Chalcogenide Letters Vol. 13, No. 4 April 2016, p. 161 - 168

COMPARATIVE STUDY OF PbS THIN FILMS GROWTH BY TWO DIFFERENT FORMULATIONS USING CHEMICAL BATH DEPOSITION

H. A. PINEDA-LEON[a], G. GUTIERREZ-HEREDIA[b], A. DE LEON[c*], R. OCHOA-LANDIN[d], R. RAMIREZ-BON[e], M. FLORES-ACOSTA[a], S. J. CASTILLO[a]

[a]*Departamento de Investigacion en Fisica, Universidad de Sonora, Hermosillo, Son, 83000, Mexico.*

[b]*Department of Material Science & Engineering, University of Texas of Dallas, Richardson, Tx, 75080, USA.*

[c]*Departamento de Ciencias Quimico-Biologicas, Universidad de Sonora, Hermosillo, Son, 83000, Mexico.*

[d]*Departamento de Fisica, Universidad de Sonora, Hermosillo, Son, 83000, Mexico.*

[e]*Centro de Investigacion y Estudios Avanzados del IPN, Unidad Queretaro, Queretaro, Qro,76001 Mexico.*

PbS thin films were obtained using the chemical bath deposition (CBD) technique at 60^{o} C. In this paper were compared two formulations: the standard and a new one. The main result of this work is to report the new chemical formulation to build the PbS thin films, where polyethyleneimine has been used as a complexing agent. With a reaction time of 7.5 minutes we obtain a thickness of 120 nm measured with a profilometer. The structural studies, using X-ray diffraction, show that the thin film is polycrystalline and strongly oriented on the (1,1,1) plane of a cubic structure, while the thin film for the traditional formulation has a preference orientation on the (2,0,0) plane. Morphology by atomic force microscopy depicts a better flatness for the new formulation than with the traditional one. Scanning electron microscopy shows clearly in images the consistency with X-ray diffraction. Also, the optical absorption and transmission for both materials are described as a comparative in the UV-vis region. Finally to reinforce this characterization of the material, to a basic science level, XPS spectra were obtained where we can be observe only those chemical element peaks expected.

(Received January 28, 2016; Accepted April 14, 2016)

Keywords: Lead sulfide, Thin film, polyethyleneimine, semiconductors.

1. Introduction

PbS thin films have been receiving attention due to its wide variety of applications such as solar cells [1], photovoltaic devices, optoelectronics devices, light emitting diodes, bio-imaging fluorescence, quantum dots, laser and optical gain media, lithography, etc. PbS can be observed in the nature as galena. This material has a narrow bulk band gap (0.41 eV) at 300 K and its largest exciton Bohr radius is 20 nm[2]. Due to these properties PbS is very suitable for applications in infrared detectors.

The optical properties depend on the size and shape of semiconductor nanocrystals and have recently motivated attempts to use them in bioengineering applications[3],[4]. PbS was synthesized using a surfactant or other templating agents, for instance oleylamine [5]. Lead sulfide was the first compound to be deposited chemically. Emerson-Reynolds got a deposition of PbS films in 1884, then in 1933 Bruckman deposited PbS thin films.[6]

* Corresponding author: d_aned@hotmail.com

Seghaier *et al* in 2005 concluded that the best crystallinity and thin film PbS is obtained by employing 0.170M of lead nitrate, 0.57 of sodium hydroxide and 0.1M of thiorea as reagents, at room temperature for a dipping time of 60 min. They obtained a FCC structure and their preference orientation was (2 0 0).[7]

In 2012 Szendrei *et al* studied the effect of the temperature on PbS nanocrystaline solar cells. They demonstrated that V_{oc} increases and J_{sc} decreases with decreasing temperature, but the Fill Factor remains constant. [8]

PbS thin films can be deposited by several methods for example chemical bath deposition (CBD). CBD is a technique has many advantages: it is cheap, easy to handle and it is possible to have a large deposition area of highly homogeneous film. In this case thiourea was the sulfide precursor.[9,10]

In the CBD method it is very the important to control the pH, because the film growth is highly dependent on this parameter.[11] Another form to control the morphology of the particles is just by adjusting the deposition temperature. Another techniques to prepare thin films are: sol-gel, chemical spray pyrolysis, electrodeposition, vacuum evaporation, sputtering [12], etc.

In this work, the CBD technique is used in the elaboration of both kinds of PbS and the comparation between these two formulations are presented, the standard and the new one. In the standard formulation the complexing agent is Triethanolamine (TEA), while in the new one, it is Polyethylenimine (PEI).

The main goal in this research consists in establishing the reliability of a new process of growing PbS thin films. We observed that the deposition time for the new formulation was lower than the classical.

2. Experimental

In this part of the paper experimental details of the essayed processes are explained. The deposition of PbS is based on joining the free Pb^{+2} and S^{-2} ions, until we get a film of 141 nm of thickness.

The chemical bath was prepared by adding the next reagents, following the order and the considered proportions: 5 ml of 0.5M lead acetate, 5 ml of 2M sodium hydroxide, 6 ml of 1M thiourea and 2 ml of 1M of triethanolamine for the traditional formulation. For the new formulation the reagants were: 5 ml of 0.5 M lead acetate, 5 ml of 2M sodium hydroxide, 4 ml of Polyethylenimine solution (3.5 ml of PEI : 50 ml of water) and 6 ml of 1M of thiourea. The solution was diluted, in both cases, adding deionized water to complete a total volume of 100 ml.

The thermodynamic conditions were around 54 and 60 ^{o}C of temperature and a pressure of 1 atm. The deposition time ranges from 6 to 15 minutes, and in this case it was of 7.5 minutes. For a typical formulation we use a temperature of 40 ^{o}C and a deposition time of 60 minutes. The structural, optical and morphological properties were studied by X-ray diffraction, UV-VIS, SEM, AFM and XPS respectively.

A diffractometer ZXS Do Discover was used to obtain the X-ray diffraction patterns of the films. The apparatus of AFM was Dimension-3100 4.43 B version. The bound energy was measured by ZPS Elmer-5100 (XPS). The reflection and transmition spectra of the films were studied using an Ocean Optic HR400-CG-UV and finally, the morphological surfaces were analyzed by scanning electronic microscopy (SEM) JMS-5300 model (JEOL Ltd).

3. Results and discussion

In this part we compare the PbS thin films properties for both formulations. Figure 1 shows the XPS patterns of PbS thin films prepared by the usual and new formulation without etching which correspond to (a) and (b), respectively. In this case there are two air pollutants: Carbon at 289 eV and Oxygen at 536 eV. On the other hand, (c) and (d) correspond to same samples, but etched with Ar ions during 60 seconds; it can be observed that the electrons which

correspond to $Pb4S_{1/2}$, $Pb4p_{1/2}$ and $Pb5d_{3/2}$ are less shielded. Also, in general all the peaks in (c) and (d) are more intense than (a) and (b).

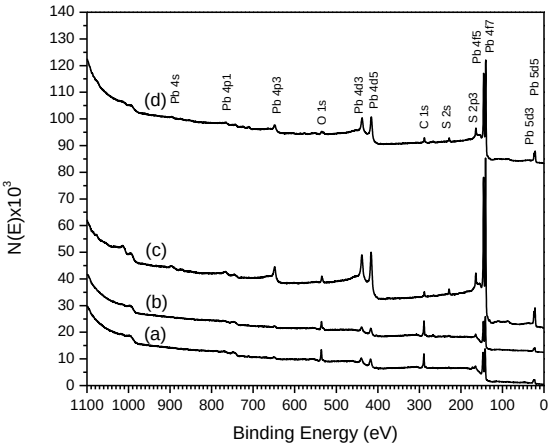

Fig. 1. Shows the spectrum of the PbS thin films. a) and b) correspond to the typical and new formulations without etching, respectively. c) and d) correspond to the usual and new formulations, but these had 60 seconds of etching time by Ar ions.

From these results it can be discerned that CBD is a very selective chemical process to form high quality materials, because the significant proportions are only the desired elements.

In table 1 the main elements that contribute to the growth of the lead sulfide layers are listed, as well as the energy values that are arranged in a decreasing way. The highest intensities are placed in 142 and 147 eV binding energies, which are associated with the 4f sub-level.

Table 1. Binding energy and the elements of the PbS thin films, except the air pollutants Carbon and Oxygen.

Energy (eV)	899	766	648	436	413	228	164	147	142	23	18
Elements	Pb $4s_{1/2}$	Pb $4p_{1/2}$	Pb $4p_{3/2}$	Pb $4d_{3/2}$	Pb $4p_{5/2}$	S $2s_{1/2}$	S $2p_{3/2}$	Pb $4f_{5/2}$	Pb $4f_{7/2}$	Pb $5d_{3/2}$	Pb $5d_{5/2}$
(a)			x	x	X	x	x	x	x		x
(b)			x	x	X	x	x	x	x		x
(c)	x	x	x	x	X	x	x	x	x	X	x
(d)			x	x	X	x	x	x	x	X	x

3.1 ATOMIC FORCE MICROSCOPY (AFM)

The PbS thin films were morphologically characterized by using AFM. Figure 2 depicts the AFM images of PbS films. For the traditional formulation, the left side corresponds to a top view and the right is a perspective view. The grain size is around 400 nm. There are isolated cluster formations up to 1 μm and their maximum height is of 161.72 nm. The morphology of these thin films is homogeneous.

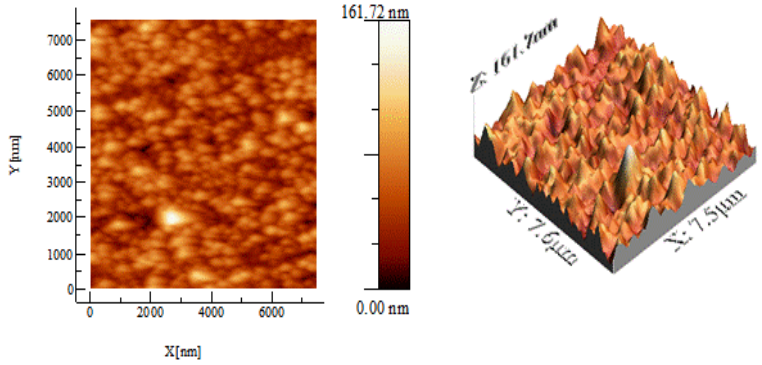

Fig. 2. Top and perspective view of PbS thin film prepared by the usual formulation.

On figure 3 the morphology of the PbS film prepared by the new formulation is shown. This figure reveals, due to the size of the grain, the uniform distribution of the film. The maximum height is around 107.56 nm. The range of the sizes of the grains are between 200 and 500nm. In this case the cluster formation is as dense as a granular background.

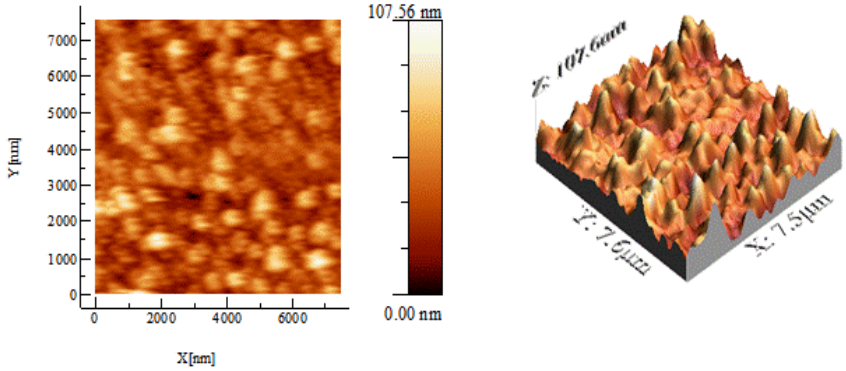

Fig. 3. Top and perspective view of PbS thin film prepared by the new formulation.

3.2 SCANNING ELECTRON MICROSCOPY (SEM)

Another way of studying the morphology was carried on by SEM. The images built form the secondary electrons, show a clear difference between the granular orientation of both layers. Micrographs were taken in two different magnifications; the first one was to look at film homogeneity at a huge scale, while the second one was to show the superficial granular orientation.

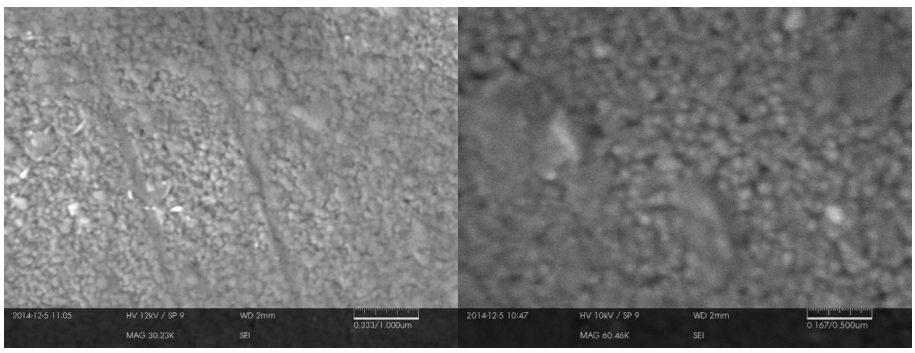

Fig. 4. SEM of PbS thin film, at a scale of 1 µm. a) New formulation. b) Typical formulation.

In figure 5 the plane vertexes which form the grains of the PbS material in the new chemical formulation can be observed. The surface morphology is regular. The same result will be correlated with the XRD results.

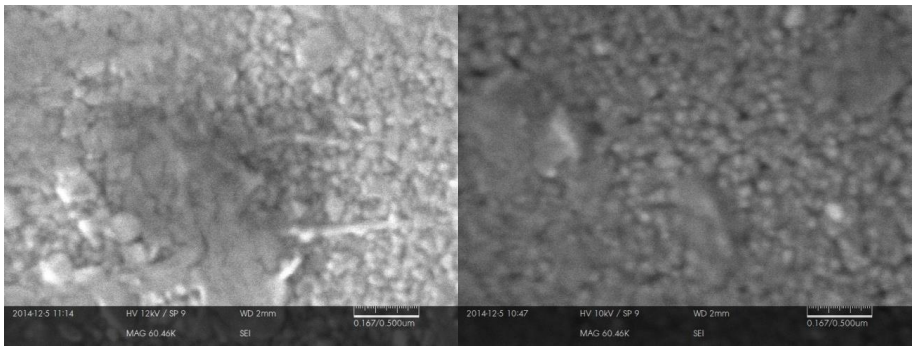

Fig. 5. SEM of PbS thin film, at a scale of 500 nm. a) New formulation. b) Typical formulation.

3.3 X-RAY DIFFRACTION

XRD was used to characterize the deposited PbS thin films. The XRD pattern of the PbS thin film with the new formulation shows a crystalline nature with preferred orientation along (111) and (200); the directions (220),(311) and (222) also appeared but with less intensity, hence it is an FCC structure. By using the Debye-Scherrer equation (1), see [12,13], the grain size was of 20 nm.

$$s = \frac{0.94\,\lambda}{BCos\theta} \tag{1}$$

where: s is the crystallite size, λ is the wavelength of X-ray radiation ($CuK_\alpha = 0.15405nm$), θ is the diffraction angle and *B* is the line width at half maximum height.

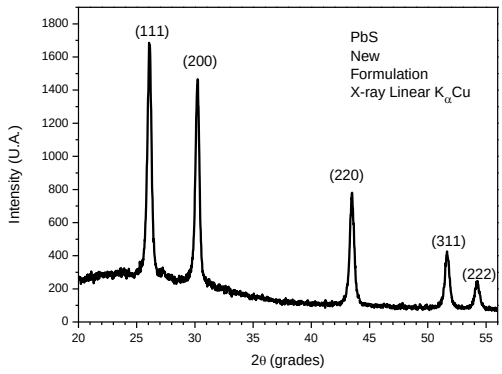

Fig. 6. X-ray spectrum of the PbS thin film made it with the new formulation.

Table 2. In this table the Miller index of the FCC structure and the angles of the PbS thin film was elaborated by the typical formulation.

Miller Index	(111)	(200)	(220)	(311)	(222)
2θ	26.11	30.24	43.49	51.65	54.28

Figure 8. XRD pattern for PbS which was prepared by the traditional chemical formulation. It can be observed that the crystallic directions are (200) and (111), hence it is a FCC structure. Similarly, the calculated grain size was of 34 nm.

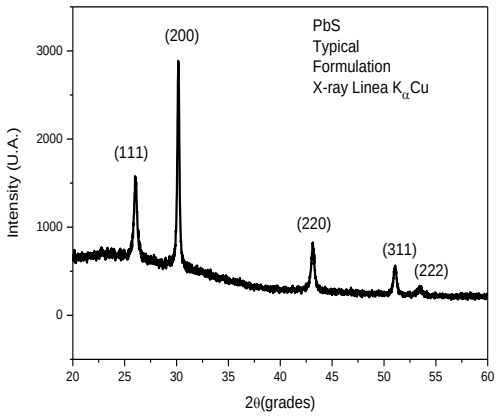

Fig. 7. X-ray spectrum of the PbS thin film made with the typical formulation.

Table 3. In this table the Miller index and the angles are shown for the PbS thin film, prepared with the new formulation.

Miller Index	(111)	(200)	(220)	(311)	(222)
2θ	26	30.16	43.15	51.08	53.42

3.3 UV-VIS

The absorption, reflection and transmistion were measured by using the UV-vis technique.

3.3.1 Absorption

PbS has its absorption edge in λ=3351 nm [5]. More than 60% of the absorption in the PbS film was between 330 and 665 nm, so the film is dark colored. However, it can be observed that there is a little absorption edge at around 700 nm. Figure 8 shows the absorption versus the wavelength (nm) spectra of PbS thin films.

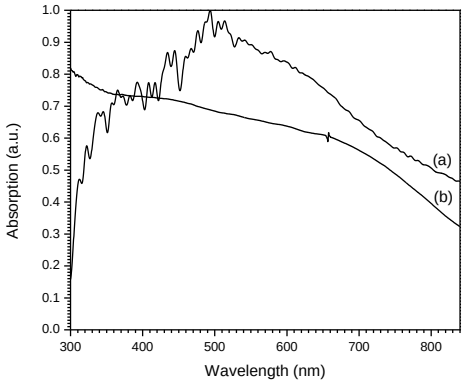

Figure 8. The variation of the absorption with respect to the wavelength of the PbS thin film is shown. (a) is associated to the PbS thin film prepared by the new formulation, and (b) corresponds to the standard formulation.

3.3.2 Transmission

Figure 8 Optical transmission which is less than 30% for both thin films. Thus, the color of the film is expected to be dark. The minimum is around 500 nm

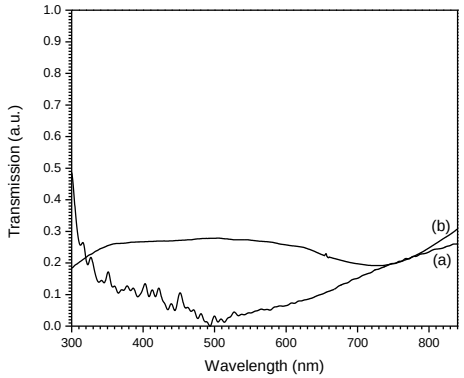

Fig. 9 Variation of transmission with respect to wavelength (nm). (a) corresponds to PbS thin film prepared with the new formulation, and (b) part to the elaborated with the typical formulation.

3.3.3 Reflection

Fig. 10 a) and b) show the optical reflection of both films obtained with the new and typical formulations, respectively. As a result, 30% of the reflection in this range was obtained.

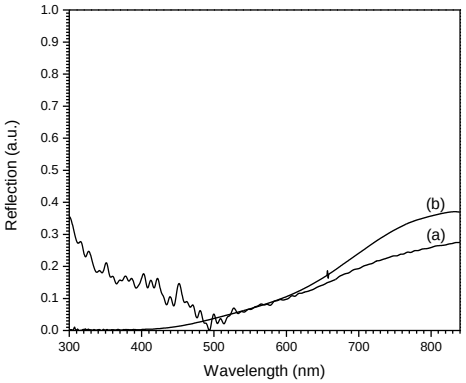

Fig. 10 Reflection responses versus wavelength (nm) of both PbS thin films. (a) and (b) are the PbS thin films made with the new and typical formulations, respectively.

Table 4. Deposition time and thickness of the thin film.

Time (min)	Thickness (nm)
6	104.3
7	115.6
8.5	141.7
15	170

A similar film was elaborated in 15 minutes, which could also be obtained with the typical formulation in two hours. The thickness is 141.7 nm; these measurements were carried on using a profilometer.

4. Conclusions

PbS thin films were obtained using the complexing agent Polyethilene-imine and a reaction temperature of 60°C. The new chemical formulation showed to be effective.

The XRD pattern shows that the crystalline structure is FCC, the preferential orientation for the new formulation is (111) meanwhile the classical formulation is (200). The grain sizes were of 20 and 34 nm for the new and the standard formulations.

In the case of XPS, for each formulation, most intensive peaks were obtained for samples of Pb with erosion. The binding energy remains invariant, but, three new peaks appeared in the case of the standard formulation with erosion. The binding energy patterns are the same in both formulations when there is no erosion. It is very important to note that the XPS pattern presents a greater diversity when the samples are erosioned, so, in this case non-stoichiometric compounds are observed.

AFM images showed a decrease in the heights of the granules in about 34% of the new formulation with respect to the traditional. Moreover, the distribution has more homogeneous granular clusters for the typical case, with a diameter of 400 nm in average, while in the new formulation these sizes varied from 200 nm to 500 nm. These observations and the preferential orientations obtained by XRD are confirmed by SEM.

To have an alternative possibility for the preparation of PbS thin films is a successful result *per se*. The polyethyleneimine was more efficient than triethalonamine, because the deposition time was less for the thin films with the same thickness, chemical and physical properties.

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