



Engineering of electronic and optical properties of PbS thin films via Cu doping



Baligh Touati ^{a,*}, Abdelaziz Gassoumi ^{a,b}, Illia Dobryden ^{c,d},
Marta Maria Natile ^e, Alberto Vomiero ^c, Najoua Kamoun Turki ^a

^a Université Tunis El Manar, Faculté des Sciences de Tunis, Département de Physique, LR99ES13 Laboratoire de Physique de la Matière Condensée (LPMC), 2092, Tunis Tunisie, Tunisia

^b King Khalid University, Faculty of Science, Physics Department, P.O. Box 9004, Abha, 61413, Saudi Arabia

^c Division of Materials Science, Department of Engineering Science and Mathematics, Luleå University of Technology, Luleå, Sweden

^d Division of Surface and Corrosion Science, Department of Chemistry, KTH Royal Institute of Technology, Stockholm, Sweden

^e CNR-IENI, Dipartimento di Scienze Chimiche, Università di Padova, via F. Marzolo 1, 35131, Padova, Italy

ARTICLE INFO

Article history:

Received 25 April 2016

Received in revised form 19 July 2016

Accepted 21 July 2016

Available online 25 July 2016

Keywords:

Cu doped PbS films

Chemical bath deposition (CBD)

Optical and electrical properties

ABSTRACT

Copper-doped PbS polycrystalline thin films were deposited by chemical bath deposition by adding small amount of Cu ($y_{\text{solution}} = [\text{Cu}^{2+}]/[\text{Pb}^{2+}]$) between 0.5 and 2 at%. The composition, structure, morphology, optical and electrical properties of the films were investigated by means of X-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoemission spectroscopy (XPS), UV–visible–near infrared (UV–Vis–NIR) spectrophotometry and Hall effect measurements. The XRD studies showed that the undoped films have PbS face centered cubic structure with (111) preferential orientation, while preferential orientation changes to (200) plane with increasing Cu doping concentration. The AFM and SEM measurements indicated that the film surfaces consisted of nanosized grains with pyramidal shape. Optical band gap was blue shifted from 0.72 eV to 1.69 eV with the increase in Cu doping concentration. The film obtained with the $[\text{Cu}^{2+}]/[\text{Pb}^{2+}]$ ratio equal to 1.5 at% Cu showed the minimum resistivity of 0.16 Ω cm at room temperature and optimum value of optical band gap close to 1.5 eV. 1.5 at% Cu-doped PbS thin films exhibit the best optical and electrical properties, suitable for solar cells applications.

© 2016 Published by Elsevier Ltd.

1. Introduction

Lead sulfide (PbS) is subject of intense research owing to its technological importance in the field of optoelectronics. PbS has important properties like small direct band-gap (0.4eV), p-type character and high absorption coefficient in the visible and infrared region ($>10^5 \text{ cm}^{-1}$), that make it a useful material as detectors for infrared radiation, gas sensors, solar control coatings, etc. [1–3]. Previous studies show the ability of blue shifting the band gap by doping. Then, it can be expected that the energy band gap (E_g) changes due to many effects like the quantum confinement (QC) and/or unit cell volume variation, etc. Proper electronic band alignment is critical for application of PbS based films as absorber material in solar cells devices, in which suitable electronic band structure is needed for the p-n junctions to operate properly under sunlight irradiation [4,5].

* Corresponding author.

E-mail address: Baligh.touati77@gmail.com (B. Touati).

There are numerous methods used to fabricate PbS films (either undoped or doped), such as spray pyrolysis, successive ionic layer adsorption (SILAR) and chemical bath deposition (CBD) [6–8]. Chemical bath deposition is a versatile method for thin film growth; it is relatively simple, capable of depositing large area coatings and, most importantly, cost effective and is a low temperature technique.

In order to improve the physical properties of PbS thin films, impurity doping is a useful approach. Typical dopants have been used to make PbS practically applicable belonging to the group 11 (Cu) and group 12 (Zn, Cd) [9–12]. However, up to now, only few reports exist on Cu-doped PbS thin films using CBD [11] and [12]. They have been used other experimental conditions (precursors, temperature deposition and doping concentration) for improving the physical properties of PbS films. In our case, Cu:PbS have been elaborated with small amount of copper (0, 0.5, 1, 1.5 and 2 at.%) employing lead nitrate $\text{Pb}(\text{NO}_3)_2$ and copper nitrate ($\text{Cu}(\text{NO}_3)_2$) as chemical precursors and with successful low temperature deposition ($T = 25^\circ\text{C}$). Therefore, the coexistence of good surface morphology, optical and electrical properties is one of the prime concerns of solar cells devices, which is the motivation of this research.

In the present work, our aim is to develop Cu doped PbS thin films with chemical bath deposition method in order to improve optoelectronic properties of PbS nanomaterial. Therefore, we are committed to a systematic study in order to investigate Cu doping effect on structural, morphological, optical and electrical properties of PbS thin films. To date, the use of small amount of copper, as a selective doping agent, in PbS binary compound with ‘p’ character to obtain optical band gap close to 1.5 eV, low resistivity of 0.16 $\Omega\text{ cm}$ and relatively smooth surface, simultaneously, has not yet been achieved. Our results demonstrate the possibility of obtaining PbS thin films with E_g and electronic conduction suitable for application in p-n junction solar cells, close to the optimum ideal condition to maximize the photoconversion efficiency, according to the Shockley–Queisser limit [13].

2. Experimental methods

2.1. Growth of thin films by CBD

The chemical bath contained lead nitrate [$\text{Pb}(\text{NO}_3)_2$], copper nitrate [$\text{Cu}(\text{NO}_3)_2$], sodium hydroxide [NaOH] and thiourea [$\text{SC}(\text{NH}_2)_2$], in appropriate concentrations and double distilled water. The reactive solution was prepared by the sequential addition of: 0.17 M lead nitrate, 0.57 M sodium hydroxide and 0.1 M thiourea. In order to get the Cu-doped PbS films, the copper nitrate was then added in desired amounts ($y_{\text{sol}} = ([\text{Cu}^{2+}]/[\text{Pb}^{2+}])_{\text{sol}}$) was varied from 0.5 to 2 at.%. Double distilled water was added to the solution to make the volume close to 50 mL. The pH value 12 was obtained by the addition of sodium hydroxide into the solution. Prior to deposition, the glass substrates of dimensions (2.5 cm \times 2.5 cm \times 2 mm) were treated with hydrofluoric acid, which provides nucleation sites facilitating the film growth. They were placed vertically in the beaker containing the solution.

Cu-doped PbS films were deposited at room temperature (25°C) for 1 h. The substrates with the deposited films were taken off from the reaction solution, washed with de-ionized water, to remove the surface impurities and minimize the particle agglomeration, and dried in air at room temperature. The prepared films were uniform and well adherent to the substrate.

2.2. Film characterization

Rutherford backscattering spectrometry (RBS) was carried out to determine film thickness and possible presence of Cu in doped films. The experimental conditions are the following. Beam: $^4\text{He}^+$; $E_0 = 2.0\text{ MeV}$; Scattering angle $\theta = 20^\circ$. Normal incidence of the beam. Geometry: IBM. We used RUMP code simulations to analyze the collected spectra [14]. Areal density-to-thickness conversion was carried out under the hypothesis of bulk density equal to 7.6 g/cm^3 , corresponding to $3.1 \times 10^{22}\text{ atoms/cm}^3$ for the films, irrespective of Cu concentration. Such estimate may introduce a slight systematic error, if film density changes with the increase of Cu doping, but it is a good approximation for our purposes. The structural properties of the PbS and Cu-doped PbS thin films were determined with a diffractometer “XPRT-PRO” model, using Cu $K\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$) with 2θ ranging from 20° to 60° . The morphology and topography of the doped PbS films were examined using tapping mode Ntegra and Solver AFM (NT-MDT) using a NSG- 01 probe (NT-MDT, with a tip curvature radius $<10\text{ nm}$ and nominal spring constant of 5.1 N/m) and high-resolution SEM (Magellan 400 XHR-SEM, FEI Company). X-ray photoelectron spectroscopy (XPS) study was done using Perkin-Elmer PHI 5600ci spectrometer with standard Al- $K\alpha$ source (1486.6 eV) working at 220 W. The working pressure was less than $7 \times 10^{-7}\text{ Pa}$. The spectrometer was calibrated by assuming the binding energy (BE) of the Au $4f_{7/2}$ line to be 84.0 eV with respect to the Fermi level. Extended spectra (survey) were collected in the range 0–1350 eV (187.85 eV pass energy, 0.5 eV step, 0.025 s step^{-1}). Detailed spectra were recorded for the following regions: Pb 4f, S 2p, Cu 2p, O 1s, and C 1s (23.5 eV pass energy, 0.1 eV step, $0.2\text{ eV s step}^{-1}$). The reported binding energies (BEs) were corrected for the charging effects by considering the adventitious C1s line at 285.0 eV. Optical measurements are performed using a UV–Vis–NIR spectrometer (Perkin Elmer lambda 950) at room temperature in the wavelength range from 250 to 2500 nm. Hall effect measurement was carried out to determine the hall mobility, carrier concentration and resistivity of samples.

Download English Version:

<https://daneshyari.com/en/article/1552538>

Download Persian Version:

<https://daneshyari.com/article/1552538>

[Daneshyari.com](https://daneshyari.com)