Research Article

Rutherford Backscattering Spectrometry Analysis and Structural Properties of $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ Thin Films Deposited by Chemical Spray Pyrolysis

Abiodun E. Adeoye, 1 Emmanuel Ajenifuja, 2 Bidini A. Taleatu, 3 and A. Y. Fasasi 2

1 Engineering Materials Development Institute, Akure 340223, Nigeria
2 Center for Energy Research and Development, Obafemi Awolowo University, Ile-Ife 220005, Nigeria
3 Department of Physics and Engineering Physics, Obafemi Awolowo University, Ile-Ife 220005, Nigeria

Correspondence should be addressed to Emmanuel Ajenifuja; eajenifuja@cerd.gov.ng

Received 8 June 2015; Revised 11 August 2015; Accepted 11 August 2015

Academic Editor: Rodrigo Martins

Copyright © 2015 Abiodun E. Adeoye et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Zinc lead sulphide ternary thin films were prepared by chemical spray pyrolysis on soda lime glass substrates using zinc acetate, lead acetate, and thiourea sources precursor. The films were characterized using Rutherford backscattering (RBS) spectrometry, energy dispersive X-ray (EDX) spectroscopy, scanning electron microscopy (SEM), and X-ray diffractometry (XRD). RBS studies revealed variation in thickness and stoichiometry of the films with respect to compositional substitution between Zn and Pb, thereby giving effective composition $\text{Zn}_x\text{Pb}_{1-x}\text{S}$, where $x=0$, 0.035, 0.069, 0.109, 0.176, and 0.217. Film thickness obtained by length conversion ranged from 81.02 nm to 90.03 nm. Microstructural analyses also indicated that the growth and particle distribution of the films were uniform across substrate's surface. Diffraction studies showed that the films possess FCC crystalline structure. Crystallite size reduced from 14.28 to 9.8 nm with increase in $\text{Zn}^{2+}$ in the $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ samples.

1. Introduction

Thin films of metal chalcogenides particularly Pb, Cd, and Zn have received much attention due to their importance in photovoltaic and optoelectronic semiconductor devices mostly due to the fulfillment of some of the requirements that are essential for device fabrication [1–3]. Most importantly, ternary chalcogenide semiconductors are of special interest in recent time based on the fact that their energy gap and lattice parameters can be adjusted to enhance their optoelectronic and photovoltaic characteristics [4, 5]. Many studies have been carried out on ternary chalcogenide semiconductor thin films. These include $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ [1], $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ [6], $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ [7, 8], $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ [9, 10], and $\text{Cd}_x\text{Pb}_{1-x}\text{S}$. However, to the authors’ knowledge little or no reports are currently available on synthesis of $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ chalcogenide thin films using spray pyrolysis method. Despite the promising and novel characteristics of chalcogenide semiconductors thin films, the use of this class of material in optoelectronic devices may be held back by the difficulty in preparing chemically stable thin films with desired properties. Hence, some technical challenges have to be surmounted in order to prepare chemically stable thin films that could be widely used in optoelectronic device fabrication such as solar cell, light emitting diode, and photodiode. Various deposition techniques such as chemical vapor deposition, vacuum deposition, solution growth, and sputtering have been widely reported for thin film preparation. Limitations such as high cost and stringent growth process conditions (e.g., temperature, pressure, environment, and time) attributed to most of these techniques. Spray pyrolysis is essentially thermally stimulated reaction between clusters of ions or atoms of different chemical species. In spray technique, a solution containing soluble salts of the constituent atoms of the desired compound is sprayed on a substrate maintained at elevated temperatures. Spray pyrolysis is a useful alternative to the traditional methods for obtaining zinc lead sulphide ternary compound thin films.
Table 1: Summary of Zn$_x$Pb$_{1-x}$S deposition precursor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursors (concentration, volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZPS1</td>
<td>Zn(CH$_3$COO)$_2$ $\cdot$ 2H$_2$O (0.1 M, 0 mL) + Pb(CH$_3$COO)$_2$ $\cdot$ 3H$_2$O (0.1 M, 10 mL) + CS(NH$_2$)$_2$ (0.1 M, 20 mL)</td>
</tr>
<tr>
<td>ZPS2</td>
<td>Zn(CH$_3$COO)$_2$ $\cdot$ 2H$_2$O (0.1 M, 0.2 mL) + Pb(CH$_3$COO)$_2$ $\cdot$ 3H$_2$O (0.1 M, 9.80 mL) + CS(NH$_2$)$_2$ (0.1 M, 20 mL)</td>
</tr>
<tr>
<td>ZPS3</td>
<td>Zn(CH$_3$COO)$_2$ $\cdot$ 2H$_2$O (0.1 M, 0.4 mL) + Pb(CH$_3$COO)$_2$ $\cdot$ 3H$_2$O (0.1 M, 9.60 mL) + CS(NH$_2$)$_2$ (0.1 M, 20 mL)</td>
</tr>
<tr>
<td>ZPS4</td>
<td>Zn(CH$_3$COO)$_2$ $\cdot$ 2H$_2$O (0.1 M, 0.6 mL) + Pb(CH$_3$COO)$_2$ $\cdot$ 3H$_2$O (0.1 M, 9.40 mL) + CS(NH$_2$)$_2$ (0.1 M, 20 mL)</td>
</tr>
<tr>
<td>ZPS5</td>
<td>Zn(CH$_3$COO)$_2$ $\cdot$ 2H$_2$O (0.1 M, 0.8 mL) + Pb(CH$_3$COO)$_2$ $\cdot$ 3H$_2$O (0.1 M, 9.20 mL) + CS(NH$_2$)$_2$ (0.1 M, 20 mL)</td>
</tr>
<tr>
<td>ZPS6</td>
<td>Zn(CH$_3$COO)$_2$ $\cdot$ 2H$_2$O (0.1 M, 1.0 mL) + Pb(CH$_3$COO)$_2$ $\cdot$ 3H$_2$O (0.1 M, 9.0 mL) + CS(NH$_2$)$_2$ (0.1 M, 20 mL)</td>
</tr>
</tbody>
</table>

It has several advantages over other deposition processes which include scalability of the process, cost effectiveness, allowance of intentional doping, and low or moderate growth temperatures (100–400°C). These unique properties create different possibilities such as use of variety of substrates, easy control of thickness, variation of film composition, and possibility of multilayer growth [11, 12].

In this study, we present results on zinc lead sulphide (Zn$_x$Pb$_{1-x}$S) thin films deposited on soda lime glass substrate using chemical spray pyrolysis. Rutherford backscattering spectroscopy (RBS) was essentially used to study thickness profile and stoichiometric compositions of the films. EDX was used as complementary technique for identification of films constituents. Surface microstructure and crystal orientation were examined by scanning electron microscopy (SEM) and X-ray diffractometer (XRD).

2. Materials and Methods

2.1. Film Deposition Procedure. Soda lime glass substrates were cleaned by washing with detergent and rinsed with distilled water before ultrasonic cleaning in acetone, methanol, and isopropyl alcohol (IPA) bath each for 20 minutes, respectively. The substrates were dried and kept in the vacuum oven in order to minimize extraneous contamination. The precursors for the Zn$_x$Pb$_{1-x}$S thin films were obtained by preparing equal molar concentration of commercially available lead acetate, zinc acetate, and thiourea in varying proportions depending on the expected concentration of each cation in the thin films. The mixing ratio of the precursors corresponding to each sample designation (ZPS1–ZPS6) is summarized in Table 1. The freshly prepared solutions were stirred thoroughly for several minutes before stepwise spraying onto preheated clean substrates maintained at (250 ± 5)$^\circ$C. Suitable Zn$_x$Pb$_{1-x}$S thin films were obtained by maintaining deposition parameters such as substrate temperature, carrier gas flow rate, and pressure that were at (250 ± 5)$^\circ$C, (3–3.5) dm$^3$/min, and 2.3 bar, respectively. The chemical reaction mechanism of Zn$_x$Pb$_{1-x}$S thin film is as shown below in

$$\text{Pb}_{1-x} (\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O} + \text{Zn}_x (\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + \text{NH}_2\text{CSNH}_2 \rightarrow \text{Zn}_x\text{Pb}_{1-x}\text{S} + 2\text{NH}_4 + 6\text{CO}_2 + 3\text{CH}_4 + 2\text{H}_2 + \text{H}_2\text{O} \quad (I)$$

2.2. Characterization Techniques. Ion beam analysis (IBA) of films was carried out at the Centre for Energy Research and Development (CERED), Obafemi Awolowo University, Ile-Ife, Nigeria. The facility has a general purpose end station for particle induced X-ray emission (PIXE), Rutherford backscattering spectrometry (RBS), elastic recoil detection analysis (ERDA), and particle induced gamma-ray emission (PIGE). Film composition, thickness, and depth profile were concurrently obtained by a 2.2 MeV helium particle. SIMNRA fitting code was used to carry out the spectra analyses of the RBS spectra. Scanning electron microscope (Carl Zeiss MA-10 SEM) with attached EDX facility was used to investigate surface morphology of the films. Structural studies were carried out using GBC EMMA X-ray diffractometer with CuKα radiation ($\lambda = 1.5418$ Å).

3. Results and Discussions

3.1. RBS Analyses. The elemental composition, stoichiometry, and thickness of the deposited Zn$_x$Pb$_{1-x}$S thin films were determined using RBS technique. The SIMNRA Simplex code was used to fit the simulation over experimental data and give information regarding the stoichiometry and areal concentration. Previous study [13] has shown that composition of compound semiconductors has a strong influence on their properties. Therefore, exact control of composition and accurate analysis of elements of these thin films are prerequisite for preparing high quality and chemically stable thin films. Both the heavy elements (Pb, Zn) and the relatively light element (S) were detected concurrently via the backscattering process. The spectra of simulated one-layer structure of Zn$_x$Pb$_{1-x}$S films with varying concentration of Zn are presented in Figures 1(a)–1(f). From distinct nature of the peaks shown in the spectra, it can be inferred that the thin films are relatively uniform and adhere to the substrate well and without diffusion between the layer of the films and the substrate. The results further suggested a thermal decomposition of the precursors to produce stable Zn-Pb-S compound with little or no trace of impurities such as carbon and hydrogen which were part of the constituents of the starting chemicals. Presence of such impurities affects film functionality. In all the spectra, it is also observed that the peaks corresponding to each element are well separated. This is due largely to the differences in the mass of the elements making up the target nuclei, namely, zinc, lead, and sulphur. Peak corresponding to Pb is more enhanced than that of S despite comparable
Figure 1: RBS spectra of deposited thin films of $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ for (a) ZPS1, (b) $x = \text{ZPS2}$, (c) $x = \text{ZPS3}$, (d) $x = \text{ZPS4}$, (e) $x = \text{ZPS5}$, and (f) $x = \text{ZPS6}$. 
concentrations during preparation. This can be attributed to distinctive interaction of the projectile ion ($^{4}$He$^{+}$) with Pb nuclei which is much heavier than sulphur in the target, thereby yielding improved backscattering signal. Compositional results of the Zn$_x$Pb$_{1-x}$S films from the RBS experiment are presented in Table 2. Notable changes are observed in the concentration of elemental composition of the films. This is as a result of incremental variation of number of Zn ions with respect to volume of the zinc acetate in the precursor solution. It therefore implies that using spraying pyrolysis, it is convenient to build into the precursor the desired concentration of dopants in thin films. Expectedly, as the concentration of zinc acetate was increased in the solution, the concentration of zinc ions increased, reaching 8.84% per mL in the 30 mL precursor. Film thickness was obtained in RBS unit (atoms/cm$^2$) as shown in Table 2. In order to obtain it in SI unit, areal density unit was approximated into the length unit using (2) [14]. Since the densities of the deposited films are not known directly and may differ from that of bulk Zn-PbS, therefore, Zn due to its relatively low concentrations in a known Zn-Pb-S mixture can be attributed to induced structural disorder in the films can be attributed to induced structural disorder in the films. The slight shifts in the diffraction peak angle could also be as a result of the increase in heterogeneity of the films due to coalescence and formation of polycrystalline and its particles are closely packed. There is no observable crack or pinhole. Images of other samples (see Figures 3(b)–3(f)) possess similar features with a number of observations: (i) particle size appears smaller than in Figure 3(a) and (ii) particles are coalesced and formation of polycrystal is enhanced as percentage contribution of Zn increases. Thus, it can be suggested that introduction of zinc can cause slight reduction in the particle size. Increasing the Zn$^{2+}$ in the Zn$_x$Pb$_{1-x}$S films caused an increase in surface diffusion.

3.3. Structural and Crystallographic Analysis. The XRD spectra were used to determine the structure and crystallographic orientation of the samples. The diffraction patterns of the Zn$_x$Pb$_{1-x}$S thin film prepared by CSP are shown in Figure 4. The diffraction patterns indicate that the prepared Zn$_x$Pb$_{1-x}$S thin films are polycrystalline in nature with the existence of sharp and well defined peaks.

As shown in Figure 4, all the 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 number 5-592) [15, 16]. The prominent peaks indicate that the crystals have preferred orientations at the planes observed at (111), (200), (220), (311), and (222). The relative diffraction peaks intensities of the most three prominent peaks ($I_{111}/I_{200}$) and ($I_{220}/I_{200}$) of the prepared Zn$_x$Pb$_{1-x}$S thin films are shown in Table 3. Both the intensity ratios ($I_{111}/I_{200}$) and ($I_{220}/I_{200}$) for thin films grown are within the range (0.14–0.24) and (0.12–0.20); these values are lower than the JCPDS standard of 0.84 and 0.57, respectively, showing that the samples prepared have (200) preferred orientation with strong intensity.

In addition, the diffraction angle of the peaks shifts slightly with the addition of Zn$^{2+}$. Also, as the concentration of Zn$^{2+}$ increases, the intensity of diffraction peaks decreases. The slight shifts in the diffraction peaks and decrease in peak intensity with increase of Zn$^{2+}$ in the Zn$_x$Pb$_{1-x}$S thin films can be attributed to induced structural disorder in the films [17]. The slight shift of the diffraction peak angle could also be as a result of the increase in heterogeneity of the films due to

### Table 2: Elemental compositions and thickness profiles of Zn$_x$Pb$_{1-x}$S thin films.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Compositions (%)</th>
<th>RBS thickness ($10^{15}$ atoms/cm$^2$)</th>
<th>Linear thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZPS1</td>
<td>—</td>
<td>155.220</td>
<td>81</td>
</tr>
<tr>
<td>ZPS2</td>
<td>1.65</td>
<td>156.147</td>
<td>82</td>
</tr>
<tr>
<td>ZPS3</td>
<td>3.15</td>
<td>156.121</td>
<td>82</td>
</tr>
<tr>
<td>ZPS4</td>
<td>4.84</td>
<td>156.318</td>
<td>82</td>
</tr>
<tr>
<td>ZPS5</td>
<td>7.45</td>
<td>157.452</td>
<td>82</td>
</tr>
<tr>
<td>ZPS6</td>
<td>8.84</td>
<td>172.465</td>
<td>90</td>
</tr>
</tbody>
</table>

Thickness = \( \frac{\text{atoms per unit area}}{\text{atoms per unit volume}} \) (2)
Table 3: $I/I_0$ ratio of prominent peaks of the prepared films and that of the JCPDS standard.

<table>
<thead>
<tr>
<th>Relative intensity ratio</th>
<th>JCPDS standard</th>
<th>ZPS1</th>
<th>ZPS2</th>
<th>ZPS3</th>
<th>ZPS4</th>
<th>ZPS5</th>
<th>ZPS6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{111}/I_{200}$</td>
<td>0.84</td>
<td>0.14</td>
<td>0.15</td>
<td>0.22</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>$I_{220}/I_{400}$</td>
<td>0.57</td>
<td>0.12</td>
<td>0.14</td>
<td>0.17</td>
<td>0.21</td>
<td>0.22</td>
<td>0.22</td>
</tr>
</tbody>
</table>

The occupation of Zn$^{2+}$ into the host lattice. Crystal size of the samples was estimated using Debye Scherer's formula [18] given by

$$D = \frac{K \lambda}{\beta \cos \theta},$$

where $D$ is the grain size, $\lambda$ is the wavelength (1.5406 Å for CuKα radiation), $\beta$ is the full width at half maximum (FWHM), and $K = 0.94$ is the shape factor approximately equal to unity.

The lattice parameters were estimated using the combination of Bragg's law and plane spacing equation for the rock salt (NaCl) structure given by (4) [19, 20]. The computed crystals size and the lattice constants ($a$) are presented in Table 3:

$$\sin^2 \theta = \frac{1}{a^2} \left(h^2 + k^2 + l^2 \right).$$

Table 4: Computed crystals size and the lattice constants for thin film samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice constant (Å)</th>
<th>Crystal size using Scherer’s formula (nm)</th>
<th>Crystal size using modified Scherer’s formula (nm)</th>
<th>Residual strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZPS1</td>
<td>5.942</td>
<td>14</td>
<td>15</td>
<td>$3.125 \times 10^{-3}$</td>
</tr>
<tr>
<td>ZPS2</td>
<td>5.952</td>
<td>13</td>
<td>13</td>
<td>$3.22 \times 10^{-3}$</td>
</tr>
<tr>
<td>ZPS3</td>
<td>5.961</td>
<td>12</td>
<td>13</td>
<td>$3.85 \times 10^{-3}$</td>
</tr>
<tr>
<td>ZPS4</td>
<td>5.973</td>
<td>12</td>
<td>12</td>
<td>$5.75 \times 10^{-3}$</td>
</tr>
<tr>
<td>ZPS5</td>
<td>5.989</td>
<td>11</td>
<td>11</td>
<td>$6.70 \times 10^{-3}$</td>
</tr>
<tr>
<td>ZPS6</td>
<td>5.995</td>
<td>10</td>
<td>10</td>
<td>$7.00 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The crystal size decreases from 14.28 to 9.8 nm as the concentration of Zn increases in the $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ thin film prepared. The lattice constant increased from 5.942 to 5.995 Å as the Zn$^{2+}$ in $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ increases from ZPS1 to ZPS6 (Table 4).

However, during thin film deposition lattice mismatch between the film and the substrate with the influence of the deposition conditions such as the temperature, composition, and deposition rate can also create strain [21]. Therefore, the
residual strain on the deposited films was calculated using the modified Scherer’s equation [22] expressed in

$$\beta = \frac{KA}{D \cos \theta} + 4\varepsilon \tan \theta, \quad (5)$$

where $\varepsilon$ is the residual strain and $D$ is the grain size. From the data obtained from the diffraction patterns of the prepared $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ thin film shown in Figure 4, the grain size $D$ and residual strain ($\varepsilon$) are deduced from the intercept and slope of the plot of $\beta \cos \theta$ versus $\sin \theta$. Hence the increase of Zn in

Figure 3: SEM micrographs of deposited thin film of $\text{Zn}_x\text{Pb}_{1-x}\text{S}$ for (a) ZPS1, (b) ZPS2, (c) ZPS3, (d) ZPS4, (e) ZPS5, and (f) ZPS6.
the Zn$_x$Pb$_{1-x}$S causes slight increase in residual strain in the film from 3.125 \times 10^{-3} to 7.0 \times 10^{-3}. This may be due to the replacement of some larger lead ions (1.21 Å) by smaller zinc ions (0.74 Å). Similar results were reported for Mn-doped CdS films [23].

### 4. Conclusion

Zinc lead sulphide thin films have been synthesized successfully by chemical spray pyrolysis without any complexing agent, otherwise using common chemical reagents. The desired composition was built into the precursors prior to deposition. Rutherford backscattering experiment revealed changes in the thickness with stoichiometry. Direct observation from the micrographs showed that the films are well crystalline with closely packed particles. Film diffraction analysis indicated direct relationship between lattice constant, residual stress, and Zn compositions. Thus, by suitably controlling the Zn composition in the layers, the Zn$_x$Pb$_{1-x}$S films may have minimum lattice mismatch compared to that of pure PbS in forming heterojunction device.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

### Acknowledgments

The authors acknowledge the immense contribution of Professor A. M. Salau who passed away recently (may his soul rest in peace (amen)). The authors thank staff of Nuclear Accelerator Laboratory at Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria, for RBS measurements and analyses. Efforts of colleagues at Department of Physics of Obafemi Awolowo University Ile-Ife are appreciated. Special appreciation goes to the management of Engineering Materials Development Institute, Akure, Nigeria, for making some of their laboratory facilities available during this study.

### References


Submit your manuscripts at http://www.hindawi.com