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Effect of Pb:S molar ratio in precursor solution on the properties of lead sulphide thin films by ultrasonic spray pyrolysis

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ABSTRACT

In this work, PbS thin films were deposited onto glass substrate at 225 °C by spraying precursor solution prepared with different molar ratio of lead acetate and thiourea as a source of Pb^{2+} and S^{2-} respectively in order to investigate the effect of Pb:S molar ratio in the precursor solution on the physical properties of PbS thin films. Structural investigations carried out by X-ray diffractometer have shown that all films have fcc cubic structure and the average crystal size increased from 11 nm to 25 nm with the increasing the thiourea ratio in the precursor solution. In order to analyze the surface morphology of PbS thin films, AFM and SEM images were taken and elemental analysis of the films was performed by EDS. Optical transmittance and absorption spectra show that all deposited films have fairly low transmittance and high absorbance in the visible region. Additionally, it was determined that optical band gap of the deposited films were varied between 1.18 eV and 1.37 eV. As a consequence of electrical investigations, it was seen that all films have p-type conductivity and electrical resistivity decreased by increasing thiourea molar ratio in the precursor solution. All examinations have revealed that the molar ratio of lead acetate and thiourea has a significant effect on the physical properties of PbS thin films.

1. Introduction

Lead sulphide (PbS) which is IV–VI group semiconductor, has direct and narrow band gap (~ 0.41 eV) at room temperature. However, its relatively large bohr exciton radius (~ 18 nm)allows that optical band gap of PbS can be tuned from 0.41eV to 2.51 eV by forming nanocrystallites [1]. This feature, called as quantum size effect, makes PbS thin films attractive in some optoelectronic applications such as infrared detectors [2], LEDs [3], field effect transistors [4] etc. Particularly, its high absorption coefficient (~ 10^5 cm^{-1}) makes them good absorber layer for thin film solar cell applications [5]. PbS thin films can be deposited by using various techniques such as chemical vapor deposition (CVD) [6], vacuum evaporation [7], RF-sputtering technique [8]. However, solution-based processes involving cheaper and easier settling techniques are essential in order to reduce manufacturing costs. Therefore, solution-based and vacuum-free techniques such as chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR) [9], spin coating [5] and spray pyrolysis (SP) [10] are one step ahead of other vacuum techniques because of their low cost. Among these techniques, SP has many advantages such as easy handling, wide area coating, easy doping of almost every element by incorporating of elements into the precursor solution [11]. It is also possible to increase the surface homogeneity of the films by replacing the conventional nozzle used for spraying with an ultrasonic nozzle.

In literature, it has been stated that physical properties of the PbS thin films are largely dependent on the deposition parameters such as bath composition and deposition time for CBD [12], precursor molar concentration and substrate temperature for spray pyrolysis [10,13], dipping cycles for SILAR deposition technique [14]. Beddek et al. examined the effect of lead source, and thiourea concentration and they expressed that increasing thiourea concentration adversely effected the crystallinity of PbS thin films in case of lead acetate as lead source and it was attributed to the low growth rate. But, it was also stated that, in the case of lead nitrate, the change in crystallinity is exactly the opposite [15]. Seghaier et al. also investigated the effect of both of lead nitrate concentration and thiourea concentration by using CBD technique. They have announced that best crystallinity and stoichiometric compound were obtained by using 0.170 M lead nitrate and 0.1 M as reactants at room temperature (RT) [16]. However, for the deposition techniques requiring higher temperatures, lower dissociation temperature of sulphide semiconductors make it difficult to obtain stoichiometric PbS thin films [17] For instance, in a study on the effect of substrate temperature on the structural and electrical properties of PbS thin films deposited by spray pyrolysis, it was reported that increasing

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substrate temperature from 150 °C to 300 °C improves the crystalline level of PbS thin films but substrate temperature which is higher than 225 °C led to switch the electrical conductivity from p-type to n-type and the changing in the electrical transport mechanism was attributed to variation from sulphide rich to lead rich films as a consequence of increased temperature [10]. This stoichiometric deviation which stem from the interstitial atoms and vacancies also lead to formation of localized states within the band gap [18,19]. Undesirable deviation from stoichiometry can be restored sulfurizing both during and after deposition of sulphide semiconductors [17,20]. It can be also achieved by altering the amount of lead and sulphide sources in the precursor solution for the spray pyrolysis technique. Veena et al., achieved by increasing lead precursor concentration from 1:1 to 2:1 with respect to sulphide concentration. However, it should be mentioned that they have stated that all films have n-type conductivity although some films have an excess of sulfur, which is contrary to reported in Ref. [10].

Due to the fact that sulphide has a lower melting temperature than the lead, it is likely that the sulphide evaporates from the surface and leads to obtain sulphide deficient non-stoichiometric PbS thin films [21] and it may be possible to compensate this undesirable case by increasing the amount of thiourea in the precursor solution. Therefore, this study mainly aims to investigate the structural, surfaces, electrical and optical properties of PbS thin films with respect to the precursors (lead acetate and thiourea) Pb:S molar ratio in precursor solution (1:1, 2:3, 1:2 and 2:5).

2. Experimental procedure

2.1. Film deposition

PbS thin films were deposited by ultrasonic spray pyrolysis technique on microscope glass substrates at substrate temperature of 225 ± 5 °C using air as carrier gas with a pressure of 1 atm for different Pb:S molar ratio. The schematic diagram and working principle of the ultrasonic spray pyrolysis technique is given in detail in our previous work [22]. Microscope glasses used as substrates were cleaned in distilled water for 30 min using an ultrasonic bath before beginning the deposition process. The spray solution was prepared by mixing dissolved lead acetate [$Pb(CH_3CO_2)_2{\cdot}3H_2O$] at 0.05 M and thiourea [CH_4N_2S] at different molarities (0.05 M, 0.075 M, 0.1 M and 0.125 M) in distilled water for lead and sulphide source, respectively. A total of 150 cc initial spraying solution was sprayed onto the glass substrates for 30 min. The solution flow rate was kept constant at 5 cc min^{-1} and checked with the aid of a flowmeter during deposition process. The distance between the nozzle and the substrate was maintained at 35 cm and the substrate temperature of 225 °C was controlled within ± 5 °C by using an iron-constantan thermocouple.

2.2. Characterization techniques

Thickness values of PbS thin films were measured by using PHE 102 Spectroscopic Ellipsometry and found to be 400, 415, 396 and 394 nm for Pb:S molar ratio at 1:1, 2:3, 1:2 and 2:5, respectively. Structural analyses of the films were carried out by using X-ray diffractometer (PANalytical Empyrean), having CuK_α radiation (λ = 1.5405 Å). A continuous scan mode was used to collect 2θ data from 20° to 80° with a step of Δ(2θ) = 0.013°. The widths of the diffraction lines are broaden due to the crystallite size, lattice strain and instrumental resolution of diffractometer [1]. In order to eliminate the contribution of the instrumental expansion of angular resolution of the diffractometer were obtained [$FWHM_R(2\theta) = \sqrt{utan^2\theta + vtan\theta + w}$] by carrying out a special experiment with cubic Si standard sample having a = b = c = 5.429507 Å lattice parameter. For the PANalytical Empyrean diffractometer, the resolution function parameter u, v and w determined as 0.007292, −0.002582 and 0.005771, respectively. Broadening of the each diffraction reflection was determined by comparing of experimentally obtained $FWHM_{Exp}$ with instrumental resolution function $FWHM_{Exp}$ according to following equation [23,24];

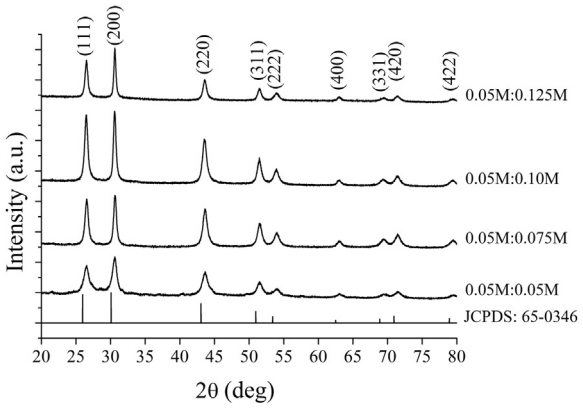

Fig. 1. XRD patterns of deposited PbS thin films.

$$\beta(2\theta) = \sqrt{(FWHM_{Exp})^2 - (FWHM_R)^2}$$

Surface morphologies and elemental analysis of the films were characterized by using a Park System XE 70 Atomic Force Microscope a JEOL SEM-7100-EDX Scanning Electron Microscope equipped with an Energy Dispersive X-ray Spectroscopy setup. For optical analysis, transmittance and absorbance spectra of all the films were taken in the wavelength range of 350–1400 nm by using Shimadzu UV-2600 spectrophotometer. Electrical characterizations were carried out by taking I-V characteristics at dark and room temperature conditions using Keithley 2400 Sourcemeter. Hot point probe technique was also adopted to determine majority carrier type of the PbS thin films.

3. Results and discussion

3.1. Structural analysis

It was seen that the XRD patterns of the films shown in Fig. 1 have multiple diffraction peaks at different intensity and width. These peaks which located at 2θ ~ 26.5°, 30.6°, 43.6°, 51.5°, 54.0°, 69.4°, 71.4°and 79.4° were indexed as (111), (200), (220), (311), (222), (400), (331), (420) and (422) crystal planes, respectively by comparing of XRD patterns with the standard JCPDS Card No: 65-0346 and it was also found that all deposited films were polycrystalline and had a face-centered cubic phase. Texture coefficient (*TC*) values for three diffraction peaks with the highest intensity were calculated by using following equation [25] and listed in Table 1;

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{1/N\left[\sum_N I_{(hkl)}/I_{0(hkl)}\right]} \quad (1)$$

where $I_{(hkl)}$ is the measured intensity of the corresponding orientation, $I_{0(hkl)}$ is the standard intensity JCPDS and N is the number of diffraction peaks. Relative intensity of the peaks according to the (200) oriented peak is also listed in Table 1. It is known that *TC* is close to 1 in the case of randomly distribution and greater than 1 for the peak which is preferentially oriented [26]. As it seen from Table 1, for this study, calculated TC values are close to 1 for PbS thin films prepared by 1:1 and 2:3 Pb:S molar ratio and it becomes to slightly increase as the thiourea concentration increase and reaches the maximum value for the (200) orientation for the PbS thin films prepared with 2:5 Pb:S ratio. Therefore it can be noted that randomly distribution exist for thin films prepared with lower thiourea concentration and (200) plane becomes the preferential orientation for PbS thin films prepared by 2:5 Pb:S molar ratio.

In addition, as it can be seen from Table 2, full width half-maximum (FWHM) of the diffraction peaks have narrowed with the increasing