Structural analysis

In Fig. 1 shown the X-ray diffraction pattern obtained from the PbS thin films. The observed diffraction peaks were indexed within a cubic rock salt (NaCl) type structure, as confirmed using a standard card (JCPDS No. 05-0592) and they are represented by their corresponding miller indices in the spectra. The peaks with \( 2\theta \) values 26.03°, 30.14° and 79° correspond to the crystalline planes (111), (200) and (422) respectively. The narrow peaks show that the material has good crystalline nature and very strong preferentially oriented along the (200) direction which intensity is mainly depending on the deposition time. Moreover, the absence of any other peaks corresponding to metallic clusters and/or impurities reveals good quality of the films. The average crystallite size (74 nm) was estimated using Debye-Scherrer formula (Yu and Shengshui, 2008).

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

where \( k \) is a constant (0.94), \( \lambda \) is the XRD wavelength (0.15418 nm) and \( \beta \) is the full width at half maximum (FWHM) of a defined diffraction peak. The crystalline size indicates the nanocrystalline of the film. To increase the band gap of the semiconducting materials as the particle size decreases this is the effect of quantum confinement. It is caused by localization of electrons and holes in a confined space resulting in observable quantization of the energy levels of the electrons and holes. This idea behind confinement is all about keeping electrons and holes trapped in a small area (Nalwa, 1999). For, PbS films deposited on glass, the nucleation rate is considered to be larger than the growth rate due to the great number of nucleation centers that exit on the surface of the substrate. This could explain why PbS films deposited on glass are compact and with a small size of crystallites. The lattice constant of the cubic rock salt structure is given by Preetha et al. (2012),

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

Deviation of the calculated lattice parameter \( a' \) from the strain face bulk sample \( (a_0 = 5.936 \text{ nm}) \) indicates that the as prepared films were under strain. The average stress and microstrain were determined by the relation (Barett and Massalski, 1996),

\[ S = \frac{\rho}{2\sigma} \]

\[ \varepsilon = \frac{a_0 - a}{a_0} \]

where \( a_0 \) is the lattice parameter of the cubic rock salt structure, \( \sigma \) is the Young's modulus of the cubic rock salt structure and \( \varepsilon \) is the Poisson's ratio of the cubic rock salt structure respectively. For PbS the value of \( y \) is 70.2 GPa and \( \sigma \) is 0.28. The correct values lattice constants are estimated from the Nelson–Riley plots. For this the lattice parameters calculated from the peak positions of individual reflections are plotted against \( 1/2\cos^2 \theta(1/\sin^2 \theta + 1/\theta) \) and the intercept of the linear plot at \( 1/2\cos^2 \theta(1/\sin^2 \theta + 1/\theta) = 0 \) gives the lattice constant. Fig. 2 represents the plot of lattice constant \( (a) \) against \( 1/2\cos^2 \theta(1/\sin^2 \theta + 1/\theta) \) of the as deposited PbS thin films. The estimated value of lattice parameter for the PbS thin film is approximately equal to 5.93 Å. This value is close to the lattice parameters reported for PbS \( (a = 5.936 \text{ Å}) \) (Barett and Massalski, 1996). The various structural parameters e.g., corrected values of lattice constant \( a' \), average internal stress \( S \) and dislocation density \( \varepsilon \) for PbS

Please cite this article in press as: Rajathi, S. et al., Structural, morphological, optical, and photoluminescence properties of nanocrystalline PbS thin films grown by chemical bath deposition. Arabian Journal of Chemistry (2015), http://dx.doi.org/10.1016/j.arabjc.2014.11.057
thin films are calculated and systematically represented in Table 1.

From the compositional analysis, the atomic percentage of PbS films has been calculated, the ratio of Pb and S is 48.98 and 51.02 respectively. Also we can observe that the composition of the films is close to stoichiometry (Pb:S).

### 3.2. Optical properties

In this work, we study the influence of the deposition parameters on the optical properties of chemically deposited PbS films. These studies constitute most important means of determining the band structures of semiconductors. The first part will be devoted to the study of the transmittance and reflectance spectra. The second will proceed in energy band gap of PbS thin films. The third part will proceed in determining the refractive index, dielectric constant, and optical constant of surface using an ellipsometer. Transmittance and reflectance measurements at near normal incidence were performed over a spectral ranging between 300 and 1100 nm on PbS thin films deposited on glass substrate with optimal deposition parameters. The optical transmission spectra of PbS films are shown in Fig. 3. In this case, the thickness of the film is 742 nm and estimated $E_g$ values are found to be 1.8 eV, respectively for films deposited at 80 °C.

Using the calculated absorption coefficient values, the type of electronic transition associated with band structure of PbS can be identified using

$$
\alpha = \frac{A(h\nu - E_g)^m}{h\nu} \text{cm}^{-1}
$$

where $m$ is a constant associated with the type of electronic transition that means the valence band to conduction band a strong electronic absorption, $E_g$ is the band gap extracted after extrapolation of the plot at $x = 0$, $A$ is a constant which is related to the effective mass associated with the bands and $h\nu$ is the energy of the incident photon. The band gap energies were determined from the transmittance by zero crossing extrapolation in a linear fitting of $(h\nu)^2$ vs $h\nu$ is the photon energy as indicated in Fig. 4. On the other hand, the extinction coefficient of the PbS films is given by following relation:

$$
k = \frac{2\lambda}{4\pi}
$$

The reflectance in terms of absorption coefficient is derived.

$$
R = \frac{1 + \sqrt{1 - \exp(-xd\nu) + \exp(xd\nu)}}{1 + \exp(-xd\nu)}
$$

The dependence of the band gap $E_g$ on the PbS films was determined from the optical transmission spectra. The spectral region most informative for determining the band gap from the optical spectra is the region, where in the transmittance exhibits a noticeable variation depending on the wavelength $\lambda$. Taking this into account, it can be supposed that the PbS films produced here exhibit a blueshift of the optical absorption band. In fact, a decrease in the size of semiconductor nanoparticles should be accompanied by a shift of the absorption band to the high frequency region. It is noticed that the transmission decreased with increasing film thickness, which leads to a decrease in light scattering losses. This finding may be attributed to the increase in particle size as film thickness increased, thus leading to a decrease in transition. Transmission increased with increasing wavelength toward near infrared (NIR) region. For low wavelengths, there is no transmission because all the light is absorbed, while the steady state in NIR regions resembles the absorption spectra. Fig. 5 shows the variation of refractive index with wavelength for PbS films deposited at RT.

The refractive index is given by

$$
n = \frac{-(R + 1) \pm \sqrt{(-3R^2 + 10R - 3)}}{2(R - 1)}
$$

Also the complex dielectric constant is related to the refractive index ($n$) and the extinction coefficient as

<table>
<thead>
<tr>
<th>$2\theta$ (°)</th>
<th>$d$ (Å)</th>
<th>Crystallite size ($D$) (nm)</th>
<th>$hkl$</th>
<th>$a$ (Å) (calculated)</th>
<th>$a$ (Å) (standard)</th>
<th>$S \times 10^6$ (N/m$^2$)</th>
<th>$\delta \times 10^{-3}$ (nm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.034</td>
<td>3.4199</td>
<td>74</td>
<td>111</td>
<td>5.9234</td>
<td>5.9392</td>
<td>0.1250</td>
<td>1.7839</td>
</tr>
<tr>
<td>30.141</td>
<td>2.9626</td>
<td>95</td>
<td>200</td>
<td>5.9234</td>
<td>5.9380</td>
<td>0.1251</td>
<td>1.0920</td>
</tr>
<tr>
<td>79</td>
<td>1.2114</td>
<td>1.12</td>
<td>422</td>
<td>5.9346</td>
<td>5.9375</td>
<td>0.1253</td>
<td>0.3099</td>
</tr>
</tbody>
</table>

Table 1 Structural parameters of PbS thin films.
where the real and imaginary dielectric constant are

\[ \varepsilon_r = n^2 - k^2 \]  

(10)

\[ \varepsilon_i = 2nk \]  

(11)

The optical conductivity is a measure of the frequency response of the material when irradiated with light

\[ \sigma_{op} = \frac{2\pi c \varepsilon_0}{\lambda} \]  

(12)

where \( c \) is the velocity of light. The electrical conductivity can also be estimated by optical method using the relation

\[ \sigma_e = \frac{2\pi \varepsilon_0 \sigma_{op}}{\lambda} \]  

(13)

These figures indicate that \( n \) decreases with increasing \( \lambda \) within the range 2.4–3.49. Figs. 6 and 7 depict the real (\( \varepsilon_r \)) and imaginary (\( \varepsilon_i \)) parts of the dielectric constants. It is clear that the variation of dielectric constant follows the same trend as \( n \), since \( k < n \) (where \( = n^2 - k^2 \)) whereas the dielectric constant variation mainly follows the behavior of \( k \) which is related to the variation of wavelength.

From the recorded absorption spectra, the optical constants of PbS calculated and the variation of optical constants as a function of wavelength is plotted. The optical conductivity and electrical conductivity are shown in Figs. 8 and 9. It is
interesting to note that the inclusion of material PbS decreased the optical conductivity, refractive index and increased the electrical conductivity of the material.

3.3. Photoluminescence properties

The room temperature photoluminescence emission spectra of the nanocrystalline PbS thin film are shown in Fig. 10. The emission peak was observed at wavelength 355 nm when the sample was excited at 490 nm. This emission wavelength peak shifted toward to blue when compared to the bulk PbS. This emission is due to the recombination of electron and hole pair. Intensity of photoluminescence has been increased due to surface passivation of PbS films. The remaining two peaks centered at longer wavelengths 399 nm and 477 nm are due to the transitions in nanocrystalline PbS films.

Figure 11  FTIR spectrum of PbS thin film.

Figure 12  Scanning electron micrograph of PbS thin film.
Properties of nanocrystalline PbS thin films

3.4. FTIR

The FTIR spectra of nanocrystalline PbS thin films are shown in Fig. 11. It shows the weak and medium Pb–S bonding for 427.53 and 477.65 cm\(^{-1}\). The spectra exhibit the vibrational frequency at 3419.10 cm\(^{-1}\) for O–H stretching. It also shows 1338.90 and 1220.10 cm\(^{-1}\) means for improved crystallinity with C–O stretching mode of vibrations. The N–H group of vibrations is observed at 1686.42 and 1597.87 cm\(^{-1}\). The CH\(_2\) bending vibrations are observed in the range of 1482.79 and 1441.44 cm\(^{-1}\). The weak peak absorbed at 1220.10 cm\(^{-1}\) is due to the presence of C–O group in the compound. These functional groups exist in irrespective of present growth conditions and similar harmonics were also found in the literature (Wu, 2003; Pasha et al., 2012; Kumar et al., 2009; Chernyshova, 2001).

3.5. Surface morphology

The morphology of the nanocrystalline PbS thin films was investigated using SEM as shown in Fig. 12. Descriptions of the films in terms of size and morphology of nanocrystalline PbS for samples prepared using CBD method. Highly uniform and adherent PbS films are obtained. It is observed that the film is smooth, homogeneous, excellently covered to the substrate and shows the individual clusters of PbS films. The surface of the deposited PbS layer shows clusters in a relatively loose compact structure. The clusters are constituted by nanocrystalline grains and separated in some cases by voids disappear in the surface. For PbS films deposited on glass the nucleation rate is considered to be larger than the growth rate due to the great number of nucleation centers that exist on the surface of the substrate. This could explain why PbS films deposited on glass are compact and with a small size of particles.

4. Conclusion

In this study, PbS nanocrystalline thin films were successfully prepared using the CBD method. The synthesized thin films were of good quality. From structural analysis we can conclude that the best crystallinity and the great adhesion of PbS on glass substrate are obtained by employing lead acetate, sodium hydroxide thiourea and triethanolamine formed by lead sulfide compound with the centered cubic structure preferentially oriented according to the (200) perpendicular direction to the plane of the substrate. The high transmittance and low reflectance properties make the film good materials for house heating for solar chick brooding and antireflection in flat-plate collectors. The band gap of nanocrystalline PbS thin films is found to be 1.8 eV which is higher than the bulk due to quantum confinement of PbS nanocrystalline. Photoluminescence spectroscopy shows the emission at 355–490 nm. The FTIR study of PbS nanocrystalline shows that the presence of difference functional groups and presence of PbS. SEM analysis revealed the formation of cubic shaped particles with uniform size of the distributions.

References


