International Journal of Scientific Research & Engineering Technology (IJSET)
ISSN: 2356-5608, Vol.3, issue 2
Copyright IPCO-2015-pp.138-142

Structural, Optical and Electrical Properties of PbS Thin Films Deposited by CBD at Different Bath pH

L. Beddek[#1], M. Messaoudi[#2], S. Guitouni[#3], N. Attaf[#4], M.S. Aida[#5]

[#] *Physics Department, Frères-Mentouri University*
Laboratoire de Couches Minces et Interfaces Faculté des Sciences, Constantine, Algeria
[1] `beddeklynda@hotmail.fr`
[2] `messaoudi_phlmd@yahoo.fr`
[3] `samira85ain@yahoo.fr`
[4] `nattaf1@yahoo.fr`
`aida_salah2@yahoo.fr`

Abstract— **PbS thin films were grown on glass substrates by chemical bath deposition (CBD). The precursor aqueous bath contained 1mole of lead nitrate, 1mole of Thiourea and complexing agents (triethanolamine (TEA) and NaOH). Bath temperature and deposition time were fixed at 60°C and 3 hours, respectively. However, the PH of bath was varied from 10.5 to 12.5. Structural properties of the deposited films were characterized by X-ray diffraction and Raman spectroscopy. The preferred direction was revealed to be along (111) and the PbS crystal structure was confirmed. Strains and grains sizes were also calculated. Optical studies showed that films thicknesses do not exceed 600nm. Energy band gap values of films decreases with increase in pH and reached a value ~ 0.4eV at pH equal 12.5. The small value of the energy band gap makes PbS one of the most interesting candidate for solar energy conversion near the infrared ray.**

Keywords*— *CBD, PbS, pH,thin films, x-ray diffraction.

I. INTRODUCTION

During these last decades, thin films have been growing in importance in the field of technology and, in particular, in the semi-conductors industry. New properties, different from those observed in the bulk, appear in the films states [1]. Generally, those properties are linked to film thickness and preparation method [2, 3] These properties can be controlled by varying the parameters of deposition. Lead sulfide (PbS) is a semiconductor arousing interest of researchers[4-8]. This material is belonging to IV-VI group with a narrow band gap (0.41eV) [9,10]. It is used in infrared optics as a material for temperature sensors and photodetectors [9, 11], and solar cells. Near infra red active solar cells based on PbS quantum dots and a conventional conjugated polymer Bi_2S_3/PbS heterojunction solar cells are fabricated by chemical bath deposition (CBD) [10]. Several other methods were used to synthesized PbS thin films such as spray pyrolysis (SP) [12], chemical vapor deposition (CVD) and vacuum evaporation [13]. CBD is the more interesting public deposition technique. It is known to be technically simple and necessitating few resources and cost [14]. A chemical bath deposition technique also offers the advantage of being able to deposit films on different kinds, shapes and sizes of substrates [15]. By CBD method the grains sizes can be controlled by varying experimental parameters. A lot of works on PbS thin films studied: the temperature effect on the PbS deposited films [16, 17], the deposition time dependence [7, 18], bath composition [8], morphology, optical and electrical properties of PbS thin films has been investigated [5]. The control of the bath pH is an important factor. Some attempts [4-6] are carried out to control this parameter to define accurately its influence on PbS thin films properties. The present study deals with the investigation of bath pH effect on PbS thin film properties.

II. EXPERIMENT DETAILS

Microscope glass slides (75 mm x25mm x2 mm) were used as substrates. Those ones were, firstly, washed with distilled water, immersed in methanol and cleaned ultrasonically for 20min. Then, they were cleaned again ultrasonically with distilled water for 20min and, finally, dried in air.

The deposition was done in a reactive bath prepared in a 50mL beaker. The bath was composed of sulfur and lead precursors, 1M of thiourea [CH_3CSNH_2] and 0.1M of lead nitrate [$Pb(NO_3)_2$]. Thriethanolamine (TEA) [$N(CH_3CH_2OH)_3$] was added as buffer solution to control the rate reaction. The pH solution was varied between 10.5 and 12.5 (10.5, 11, 11.5, 12, 12.5) by adding sodium hydroxide NaOH. Cleaned substrates were vertically dipped in the heated solution by external hot plate set at 60°C for 3hours. For the first 5min, the solution remained transparent, indicating the occurrence of decomposition reactions. After 5min, the solution became dark gray which indicates the PbS compound formation.

The reaction process for forming lead sulfide films is considered as follows:

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

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

$Na_4Pb(OH)_6 \rightarrow 4Na^+ + HPbO^- + 3OH^- + H_2O + 1/2O_2$

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

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

After the deposition elapsed time, the synthesized samples were removed from the bath and rinsed with distilled water. The mirror-like gray obtained were characterized by X-ray diffraction using a X'PERT PRO diffractometer using copper wavelength of 1.54A°, associated to the American Society for Testing Materials (ASTM) data base.

The optical properties of the PbS films were investigated using a SHIMADZU 3100S double-beam spectrometer having a wavelength range 200-3000 nm.

The ECOPIA Hall Effect measurement system (HMS-3000) was used to measure the electrical properties of the deposited thin films.

III. STRUCTURAL PROPERTIES

Fig.1.a and fig.1.b showed the XRD patterns of the PbS thin films deposited with different bath pH: 10.5 and 12.5. The patterns display four prominent diffraction peaks at 2θ values of 26°, 30°, 43° and 51° corresponding to the diffraction lines produced by the (111), (200), (220) and (311) planes. They were confirmed by comparing the peaks positions (2θ) of the XRD patterns of the films with the standard X-ray data file (card no. 77-0244). The absence of any other diffraction peak indicates that no other crystalline phases exist with detectable concentration within the deposited films. The preferred orientation growth of the deposited films was along (111) direction. From the fig.1.a and fig.1.b, it could be concluded that the intensity of the peaks increased when the pH of the chemical bath increased. This effect can be justified by the increase in thicknesses and crystallites sizes of the PbS films deposited while increasing the pH. Same observations were done in several studies [4-6].

The average crystallites sizes *D* and strains ε in the PbS films were deduced from the Scherrer equation (1) for (111), (200) and (220) reflections. The results were reported in table. 1.

$$\beta \cos\theta = k\lambda/D + \varepsilon \sin\theta \qquad (1)$$

Where β is the peak width at mid height, θ is the diffraction angle, *k* is constant having a value of 0 .9, the constant λ=1.54 Å, *D* the crystallites size and ε represents the strains in the film.

The grains size *D* increased from 10 nm to 70 nm for PbS films deposited with increasing bath pH, as shown in table. 1. For pH greater than 12, an important variation of crystallites size was observed, from 18nm to 70nm, which can be explained by a changement in growth mechanism. When pH was less than 12, the PbS films grew by mechanism which products small sizes loading to nanostructured films. This first growth process was probably carried out ion by ion. However, for a highly basic bath (pH>12), the film was built up via cluster by cluster process which formed a bigger crystallites size then lead to microcrystalline PbS thin film.

The texture coefficient TC along the diffraction lines produced by (111) and (200) crystalline planes of PbS was calculated using equation (2) [19]. This coefficient represent the texturation of films in particular planes related to the preferred growth directions during the deposition process:

$$TC(hkl) = (I(hkl)/I_0(hkl))/ \{(\Sigma_n(I(hkl)/I_0(hkl))\} \times 100\% \qquad (2)$$

TABLE I
TEXTURE COEFFICIENT TC, STRAINS E AND GRAINS SIZE D OF PbS THIN FILMS DEPOSITED WITH TWO DIFFERENT PH :(10.5 AND 12.5).

pH	2θ (°)	hkl	I_{hkl}	TC (111) %	TC (200) %	ε	*D* *nm*
10.5	26.12 30.03 43.16 51 .08	(111) (200) (220) (311)	255.38 217.08 101.47 74.44	31.83	25.88	0.68	11
12.5	25.89 30.07 43.02 51.13	(111) (200) (220) (311)	3159.57 2839.23 1378.96 1044.02	28.71	27.04	0.13	67

Where *I (hkl)* and *I₀ (hkl)* are, respectively, the measured intensity and the standard intensity of (*hkl*) plane based on standard data file. n is the number of diffraction peaks.

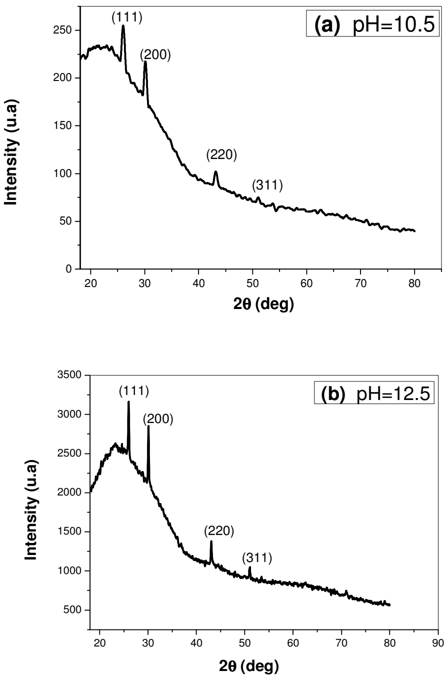

Fig. 1 XRD patterns of PbS thin films deposited with two different pH: a) pH=10.5; b) pH=12.5

The TC (*hkl*) values represent the abundance of crystallites oriented in a given (*hkl*) direction. The variation of TC for the diffraction peaks of the deposited films at pH=10.5 and 12.5

are showed in table. 1. The highest TC were along (111) plane but slightly smaller for the sample deposited at pH=12.5 for which the other diffraction peaks, along (220) and (311) directions, became relatively more important. As can be seen in fig.1 and table.1 a preferred orientations growth of PbS for the two used pH are (111) and (200) with a higher intensity in the first direction. In addition, it could be observed that the TC(111) decreased with increasing pH. However, the TC along (200) increased. This result shows a small variation along the growing direction with pH changing.

AFM images as shown in fig.2 showed dense surface of the deposited film at pH=12.5. The PbS films were revealed to be crystalline from XRD patterns and confirmed by AFM. . As showed in this figure, the film was grown by columnar mechanism.

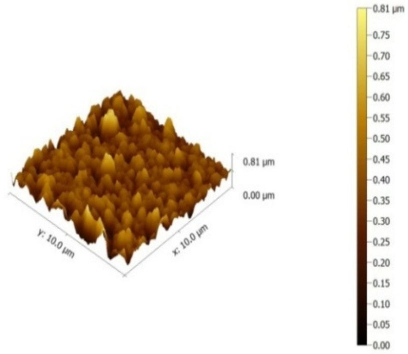

Fig. 2 AFM images of PbS thin films deposited at pH=12.5

IV. STRUCTURAL PROPERTIES

The transmittance spectra of PbS films is display in fig.3. The spectra showed that PbS films deposited with different bath pH present transmittance values between (2-40%). A decreasing in transmittance was observed while bath pH increased until it reached 12, above this value the transmittance increased. The decrease of transmittance can be explained by the increase in thicknesses of deposited films when the pH increased until the maximum value of 12. After that, the films thicknesses decreased, as shown in fig.4, thus increasing the transmittance. In the reported study [4], PbS thin films deposited with TEA and lead acetate by CBD gave thicknesses decreasing as a measure of decrease in bath pH. Beyond the value 10.5, the film thickness became independent of pH. In another study [5], thicknesses of the PbS films, deposited by SILAR, increased with the pH bath increasing. This last result is in agreement with ours.

The energy band gap Eg of the PbS films was calculated using the known formula [9]:

$$\alpha h\upsilon = A(\alpha h\upsilon - Eg)^n \qquad (3)$$

Where υ is the frequency of the incident photon, *h* is Planck's constant, A is constant, α is absorption coefficient and n is the number which characterizes the optical process (n=1/2 for direct transition). The plot of $(\alpha h\upsilon)^2$ as a function of $h\upsilon$ gave the results reported as function of bath pH in fig.5. The present figure revealed that optical gap varied between 0.46 eV and 0.59 eV.

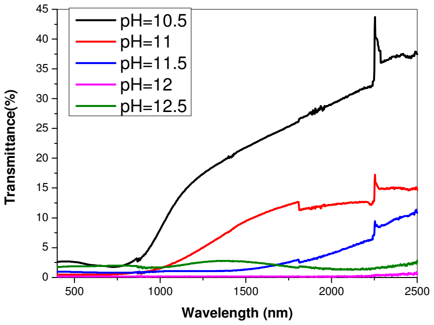

Fig. 3 Transmittance spectra of the PbS thin films deposited at various pH

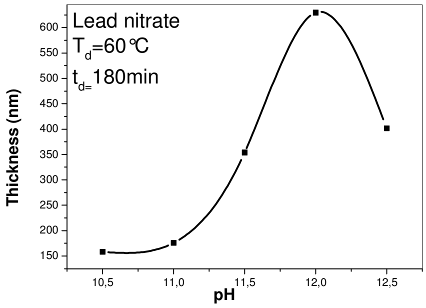

Fig. 4 Thicknesses of PbS thin films deposited at various pH

It has been found that Eg decreased with increasing of bath pH, certainely due to the increasing of crystallites size. Same behavior has been observed in many studies [16, 18].

The tail width E_u in the energy gap was obtained by plotting $\ln\alpha$ as a function of $h\upsilon$. The extraction of the reciprocal slope of the linear part gave the E_u for PbS films deposited, as reported in fig.6. The E_u values increased with increasing of bath pH until it reached the value of 12 after which tail width decreased. This result may be related to the fact that the increase in bath pH leads to an increase in films thicknesses (until pH=12) and that it leads to an increase in films defects and localized state in the gap [16].

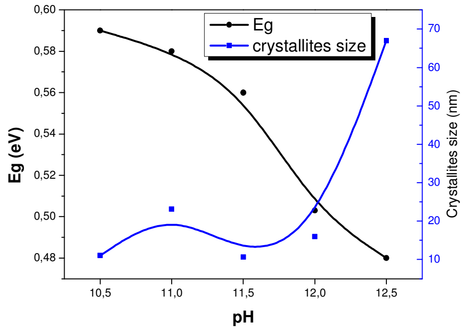

Fig. 5 Energy band gap and crystallites size of the PbS thin films deposited at various bath pH

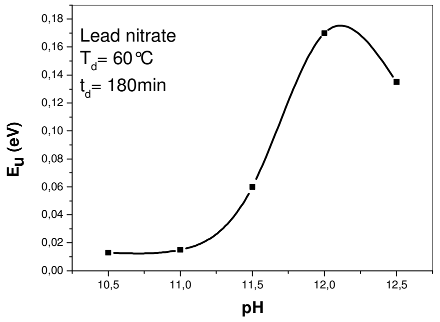

Fig. 6 Urbach energy E_u of the PbS thin films deposited at different bath pH

V. STRUCTURAL PROPERTIES

Resistivity and Hall measurements were performed on PbS samples. The variation of resistivity as functin of bath pH was shown in fig.7. It was found to be linked to films strains and crystallites size. Films with big crystallites size (sample deposited at pH=12.5) or high strains value (the one deposited at pH=11.5) had a low resistivity. Films with small crystallites size showed a high resistivity despite the small strains value. Rakesh K. and al. [6] have reported in their study that the increase in resistivity is attributed to the decrease in particle packing density with decrease in grains size. K.C. Preethaand al. [5] have found an increasing conductivity with increasing strains in PbS films deposited by SILAR.

Hall mobility values were represented in fig.8. It was found decreasing with bath pH decreased, probably, due to the reducing grains size. Similar remarks were done in other studies [6].

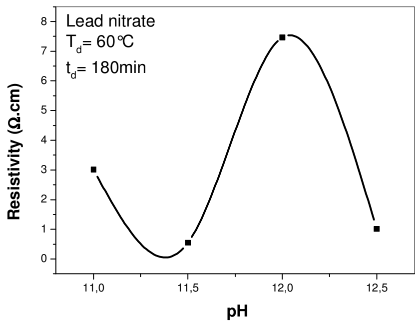

Fig. 7 Resistivity of PbS samples deposited at different bath pH

Sheet concentration, represented in the same figure, had almost an inverse behavior. The highest sheet concentration corresponds to the smallest mobility.

The value of sheet concentration varied between 3 x $10^{13}/cm^2$ and 1 x $10^{14}/cm^2$ while increasing pH until 12. At pH=12.5, PbS films showed a big decreasing of sheet concentration ($10^{11}/cm^2$).

All the fims were found to be n-Type from which it can be concluded that the films type are independent of pH.

VI. CONCLUSIONS

PbS thin films were synthesized by a simple chemical bath deposition at low temperature (60°C). The reaction bath included cationic, anionic precursors and complexing agents. The effect of bath solution pH on the films properties has been studied. XRD patterns showed that PbS thin films are crystalline. Optical properties have been investigated. Results showed that PbS films have allowed direct transition and the optical band gap was strongly dependant on pH solution: when 10.5<pH<12, Eg varied slightly between 0.56 eV and 0.59 eV. When pH exceed 12, the gap narrowed considerably. The grains size calculated from X-ray patterns explained this narrowing by a by a shift in dimensions, nanocrystallites became microcrysctallites.

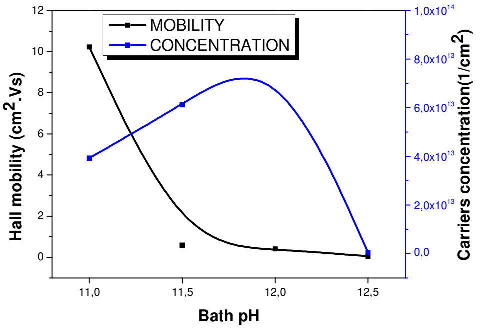

Fig. 8 Mobility and sheet concentration of PbS films deposited at different bath pH

Acknowledgment

The heading of the Acknowledgment section and the References section must not be numbered.

Causal Productions wishes to acknowledge Michael Shell and other contributors for developing and maintaining the IEEE LaTeX style files which have been used in the preparation of this template. To see the list of contributors, please refer to the top of file IEEETran.cls in the IEEE LaTeX distribution.

REFERENCES

[1] C.D. Lokhande, A.U. Ubale, P.S. Patil, Thin Solid Films 1 (1997) 302.
[2] Bull. Mater. Sci. Indian Acad. Sci. 30 (N°2) (April 2007) 147.
[3] Y. Wang, A. Suna, W. Mahler, R. Kawoski, J. Chem. PhyS. 87 (1987) 7315.
[4] A.N. Chattarki, S.S. Kamble, L.P. Deshmukh, Role of pH in aqueous alkaline chemical bath deposition of lead sulfide thin films, Materials Letters 67 (2012) 39–41.
[5] K.C. Preetha, K.V. Murali, A.J. Ragina, K. Deepa, Effect of Cationic Precursor pH on Optical and Transport Properties of Silar Deposited Nano Crystalline PbS Thin Films, Current Applied Physics 12 (2012) 53-59.
[6] Rakech K. Joshi, Aloke Kanjilal, H.K. Sehgal, Solution grown PbS nanoparticle films, Applied surface science 221 (2004) 43-47
[7] J.A. Amusan, G.R. Fajinmi and Y.K. Sanusi, Deposition Time Dependence on Absoptivity of Chemically Deposited Lead Sulfide Thin Films, Research Journ. Appl. Sci. 2 (9) : 931-934, 2007.
[8] R. Thiagarajan, M. Mahaboob Beevi, M. Anusuyaa, T. Ramesh, Influence of reactant concentration on nano crystalline PbS thin films prepared by Chemical Spray Pyrolysis, OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS, Vol. 6 (2012) 132-135
[9] A.A. Rempel, Uspekhi Khimii 76 (2007) 474-500. (in Russian) (Engl. Transl. : Russian Chem. Reviews 76 (2007) 435-461)
[10] H. Moreno-Garcia, M.T.S. Nair, Thin Solid Films 519 (2011) 7364-7368.
[11] G. Bauer, H. Clemens, Semicond. Sci. Technol. 5 (1990) S122-S130.
[12] H. Ben Haj Salah, H. Bouzouita, B. Rezig, Preparation and characterization of tin sulfide thinn films by a spray pyrolysis technique, Thin Solid films 480-481 (2005) 439-442.
[13] Sushil Kumar, T.P. Sharma, M. Zulfequarb, M. Husain, Characterization of vacuum evaporated PbS thin films, Physica B 325 (2003) 8–16.
[14] A.A. Rempela, N.S. Kozhevnikovab, A.J.G. Leenaersa, S. Van der Berghe. Towards particle size regulation of chemically deposited lead sulfide (PbS). J. Crist. Growth 280 (2005) 300-308.
[15] Eya. D.O. 2006. Influence of thermal annealing on the structural and optical Properties of lead oxide thin films deposited by chemical bath deposition technique. Pacific Journal of Science and Technology. 7 (1):114.
[16] M.M. Abbas, A. Ab-M. Shehab, N-A. Hassan, A-K. Al-Samuraee, Effect of Temperature and Deposition Time on the Optical Properties of Chemically Deposited Nanostructure PbS Thin Films, Thin Solid films 519 (2011) 4917-4922.
[17] J.J. Valenzuela-Jauregui, R. Ramirez-Bon, Optical Properties of PbS Thin Films Chemically deposited at Different Temperatures, Thin solid Films 441 (2003) 104-110.
[18] 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 (2011) 241-250.
[19] G. Bauer, H. Clemens, Semicond. Sci. Technol. 5 (1990) S122-S130 802.11,