RESISTANCE AND RESISTIVITIES OF PbS THIN FILMS USING POLYETHYLENIMINE BY CHEMICAL BATH DEPOSITION

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In this work resistance and resistivities of PbS thin films by chemical bath deposition using Polyethylenimine as complexing agent are presented. A series of resistance and resistivity values of thin films obtained at different deposition times of 7, 10 and 13 minutes were evaluated and compared. The obtained films were chemically characterized by X-Ray Photoelectron and Raman spectroscopy confirming the presence of lead and sulfur as PbS. Thickness of the films was measured by ellipsometric spectroscopy; the values were in the range of 80 to 100 nm. Resistivity of the films was measured indirectly using an integrator circuit, the results show that resistivity values vary as a function of the deposition time. PEI films showed a low transmission in the visible range about 2 to 5% and an irregular absorption in the range of 300 to 1050 nm. Roughness of the films was characterized by atomic force microscopy showing values of mean square roughness of 16 nm, presenting different orientation of the clusters and pyramidal shapes.

1. Introduction

Most studied nanostructured semiconductors belong to the II - VI and IV - VI groups as they are relatively easy to synthesize and generally are prepared as particles or thin films [0]. Semiconductor thin films have been synthesized by wet and dry deposition techniques. Vacuum evaporation [0] and molecular-beam epitaxy [0] are among the most successful dry methods for PbS films synthesis. Most of the applied wet methods include spray pyrolysis [0], chemical bath deposition [0], [0], [0] and electrochemical deposition [0]. Chemical Bath Deposition (CBD) is a simple, cheap, and feasible technique for different semiconductor thin films being possible to obtain high quality films even at room temperature. To ensure films quality and homogeneity is necessary to control the following parameters pH, temperature, reagents concentration and reaction time [0], [0], [0]. Lead sulfide (PbS) has a relatively small band gap (0.41 eV at 300 K) [0] and a cubic structure and is used in infrared light detectors in order to sense radiation between 1 to 3 μm wave lengths range [0]. It is well known that polycrystalline lead sulfide films are used as the base to build photodetectors. The lead sulfide photodetector was brought to the manufacturing stage of development in Germany about 1943. After 7 decades, lead sulfide detectors are still in great

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demand as sensors for major military systems, as well as industrial, commercial and medical applications. [0], [0], [0]

In this work, two different formulations were used to synthesize PbS thin films, the traditional one with triethanolamine (TEA) as complexing agent and a another formulation using Polyethylenimine (PEI) instead of TEA. The obtained films were characterized by X-ray Photoelectron (XPS) and Raman spectroscopy for chemical composition, thickness was measured by ellipsometric spectroscopy, electrical resistivity and electrical resistance, optical properties by spectrophotometry, morphology by atomic force microscopy (AFM) and scanning electronic microscopy (SEM).

2. Experimental

Two series of PbS thin films using TEA and PEI as complexing agents were grown on glass substrates from an alkaline solutions in a chemical bath. For the traditional formulation with TEA, 82 ml of deionized water, 6 ml of thiourea, 5 ml of lead acetate, 5 ml of sodium hydroxide and 2 ml of Triethanolamine were mixed and placed in hot bath at 55°C. The glass substrates were retrieved at 30 minutes and cleansed with deionized water and then dried at ambient temperature. The PEI solution was prepared mixing 82 ml of deionized water, 6 ml of thiourea, 5 ml of lead acetate, 5 ml sodium hydroxide and 2 ml of Polyethylenimine then placed in a hot bath at 55°C. For this series, the glass substrates were retrieved at three different reaction times of 7, 10 and 13 min and cleansed with deionized water. For both types of formulations, the reaction was performed under dark conditions due to material photosensibility. The reaction mechanism for PbS formation using TEA as complexing agent is as follows [0]:

$$[Pb(CH_3COO)_2 \cdot 3H_2O + 2NaOH] \rightarrow Pb(OH)_2 + 2Na(CH_3COO) + 3H_2O$$
$$SC(NH_2)_2 + 2H_2O \xrightarrow{:OH^-} H_2S_{(g)} + CO_{2(g)} \uparrow + 2NH_{3(g)} \uparrow \xrightarrow{:OH^-} S^{2-} + H_2O$$
$$2Pb(OH)_2 + 2[C_6H_{15}NO_3]_n \xrightarrow{55°C} 2[Pb\,(TEA)_n] + 2H_2O + O_2$$
$$[Pb\,(TEA)_n] \xrightarrow{55°C} Pb^{2+} + n(TEA)$$
$$Pb^{2+} + S^{2-} \xrightarrow{55°C} Pb\,S$$

Then a reaction mechanism for the PEI formulation is proposed from the previous mechanism, taking into account that PEI is substituting TEA as complexing agent. The proposed reaction mechanism is:

$$[Pb(CH_3COO)_2 \cdot 3H_2O + 2NaOH] \rightarrow Pb(OH)_2 + 2Na(CH_3COO) + 3H_2O$$

$$SC(NH_2)_2 + 2H_2O \xrightarrow{:OH^-} H_2S_{(g)} + CO_{2(g)} \uparrow + 2NH_{3(g)} \uparrow \xrightarrow{:OH^-} S^{2-} + H_2O$$

$$2Pb(OH)_2 + 2[C_2H_5N]_n \xrightarrow{55°C} 2[Pb\,(PEI)_n] + 2H_2O + O_2$$

$$[Pb\,(PEI)_n] \xrightarrow{55°C} Pb^{2+} + n(PEI)$$

$$Pb^{2+} + S^{2-} \xrightarrow{55°C} Pb\,S$$

Chemical composition of the PbS thin films was characterized by Raman and XPS spectroscopies. The Raman dispersion was analyzed in a Micro Raman XPloraBXT40 with a resolution of 2400T. XPS was performed in a Perkin- Elmer Phi-5100 model spectrometer with a non-monocromated Mg source emiting a Kα radiation of 1254 KeV. The surface of the films was etched with an Argon ion beam with an emission voltage of 3KV during 15 seconds to remove contaminants present on the surface. Afterwards, wide surveys scans of the films were taken with a

pass energy of 72 eV in 5 sweeps. Morfology of the films was characterized by atomic force microscopy (AFM) using a JSPM-4210 scanning probe microscope (JEOL Ltd) and scanning electron microscopy (SEM) using a JMS-5300 model (JEOL Ltd). Thickness of the PbS films was measured by ellipsometric spectroscopy in a 200 mm Phillips Laser ellipsometer a series of 36 measurements along the coated substrate were taken for each film. Resistance measurements were done using a multimeter GWstek GDM-8034 model, an integrator circuit, a digital power supply and an Agilent S4624A digital Oscilloscope 100 MHz. Optical transmission spectrum of the layers was recorded by an Ocean Optics USB4000-UV-VIS spectrometer in the 250-1100 wavelength range.

3. Results and discussion

PbS films grown on glass substrates by CBD using both TEA and PEI formulations were obtained. The films were homogeneous in thickness and with good adherence in visual evaluation for all reaction times considered in this study. The samples were characterized and the results are presented and discussed as follows.

3.1 Chemical composition

3.1.1 X-ray photoelectron spectroscopy

In Fig. 1 wide-scan survey XPS spectra of PbS films obtained at two reaction times are presented. The films are composed principally of lead and sulfur suggesting the formation of PbS. The O 1s core level peak is located at 531.75 eV which corresponds to oxygen forming an hydroxide [0], then it is possible that lead hydroxide is present on the films surface since is an intermediary compound according to the reaction mechanism of PbS as it was described previously. The presence of the C 1s core level peak is related with adventitious carbon which is still detected after 15 seconds of etching. In addition, in Fig. 1 the inset graph shows in detail the Pb 4f doublet of TEA and PEI 7 min films and the position of the Pb 4 f7/2 of 137.5 eV is the same for both films and is in good agreement with reported values in literature for PbS [0], [0].

The S 2p core peaks for both films are located at 160.75 eV which corresponds to sulfur as PbS [0] Therefore, PbS films are obtained using PEI as complexing agent according to the surface analysis from XPS spectra.
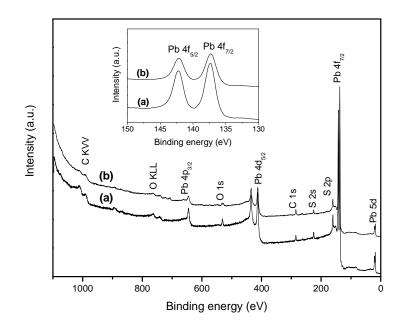

Fig. 1. XPS spectra of a) PbS TEA film and b) PbS PEI 7min film and the inset graph shows details of the same films of the Pb 4f doublet.

3.1.2 Raman scattering

Natural PbS (Galene) may observe two peaks, a peak at 209 cm^{-1} as reported in RRUFF database (Galene R060187) and [0],[0]; and a second peak at 459 cm^{-1} as reported in [0] and [0]. Figure 7 shows the formation of three Raman scattering peaks characteristic of the lead sulfide obtained from TEA and PEI formulations, the Raman spectra was obtained at 300K. In the presented spectra, the first peak occurs at 201.6 cm^{-1} for TEA formulation and 207 cm^{-1} for PEI formulation, which is a doublet related to two acoustic phonons [0]. Meanwhile, the second peak correspond to PbO_2 excited with a laser source at 780 nm [RRUFF R070605 database], and is positioned at 321.3 cm^{-1} for TEA formulation and 323.9 cm^{-1} for PEI formulation. PbO_2 can form due to lead oxidation from environmental exposure to the atmospheric oxygen during and after the synthesis. The third peak at 448.4 cm^{-1} for TEA formulation and 449.1 cm^{-1} for PEI formulation is a doublet and has already been related to the generation of two optical phonons associated with the 2LO and 3LO modes of PbS [0]. The shift of the films compared to natural galene can be associated to the growth orientation of the PbS films on the glass substrates for both formulations.
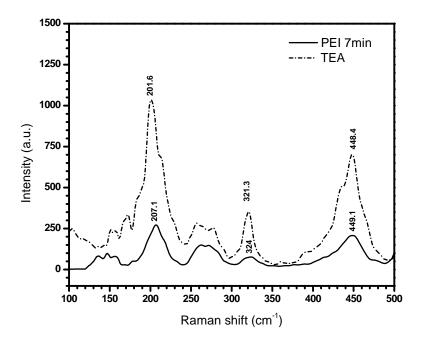

Fig. 2: Raman scattering for traditional and PEI formulation of PbS thin films.

3.2. Resistance and resistivity

To estimate the resistivity of the films is necessary to determine the thickness of the films which were measured by ellipsometry. Results of the thicknesses values of all synthesized films are presented in Fig. 3, as it is expected PbS PEI films are thicker as the reaction time is incremented. At 13 minutes of reaction the film reach a thickness of 100 nm and is very homogeneous. Noticeably, the PEI7min film has a thickness very similar to that of the TEA film obtained after 30 minutes of reaction. In general terms, using PEI as complexing agent accelerates the deposition of homogeneous PbS films compared with the film using a formulation with TEA. This can be explained in terms of the major number of amino groups present in the PEI molecule to form complex centers for the lead atoms compared to the TEA which only has one amine group. It has been reported by Aned de Leon et al. [0] that $Pb(TEA)_2$ is the most stable complex structure and since two molecules of TEA are needed to form a complex, it means a slower rate of Pb atoms free to react with sulfur from thiourea. According to this result, the film thicknesses obtained from

both formulations can be used to fabricate the active layer of devices as thin films transistors (TFT) or IR detectors. These values were used for the resistance and resistivity measurements.

The electrical resistivity of the films was measured using two different methods and all the experiments were carried out at ambient temperature. In the first method, the electrical resistance was measured by a GDM8034 multimeter and the obtained results were as follows: 13.6 MΩ for TEA PbS thin film; and for PEI PbS thin films were 4.9 MΩ, PEI 7 min; 6.9 MΩ, PEI 10 min; and 8.7 MΩ, PEI 13 min. The second method proposed for the electrical resistance measurements uses an integrator circuit as is schematically represented in Fig 4. The electrical resistance values of the samples were: 13 MΩ for the TEA PbS film; and 4.9 MΩ, 6.8 MΩ Ω for the PEI PbS films at 7 min, 10 min and 13 min, respectively. These values are very similar to those obtained with the first method and can be used to estimate the resistivity of the films. The advantage is that resistance values with less error associated with the fluctuation of the multimeter can be measured; the variation in the measurements is related to the high resistance of the material.
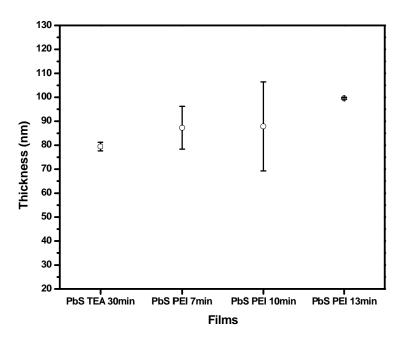

Fig. 3: Comparison of Thickness of PbS thin films. The figure showed thickness comparison of different formulations of PbS thin films.
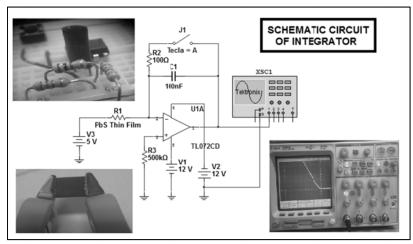

Fig. 4. Schematic representation of the integrator couple to PbS semiconductor thin film for electrical resistance measurements.

The resistivity was calculated by the formula:

$$R = \rho \cdot \frac{L}{A} \tag{1}$$

where R is the electrical measure resistance, ρ is the resistivity, L is the separation between electrodes and A is the transversal area where is crossing the current. The results for these resistivities at room temperature were 92 Ωcm for PbS TEA and 38 Ωcm at 7 min, 53 Ωcm at 10 min y 77 Ω cm at 13 min for PbS PEI formulation films. The separation between electrodes was 9 mm in all cases and the length was 8 mm while the considerate thickness was the average of the measurement by laser ellipsometry. In Table 3 all the features considered to estimate the resistivity are compiled. These values are lower than those reported elsewhere [0].

Table 3: Resistivities and features correlated for Resistivity estimation for TEA and PEI PbS thins films

	Resistance R (MΩ)	Length (cm)	Thickness (nm)	Width (cm)	ρ (Ω•cm)
PbS TF 30min	13	0.9	79 ± 2	0.8	92.4
PbS PEI 7min	4.9	0.9	87 ± 9	0.8	37.9
PbS PEI 10min	6.8	0.9	88 ±18	0.8	53.2
PbS PEI 13min*	8.7	0.9	100 ±0.4	0.8	77.3

*This film was only measured with the multimer.

3.4. Morphology

3.4.1 X-Ray Diffraction

The figure 5 shows typical XRD spectra of PbS TEA and PbS PEI films. In the case of PbS TEA films sharp peaks at 2θ ≈ 26.0°, 30.1°, 43.1°, 51.0° and 53.5° were observed; these positions coincide with the fcc structure of PbS, galene (JCPDS-ICCD PDF # 5-05920) and each one is identified by its Miller index. Only galene related peaks were detected in the PbS TEA film confirming the good quality of the films. For the PbS PEI films a small shift in the position of the peaks was observed; the peaks are slightly shifted towards higher 2θ values from those reported for PbS galene. This can be attributed to lattice strain from the PbS growth during deposition process and in this case to the effect of the PEI as complexing agent. Moreover, another peak not related to PbS in PbS PEI films was found and it corresponds to the orthorhombic structure of NaOH (JCPDS-ICCD PDF # 35-1009). It was only possible to differentiate the most intense peak with regarding NaOH diffraction pattern while others peaks were less intense to be clearly detected. Sodium hydroxide is used to obtain a solution with a high pH of ~ 11 in order for the reactions to take place, however the presence of NaOH in the film affect the quality of the film and the final properties will be influenced. Another distinguishable feature about the XRD spectra of the films is that for the case of the PbS PEI films the peak related to the crystallographic plane (111) is more intense than that of the (200) plane, which is normally the most intense peak for the fcc structure of PbS. According to this PEI promotes another preferred orientation during growth compared to TEA films, and as it was mentioned above this can be attributed to the overall capacity of PEI to chelate Pb^{+2} ions. However, further studies in this direction are needed to have a better understanding of the chelation process.
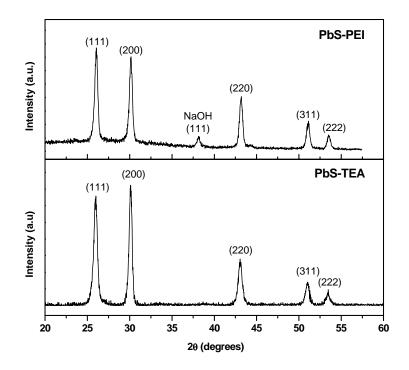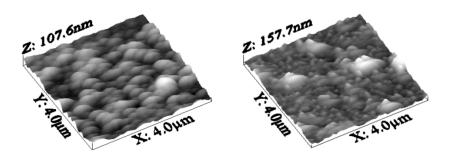
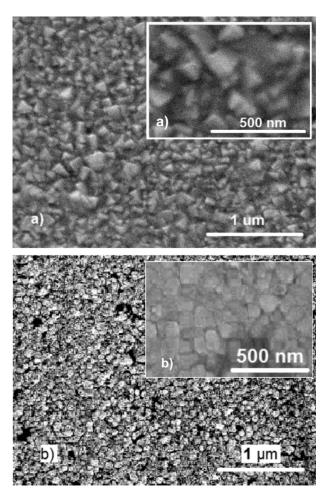*Fig. 5: XRD patterns of the PbS films obtained from TEA and PEI formulations.*

3.4.2. AFM and SEM

Surface images were obtained by AFM and SEM to observe the morphology of the obtained PbS films. AFM images were taken in a 4x4 μm^2 surface area. In Figure 6 a), AFM image of TEA films is presented, the surface shows the formation of rounded grains of similar shape and size. In the case of the PbS PEI 7 min film in Fig.6 b) the surface of this film shows peaks formation all over the scanned area revealing a pyramidal-like shape of the clusters from that of the PbS TEA film. The mean square roughness, *Rq*, of the samples was estimated using the WSxM software [0], the results are 16.6 nm and 20.3 nm for the PbS TEA and PbS TEI 7 min films, respectively. These values demonstrate the smoothness of both films.

a) PbS TEA film   b) PbS PEI 7min film

Fig. 7 The morphology for traditional and PEI formulation of PbS thin films by atomic force microscopy (AFM). In a) AFM PbS TF 30 min, b) AFM PbS PEI 7 min.
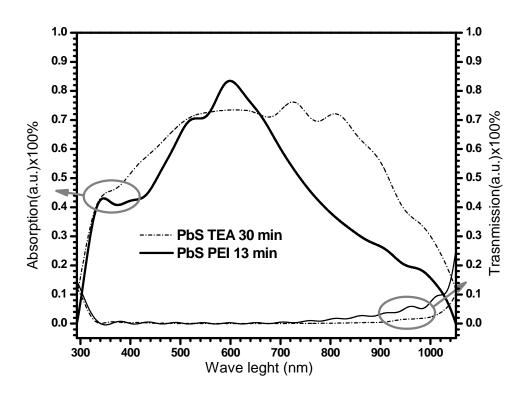
In order to observe more details about the films microstructure, the surface was analyzed by SEM and it revealed that the PEI 7min film shows a clusters with a pyramidal shape as it can be seen in Fig. 7 a). The morphology of this film consist of pyramidal vertices oriented emerging

from the substrate surface while for the TEA film in Fig 7 b) has a surface with cubic grains parallel to the substrate surface plane. For more detail an inset image at higher magnifications is presented in each case where the cubic shape clusters of the TEA films are very distinguishable from the pyramidal ones formed on the PEI 7min films. Thus, this is the effect of what it was observed in XRD results were PbS film growth with PEI formulation show a different preferred orientation than that of the PbS growth with TEA as complexing agent.

Fig, 7: The morphology for traditional and PEI formulation of PbS thin films by scanning electronic microscopy (SEM). In a) SEM PbS PEI 7 min, b) SEM PbS TEA 30 min.

3.5. Optical Properties

In Figure 8, absorption and transmission optical responses of the films are depicted. The absorption increases from 300 to 600 nm and decreases towards higher wavelengths. The broadband is wider for PbS TEA films. Moreover, transmission of the film remains constant and oscillating from 340 to 900 nm with an approximate value of 2% for both formulations.

Fig. 8: Optical responses: absorption and transmission.

4. Conclusions

We got PbS thin films by chemical bath deposition, the synthesis is new compared with traditional formulation used in [0]. For the XPS a result, the chemical bath deposition technique is clean because there are no contaminants and confirm that the main components of this thin film are Lead and Sulfur. The resistance of both films was very similar. The PbS thin films gives the highest resistances, resulting 12.97 MΩ for the traditional formulation of PbS and 4.92 MΩ at 7 min, 6.79 MΩ at 10 min and 8.68 MΩ at 13 min, for PEI formulation of PbS thin films. The thickness for the PbS thin film is about 80 nm for traditional formulation, while several thicknesses were measured for PEI formulation, 87 nm at 7 min, 88 nm at 10 min and 100 nm for 13 min. The studies of morphology showed roughness average of the order of 16 nm for both formulations that correspond to smooth films and the SEM showing different orientation of the clusters and obtained pyramidal shapes as reported in [0] at PEI formulation, similar to galena, reported in [0], [0], [0], [0], [0]. This film could be used as an optical detector.

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