

Effect of Thickness on the Structural and Electrical Properties of Spray Pyrolysed Lead Sulfide Thin Films

Mohammad Ghaffar Faraj

Department of Physics, School of Science, Faculty of Science and Health, University of Koya, Koya, Iraq

Abstract Lead sulfide (PbS) thin films of different thicknesses ranging from 100 to 300 nm were prepared on glass substrates at 325°C by chemical spray pyrolysis (CSP) technique. PbS thin films were prepared using a solution of Lead nitrate and thiourea. The structural properties were carried out by X-ray diffraction (XRD). X-ray diffraction patterns reveal that the films exhibit the cubic rock salt (NaCl) type structure. The crystalline grain sizes of the films increase with increasing film thickness. The root mean square (RMS) roughness of the films was measured using scanning tunneling microscope (STM). The root mean square roughness of the films increases as the film thickness increases. At room temperature, electrical resistivity and charge-carrier concentration of the PbS film varies from 53.72×10^3 to $1.1 \times 10^3 \Omega \cdot \text{cm}$ and 2.98×10^{10} to $1.2 \times 10^{12} \text{ cm}^{-3}$, respectively.

Keywords Lead Sulfide, Chemical Spray Pyrolysis, Thin Film, Semiconductor

1. Introduction

Among the IV-VI semiconductors, PbS thin films have been used in a lot of applications, including electronic and optoelectronic devices [1-3]. PbS is an important direct narrow gap semiconductor material with band gap energy of 0.4 eV and has a cubic lattice with unit cell face center cube [4-6].

Many techniques have been reported for the deposition of PbS thin films such as chemical bath deposition (CBD) [7], electrodeposition (ED) [8], Chemical spray deposition (CSP) [9] and thermal evaporation technique [10]. Of the various techniques, spray technique is an attractive method because large-area films with good uniformity can be grown at a low cost [10, 11].

In this present work, an attempt has been made to study the structural and electrical properties of the PbS thin films with different thicknesses ranging from 100 to 300 nm grown by Chemical Spray Pyrolysis technique on glass substrate. An effort has also been made to see the effect of thickness on structural and electrical properties of prepared films.

2. Experimental Detail

2.1. Glass Substrate Cleaning

Glass slides with the dimensions of $75 \times 25 \times 2$ mm were used as substrates. In the (CSP) technique, cleaning the substrate surface is very important due to its effect on adherent thin film properties. Firstly, the substrates were cleaned by alcohol for 10 min to remove contamination. After the cleaning process, all of the substrates were rinsed with distilled water. The samples were dried with nitrogen (N_2) gas.

2.2. Materials

Lead (II) acetate trihydrate ($\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$; 99.999%), Thiourea ($\text{CS}(\text{NH}_2)_2$, 99.0%) were acquired from Acros Organics.

2.3. Preparation of PbS Solutions

A typical PbS solution procedure involves:

1. Thiourea solution [$\text{CS}(\text{NH}_2)_2$]: This solution was prepared with molarities (0.1M), from solving (0.761gm) of thiourea in (100ml) of distilled water and was marked solution 1. This solution was vigorously stirred using a magnetic stirrer about 10 minutes.
2. Lead Nitrate solution [$\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$]: This solution was prepared with molarities (0.1M), from solving (2.78gm) of lead acetate in (100ml) of distilled water and was marked Solution 2. This solution was vigorously stirred using a magnetic stirrer about 10 minutes. A solution 1 was added to solution 2 and vigorously stirred using a magnetic stirrer and was marked solution 3.

PbS thin films were deposited from a solution 3 by chemical spray pyrolysis technique on glass substrate. In

* Corresponding author:

mohammad.ghaffar@koyauniversity.org (Mohammad Ghaffar Faraj)

Published online at <http://journal.sapub.org/ajcmp>

Copyright © 2015 Scientific & Academic Publishing. All Rights Reserved

order to get uniform thin films, the height of the spraying nozzle and the rate of spray process were kept constant during the deposition process at 35 cm and 15 cm³/min. The spraying process lasted about 6 sec. The period between spraying processes was about 1 min; this period was enough to avoid excessive cooling of the substrate. PbS thin film was deposited on glass substrate at a temperature of 325°C and a concentration of 0.1 M. The crystallographic structure of the PbS thin films deposited on the glass substrates was determined with a high resolution X-ray diffractometer system (Model: Panalytical Empyrean) with CuK α radiation (λ) of 0.154 nm. The surface morphology of PbS thin films was determined with Scanning Tunneling Microscope (STM) (Model: NT-MDT Solver Nano). The film thickness was measured by the gravimetric method. The electrical properties of PbS thin films was measured by Hall measurements (HL5500PC) system.

3. Results and Discussion

3.1. Structural Properties

The X-ray diffraction patterns of PbS films with different thickness are shown in **Fig. 1**. All PbS films have cubic rock salt (NaCl) type structures. XRD patterns of all the PbS thin films showed sharp [1 1 1] and [2 0 0] peaks along with minor peaks of [2 2 0], [3 1 1], [2 2 2] and [4 0 0] planes to cubic structure of PbS thin films, as confirmed by standard ASTM card (No. 030660020). It has been observed that the intensity of the peaks increased and the crystallization of PbS thin films were improved with increasing film thickness, similar to other reports [12].

For all films the preferential orientation value of [200] plane has the highest value compared to other planes. This result indicates a strong orientation growth along that plane. This behavior is in agreement with that reported in standard literature [4]. The crystalline grain size (t) of the PbS films was determined with the Scherrer formula [13].

$$t = 0.9 \lambda / \beta \cos \theta \quad (3.1)$$

where β is the full width at half maximum (FWHM) of the peak, λ is the wavelength of the X-ray, 1.5406 Å, and θ is the peak position. Based upon the line width of the [200] diffraction peak, the crystalline grain size for the PbS films with differing thickness were 24.49–47.66 nm for films with thickness of 100–300 nm. That is, the grain size of the PbS films increased with increasing thickness [13, 14] as **Fig.2** shows. It was observed that the increase of the thickness increase the diffraction peak intensity of (200) plane which resulted in increase in grain size and good crystallinity of the films. The full width at half maximum (FWHM) of [200] plane decreases from (0.38° to 0.204°) with increasing the thickness, similar to other reports [15] as **Fig.3** shows.

STM images for surface morphologies of PbS thin films are as shown in **Fig.4**. The surfaces of the products of PbS thin films were obviously smooth. The evaluated root mean

square (RMS) surface roughness of the films was 11.084, 11.448 and 12.551 nm for films with thickness of 100–300 nm, as seen in **Fig. 5**. The increase of RMS roughness with the increase of film thickness was due to the larger size grains formation as well as increase in the porosity [16]. In all cases, conical features clearly seen on the films surface were the cause of the surface roughness. This behavior is in agreement with other reported [17].

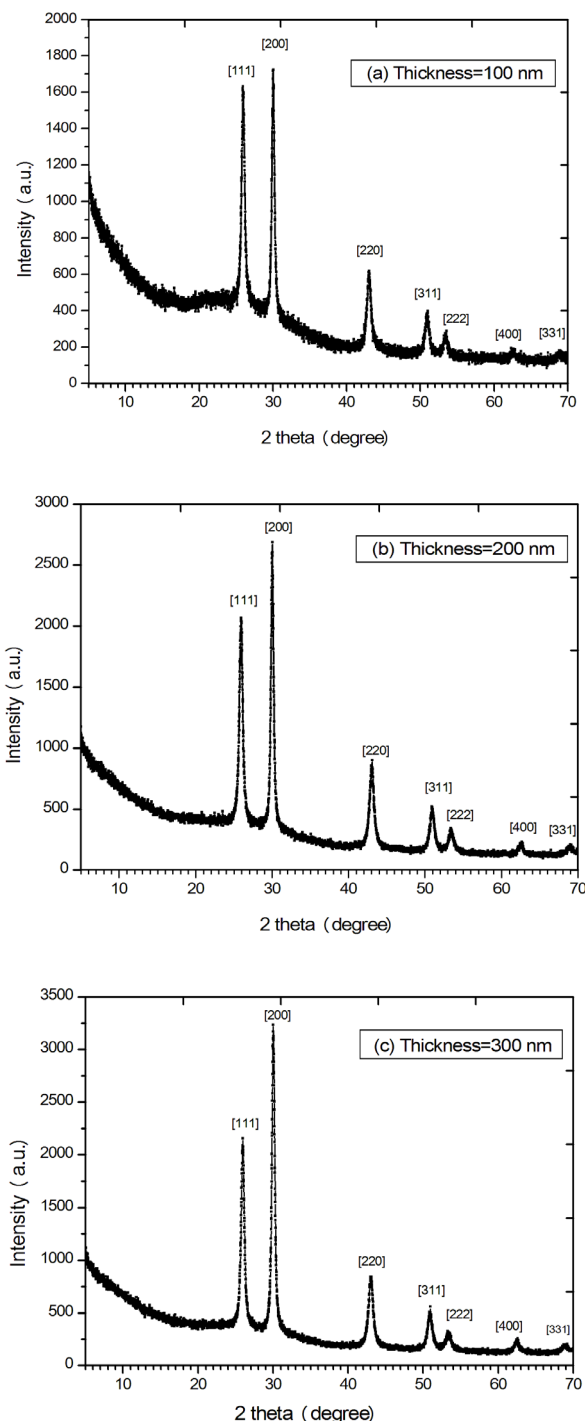


Figure 1. X-Ray diffraction patterns of PbS thin film of different thicknesses: (a) 100 nm, (b) 200 nm and (c) 300 nm

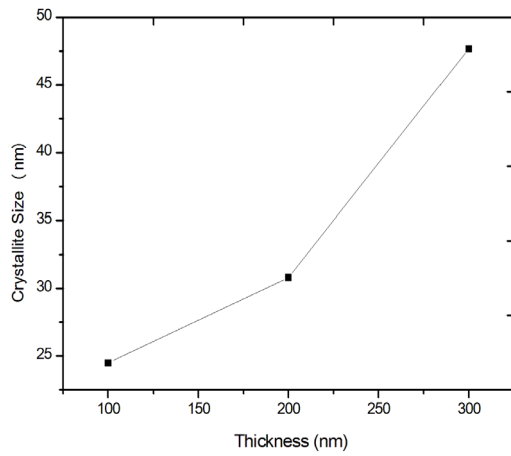


Figure 2. Crystalline grain sizes as a function of thickness

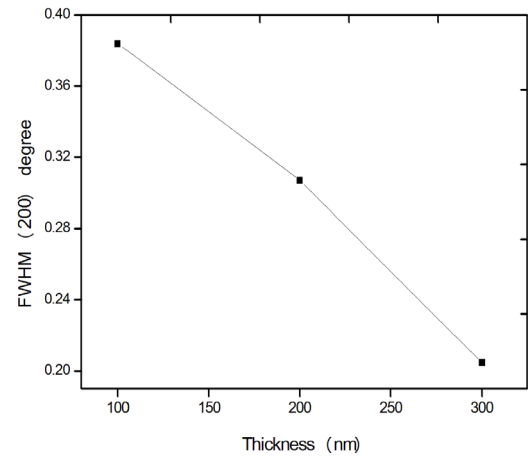


Figure 3. Variation of FWHM of (200) plane of PbS films with thickness

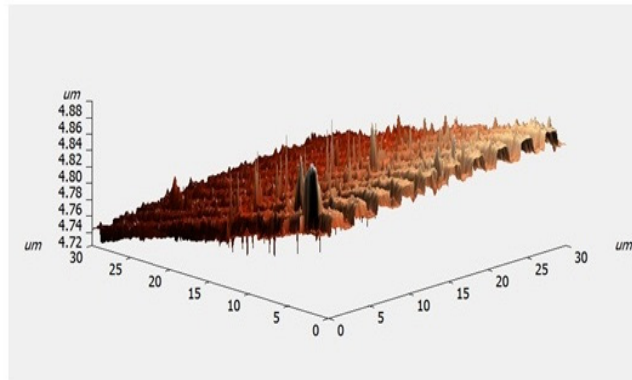
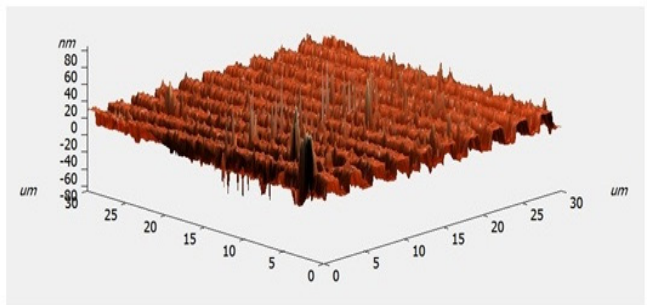
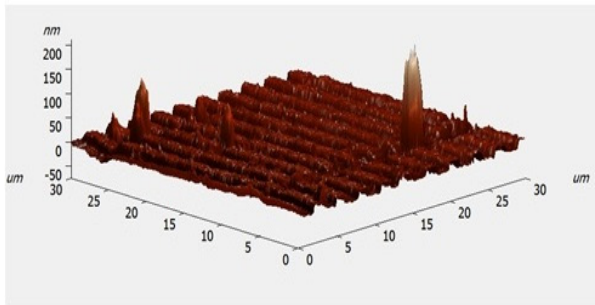


Figure 4. STM analysis of PbS films deposited on glass substrates with different thicknesses

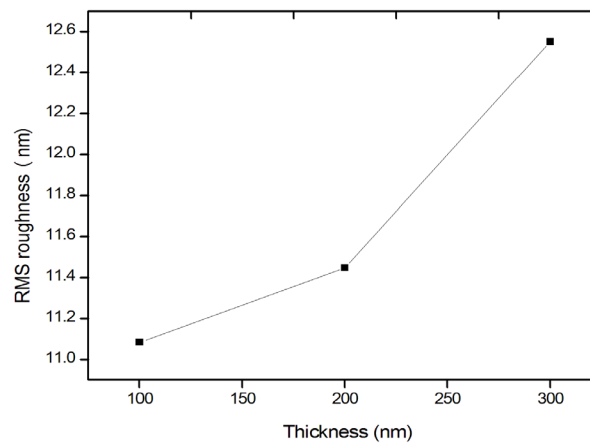


Figure 5. Variation of the RMS roughness with different thicknesses

3.2. Electrical Properties

Table 1. Dependence of electrical resistivity and carrier concentration on the thickness films

Thickness nm	Resistivity $\Omega \cdot \text{cm}$	Carrier concentration (cm^{-3})	Conduction type
100	53.72×10^3	2.98×10^{10}	p
200	2.4×10^3	1.1×10^{11}	p
300	1.1×10^3	1.2×10^{12}	p

Table 1 shows the dependence of the electrical resistivity and carrier concentration on the thickness films. The results indicate that PbS films exhibit p-type conductivity. The decrease in the resistivity of the PbS film with increasing the thickness. This behavior is in agreement with other reported [18, 19]. The carrier concentration of the films increases with the increasing film thickness. It can be explained with the fact that resistivity is known to be inversely proportional to the carrier concentration.

4. Conclusions

Lead sulfide (PbS) thin films were deposited on glass substrates with chemical spray pyrolysis. The thickness of the films varied from 100 to 300 nm. Effects of thickness on the structural and electrical properties of the films deposited were studied. The characteristics of PbS thin films were investigated by various tools. X-ray diffraction patterns confirm the proper phase formation of the PbS. For all films the preferential orientation value of (200) plane has the highest value compared to other planes. The grain size of the PbS films increased with increasing thickness. The values of crystallite size were found to be in the range 24.49-47.66 nm. From STM images it was found that the root mean square roughness of film surface increased as the film thickness increased. From the electrical properties, it was found that PbS films with different thickness always show p-type conductivity.

ACKNOWLEDGEMENTS

Author wishes to thank department of physics/ Faculty of Science and Health/ University of Koya/ Kurdistan Iraq.

REFERENCES

- [1] X. Lui, M. Zhang, Studies on PbS and PbSe Detectors for IR System, International Journal of Infrared and Millimeter Waves 21, 1697–1701 (2000).
- [2] D. Kumara, G. Agarwal, B. Tripathi, D. Vyas, V. Kulshrestha, Characterization of PbS nanoparticles synthesized by chemical bath deposition, Journal of Alloys and Compounds 484, 463–466 (2009).
- [3] N. I. Fainer, M. L. Kosinova, Yu. M. Rumyantsev, E. G. Salman, F. A. Kuznetsov, Growth of PbS and CdS thin films by low-pressure chemical vapour deposition using dithiocarbamates, Thin Solid Films 280, 16-19 (1996).
- [4] S. Seghaier, N. Kamoun, R. Brini, A. B. Amara, Structural and optical properties of PbS thin films deposited by chemical bath deposition, Materials Chemistry and Physics 97, 71-80 (2006).
- [5] I. Pop, C. Nasu, V. Ionescu, E. Indrea, I. Bratu, Structural and optical properties of PbS thin films obtained by chemical deposition, Thin Solid Films 307, 240-244 (1997).
- [6] N. Choudhury, B. Sarma, Structural characterization of lead sulfide thin films by means of X-ray line profile analysis, Bulletin of Materials Science 32, 43-47 (2009).
- [7] L. Raniero, C.L. Ferreira, L.R. Cruz, A.L. Pinto, R.M.P. Alves, Photoconductivity activation in PbS thin films grown at room temperature by chemical bath deposition, Physica B: Condensed Matter 405, 1283-1286 (2010).
- [8] M. Sharon, K.S. Ramaiah, Mukul Kumar, M. Neumann-Spallart, C. Levy- Clement, Electrodeposition of lead sulphide in acidic medium, Journal of Electroanalytical Chemistry 436, 49-52 (1997).
- [9] B. Thangaraju, P. Kaliannan, Spray pyrolytically deposited PbS thin films Semiconductor Science and Technology 15, 849–853 (2000).
- [10] S. Kumar, T.P. Sharma, M. Zulfequar, M. Husain, Characterization of vacuum evaporated PbS thin films Physica B: Condensed Matter, 325, 8-16 (2003).
- [11] H.H. Afifi, S.A. Mahmoud, A. Ashour, Structural study of ZnS thin films prepared by spray pyrolysis, Thin Solid Films 263, 248-251 (1995).
- [12] M.M. Abbas, A. Ab-M. Shehab, A-K. Al-Samuraee, N-A. Hassan, Effect of Deposition Time on the Optical Characteristics of Chemically Deposited Nanostructure PbS Thin Films, Energy Procedia 6, 241–250 (2011).
- [13] L.S. Birks, H. Friedman, Particle Size Determination from X-Ray Line Broadening, Journal of Applied Physics 17, 687–692 (1946).
- [14] J. P. Enriquez, X. Mathew, Influence of the thickness on structural, optical and electrical properties of chemical bath deposited CdS thin films, Solar Energy Materials and Solar Cells 76, 313–322 (2003).
- [15] M. Mosleh, N. Pryds, P.V. Hendriksen, Thickness dependence of the conductivity of thin films (La,Sr)FeO₃ deposited on MgO single crystal, Materials Science and Engineering B 144, 38– 42 (2007).
- [16] N. Kakati, S. Hyun Jee, S. H. Kim, J. Y. Oh, Y. S. Yoon, Thickness dependency of sol- gel derived ZnO thin films on gas sensing behaviours, Thin Solid Films 519, 494-498 (2010).
- [17] M.G. Faraj, K. Ibrahim, M.H. Eisa, Investigation of the optical and structural properties of thermally evaporated cadmium sulphide thin films on polyethylene terephthalate substrate, Materials Science in Semiconductor Processing 14, 146-150 (2011).

- [18] S.A. Al Kuhaimi, Influence of preparation technique on the structural, optical and electrical properties of polycrystalline CdS films, Vacuum 51, 349-355 (1998).
- [19] F. Lacy, Developing a theoretical relationship between electrical resistivity, temperature, and film thickness for conductors, Nanoscale Research Letters 6, 636 (2011).