Synthesis, Structural and Optical Characterizations of Sprayed PbS Thin Films

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1. INTRODUCTION

Lead sulfide (PbS) is a group IV-VI semiconducting material that has attracted considerable attention due to its small direct band gap, with low resistivity, and polycrystalline cubic structure (Aadim et al., 2017; Ravi Shankar et al., 2015; Pathan and Lokhande, 2004; Obaid et al., 2012). During the last few years, the research on the growth of nanoparticle PbS films has increased, for its technological applications. It is one of the earliest semiconducting materials and has been employed in various technological applications such as solar control coatings, solar absorber, photography, sensors, optical switch, infra-red detectors (Nair and Nair, 1990; Adachi et al., 2013; Nair et al., 1992; Saran and Curry, 2016; Peterson and Krauss, 2006; Subramanian et al., 2006).

PbS thin films can be obtained by several methods, like pulsed laser deposition, ion beam sputtering, thermal evaporation, vacuum deposition, chemical vapor deposition, co-precipitation, sol-gel, chemical bath deposition etc. (Atwa et al., 2011; Martin et al., 1982; Shyju et al., 2014; Poling and Leja, 1963; Mattoo, 1998; Katayama et al., 2004; Martucci et al., 1999; Valenzuela et al., 2013). Owing
into simplicity and inexpensiveness, the chemical spray pyrolysis technique is a better chemical method at a lower cost for the preparation of thin films with a larger area (Thangaraju and Kaliannaan, 2000). This method is convenient for preparing pinhole free, homogenous, smoother thin films with the required thickness.

In the present study, spray pyrolysis method utilized for growing PbS thin films on glass substrate at different substrate temperatures. The main goal in this research consists in establishing the role of substrate temperatures on growth and properties of the prepared thin films. The structural, morphological and compositional characteristics were investigated. The optical properties were also measured and the relative parameters were calculated and investigated.

2. MATERIALS AND METHODS

PbS thin films deposited by using spray pyrolysis technique on cleaned microscopic glass slide of dimensions, (76.2 mm × 25.4 mm × 1 mm) as a substrate. The films were formed from aqueous solution of lead acetate [Pb(CH3COO)2.3H2O] and thiourea [CS(NH2)2] with the molar ratio (Pb:S=1:2) at a different substrate temperature in the range (150-350) °C.

The solution was prepared by solving the salts in double distilled water with the hydrochloride acid (HCl). In order to distribute the sprayed solution regularly on the substrate to get uniform thin films, the distance between the nozzle and the hot plate was fixed at (30 cm) and the spray rate kept constant (4 ml/min). The nitrogen (N2) gas is used as carrier gas with pressure rate (2.5 bar), the spraying period is 10 sec and stopping for 10 min to avoid the excessive cooling of the substrate. The possible chemical reaction that takes place is as follows (Rajashree et al., 2014; Zaman et al., 2014):

\[
Pb(CH_3COO)_2 + SC(NH_2)_2 + 2H_2O -> PbS \downarrow + 2CH_3COOH \uparrow + 2NH_3 \uparrow + CO_2 \uparrow
\]

The experimental set-up of (SPT) is shown in Figure (1) bellow.

**Figure 1:** Schematic diagram of spray pyrolysis system.

3. RESULTS AND DISCUSSION

Daily oral administration of fluoxetine for one month caused several histological alterations in liver, kidney and cerebrum of rats.

3.1 Structure properties

Figure (2) shows the X-ray diffraction pattern of PbS thin films deposited at different substrate temperatures in the range (150-350) °C with a molar ratio of (Pb: S=1:2). XRD patterns of all the PbS thin films showed sharp [2 0 0] peak along with minor peaks of [1 1 1], [2 2 0] and [3 1 1] planes matched by Inorganic Crystal Structure Database (ICSD- Reference code 00-005-0592). All PbS films have a face center cubic structure as confirmed by standard ASTM data (Faraj, M. G. 2015). The films deposited at (Ts=300°C) show narrow and sharper of main [200] peak at 2θ = 30.173° indicating an improvement of the film crystalline. If the deposition temperature is too high (>400°C), no film for PbS will be formatted, where at high temperature the spray
solution gets vaporized before reaching the substrate and the film becomes almost powdery (white color, and poor adhesion with substrate).

Figure 2: X-ray diffraction (XRD) patterns of PbS thin films prepared at different substrate temperatures (150-350) °C.

The determined structural parameters, such as peak position (2θ), Full Width Half Maximum (FWHM), interplanar spacing (d), intensity (Int.%), and miller indices (h k l) of the X-ray patterns of PbS thin films examined with the Inorganic Crystal Structure Database (ICSD) are summarized in table (1):

The crystalline grain size (D) is calculated using Scherrer formula (Birks and Friedman, 1946):

\[ D = \frac{K\lambda}{B \times \cos \theta} \]  

Equation 3

Where K is the shape factor equal to 0.9 for the unknown shape of grain size, λ is the wavelength of the X-ray used (1.5460 Å), B is the full-width at half maximum of the peak which has the maximum intensity and θ is the incident angle (Braggs angle). To know the effect of the substrate temperature on the structure of the prepared films in details, the determined values of the important structural parameters such as lattice constant, grain size (D). The grain size increase with increasing substrate temperature till 300 °C gain the maximum value, after that the grain size decreased with increasing temperature. The results are shown in the table (2):

Table 1: XRD results identify the structure parameters for strongest 3 peaks of PbS films deposited at different substrate temperatures.

| T_s [°C] | Pos. [2θ] | FWHM | d-spacing [Å] | I/I_0 | Matching code | Pos. [2θ] | d-spacing [Å] | h   | k   | l   |
|----------|-----------|------|---------------|-------|---------------|-----------|---------------|------|------|------|
| 150      | 30.357    | 0.4017 | 2.94202       | 100   | 00-005-0592   | 30.0738   | 2.969         | 2    | 0    | 0    |
| 200      | 30.2172   | 0.2082 | 2.95531       | 100   | 00-005-0592   | 30.0738   | 2.969         | 2    | 0    | 0    |
| 225      | 30.2372   | 0.1946 | 2.9534        | 100   | 00-005-0592   | 30.0738   | 2.969         | 2    | 0    | 0    |
| 250      | 30.2246   | 0.1858 | 2.9546        | 100   | 00-005-0592   | 30.0738   | 2.969         | 2    | 0    | 0    |
| 275      | 30.1559   | 0.1788 | 2.96118       | 100   | 00-005-0592   | 30.0738   | 2.969         | 2    | 0    | 0    |
| 300      | 30.173    | 0.1681 | 2.95954       | 100   | 00-005-0592   | 30.0738   | 2.969         | 2    | 0    | 0    |
| 325      | 30.1371   | 0.2057 | 2.96298       | 100   | 00-005-0592   | 30.0738   | 2.969         | 2    | 0    | 0    |
| 350      | 30.141    | 0.1722 | 2.96261       | 100   | 00-005-0592   | 30.0738   | 2.969         | 2    | 0    | 0    |

The lattice constant (a) of the unit cell for cubic crystal structure was evaluated according to the relation (Barrett and Massalski, 1980):

\[ d = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}} \]  

Equation 1

Where d is inter-planer spacing.

\[ a = d\sqrt{h^2 + k^2 + l^2} \]  

Equation 2
Table 2: XRD results identify the determined structure parameters for dominate peak of PbS films deposited at different substrate temperatures.

| $T_s$ (°C) | Lattice Constant (Å) | Grain Size (nm) |
|------------|----------------------|-----------------|
| 150        | 5.88404              | 19.07932526     |
| 200        | 5.91062              | 36.82370735     |
| 225        | 5.9068               | 39.39534683     |
| 250        | 5.9092               | 41.2624445      |
| 275        | 5.92236              | 42.88479886     |
| 300        | 5.91908              | 45.61269295     |
| 325        | 5.92596              | 37.27827343     |
| 350        | 5.921050             | 44.53002658     |

3.2 Morphology and Compositional

Scanning electron microscope (SEM) was used for the morphological study of PbS thin films. Figure 3 (a, b and c) shows SEM images of PbS thin films that are prepared at different substrate temperatures 150°C, 300°C and 350°C respectively, with higher magnification SEM image at upper-right inset for the sample deposited at substrate temperature 300°C. Different shapes of crystals for the films deposited at different substrate temperatures were observed. It is shown that the morphology of the PbS thin films is strongly affected by the substrate temperature and especially the grain dimensions throughout the films. The SEM micrograph of the films clearly shows the improvement in crystallite size of PbS after increasing the substrate temperature. The thin films had a lot of agglomerations, the grain size of PbS thin films becomes larger and the morphology becomes denser. The film deposited at low substrate temperature 150°C is poorly crystalline as shown in Figure 3(a) due to a big drop of solution arrived on the substrate and the low temperature is not enough for the chemical reactions to create a good quality thin film. The creation of larger grains is as a result of coalescence of small grains into bigger one, which can be seen from Figure 3(b) for the film deposited at the substrate temperature of 300°C. On the other hand, more increasing of the substrate temperature leads to an unclear surface morphology which can be seen from Figure 3(c) for the film deposited at the substrate temperature of 350°C. It is observed that the films deposited at substrate temperature of 300°C uniform, well substrate covered and smooth throughout all the regions. The films are without pinhole or cracks; we clearly observe the nanocrystalline nature of PbS thin films.
3.3 Optical properties

To study the effect of substrate temperature on the optical properties of the PbS thin films, the optical absorbance, transmittance and reflectance spectra of all films were obtained. The action spectra were taken in the range of 300–2500 nm. The absorbance spectra of PbS thin films at three different substrate temperatures (150, 300 and 350) °C with a molar ratio of (Pb: S=1:2) were measured by the UV-VIS-NIR spectrophotometer. The optical transmittance spectra for the deposited PbS thin film can be calculated by using the equation bellow:

$$ T = 1 - (A + R) $$

Equation 4

Figure 5, 6 and 7 shows a variation of absorbance, transmittance and reflectance spectra of the PbS thin film with wavelength (λ) at three different substrate temperatures. The result shows that all films had a high absorbance in the visible region; however, the absorbance is decreased smoothly from visible to near IR region.

![Figure 3(a, b, c): SEM image of PbS thin films with molar ratio 1:2 deposited at substrate temperature of a-150°C, b-300°C and c-350°C, with higher magnification SEM image at upper-right inset for the film deposited at 300°C(b).](image)

![Figure 4: EDX spectrum of PbS film deposited with a molar ratio of Pb:S=1:2 deposited at substrate temperature of a-150°C, b-300°C and c-350°C, with higher magnification SEM image at upper-right inset for the film deposited at 300°C(b).](image)

![Figure 5, 6 and 7: Variation of absorbance, transmittance and reflectance spectra of the PbS thin film with wavelength (λ) at three different substrate temperatures.](image)
Figure 5: Absorbance spectra for PbS thin films at three different temperatures.

Figure 6: Transmittance spectra for PbS thin films at three different temperatures.

Figure 7: Reflectance spectra for PbS thin films at three different temperatures.

The reflectance is high in near infrared and near visible regions this means that PbS films can be used as solar control coatings as they have a low optical transmittance in the UV region and an appreciable reflection in the NIR region (Kanazawa and Adachi, 1998).

The absorption coefficient ($\alpha$) was calculated from absorbance spectra ($A$) and the thin film thickness ($t$) which was calculated by using the relation below (Obaid et al., 2012):

$$\alpha = 2.3026 \times \frac{A}{t} \quad \text{Equation 5}$$

The calculated values of $\alpha$ were drawn versus wavelength for the three deposited substrate temperatures and the result is shown in Figure (8).

Figure 8: Absorption coefficient as a function of wavelength for PbS thin films at three different temperatures.

The general band gap formula is found by relation below (Obaid et al., 2012):

$$\alpha(h\nu) = A(h\nu - E_g)^{\gamma} \quad \text{Equation 6}$$

Where $\gamma$ constant = 1/2, 3/2 and 2, 3 for direct allowed, direct forbidden, indirect allowed, indirect forbidden transitions respectively. Figure 9 (a, b and c) show the
variation of \((\alpha h\nu)^2\) versus \((h\nu)\) for all the samples. The nature of the plots indicates the existence of direct optical transitions. The band gap \((E_g)\) is determined by extrapolating the straight-line portion of the plot to the energy axis. The intercept on energy axis at zero absorption gives the value of band gap energy \(E_g\) for all the samples. The determined values of \(E_g\) were found to be \((2.1, 1.85 \text{ and } 1.9)\) eV for PbS thin films deposited at substrate temperatures \((150, 300 \text{ and } 350)\) °C respectively.

\(\begin{align*}
\text{Figure 9 (a, b and c): Variation of } (\alpha h\nu)^2 \text{ versus } h\nu \text{ for the films deposited at difference substrate temperatures.}
\text{The refractive index } (n) \text{ can be calculated from equation (7) below (Obaid et al., 2012):}
\end{align*}\)

\[n = \frac{(1 + \sqrt{R})}{(1 - \sqrt{R})}\]

Equation 7

Figure (10), shows the calculated refractive index \((n)\) versus wavelength \((\lambda)\) for the films deposited at \(T_s = (150, 300 \text{ and } 350)\) °C. The figure indicated that all films had a low refractive index in the low wavelength region and it increases with increasing wavelength due to change in reflectance of the film.

\(\begin{align*}
\text{Figure 10: Refractive index versus wavelength for PbS thin films at three different temperatures.}
\end{align*}\)
The extinction coefficient can be determined from Maxwell equations (Kasar, 2006):

\[ k = \frac{\alpha \lambda}{4\pi} \]  

**Equation 8**

Figure (11) shows the variation of the determined extinction coefficient versus wavelength (\( \lambda \)) for PbS thin films deposited at three different temperatures. It can be seen that the extinction coefficient increased with the wavelength for all the films.

![Figure 11: The extinction coefficient versus wavelength for PbS thin films at three different temperatures.](image)

4. CONCLUSION

In this study, PbS thin films were deposited on glass substrates by spray pyrolysis technique at substrate temperatures in the range (150-350) °C. Structural and optical properties have been investigated, and the following conclusions can be drawn on the basis of the experimental data.

- XRD studies revealed that the films were crystalline in nature with face centered cubic phase and a preferential orientation along the (200) plane. The films which were formed at a substrate temperature of 300°C were well crystalline compared with the films formed at others substrate temperatures.
- SEM analysis revealed that the morphology of the films is strongly affected by the substrate temperature. The prepared films at a substrate temperature of 300°C exhibited very smooth surfaces and good crystallographic structure.
- EDX spectrum exhibits the purity of the films and clear existence of Pb and S elements with stoichiometric ratio for the films deposited at 300°C substrate temperature.
- Optical studies revealed that the films are good absorbers with a direct band gap in the range of (1.85-2.1) eV, and transmittance below 50%. The spectra measurements showed a high absorbance coefficient of the films and their absorption edges at near infrared region. The low transmittance in the UV-VIS region and high reflectance in the IR region makes the films suitable for solar control coatings.

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