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# Effect of temperature on the structural and optical properties of chemically deposited PbS thin films

P. Srinivasan and P. Rajesh

Department of Physics, Anna University of Technology, Tiruchirappalli, Panruti Campus, India.

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**ABSTRACT**

Lead sulphide (PbS) thin films have been deposited on glass slide substartes by chemical bath deposition technique from an aqueous alkaline bath containing lead nitrate $[Pb(NO_3)_2]$and thiourea $[SC(NH_2)_2]$. The influence of bath temperature on the properties of the films were investigated . The structural, surface morphological and optical properties of films were studied by X-Ray diffraction, scanning electron microscopy and UV-Vis spectroscopy, respectively. The X-Ray diffraction studies reveal that the PbS films were polycrystalline in nature with preferrential orientation along (200) plane. The scanning electron microscopy results indicate that the films were smooth, uniform and adherent to the substrate. The band gap energy was decreased from 1.2 eV to 0.9 eV as the bath temperature was increased from 30 $^{O}$C to 60 $^{O}$C. The films deposited at 60 $^{O}$C have shown good crystallinity and uniformly distributed over the surface of substrate with larger grain sizes. Therefore, the optimum bath temperature is 60 $^{O}$C.



## Introduction

Lead sulphide (PbS) is an important direct narrow band gap semiconductor material (band gap ≈ 0.4eV) [1] with cubic structure and has been widely used in many fields such as $Pb^{2+}$ ion-selective sensors [2], IR detector [3], photography [4] and solar absorption [5]. Due to these reasons, PbS has been considered as the material of great importance and interests have been shown in the study and development of this material. Various deposition processes such as electrodeposition [6], spray pyrolysis [7], photoaccelerated chemical deposition [8], microwave heating [9, 10] and chemical bath deposition (CBD) [11-15] can be used for preparing PbS films. Chemical bath deposition technique is widely used as it is less expensive, easy to handle, convenient for large area deposition capable of yielding good quality films [1]. The deposition conditions strongly influence the material property of chemicaly deposited PbS thin films [15]. In this paper, we report the structural and optical properties of PbS thin films obtained by CBD method at various temperatures.

## Experiment

The glass slides of dimension 7 cm x 2.5 cm x 2 mm were cleaned as the cleanliness of the substrate has a direct bearing on the adherence of the film. The solution was prepared in a 100 ml beaker containing 0.06 M of lead nitrate $[Pb(NO_3)_2]$. The alkaline aqueous solution is prepared with 0.24 M of thiourea $[SC(NH_2)_2]$. The alkalinity is set using sodium hydroxide of 0.60 M. These solutions were mixed and bidistilled water was added to attain the total volume of 100 ml. Cleaned substrates were vertically inserted into the solution with the help of a substrate holder. The beaker is then kept in a water heating bath circulator placed over the heating magnetic agitator and left undisturbed for 60 min. The films were deposited at various temperatures from 30 $^{O}$C, 40 $^{O}$C and 60 $^{O}$C. After 60 min the substrates were taken out of the chemical bath and rinsed with bidistilled water and dried in air. The reaction process for forming lead sulphide films is considered as follows [16]:

$$Pb(NO_3)_2 + 2NaOH \rightarrow Pb(OH)_2 + 2NaNO_3$$

$$Pb(OH)_2 + 4NaOH \rightarrow Na_4Pb(OH)_6$$

$$Na_4Pb(OH)_6 \rightarrow 4Na^+ + HPbO_2^- + 3OH^- + H_2O$$

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

$$HPbO_2^- + SH^- \rightarrow PbS + 2OH^-$$

X-ray diffraction pattern of the deposited films were recorded using Philips X-pert Pro diffractometer (PW 1830) at room temperature with CuKα radiation (λ = 1.5418 Å). The absorption spectra (A) of the deposited thin films were recorded with a double beam (Pye-Unico UV–2102 PC) spectrophotometer.

## Results and discussion

### Structure and surface morphology

Fig 1 shows the XRD pattern of PbS thin films deposited at 30 $^{O}$C, 40 $^{O}$C and 60 $^{O}$C. The diffraction pattern displays diffraction peaks at (111), (200), (220) and (311) which correspond to the diffraction angles (2θ) 26, 30, 43 and 51$^{O}$. It is observed that the crystallinity of films were improved when the temperature was increased from 30 $^{O}$C to 60 $^{O}$C with the preferred orientation growth along (200). The structure of polycrystalline PbS is determined as face centered cubic by comparison of the obtained data with the galena, JCPDS 78-1054. It is reported that the grain size of PbS films increases with the increase in deposition temperature [15]. Table 1 gives the grain size of the PbS films determined using Debye-Scherrer formula at temperatures 30 $^{O}$C, 40 $^{O}$C and 60 $^{O}$C.

**Tele:**

**E-mail addresses: sril35@gmail.com**

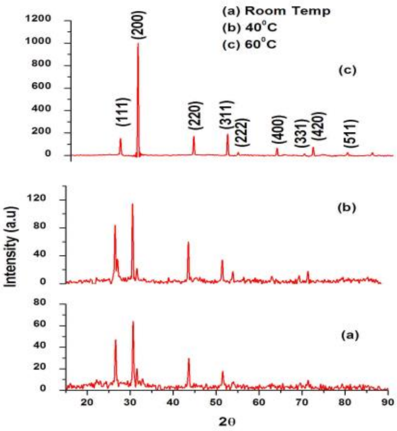


**Fig.1 XRD pattern of the PbS thin films deposited at (a) 30 $^{O}$C (b) 40 $^{O}$C and (c) 60 $^{O}$C**

**Table 1 Grain size of the PbS thin films at various temperatures**

| Sample | Temperature (°C) | Crystal Structure | Lattice parameter (Å) | Grain size (nm) |
|---|---|---|---|---|
| 1 | 30 | FCC | 5.8738 | 40.228 |
| 2 | 40 | FCC | 5.8738 | 54.326 |
| 3 | 60 | FCC | 5.8738 | 70.621 |

The SEM micrograph of the film deposited at 60 $^{O}$C shown in Fig 2 indicates that the surface of the film is smooth, uniform and compact surface, which does not show any fissures, faults and disturbances. Round shaped clusters constitute the film surface and there is no empty space found between them. The larger number of both $Pb^{2+}$ and $S^{2-}$ ions present in the reaction solution at higher temperatures change the structural and surface morphology properties of the PbS films. At higher temperatures the release of metal ions by the complexing agent and the double hidrolisation of thiourea to produce $S^{2-}$ ions will be more [17].

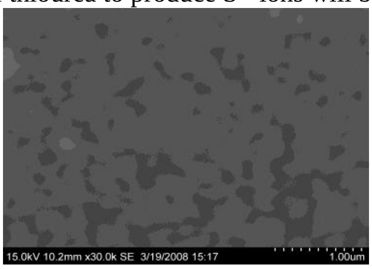


**Fig.2 SEM micrograph of the film deposited at 60 $^{O}$C**

Fig 3 Shows the EDAX spectrum of PbS thin film deposited at 60°C. The strong peaks for Pb and S were found in the spectrum, and no other impurities were detected confirming high purity of the PbS thin film.

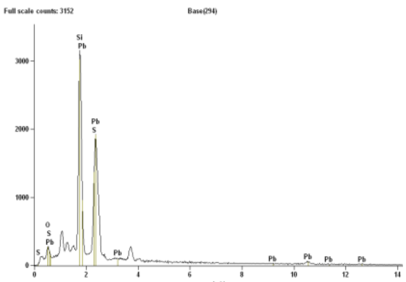


**Fig.3 EDAX spectrum of the PbS thin film deposited at 60$^{O}$C**

**Optical properties**

The effect of temperature on the optical properties of PbS thin films were studied. The optical absorbance and transmission studies were carried out with a UV-VIS-NIR spectrophotometer in the range of 350–850 nm. Fig 4 shows the variation of optical absorption with wavelength of the PbS thin films deposited at temperatures 30 $^{O}$C to 60 $^{O}$C . We observe the increase of temperature decreases the percentage of absorption. The increase of transmission is explained in Fig 5 with the increase of temperature.

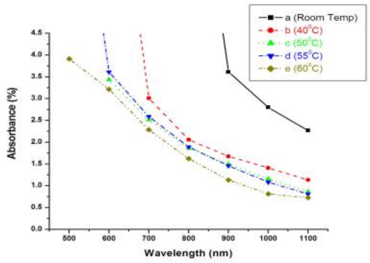


**Fig.4 Plot of optical absorption vs wavelength for PbS thin films with different temperatures**

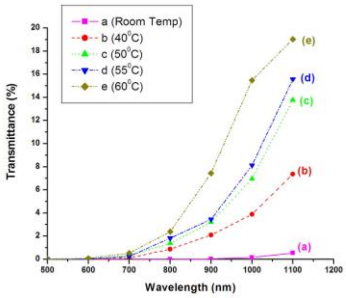


**Fig. 5 Plot of optical transmission vs wavelength for PbS thin films with different temperatures**

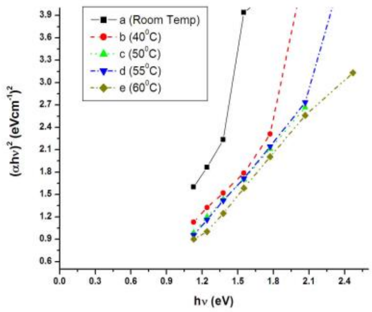


**Fig.6 Plot of $(\alpha h\nu)^2$ versus hν for PbS films with different temperatures**

Mathematical treatment of data obtained from optical absorbance versus wavelength gives the band gap and the type of transition for near edge absorption. The following equation is used to determine the band gap and the type of transition

$\alpha = k\,(h\nu - E_g)^{n/2}/h\nu$

where $\nu$ is the frequency, h Planck's constant, k is a constant and n carries the value 1 for direct transition and 4 for indirect transition. Fig 6 shows the plot of $(\alpha h\nu)^2$ versus hν for PbS films deposited at various bath temperatures. The linear nature of the plot indicates the existence of direct transitions. The band gap energy is obtained by extrapolating the linear portion of $(Ah\nu)^{2/n}$ versus $h\nu$ to the energy axis at $(Ah\nu)^{2/n} = 0$. The results reveal that the band gap energy decreases linearly from 1.2 eV to 0.9 eV when the bath temperature was increased from 30 $^{O}$C to 60 $^{O}$C.

**Conclusions**

The structural and optical properties of chemically deposited PbS thin films at different temperatures, were studied. The structural study indicate the best crystallinity with the face centered cubic structure. It revealed that the grain size of the PbS films increases with the increase in temperature. The SEM micrograph shows that the film is uniform and compact and is well adhered to the substrate. The stoichiometric compound is confirmed by the EDAX measurements. The Optical absorption study reveals that PbS thin films have allowed direct transitions. The optical band gap energy varies from 1.2 eV to 0.9 eV with temperature.

**References**

1. S. Seghaier, N. Kamoun, R. Brini, A. B. Amara, Mater. Chem. Phys., 97, 71, (2006).
2. H. Hirata, K. Higashiyama, Bull. Chem. Soc. Jpn., 44, 2420, (1971).
3. P. Gadenne, Y. Yagil, G. Deutscher, J. Appl. Phys., 66, 3019, (1989).
4. P. K. Nair, O. Gomezdaza, M. T. S. Nair, Adv. Mater. Opt. Electron., 1, 139, (1992).
5. T. K. Chaudhari, S.Chatterjes, Proc. Int. Conf. Thermo electronics, 11, 40 (1992).
6. Maheshwar Sharon, K.S. Ramaiah, Mukul Kumar, M. Neumann-Spallart, C. Levy-Clement, Electroanal. Chem., 436, 49–52, (1997).
7. B. Thangaraju, P. Kaliannan, Semicond. Sci. Technol., 15, 849–853, (2000).
8. P.K. Nair, V.M. Garcia, A.B. Hernandez, M.T.S. Nair, J. Phys. D: Appl. Phys., 24, 1466–1472, (1991).
9. Yonghong Ni, Fei Wang, Hongjiang Liu, Gui Yin, Jianming Hong, Xiang Ma, Zheng Xu, Cryst. Growth., 262, 399–402, (2004).
10. Yu Zhao, Xue-Hong Liao, Jian-Min Hong, Jun-Jie Zhu, Mater. Chem. Phys., 87, 149–153, (2004).
11. Cristina Nascu, Valentina Vomir, Ileana Pop, Violeta Ionescu, RodicaGrecu, Mater. Sci. Eng. B 41, 235–240 (1996).
12. E.M. Larramendi, O. Calzadilla, A. Gonzalez-Arias, E. Hernandez, J. Ruiz-Garcia, Thin Solid Films, 389, 301–306, (2001).
13. E. Pentia, L. Pintilie, C. Tivarus, I. Pintilie, T. Botila, Mater. Sci. Eng. B 80, 23–26 (2001).
14. Rakesh K. Joshi, Aloke Kanjilal, H.K. Sehgal, Appl. Surf. Sci., 221, 43–47, (2004).
15. J.J. Valenzuela-Jauregui, R. Ramirez-Bon, A. Mendoza-Galvan, M. Sotelo-Lerma, Thin Solid Films, 441, 104–110, (2003).
16. S. Mahmoud, O. Hamid, FIZIKA A (Zagreb), 10, 21–30, (2001).
17. K.L. Chopra, S. Ranjan Das, Thin Film Solar Cells, Plenum Press, New York and London, p. 229, 1983.