GROWTH AND CHARACTERIZATION OF LEAD-SULFIDE FILMS
DEPOSITED ON GLASS SUBSTRATES

SIHAM MAHMOUD and OMAR HAMID

Physics Department, National Research Centre, Cairo, Egypt

Received 31 March 2000; revised manuscript received 3 November 2000
Accepted 7 May 2001

Lead-sulfide (PbS) films have been deposited by chemical deposition method on
glass substrates. The details of the preparation method are described. The advantage
of this method is simple, relatively inexpensive and easily controlled method
that is producing large-area films. Some data about the electrical properties, struc-
ture, composition of the films and thermal stability of the powder samples are also
presented. The structure and crystallite sizes were determined by X-ray diffraction
studies. The films are very adherent to the substrates. The films are polycrystalline
and average crystallite sizes are 15 nm. The surface morphology of the as-deposited
and heated films was studied with a scanning electron microscope. The rate of de-
position and terminal thickness have been determined. Hall measurements were
performed at room temperature for films deposited on glass substrate to determine
the carrier density, Hall mobility and the mean free path of the carriers.

PACS numbers: 73.61.Jc

Keywords: PbS films, chemical deposition method, structure, composition, thermal sta-
bility, crystallite sizes, carrier density, Hall mobility, mean free path of the carriers

1. Introduction

From the point of view of cost reduction of photovoltaic devices, thin film tech-
nology has been identified as a possible solution. The efficiency of the devices
depends largely on the properties of the used materials and on the applied deposi-
tion technique. Various techniques are available for the deposition of polycrystalline
films of semiconducting materials. The growth from the solution is least demanding
and with its simplicity makes it very attractive [1–3].

Lead sulfide, an IV – VI semiconductor with a narrow band gap, has been em-
ployed usually for the detection of infrared radiation, applications in decorative
coating and in imaging techniques. The samples of lead-sulfide films were prepared by the chemical deposition method. The chemical deposition of PbS has been reported previously by other researchers under different conditions [4–10]. The variations have involved changes in the concentration of the lead acetate or nitrate and thiourea solutions, the temperature of deposition and the use of surface seeding nuclei as a means of improving the properties of the films. Pick [11] discussed the factors which influence film formation in homogeneous precipitation reactions. These include the rate of diffusion of colloidal particles to the glass surface and the influence of crystallization nuclei, which can be formed by the addition of metal ions. The growth and characterization of PbS thin films, deposited on glass, ferroelectric ceramic and single crystals (CdS and Ge) substrates from a water solution of reacting chemicals were investigated [4,6,12]. The experimental results indicate that the properties of the PbS films can vary, depending on the nature of the substrate. The growth rate of PbS films grown by the chemical vapour deposition in the temperature range 698 to 733 K depends on the type of substrate material and increases with increasing temperature. The black films formed that way are polycrystalline PbS with cubic structure [3]. The measurements of Seebeck effect at room temperature show that the conduction is p-type for PbS films deposited on glass. Carrier densities derived from measurements of the Hall effect are equal to those derived from the thermoelectric-power measurements. Therefore, they are interpreted to be equal to the carrier density in the grains of the PbS layer [3].

In the present work, X-ray diffraction pattern (using Philips PW 1390 diffractometer), scanning-electron microscope (JOEL-JSM-T20) and the thermal analysis (DCS-50) investigations were carried out with films prepared by the chemical deposition of PbS. The composition of the films was determined by chemical analysis. The carrier density and the mean-free path of the carriers were measured, and the Hall mobility of the films were determined by Hall-effect measurements.

2. Experimental procedure

The lead sulfide films were deposited by the chemical deposition method. Before the deposition, the glass substrates were washed in HNO$_3$ and distilled water. Then, they were mounted vertically and immersed into the deposition bath containing an aqueous solution of the following constituents mixed in the sequence: 0.175M Pb(NO$_3$)$_2$, 0.57M NaOH, 0.1M CS(NH$_2$)$_2$ and H$_2$O. The reaction process is considered as follows:

$$\text{Pb(NO}_3\text{)}_2 + 2\text{NaOH} \rightarrow \text{Pb(OH)}_2 + 2\text{NaNO}_3,$$  \hspace{1cm} (1a)

$$\text{Pb(OH)}_2 + 4\text{NaOH} \rightarrow \text{Na}_4\text{Pb(OH)}_6,$$  \hspace{1cm} (1b)

$$\text{Na}_4\text{Pb(OH)}_6 \rightarrow 4\text{Na}^+ + \text{HPbO}_2^- + 3\text{OH}^- + \text{H}_2\text{O}.$$  \hspace{1cm} (1c)
In the alkaline medium, the thiourea decomposed and released $S^{2-}$ ions which precipitate $Pb^{+2}$ ions from the solution.

$$SC(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + SH^-,$$

$$HPbO_2^- + SH^- \rightarrow PbS + 2OH^-.$$ (1d) (1e)

The deposition of the films from a solution involves a nucleation phase in which an initial layer of $Pb(OH)_2$ formed on the glass substrate is chemically converted into $PbS$ by the reaction with $S^{2-}$ ions available in the bath from the hydrolysis of thiourea. The presence of $Pb(OH)_2$ in the as-prepared bath is very vital for the deposition of $PbS$ thin films [9,10]. However, too much of a turbidity would lead to the incorporation of $Pb(OH)_2$ in the films for deposition of longer duration [9,10]. It is speculated that the deposition rate at a constant temperature should be affected mainly by the concentration of thiourea and NaOH. It was found that the increase in the NaOH concentration makes the surface of the deposited film darker and the growth rate decreases slightly. Also, the quantity of thiourea predominantly affects duration of the deposition, while lower concentrations of thiourea give lower growth rates and longer incubation times.

The deposition of the $PbS$ films was done at the room temperature. The advantage of the low temperature used is that during the growth process there is a small possibility for the diffusion of the constituents of the depositing film into the substrate. After the deposition, the slides were removed from the chemical bath after different dipping times, rinsed with distilled water, dried and placed into a desiccatior. A mirror-like surface was obtained. The thickness of each grown film was calculated from the known mass of the deposit, surface area and density. It was assumed that the film has a density of 7.596 g/cm$^3$ (of bulk $PbS$), although these films are expected to have a somewhat lower density than the bulk $PbS$ due to the lower stoichiometry and poorer crystallinity. This method has been in use for finding the thickness of thin films [13,14]. The film thickness is in the 120 to 220 nm range. The bulk ingot material of $PbS$ was prepared by direct fusion of a mixture of the constituent elements (purity 99.999%) in stoichiometric proportions in vacuum sealed silica tube. Hall measurements were made in a standard DC Hall-effect apparatus with a vibrating-read electrometer. Ohmic contacts were made by a simple vacuum evaporation of gold.

3. Results and discussion

Lead sulfide ($PbS$) is known to crystallize in cubic crystalline lattice with the lattice constant $a = 0.59458$ nm [15]. Atomic coordinates are (0,0,0) and (0,1/2,1/2) for $Pb$ and (1/2,1/2,1/2) and (1,1,1/2) for S. Distances between closest $Pb$ atoms and closest $S$ atoms are 0.42 nm.

Figure 1 shows the XRD patterns of the $PbS$ thin films deposited on a glass slide (a), of the powder collected from the chemical-deposition bath (b) and of the
powder from the thermal ingot (c). The $d$-values of the lines obtained from XRD patterns were calculated and compared with the corresponding values for PbS in the JCPDS card in Table 1. The derived $d$-values are in good agreement with the standard values, which conform that the film constitutes of PbS. Well-defined (111), (200), (220), (311) and (222) peaks are observed in the XRD pattern. The film is polycrystalline. The average crystallite sizes of 15 nm were determined by measuring the full width at half maximum of the (111), (200) and (220) peaks and using the Scherrer formula [16]

$$T = \frac{k\lambda}{D\cos \theta}.$$  

Fig. 1. X-ray results for chemically deposited PbS: a) thin film, b) powder, c) powder from the thermal ingot and d) JCPDS card.
For PbS films deposited on glass, the nucleation rate is considered to be larger than the growth rate due to the great number of nucleation centres that exist on the surface of the substrate [4]. This could explain that PbS films deposited on glass are compact and with crystallites of small size.

**TABLE 1.** Comparison of the observed \( d \)-values (in units of \( 10^{-10} \) m) for PbS (derived from Fig. 1) with the JCPDS card.

<table>
<thead>
<tr>
<th>hkl</th>
<th>JPCDS (d)</th>
<th>Film-chem. (a)</th>
<th>Powder-chem. (b)</th>
<th>Ingot (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>3.429 84</td>
<td>3.43 90</td>
<td>3.426 85</td>
<td>3.428 83.9</td>
</tr>
<tr>
<td>200</td>
<td>2.969 100</td>
<td>2.986 100</td>
<td>2.969 100</td>
<td>2.969 100</td>
</tr>
<tr>
<td>220</td>
<td>2.099 57</td>
<td>2.096 38</td>
<td>2.095 76</td>
<td>2.098 74</td>
</tr>
<tr>
<td>311</td>
<td>1.79 35</td>
<td>1.789 21</td>
<td>1.788 56</td>
<td>1.79 55</td>
</tr>
<tr>
<td>222</td>
<td>1.714 16</td>
<td>1.713 15.6</td>
<td>1.715 37</td>
<td>1.715 29</td>
</tr>
<tr>
<td>400</td>
<td>1.484 10</td>
<td>1.482 9.9</td>
<td>1.483 28</td>
<td>1.482 37</td>
</tr>
<tr>
<td>331</td>
<td>1.362 10</td>
<td>1.36 9.9</td>
<td>1.361 28.2</td>
<td>1.362 21</td>
</tr>
<tr>
<td>420</td>
<td>1.327 17</td>
<td>1.326 11.9</td>
<td>1.325 37.7</td>
<td>1.325 32.2</td>
</tr>
<tr>
<td>422</td>
<td>1.212 10</td>
<td>1.211 8</td>
<td>1.212 30.3</td>
<td>1.211 23</td>
</tr>
<tr>
<td>511</td>
<td>1.142 3</td>
<td>1.142 6.3</td>
<td>1.142 27</td>
<td>1.142 18</td>
</tr>
<tr>
<td>440</td>
<td>1.0489 6</td>
<td>1.049 5.1</td>
<td>1.049 22</td>
<td>1.049 14.5</td>
</tr>
<tr>
<td>531</td>
<td>1.0034 5</td>
<td>1.003 5.1</td>
<td>1.0029 23.7</td>
<td>1.0031 17</td>
</tr>
<tr>
<td>600</td>
<td>0.9893 6</td>
<td>0.988 5.9</td>
<td>0.989 25.1</td>
<td>0.988 20</td>
</tr>
<tr>
<td>620</td>
<td>0.9386 4</td>
<td>0.937 5.1</td>
<td>0.939 22.5</td>
<td>0.938 17</td>
</tr>
<tr>
<td>533</td>
<td>0.905 2</td>
<td>0.903 4.7</td>
<td>0.904 20</td>
<td>0.904 5</td>
</tr>
<tr>
<td>622</td>
<td>0.8952 4</td>
<td>0.893 5.1</td>
<td>0.894 22.9</td>
<td>0.894 16</td>
</tr>
</tbody>
</table>

The differential-scanning calorimeter (DSC) spectra for the powder samples (chemical deposition and thermal ingot) are shown in Fig. 2. Figure 2a shows two exothermic peaks, the first at \( 260.59 \pm 5^\circ C \), which can be attributed to the growth of grain size. The second peak (at \( 432.04 \pm 4^\circ C \)) indicates that at higher annealing temperatures a transformation to another crystalline state may occur. The thermal-ingot powder (Fig. 2b) shows a high-intensity exothermic band at \( 278.72 \pm 4^\circ C \) and an endothermic band (\( 398.59 \pm 5^\circ C \)) at higher temperatures.

Lead sulfide is formed when the ionic product (\( IP \)) of Pb\(^{2+} \) and S\(^{-2} \) exceeds the solubility (\( SP \)) of PbS. The ratio \( IP/SP = S \) defines the super-saturation of the ions over the PbS and can be varied by choosing the appropriate initial concentration of the reactants. When \( S > 1 \), the ions combine on the substrate and in the solution to form PbS nuclei which grow with time to give film and precipitate, respectively. Once PbS is formed, it acts as a catalyst for preferential further deposition of fresh portions of PbS. As the catalytic PbS surface develops both on the surface and in the volume of the solution, the proportion of PbS formed on the substrate is determined by the ratio of nuclei formed on the substrate and in the solution.
Fig. 2. Differential scanning calorimeter spectra of PbS powder samples, a) chemical deposition, b) thermal ingot.

Fig. 3. Thickness of PbS films as a function of deposition time.
Figure 3 shows a typical curve for film thickness as a function of the dipping time. In the initial stage of the growth, the thickness increases at a fast rate. Subsequently, the rate decreases, resulting in a terminal thickness. The rate of deposition is high in the initial stages of growth because the concentration of Pb$^{+2}$ and S$^{-2}$ ions is high. As more and more PbS is formed, the solution becomes depleted of ions, resulting in a lower rate of deposition. The rate of deposition becomes zero, resulting in a terminal thickness, when the concentration of Pb$^{+2}$ and S$^{-2}$ ions decreases to a values such that $S < 1$.

The growth mechanism of formation of PbS films, deposited on glass substrate for different dipping times and for different annealing, is supported by the investigations with the scanning electron microscope, as seen in a series of electron micrographs in Fig. 4. The photographs were taken under the same conditions of the electron energy (20 keV) and magnification (6000×) to compare the size of the crystallites. The figures show a cross-like needle-shaped crystalline structure with a fair amount of inter-crystallite space. As the film thickness increases, these needle-like crystallites grow in size and more inter-spaces appear. The sample shown in Fig. 4d was annealed at 473 K for one hour; the formation of large, irregular clumps of PbS could be observed. The electron micrograph indicates the presence of randomly oriented inter-grown aggregate crystals in a heterogeneous size distribution (Fig. 4e).

In single-crystal semiconductors, there is a simple relationship between the Hall coefficient $R_H$ and the free-carrier density $N$

$$N = \frac{r}{eR_H},$$

where the scattering factor $r$ is close to unity. Combined with the measurement of conductivity $\sigma$, this yields the well-known equation for the Hall mobility

$$\mu_H = R_H\sigma.$$

The mean free path $\ell$ of the carriers can be estimated from the following relation

$$\ell = \frac{h}{2e} \left( \frac{3n}{\pi} \right)^{1/3} \mu_H,$$

where $h$ is the Planck constant and $e$ the electron charge.

In the case of polycrystalline films, difficulties arise due to the fact that the electrical properties of such films are usually dominated by charge trapped at grain boundaries, resulting in carrier depletion over part or all of the grains. In other words, the carrier density is spatially inhomogeneous, and the interpretation of Hall-effect measurements is no longer straightforward. Volger [17] proposed a geometric model for an inhomogeneous material consisting of conducting grains separated by more-resistive inter-granular material. He showed how the measured Hall effect could deviate appreciably from the Hall effect appropriate to the grains.
in such a configuration. Measurements of the carrier density by Hall effect or by thermoelectric power give the density of free holes in the grains [18].

Fig. 4. Scanning electron micrographs of PbS films prepared in different ways, enlargement 6000×. Dipping times and the thickness of the films were: a) 10 min, \( d = 141 \text{ nm} \), b) 20 min, \( d = 171 \text{ nm} \), c) 30 min, \( d = 196 \text{ nm} \), d) 40 min, \( d = 201 \text{ nm} \), e) 40 min, \( d = 201 \text{ nm} \), but also annealed at 473 K for 1 hour.

Equations (3) to (5) were applied for the calculation of the carrier density, Hall carrier mobility and the mean free path of the as-deposited PbS thin films prepared
in this work. The thickness and the resistivity of the films were approximately 0.2 μm and 5 Ωcm, respectively. The measurements of the Hall effect confirmed the p-type conduction for PbS films deposited on glass substrate. The carrier concentration was estimated at about $2.5 \times 10^{17}$ cm$^{-3}$ and the mobility is about 5 cm$^2$/Vs. These values give the mean free path of the carriers, $\ell$, of 0.642 μm. These results are in a good agreement with the results in the literature [4,19]. The measured Hall mobility is very small compared to the value of 500 cm$^2$/Vs, expected at room temperature for a single crystal of PbS [20].

4. Conclusion

Microstructure characterization was carried out by X-ray diffraction and scanning electron microscopy in order to determine the crystallite size and to study the surface morphologies of the as-deposited and of heat-treated films of PbS. The grain size of the films, as observed by SEM, is found to increase with increasing thickness, and a clear change in the films was observed due to annealing. It was established by X-ray analysis that PbS films prepared on glass substrates are polycrystalline and the primary direction was (111). The as-deposited PbS films have p-type conductivity and a low resistivity (5 Ωcm). The carrier density, Hall mobility and the mean free path of the carriers of PbS films are in the range $2.5 \times 10^{17}$ cm$^{-3}$, 5 cm$^2$/Vs and 0.642 μm, respectively.

References

RAST I PROUČAVANJE TANKIH SLOJEVA OLOVNOG SULFIDA TALOŽENOG NA STAKLENU PODLOGU