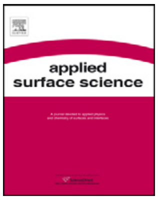
Applied Surface Science 258 (2011) 1869–1875

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc



Facile and low cost chemosynthesis of nanostructured PbS with tunable optical properties

S.B. Pawar[a,*], J.S. Shaikh[b], R.S. Devan[c], Y.R. Ma[c], D. Haranath[d], P.N. Bhosale[a], P.S. Patil[b]

[a] *Materials Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur 416 004, M.S., India*
[b] *Thin Film Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416 004, M.S., India*
[c] *Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan, ROC*
[d] *National Physical Laboratory, Council of Scientific and Industrial Research (CSIR), New Delhi 110 012, India*

ARTICLE INFO

Article history:
Received 19 July 2011
Received in revised form 13 October 2011
Accepted 13 October 2011
Available online 20 October 2011

Keywords:
Chemical bath deposition of PbS
Quantum size effect
Optical
PL
XRD
XPS
FT-IR

ABSTRACT

The present work reports on the chemosynthesis of nanocrystalline lead sulphide (PbS) thin films by a facile and cost-effective chemical bath deposition (CBD) method onto soda-lime glass substrates. The X-ray diffraction (XRD) pattern shows the formation phase pure PbS with cubic crystal structure. Electronic structures and chemical states of PbS film have been performed by X-ray photoelectron spectroscopy (XPS). Field emission-scanning electron microscopy (FESEM) images show the transition from granular-to-cubic-to-cubo-octahedra like surface morphology with the increase in the deposition time from 20 to 90 min. The UV–vis–NIR absorption spectra of PbS thin films are measured, and a classical Tauc approach was employed to estimate their band gap energies. The increase in band gap energy from 0.99 to 2.06 eV with the reduction in crystallite size evinces quantum size effect. This work demonstrates a simple and effective solution approach to deposit PbS nanostructured thin films having predominant quantum confinement. This approach would be helpful in nano-PbS sensitized oxide based solar cells, which are recently under intensive investigations.

1. Introduction

The lead sulphide (PbS) is an important direct narrow-band gap IV–VI semiconducting material with a bulk band gap of 0.41 eV at 300 K [1]. The optical properties of nanocrystals are strongly depending on its size and shape [2]. The exciton Bohr radius for PbS, PbSe and PbTe chalcogenides are 18, 46 and 152 nm making them an interesting material to study the quantum effects over the wide range of particle size [3]. Quantum size effects are usually characteristic of nanocrystallites measuring less than 10 nm. Due to this effect band gap of the material increases as the size of the particle decreases. This property makes it an excellent candidate for opto-electronic applications in many fields such as photography, IR detectors, solar absorbers, light emitting devices and solar cells [4–8]. Various nanostructures such as nanotubes, nanorods, star-shaped and dendrites of PbS have been synthesized using surfactant-assisted solution growth, chemical bath deposition (CBD), nonhydrolytic colloidal routes, polyol-mediated synthesis and electrochemical methods [9–12].

Among aforementioned methods, CBD has its own advantages such as simplicity, reproducibility, nonhazardous, cost effective and well suitability for large area deposition. Moreover, we can grow various morphologies of semiconducting materials by adjusting the growth parameters like pH of growth solution, deposition time, temperature and addition of different additives in bath. Furthermore, it facilitates better orientation of crystallites with improved grain structure.

In the present work, we have reported the synthesis of nanostructured PbS thin films with tunable optical properties by CBD method. The deposited PbS films exhibit highly dense and well-defined grains with compact structure over the entire substrate. Further, the effect of deposition time on crystallinity, morphology and optical properties is studied in detail. The possible growth mechanism of nanosphere and nano cubo-octahedron is discussed.

2. Experimental details

2.1. Thin film deposition

Aqueous solutions of 0.1 M lead acetate [$Pb(CH_3COO)_2{\cdot}3H_2O$] and 1 M tri-sodium citrate [$Na_3C_6H_5O_7$, c.a. TSC] was taken in a beaker. Initially, the solution becomes turbid and milky due to the complex formation. Then the solution of 1 M sodium hydroxide [NaOH] was added into above solution to dissolve the complex and

---

* Corresponding authors. Tel.: +91 231 2609229; fax: +91 231 2691533.
E-mail addresses: pawar_sarita@yahoo.com (S.B. Pawar), psp_phy@unishivaji.ac.in (P.S. Patil).

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.10.069

to keep pH of solution at ∼12. Finally, 0.5 M thiourea [$(NH_2)_2CS$] was added into the above solution with constant stirring. The glass substrates were immersed in the bath at room temperature. The temperature of the bath was around 27° C. The samples dipped in the bath, were extracted after a time interval of 20, 30, 40, 50, 60, 70, 80 and 90 min and are abbreviated as PbS_{20}, PbS_{30}, PbS_{40}, PbS_{50}, PbS_{60}, PbS_{70}, PbS_{80} and PbS_{90} respectively. The deposited films were rinsed with double distilled water and allowed to dry at room temperature. The as-deposited films were found to be uniform, specularly reflective (mirror-like) to the glass substrates.

The precipitation of metal chalcogenides in CBD occurs only when the ionic product exceeds the solubility product of metal chalcogenides (PbS in our case) [13]. The film growth takes place via ion-by-ion condensation of the materials or by adsorption of colloidal particles from the solution onto the substrate. The complexing agents help to control the reaction rate. PbS forms via the overall reactions to take place inside the bath:

$$Pb^{+2} + OH^- + Cit^{3-} \rightarrow Pb(OH)Cit^{2-} \tag{1.1}$$

$$NH_2–SC–NH_2 + OH^- \rightarrow NC–NH_2 + HS^- + H_2O \tag{1.2}$$

$$HS^- + OH^- \rightarrow H_2O + S^{2-} \tag{1.3}$$

$$Pb(OH)Cit^{2-} + S^{2-} \rightarrow Pbs + OH^- + Cit^{3-}. \tag{1.4}$$

In this reaction process initially lead acetate dissociates as Pb^{+2} and (CH_3COO^-) ions. After addition of tri-sodium citrate it forms complex with Pb^{+2} as $Pb(OH)Cit^{2-}$, then the solution became milky turbid. Further addition of excess alkaline NaOH causes dissolution of turbidity leading to a homogeneous solution. Due to excess of NaOH in solution provides OH^- ions, thiourea hydrolyzed into cyanamide ($NC–NH_2$), which is unstable in an aqueous medium and readily converts into urea ($O{=}C–(NH_2)_2$) following base catalyzed reaction and release S^{2-} ions into solution [14]. The deposition of the films from the solution involves a nucleation phase in which an initial layer of $Pb(OH)Cit^{2-}$ formed on the glass substrate and is subsequently converted into PbS by the reaction with S^{2-} ions available in the bath.

2.2. Characterization of PbS films

The thickness of the films was measured by using Ambios XP-1 surface profiler. The room temperature optical absorption measurements were performed in the wavelength range over 400–2000 nm by using a Hitachi-330 (Japan) UV–vis–NIR double beam spectrophotometer. Room temperature photoluminescence (PL) was studied on Luminescence Spectrometer (model: F900, resolution: 0.1 nm, Edinburgh Instruments, UK).

The XRD spectrum of the films was recorded using X-ray diffractometer (Bruker AXS B8 model). The elemental information of the films was analyzed using an XPS Thermo K-Alpha with multichannel detector, which can suffer high photonic energies from 0.1 to 3 keV. Surface morphology of deposited films was examined using FESEM (JEOL JSM-6500F). The Fourier transform infrared (FT-IR) spectra of samples were collected using a Spectrum 100 Perkin Elmer FT-IR spectrophotometer using pellets made by mixing the sample with KBr, to investigate the functional groups of the PbS nanoparticles.

3. Results and discussion

3.1. Thickness measurement

The thickness of the films was found to vary from 712 to 3256 nm with an increase in deposition time from 20 to 90 min. The values of film thickness of all films are given in Table 1. It was observed that the thickness increases with deposition time up to PbS_{70} thereafter, it decreases rapidly. The saturation can be related to insufficient quantity of reactive species after PbS_{70}.

Table 1
Tabulation of the thickness, optical band gap and crystallite size of the films deposited at various deposition time – 20, 30, 40, 50, 60, 70, 80 and 90 min.

Sample	Time (min)	Thickness (nm)	Optical band gap (eV)	Crystallite size (nm)
PbS_{20}	20	712	2.06	23
PbS_{30}	30	1057	1.67	26
PbS_{40}	40	2004	1.50	27
PbS_{50}	50	2336	1.12	29
PbS_{60}	60	2506	1.10	30
PbS_{70}	70	3256	0.99	34
PbS_{80}	80	2375	1.05	30
PbS_{90}	90	2207	1.07	26

3.2. Optical absorption studies

The optical absorption spectra for the films were recorded in the wavelength range of 400–2000 nm at room temperature. Fig. 1(a) shows variation in the optical absorption with wavelength. The absorption coefficient for all the films was found to be of the order of 10^{-10} cm^{-1}. The optical band gap energy of all films is calculated using a classical equation:

$$\alpha = \frac{\alpha_0 (h\nu - E_g)}{h\nu}^{1/2} \tag{1.5}$$

where, E_g is the separation between the bottom of conduction band and top of the valence band, $h\nu$ is the photon energy and n is the constant. For allowed direct transitions $n = 1/2$ and for indirect transition $n = 2$. The plots of $(\alpha h\nu)^2$ against $h\nu$ for all the films are shown in Fig. 1(b). The extrapolation of straight line portions to zero absorption coefficient ($\alpha = 0$), leads to the estimation of the band gap energy values. It is noted that the band gap energy varied ranging from 2.06 to 0.99 eV with deposition time. The variation in E_g is attributed to the quantum confinement effect. Because, for a semiconductor crystal, electronic excitation consists of a loosely bounded electron–hole pair, usually delocalized over a length much longer than the lattice constant. As the diameter of the semiconductor crystallite approaches this exciton Bohr diameter, its electronic properties start to change. This quantum confinement effect can be explained qualitatively by considering a particle-in-a-box like situation where the energy separation between the level's increases as the dimensions of the box is reduced. In addition, quantum confinement leads to a collapse of the continuous energy bands of a bulk material into discrete, atomic like energy levels. The discrete structure of energy states leads to a discrete absorption spectrum of QDs. Thus, one observes an increase in the band gap of the semiconductor with a decrease in the particle size [15].

It is interesting to note that this facile and low cost chemosynthesis method enables band gap energy tuning from as low as 0.99 eV to 2.06 eV, capable of harnessing photons over visible and NIR regime. This would help to prepare an efficient solar absorber with minimum interfacial stress and to absorb the maximum span of the solar spectrum in PbS-based solar cells.

Photoluminescence (PL) is an important tool to investigate quality of the thin film, which depends on size of crystallites, morphology and chemical environment. PL measurement of the PbS films was carried out at room temperature with an excitation wavelength of 416 nm, as is laid out in Fig. 1(c). Twin peaks at 405 nm and 393 nm, along with low intense peak at 460 nm are observed in the PL spectra. It shows variation in the peak intensity little change peak position. Cao et al. [16] also observed a large blue shift of the absorption edge for their synthesized PbS nanocubes. Chattopadhyay and co-workers [17] reported a blue shift for their prepared