Surface microstructure, optical and electrical properties of spray pyrolyzed PbS and Zn-PbS thin films for optoelectronic applications

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Lead sulphide (PbS) and zinc- doped lead sulphide (Zn–PbS) thin films were prepared by chemical spray pyrolysis on soda lime glass substrates at a temperature of 250 °C. Precursors were prepared from chemical reagents including zinc acetate, lead acetate and thiourea. The deposited films thicknesses and elemental composition were studied by Rutherford backscattering spectroscopy (RBS); the percentages of Pb and S were estimated as 40.58 % and 59.42 %, respectively, while for the Zn-doped sample, the percentages of Zn, Pb and S were respectively 4.84 %, 44.57 % and 50.59 %. Morphological studies revealed that the films were continuous and the particles were uniformly distributed across the substrate surface. AFM probe revealed nanostructured films with particles densely distributed across the substrates surfaces with incorporation of Zn²⁺. Statistical distribution of the grains over a specific projected area indicated average growth height of about 47 nm. Optical studies indicated that the transmission in visible light region of Zn-PbS thin film was superior to that of the undoped sample. Interband transition of both PbS and Zn–PbS films is directly allowed and their energy band gaps were found to be 0.43 eV and 1.45 eV, respectively. Electrical characterization showed that both films are of p-type conductivity with surface resistivity values of the order of $10^4 \,\Omega$ -cm.

Keywords: pyrolysis; nanostructure; thiourea; optoelectronics; resistivity

1. Introduction

Renewed and growing interest has been focused on PbS, one of narrow band gap (IV-VI) semiconductor compounds, for nanocrystalline solar cells, electroluminescent devices, gas sensors and some optoelectronic devices [1–4]. This interest arose because of certain intriguing properties such as large excitation Bohr radius of PbS (\sim 18 nm) [5, 6] which results in strong quantum confinement of both electrons and holes in nanosized structures [7] and the potential of tailoring both lattice parameters and optical band gap for effective solar devices [8]. Studies on the influence of transition metal and rare-earth metal doping on the properties

of PbS indicate that doped PbS can be employed in the production of optoelectronic devices such as solar cells, flat panel displays, high efficiency electroluminescent and field emission devices [9]. Electronic band structure as well as low refractive index of doped PbS enables it to easily allow light transmission in the visible part of the solar spectrum. Effective electron transport at high electric field and chemical stability can make some sulfide thin films a perfect candidate for microelectronic device applications [10, 11]. Sometimes, they may be poorly crystalline or highly defective. These structural anomalies can be linked to the growth or production processes [12]. One of the very efficient techniques of growing durable thin films is chemical spray pyrolysis (CSP) [13]. In the process, reacting solution made from relevant

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chemical reagents is sprayed onto a substrate to obtain the desired film. This growth process has some advantages over many deposition techniques. These include scalability of the process, cost-effectiveness, allowance of intentional doping, low or moderate growth temperatures (100 °C to 400 °C) and so on. These attributes conveniently allow the use of variety of substrates, easy control of thickness, variation of film composition and possibility of multilayer growth [13–15]. To the best of our knowledge, detailed studies on properties of spray pyrolyzed Zn-doped PbS thin films have not been reported in the literature.

In the present study, the authors investigate some properties of nanocrystalline PbS and Zn– PbS thin films for optoelectronic application. The aim of the current research is to deposit PbS and Zn–PbS thin films using chemical spray pyrolysis and ultimately study the effect of dopant material (Zn) on the microstructure, optical and electrical characteristics of the thin films in regards to its potential application in optoelectronics devices.

2. Materials and methods

2.1. Precursor preparation and film deposition

Solution precursors for growing PbS and Zn-PbS thin films were formed from common chemical reagents, namely lead acetate, zinc acetate and thiourea. The principle of selection of constituents concentration ratios was based on previous studies [16, 17]. The reagents prepared at equal concentration (0.1 M) reacted together at varying volume to obtain desired film stoichiometry. Details of the reagents and reacting volume are collected in Table 1. The films were prepared by pyrolysing the freshly prepared precursors on a soda lime glass substrate using a conventional chemical spray pyrolysis arrangement shown in Fig. 1. The setup consists of air atomizer nozzle, flow meter, receptacle, air compressor, hot plate and iron-constantan thermocouple. Prior to film deposition, some pieces of sodalime glass substrates were cleaned using the procedure already stated in one of our previous work [13]. The cleaned substrates were dried in an oven and kept in air tight container. The precursors after being thoroughly stirred for several minutes were stepwisely sprayed onto preheated substrates maintained at about 250 °C. Apart from substrate temperature, flow rate and pressure of the carrier gas were stabilized at \sim 3.5 dm³/min and 2.3 MPa to achieve optimum film deposition. The respective chemical reaction mechanisms for both films are stated in equation 1a and equation 1b:

$$Pb_{1-x}(CH_{3}COO)_{2} \cdot 3H_{2}O + NH_{2}CSNH_{2} \rightarrow$$

$$Pb_{1-x}S_{x} + 2NH_{4} + 6CO_{2} + 3CH_{4} + 2H_{2} + H_{2}O$$
(1a)

 $\begin{aligned} & Pb_{1-x}(CH_{3}COO)_{2} \cdot 3H_{2}O + NH_{2}CSNH_{2} + \\ & Zn_{x}(CH_{3}COO)_{2} \cdot 2H_{2}O \rightarrow Zn_{x}Pb_{1-x}S + 2NH_{4} + \\ & 6CO_{2} + 3CH_{4} + 2H_{2} + H_{2}O \end{aligned} \tag{1b}$



Fig. 1. Sketch of chemical spray pyrolysis setup.

2.2. Characterization techniques

Elemental composition and thickness of the films were obtained by Rutherford backscattering spectroscopy. The characterization was carried out using 1.7 MeV tandem accelerator. Particles shape and distribution were observed by scanning electron microscope (Zeiss crossbeam series with Gemini FESEM column). Surface roughness and growth height were examined in tapping mode using atomic force microscope (AFM). UV-Vis spectrophotometer Jenway 5400 was used to measure the transmittance of the film at room temperature

Sample name	Reacting solution (concentration and volume)			
PbS thin film	$Pb(CH_3COO)_2 \cdot 3H_2O (0.1 \text{ M}, 10 \text{ ml}) + (CS(NH_2)_2(0.1 \text{ M}, 20 \text{ ml}))$			
Zn–PbS thin film	$\begin{array}{l} \mbox{Pb}(\mbox{CH}_3\mbox{COO})_2 \cdot 3\mbox{H}_2\mbox{O}(0.1\mbox{ M}, 9.4\mbox{ ml}) + (\mbox{CS}(\mbox{NH}_2)_2(0.1\mbox{ M}, 20\mbox{ ml}) + \\ \mbox{Zn}(\mbox{CH}_3\mbox{COO})_2 \cdot 2\mbox{H}_2\mbox{O}(0.1\mbox{ M}, 0.6\mbox{ ml}) \end{array}$			

Table 1. Solution precursor for deposition of PbS and Zn–PbS thin films.

in the wavelength range of 300 nm to 1100 nm. Electrical resistivity and conductivity of the films were also examined using a Stignatone four point probe coupled with Keithley source meter 2400.

3. Results and discussion

3.1. Crystallographic analysis

The obtained XRD spectra were used to determine the structure and other crystallographic parameters of the samples. The diffraction patterns of PbS and Zn–PbS thin films are shown in Fig. 2. The patterns indicate that the prepared films are polycrystalline in nature with the existence of sharp and well defined peaks. All prominent peaks of each spectrum are indexed to the rock salt (NaCl) structure of PbS, according to the value of the reference standard JCPDS Card No. 5-592 [18]. The most prominent peaks indicate that the crystals have preferred orientations at the planes observed at (1 1 1), (200), (220), (311) and (222). Using Scherer formula, the crystallographic parameters were estimated as shown in Table 2. A reduction in crystal size from 14.28 nm to 11.680 nm with the incorporation of Zn^{2+} into the PbS thin film was noticed.

Table 2. CrystallographicparametersforPbSand Zn-PbS thin film samples.

Sample	Lattice constant (± 0.021) [Å]	Crystal size (±1.84) [nm]
PbS	5.94	14.28
Zn–PbS	5.97	11.68

3.2. Surface morphology

Surface microstructure and grain distribution of the films were observed. Fig. 3 shows



Fig. 2. XRD spectra for thin film samples of PbS and Zn–PbS.

morphology of PbS and Zn–PbS thin films taken at the same magnification under stabilized machine beam resolution. In the two images, it can be seen that the deposited films are composed of regularly shaped crystallites and the particles are uniformly distributed across the substrate surface. Surface adhesion and uniformity indicate a good growth environment of the deposited nanostructure [19]. From Fig. 3b, the surface of Zn–PbS thin film shows the morphology composed of dense and coalesced particles with no observable cracks or pinholes. The coalescence can be attributed to incorporation of Zn²⁺ ions during growth. It can, thus, be suggested that Zn²⁺ in the sample enhanced surface diffusion with respect to incoming flux of the precursor.

AFM images showing surface roughness and growth height of the films particles are presented in Fig. 4. From the image of PbS film acquired on a scan area of 1.0 m² (Fig. 4a), statistical distribution showed that the average growth height and surface roughness within a projected surface area of 0.281 m² are 47 nm and 48 nm, respectively, whereas for the image of Zn–PbS film (Fig. 4b), the average growth height and surface roughness

reduced slightly to 46 nm and 47 nm. Thus, the AFM studies further confirmed that the slight change in microstructure of the doped sample was due to introduction of Zn^{2+} ion.





(a)



Fig. 3. SEM images of thin films (a) PbS and (b) Zn–PbS.

Fig. 4. AFM micrographs of deposited thin films (a) PbS and (b) $Zn_xPb_{1-x}S$.

3.3. Elemental composition and thickness

SIMNRA code was used to fit the RBS data with elemental depth profiles [20]. RBS spectra of PbS and Zn–PbS thin films are presented in Fig. 5a and Fig. 5b, respectively. Backscattered data and elemental profiles were fitted using SIMNRA code. For PbS film, a reasonable match was obtained between the experimental data and the fit at channels 200 and 800 while for Zn–PbS film, the match occurred at channels 200, 800 and 1000. Thus, the observed sharp emission edges correspond to each elemental constituent of the films. These observations suggest that (i) there is complete thermal decomposition of precursors during pyrolysis, (ii) there is no visible interfacial or adsorbed impurity in the deposited films, and (iii) there is little or no interatomic diffusion between the films and substrate constituents. Spectra analysis revealed that percentage compositions of Pb and S in the PbS film are 40.58 % and 59.42 %. This implies that the stoichiometric ratio of Pb:S is approximately 2:3. For the Zn–PbS sample, the percentage composition of Zn, Pb and S was estimated as 4.84 %, 44.57 % and 50.59 %, respectively. This shows that Zn^{2+} is present in very small amount compared to Pb and S. Thus, the stoichiometry of this film could be given as $Zn_xPb_{1-x}S$ where x = 0.11. From these analyses, it could be deduced that traces of elemental impurities such as environmental carbon or atomic oxygen were not found or could not be sufficiently counted by the backscattered spectroscopy.

Film thickness was estimated by approximating areal density unit into length unit according to equation 2:



Fig. 5. RBS spectra of deposited (a) PbS thin film and (b) Zn–PbS thin film.

3.4. Optical properties

Characteristic behavior of PbS and Zn-PbS thin films from UV to visible range of electromagnetic wave spectrum was studied. Optical transmittances of the films are presented in Fig. 6. Influence of doping on transmittance of Zn-PbS film is observed in the bandgap plot. It can be seen that the maximum transmittance of the films lies mostly in the far-visible and near-IR regions. It is shown that the zinc doped film has a maximum transmittance of about 38 %. Slight shift in absorption edge towards the shorter wavelength could be attributed to the introduction of Zn^{2+} ions. In addition, the blue shift of the absorption edge of Zn-PbS thin film can be attributed to an increase in carrier concentration, which can be explained by Burstein-Moss (BM) effect [21, 22]. From the measured spectrophotometric data, absorption coefficient, α , was obtained as a function of wavelength using equation 3:

$$\alpha = \frac{1}{t} \ln\left(\frac{1}{T}\right) \tag{3}$$

where t and T are film thickness and transmittance, respectively. PbS thin film is considered as a direct bandgap material [6, 23], and effect of Zn^{2+} on its band structure was investigated. This was done by plotting the graph of α^{m} versus photon energy as shown in Fig. 7a, where $m = \frac{1}{2}$ and 2 according to equation 4 assuming that densities of state of the valence and conduction band are parabolic:

$$\alpha \left(hv \right) = A \left(hv - E_g \right)^m \tag{4}$$

where $h\nu$ is photon energy, E_g is energy bandgap, m is a power factor and A is an empirical constant. Bandgap was determined by extrapolating linear region of the plot to energy axis where $\alpha^2 = 0$. Thus, the estimated values of E_g of the deposited PbS and Zn-PbS thin films have been found as 0.52 eV and 1.45 eV, respectively (Fig. 7b). The E_g obtained for PbS film is consistent with the literature [24], while that of the Zn-PbS film is higher. This value matches the step like profile of solar radiation spectrum for maximum light absorption. Fundamental optical transition is observed in Zn-PbS thin film, and this can be attributed to complete dispersion of Zn²⁺ ions into PbS matrix, thereby providing a strong intermetallic bonded compound. Similar intermetallic bonding of Ni²⁺ ions in PbS matrix was reported by Portillo et. al. [25]. Higher Eg values of Zn-PbS indicate a widening of the forbidden gap due to the inclusion of zinc ions. Since both Pb and Zn have the same valency, it is unfeasible for Zn to play a role like a usual donor or acceptor. It means, it is not possible to decrease the bandgap by Zn doping like in traditional n- or pdoped semiconductors. However, a blue shift is observed, which represents an increase in the bandgap energy. The observed behavior is in agreement with recent studies [26, 27].

3.5. Electrical analysis

A simple hot point probe arrangement was used to determine the majority carrier



Fig. 6. Optical transmittance of PbS and Zn–PbS thin films.



Fig. 7. (a) graph of $\alpha^{1/2}$ vs. photon energy and (b) estimation of energy bandgap of PbS and Zn–PbS thin films.

and conductivity type of the deposited films. The tip of the hot probe (heated to ~ 120 °C) and that of cold probe with a separation of 10 mm were placed on the Zn-doped sample. A deflection in anticlockwise direction from the voltmeter implies that the deposited Zn-PbS thin film is p-type conductive. It could be deduced that energy in the form of heat is transferred to the film and enhances majority carriers to migrate away from the hot site. This charge migration often leads to potential build-up which tends to hinder the migration. At room temperature, sheet resistance R_s , electrical resistivity ρ and conductivity σ of the deposited films were determined. The values are presented in Table 3. From these results, it can be seen that with introduction of Zn^{2+} into PbS microstructure, there was a slight improvement in electrical conductivity of the sample with corresponding remarkable reduction in the values of resistivity and sheet resistance. Resistivity reduction can be attributed to the decrease in grain size, recrystallization and increase in the number of faults at the grain boundaries due to grain size refinement by Zn dopants. As a consequence, the promising characteristics of the film increased with enhanced surface smoothness of the Zn-PbS as observed in the microstructure. Moreover, it is shown that resistivity values confirmed the results obtained from optical analysis for transmittance and bandgap energy. Potentially transparent conducting films (TCFs) should have a widened E_{α} , hence, the deposited Zn-PbS film can be a good candidate as a p-type absorber layer in photovoltaic devices.

4. Conclusions

Nanostructured PbS and Zn-doped PbS thin film have been deposited successfully by chemical spray pyrolysis. The desired compositions were built in the precursors prior to deposition. The performed analysis showed that the deposited films are polycrystalline and continuous. Both films exhibit p-type conductivity. Introduction of Zn^{2+} into PbS led to significant reduction in electrical resistivity and sheet resistance. Optical analyses indicated a relatively high transmission in the far-visible and

Sample	Film thickness	Sheet resistance	Resistivity	Conductivity	Conductivity
	[nm]	[Ω]	[Ω·cm]	$[\Omega \cdot cm]^{-1}$	type
PbS	81	7.42×10^{9}	6.01×10^{4}	$1.35 imes 10^{-10}$	р
Zn–PbS	82	$2.84 imes 10^9$	$2.33 imes 10^4$	$3.52 imes 10^{-10}$	р

Table 3. Electrical measurements of deposited PbS and Zn–PbS thin films.

near infrared (NIR) regions for Zn–PbS. In addition, a significant shift in the lattice absorption edge due to the inclusion of Zn²⁺ in the film was observed. The absorption edge of the grown Zn–PbS film occurred at $\lambda \sim 918$ nm (near infrared region), while direct energy bandgap value of 1.45 eV was obtained. The blue-shift of the bandgap energy following Zn doping is attributed to Burstein-Moss effect. With the enhanced microstructural, optical and electrical properties, Zn–PbS films could be a desired candidate for future optoelectronic application.

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