Full length article

Elucidating doping driven microstructure evolution and optical properties of lead sulfide thin films grown from a chemical bath

Bhaskar Chandra Mohanty [a,*], Keerti Bector [a], Ranjit Laha [b]

[a] School of Physics and Materials Science, Thapar University, Patiala, Punjab, 147004, India.
[b] Department of Physics, Indian Institute of Technology Patna, 801103, Bihar, India

ARTICLE INFO

ABSTRACT

Doping driven remarkable microstructural evolution of PbS thin films grown by a single-step chemical bath deposition process at 60 °C is reported. The undoped films were discontinuous with octahedral-shaped crystallites after 30 min of deposition, whereas Cu doping led to a distinctly different surface microstructure characterized by densely packed elongated crystallites. A mechanism, based on the time sequence study of microstructural evolution of the films, and detailed XRD and Raman measurements, has been proposed to explain the contrasting microstructure of the doped films. The incorporation of Cu forms an interface layer, which is devoid of Pb. The excess Cu ions in this interface layer at the initial stages of film growth strongly interact and selectively stabilize the charged {111} faces containing either Pb or S compared to the uncharged {100} faces that contain both Pb and S. This interaction interferes with the natural growth habit resulting in the observed surface features of the doped films. Concurrently, the Cu-doping potentially changed the optical properties of the films: A significant widening of the bandgap from 1.52 eV to 1.74 eV for increase in Cu concentration from 0 to 20% was observed, making it a highly potential absorber layer in thin film solar cells.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Lead sulfide has been extensively investigated over last few years owing to its exotic optical and electrical properties highly useful for applications in photovoltaic solar cells, infrared emission and detection, catalysis, sensing, etc. [1–5]. For instance, nano-sculptured PbS thin films can be designed to obtain high value of birefringence in near IR region, to reflect poorly depending on the incident polarization and also to sense flow of fluids due to high porosity [5]. The other important reason of research interest on PbS is of more fundamental character: the unique structural anisotropy manifested as the reported wide range of branched and faceted nanostructures [6–13]. For example, Safrani et al. have studied the effect of reagent concentration, pH, deposition time and temperature on properties of PbS thin films grown by the chemical bath deposition (CBD) method [13]. They have found that optimally grown films are potentially suitable for use as photoreceptors in optically addressed spatial light modulators. Considering the profound influence of surface microstructure on properties of

nanocrystals, in general [14–17], the understanding of microstructural evolution and hence, the ability to control/predict it in given experimental work flow is rather important.

PbS crystallizes typically in cubic (galena) phase wherein the charged {111} and charge-neutral {100} are the two main morphology-related planes and the growth rates along normal to these planes determine the microstructure of the nanocrystals [18]. The surface energy of the {111} planes is intrinsically higher than that of the {100} ones suggesting that rapid growth along <111> to minimize the surface energy is expected [19]. However, this tendency has often been observed to be overruled by a number of factors including (i) the ratio of sulfur to lead concentration ($R_{S/Pb}$), (ii) the presence of capping agents/stabilizing surfactants, (iii) the duration and ambient temperature, etc. [20]. For example, Liu et al. have demonstrated that with decreasing $R_{S/Pb}$, morphology of sub-micrometer PbS particles evolved from small cubes to hierarchical cube-like ones consisting of eight polyhedral subunits as a consequence of varied growth rates along <111> and <100> directions [7]. In literature, one can find reports of various methods such as solvothermal, microwave, thermal decomposition, aqueous routes, etc. and the use of surfactants such as 1-oleic acid, 1-octadecene, cetyl-trimethyl-ammonium bromide (CTAB), sodium dodecyl sulfate, amino acids, aminocaproic acid, polyvinylpyrrolidone, etc. to

---

* Corresponding author.
  E-mail address: bhaskar@thapar.edu (B.C. Mohanty).

prepare PbS nanocrystals of different microstructures and in the eventual form of powders [11,21–24].

Differently with the earlier studies, in this work we report an unusual copper-doping driven interface modification that led to a distinctly different microstructure compared to that of the undoped PbS thin films grown by the CBD technique using simple compounds of lead acetate and thiourea as sources of Pb and S in the presence of pH stabilizer NaOH and complexing agent triethanolamine (TEA) in distilled water at a low temperature of 60 °C. An extended range of doping concentration of 0 to 20% was investigated to bring out the distinct effect of doping on the microstructure of the resulting films. Besides elucidating whether a dopant can modulate the microstructure at all, the other motivation of this work is to manipulate the bandgap of PbS (0.41 eV for bulk PbS) as relevant for solar cell applications through copper doping. Although solar cell efficiency of as high as ∼10% has been obtained by colloidal PbS quantum dots as a consequence of widening of bandgap due to quantum confinement [25], the multi-step processing and necessary surface passivation limit its wider acceptability. Recently, the CBD has been shown to be a scalable route of synthesis of PbS thin films where facile modulation of bandgap by varying bath temperature can be achieved [26]. A wide range of bandgap from 0.5 to 1.61 eV has been reported for the PbS-based thin films depending on the film quality and processing conditions [26–28]. Though limited, there are some examples of conversion efficiency >3.0% for the PbS based solar cells when the bandgap is ∼1.6 eV [26,29]. Several research groups have attempted to tune the bandgap by substituting Pb sites in PbS films with metal elements such as Sb, Fe, Cd, Cu and Hg [30–34]. CuS being a p-type semiconductor, similar to PbS, and expecting d-orbitals of Cu to provide deep acceptor states in metal sulfides [35], it is reasonable to believe that Cu-doped PbS thin films can be potentially used as absorber layer in thin film photovoltaics.

2. Experimental

Lead acetate (Pb(CH$_3$COO)$_2$·3H$_2$O) (99.9%, Loba Chemicals, India) and thiourea (NH$_2$.CS.NH$_2$) (99.9%, Loba Chemicals, India) were used as sources for Pb and S in the CBD process. Stock solutions of 10 ml of 0.5 M lead acetate, 12 ml of 1 M of thiourea, 10 ml of 2M NaOH (99.9%, Sigma-Aldrich) and 8 ml of 1 M triethanolamine (TEA) (99.9%, Loba Chemicals, India) were prepared in distilled water. The total volume of the bath was made 400 cm^3 by adding DI water. The reagents namely Pb(CH$_3$COO)$_2$, TEA and NaOH were added under constant stirring. The glass slides were first washed with detergent solution, followed by ultrasonic cleaning with DI water and acetone for 10 min each. The cleaned glass slides were kept vertically in the solution. After inserting the glass slides, thiourea solution was added under constant stirring. In typical conditions, only one substrate was used. Stirring of the solution was carried out at a speed of about 1000 RPM for the entire duration of deposition (from starting to end till the substrates removed from solution). All films were made in single step. To study the evolution of film properties, films were grown for various durations ranging from 2 to 30 min. After the injection of thiourea, the colour of the solution slowly changed to black. The rate of change of colour depended on the deposition time. For temperature measurement, a thermometer (with an accuracy of ±1 °C) was dipped inside the solution for the whole period of deposition. After the specified period of time, the deposited thin films were removed from the solution and were ultrasonically cleaned in DI water followed by air drying. For Cu doping of the films, appropriate amount of the copper chloride (CuCl$_2$·2H$_2$O) (99.9%, Loba Chemicals, India) was added to the solution. The depositions process remained the same. In this work the percentage of copper doping was in the range from 1 to 20 mol%.

Correspondingly, the samples are noted as XCu when X (= 0, 1, 2, 5, 10 and 20) indicated the percentage of Cu doping. The bath temperature was 60 °C.

X-ray diffraction (XRD) measurements were performed on a Pan Analytical (model: X Pert Pro) diffractometer using Cu-K$_\alpha$ radiation in the conventional θ-2θ mode. Field emission scanning electron microscopy (FESEM) images were obtained using a ZEISS (Ultra-Plus) electron microscope operated at an accelerating voltage of 15 KV. High resolution transmission electron microscopy (HRTEM) images were acquired using a FEI (TECHNAI G^2) microscope operated at an accelerating voltage of 200 kV. Room temperature Raman measurements were carried out using Renishaw inVia Raman spectroscope with a laser source of wavelength of 632.8 nm. Optical transmittance of the films as a function of wavelength in the near visible regions was measured using a Shimadzu UV–vis spectrophotometer (model: UV-2600/2700).

3. Results and discussion

3.1. Evolution of microstructure

Fig. 1 depicts the surface microstructure of the films deposited at a bath temperature 60 °C for a duration of 30 min. The FESEM images showed that the film without any Cu doping (i.e., 0Cu sample) is discontinuous with separated but well-developed crystallites. The crystallites are faceted resembling octahedrons of sides of about 100 nm and have a uniform distribution of size. Remarkable changes in the form of continuous films with very contrasting microstructure were obtained when films were doped with Cu even with an amount as small as 1%. Apparently, doping yielded continuous films with their surface covered by crystallites whose size continuously decreased with the increase in Cu concentration. For the 1Cu films, a bimodal surface structure was observed. A majority of the crystallites were elongated with a high aspect ratio, and the others were of small dimensions and having an aspect ratio of nearly 1:1. This non-uniformity disappeared as the Cu amount in the films was increased. For instance, the surface was found to be covered by crystallites of similar type (marginally elongated) in the 10Cu and 20Cu films. These crystallites had similar aspect ratio and similar dimensions. The sharp contrasts in the surface microstructure of the films are thought to arise as a consequence of the doping and the doping concentration. The effects of thickness is ruled out based on the fact that all films were grown for the same duration and cross-sectional images of the films showed that thickness of all films was about 170 nm.

The typical growth process of lead chalcogenide nanocrystals includes initial nucleation, characterized by polyhedra of six {100} and eight {111} facets because of the cubic rock-salt structure, followed by process parameter-dependent growth of faces [36,37]. Thus, the eventual microstructure of the nanocrystals is decided by the preference or inhibition of growth in a direction normal to either of these faces. Peng et al. [6] and Zhang et al. [38] have reported that PbS nanocrystals of different morphologies exhibit distinct variation in the intensity of the Bragg reflection peaks corresponding to the (111) and (200) compared to the reference data. A very high intensity ratio I$_{(111)}$/I$_{(200)}$ is indicative of restricted growth of (200) planes, resulting in octahedral-shaped crystals. In this view, more insight to the growth habits was obtained from the analysis of corresponding XRD patterns of the films, which are shown in Fig. 2a. All patterns are characterized by six distinct peaks attributed to the reflections from the (111), (200), (220), (311), (222), and (420) planes of the PbS cubic phase [JCDPS card no. 05-0592]. The absence of any peak corresponding to secondary phases indicates the growth of phase pure films. However, the notable difference between the films with and without Cu lies in the peak