

EFFECT OF CHEMICAL BATH DEPOSITION PARAMETERS ON THE GROWTH OF PbS THIN FILMS FOR TFTs APPLICATIONS

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Lead sulfide (PbS) thin films were prepared by chemical bath deposition (CBD) as function of deposition time, pH and deposition rate and the impact of the resulting film structure on the thin film transistor (TFT) electrical characteristics was evaluated. Structure and morphology were investigated by X-ray diffraction (XRD) and scanning electron microscopy respectively (SEM). The deposited films show a cubic phase (galena) with an average crystallite size of ~25 nm. Three different PbS deposition conditions were evaluated in TFTs using source and drain gold contacts. The best electrical performance was observed for films deposited at high deposition rates. These transistors, showed field effect mobility and threshold voltage of $\sim 3 \times 10^{-3}$ cm²/V-s and ~6 V, respectively.

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1. Introduction

Amorphous silicon (a-Si:H) TFT is the most mature n-type TFT technology and is currently used in active matrix liquid crystal displays [1]. While the a-Si:H TFT technology has emerged as the industry leader in applications such as active matrix liquid crystal display backplanes, its relatively low mobility (1cm²/V-s) and threshold voltage instability [2-3] limits its use in applications that require significant device performance. Efforts to synthesize other n-type semiconductor materials to reduce the high-cost deposition techniques and high process temperatures that a-Si:H requires have not been successfully achieved. In addition, there is still the need to develop air-stable p-type semiconductor materials to be able to fabricate high performance complementary metal-oxide-semiconductor (CMOS) circuits. Among p-type materials, organic semiconductors have been investigated for a long time, but its instability when exposed to air and their incompatibility with some photolithographic processes are limiting its incorporation in functional devices [4]. Therefore, the development of alternative TFT semiconductor materials is very relevant and is currently mostly driven by improved carrier mobility, device stability and reduced processing costs [5]. In addition, in recent years a low cost solution-based fabrication of thin film field-effect transistors (TFTs) has become a key goal among the materials science community. Among these techniques chemical bath deposition is one of the most suitable

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techniques for chalcogenides thin films synthesis because it is a relatively simple and inexpensive method for large area deposition and, at the same time, allows depositing films at a relatively low temperature [6]. In fact, chalcogenide materials have shown to be good candidates for p-type semiconductors [7-8] and have been demonstrated using chemical bath deposition (CBD) [9]. In particular, PbS thin films have been demonstrated using various chemical methods including CBD [9], electrodeposition [10], successive ionic layer adsorption and reaction [11], spray pyrolysis [12] etc.

Chemical bath deposition can be used to carefully control the crystallinity of the thin film semiconductors by adjusting the deposition temperature [13]. In general, this technique can be used to deposit any compound that satisfies four basic requirements: the material can be prepared by simple precipitation, the compound is highly insoluble in the solution used, the compound is chemically stable in the solution and the reaction should proceed with a free anion that is slowly generated [14]. Another important variation in the deposition of PbS films by CBD is the deposition under light. Visible light increases the growth rate of CBD-deposited PbS films [15]. The enhanced deposition rate is a cumulative effect of the increased bath temperature due to photothermal conversion as well as to photo-activated deposition of the PbS film [16]. The morphological structure characteristics of chemically deposited PbS films evidenced in scanning electron microscopy images has also effects on its electrical and optical properties [15-17].

The aim of the present work is to optimize the various processing parameters to synthesize PbS thin films by the chemical bath deposition method and understand the growth mechanism and its impact in device (TFT) performance. The films were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) to understand the PbS structure, morphology and finally correlate CBD process parameters with device performance. The transistor fabrication process was carried out using conventional thin film transistors with gold source and drain top contacts defined using a shadow mask process. Field effect mobilities of $3 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were achieved, which are comparable to those obtained in organic thin film transistors [18-19].

2. Experimental details

a) Substrate preparation

The PbS films were deposited on 90 nm thick HfO₂ films [20]. The HfO₂ dielectric was deposited using atomic layer deposition (ALD) at 100°C on a heavily doped Si wafers (p-type: boron; <0.005 ohm-cm). The HfO₂/Si substrates were then cleaned in an ultrasonic bath with acetone followed by isopropanol and finally rinsed with distilled water and dried with N₂ gas.

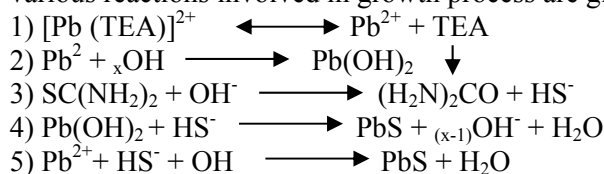
b) Lead sulphide deposition

The PbS films were deposited by immersion in a CBD solution prepared from lead acetate (Pb(CH₃COO)₂), sodium hydroxide (NaOH), triethanolamine (C₆H₁₅NO₃) and thiourea (SC(NH₂)₂) in a volumetric ratio of 2.5 ml (0.5M):2.5 ml (1.1M-2.5M):1 ml (1M):3 ml (1M). The total reaction volume was adjusted with water to 70 ml. The pH was measured with a digital pH-meter Excel XL15. The temperature of the solution was kept at 40 °C ±1 °C. All depositions were performed under dark conditions to avoid variations on the films growth rate due to photo enhancement effects. After deposition, the PbS films were cleaned in an ultrasonic bath with methanol followed by rinsing in distilled water and dried with N₂ gas. Finally, 100 nm thick Au contacts were deposited by e-beam evaporation to form, through a shadow mask process, the source and drain contacts of the transistor structure.

The crystalline structure of the PbS films was analyzed in a Rigaku Ultima III X-ray diffractometer with CuK α (λ)= 1.54 Å, operated at 40kV and 44mA. The 2 θ scan rate was 0.5°/min. The morphology was studied in a SEM Zeiss SUPRA 40 with operating voltage of 5 kV. The electrical characteristics of the TFTs were determined using current–voltage (*I-V*) measurements at room temperature in a 4200 Keithley semiconductor characterization system under dark conditions.

3. Results and discussions

Hydroxyl ions in the chemical bath precursor solution are necessary for the growth of PbS thin films. [19]. For the PbS films deposition, triethanolamine (TEA) acts as the complexing agent to control the release of Pb ions [Eq. (1)]. Hydrolysis of the thiourea provides the S^{2-} ions. The various reactions involved in growth process are given in Equations (1)–(5) [19]:



The pH of the reaction mixture depends on the OH^- ions concentration and may have an impact on the film growth rate as demonstrated by A. Antony et al [21]. In such work, the thickness of as-deposited ZnS thin films increases with pH. In the present study it is also observed that the PbS thicknesses deposited on HfO_2 increases as the pH increases. The depositions of thin films were studied between 12 and 48 minutes, depending of pH. The pH was controlled by using NaOH with concentrations ranging from 1.1 - 2.5M. The alkaline character of the solution helps hydrolysis of the thiourea, with the subsequent release of S^{2-} ions [Eq. (3)][8].

Fig. 1a shows the variation in PbS film thickness as function of deposition time at different pH. For equivalent deposition times, films deposited at low pH results in thinner films while films deposited at high pH results in thicker films. This effect is likely due to the lack of thiourea hydrolysis at low pH, as explained below. In general, Fig 1a shows an initial slow corresponding to an induction phase where the thickness follows a linear dependence.

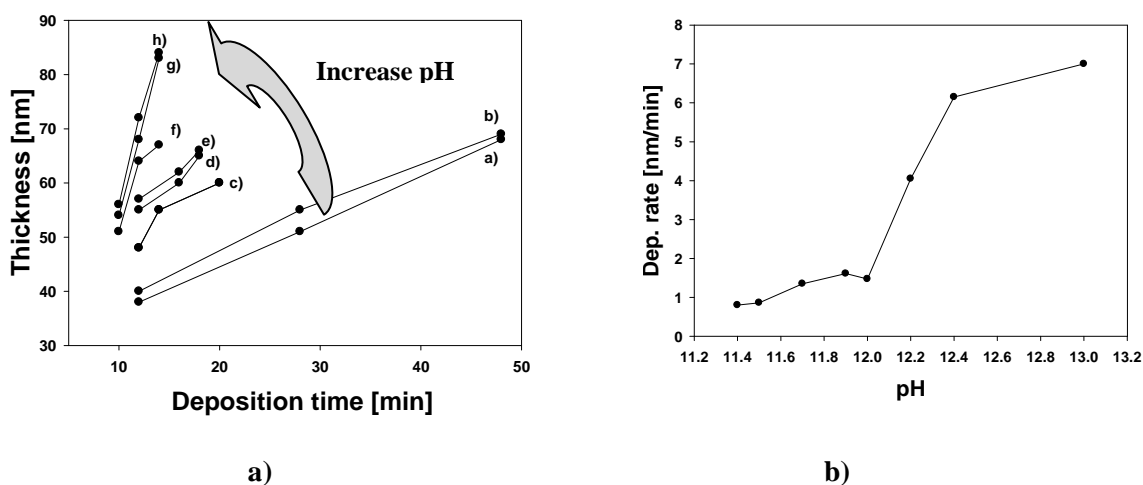


Fig. 1. a) Variation thickness of PbS films with pH and time of deposition. PbS films deposited at: a) pH-11.4, b) pH- 11.5, c) pH- 11.7, d) pH- 11.9, e) pH- 12, f) pH- 12.2, g) pH- 12.4, h) pH-13. b) Variation of deposition rate with pH. The deposition rate of PbS films increase with pH.

Average PbS thicknesses were measured by SEM cross-section. Also, in order to analyze the impact of pH in the resulting PbS morphology, films grown with similar thicknesses were analyzed by SEM. Fig. 2 shows the SEM results. Homogeneous PbS films are observed for low pH (11.4-11.7). At low pH, high Pb^{2+} free ions concentration in the CBD solution is expected due to lower complexation of the Pb^{2+} ions; however, the lower hydrolysis of the thiourea also limits the concentration of S^{2-} free ions, resulting in thinner films. PbS films grown at high pH values results in denser films, but also shows clusters at the PbS surface. This formation is likely due to the high deposition rate at higher pH. At high pH the Pb^{2+} free ions concentration is lower due to

higher complexation, but S^{2-} free ions concentration is higher and results in higher deposition rates. Fig. 1b shows the deposition rate variation as function of pH. The sudden increasing in deposition rate at pH 12 might be due to the increase of OH^- ions concentration in the solution, thereby favoring thiourea hydrolysis [Eq. (3-5)].

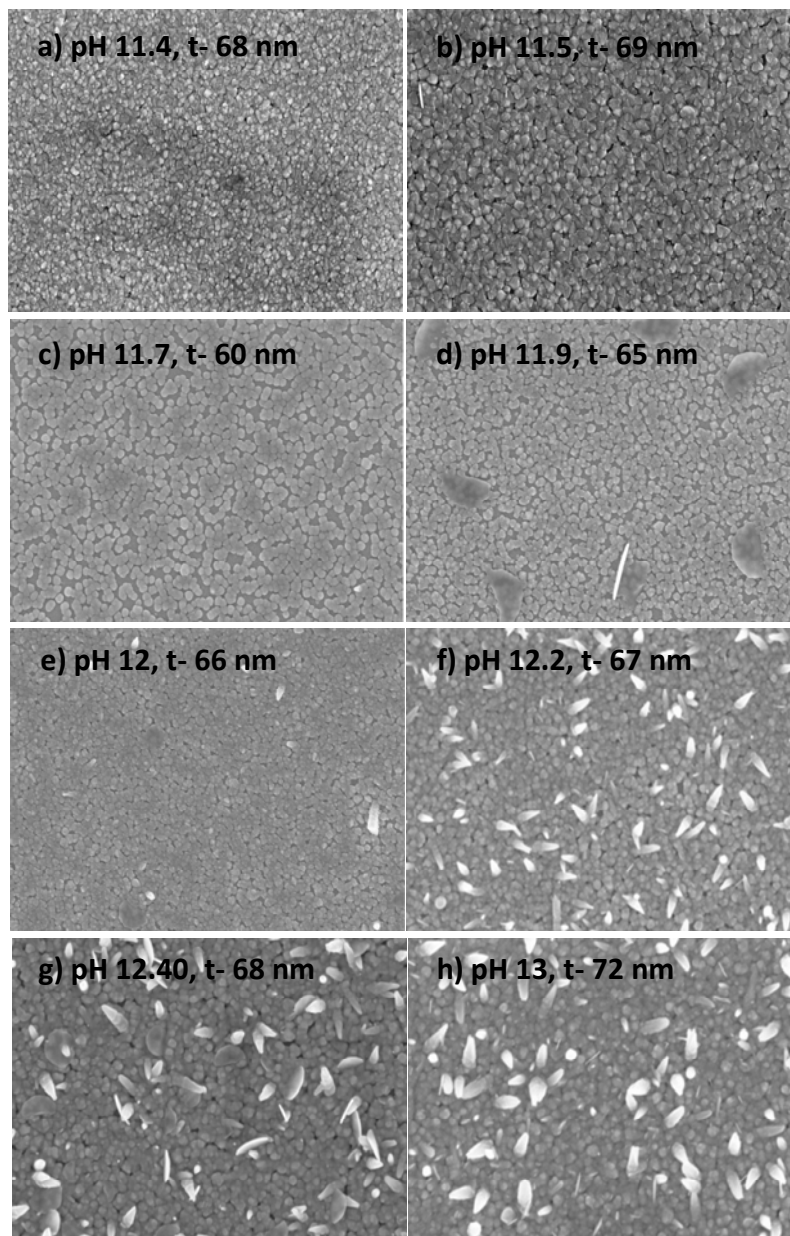


Fig. 2. SEM for PbS films deposited at different pH. PbS films with ~64 nm of thickness. An increase of cluster size on the surface for PbS films is observed with the increase of pH.

Fig. 3 shows the XRD patterns for as-deposited PbS layers corresponding to the (111), (200), (220), (311) and (222) crystalline planes of the cubic PbS phase. All PbS films, regardless of the pH, showed preferred orientation in the (200) direction, with an average crystallite of 25 nm.

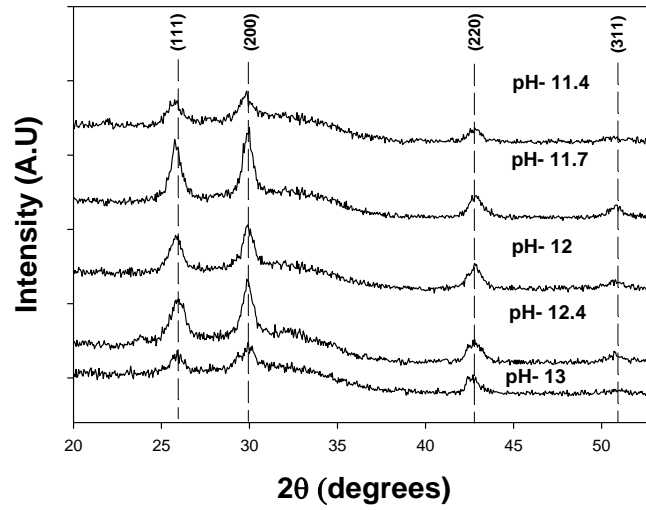


Fig. 3. XRD patterns for PbS films deposited at different pH. No change in the film microstructure was observed with the pH variation on the deposition.

The characteristic transfer curves in saturation for TFTs fabricated with PbS films grown at three different pH values (high, medium and low) are shown in Fig. 4. Here, the $I_{DSAT}^{1/2}$ versus V_G curves are plotted for $V_D = -20$ V. The channel mobility (μ_{SAT}) and the threshold voltage (V_T) were obtained by fitting the linear region of the saturation regime using equation [6] [22]:

$$I_{DSAT} = C_i \frac{W}{2L} \mu_{SAT} (V_G - V_T)^2 \quad (6)$$

where C_i is the dielectric capacitance per unit area, W is the channel width and L is channel length. Table 1 shows the results of the mobility and V_T for TFTs shown in Fig.4. The Table also shows the I_{on}/I_{off} ratios for the three devices. The I_{on}/I_{off} ratios and mobility values are of the same order for the three devices fabricated with PbS films grown at different pH only the V_T value was affected.

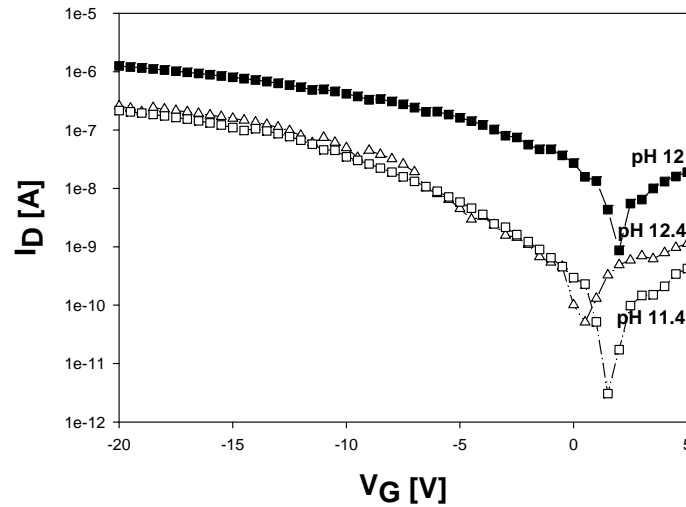


Fig. 4. Characteristic $(I_{DSAT})^{1/2}$ versus V_G plots for $V_D = -20$ V with different sweep number for PbS as deposited- TFTs, with 500- 20 μ m channel width- channel length respectively for PbS TFTs to different pH (11.4,12 and 12.4) .

Devices fabricated with PbS film deposited at high pH (high deposition rate) showed V_T of ~ 6 V and for devices fabricated with PbS film deposited a medium pH (medium deposition rate) showed a V_T of ~ 20 . Films prepared with PbS film grown at low pH (low deposition rate) showed a V_T of ~ 5 . There is not tendency on the V_T values can be related to the interface changes in the dielectric-semiconductor due to different growth mechanism showed different morphology for the PbS films deposited at different pH.

Table 1. Electrical measurements for TFTs with PbS films as semiconductor deposited at different pH.

Measurements pH	Mobility [cm ² /V- s]	VT [V]	I _{on} /I _{off} ratios
11.4	2×10^{-3}	5	10^3
12	3×10^{-3}	20	10^3
12.4	3×10^{-3}	6	10^3

More importantly, regardless of the pH, the extracted channel field mobility was similar for the three PbS film ($\sim 3 \times 10^{-3}$ cm²/V-s). This is likely due to the crystal size of the films is not changed with the pH variation only the cluster size is influenced for this parameter (Fig. 2), therefore the layer transport is not affected by the morphology due to the crystal size remains constant. These mobility values are still higher than many p-type organic semiconductors [23-25]. Furthermore, the fabrication process reported here eliminates the need for high temperature and expensive semiconductor deposition techniques. The soft chemistry solution-based processing used in this work to deposited p-type semiconductor offers an alternative solution to deposit inorganic p-type materials for large-area manufacturing technologies for inorganic thin-film transistors (TFTs).

4. Conclusions

We have successfully deposited PbS thin films by using the CBD method on HfO₂ substrate as function of deposition time, pH and deposition rate. These processing conditions play an important role in the processing of thin films especially in the deposition rate. XRD confirms that the PbS has a cubic phase (galena), with an average crystallite of 25 nm. We also demonstrated p-type thin film transistors using simple, inexpensive and low-temperature chemical bath deposition method. The best electrical performance of TFTs was achieved by PbS films grown at high deposition rates where the field effect mobility and threshold voltage are 3×10^{-3} cm²/V-s and ~ 6 V, respectively. The maximum temperature the devices see is due to the dielectric ALD process at 100°C.

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