STUDY OF THE GROWTH OF PbS THIN FILMS ON COMMON GLASS, HfO_2/Si AND SiO_2/Si SUBSTRATES, PREPARED BY CBD

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The goal of this work is to compare Lead Sulfide Thin Films grown on three different substrates: common glass a Hafnium oxide layer and a silicon dioxide layer. The morphology and cross section was characterized through SEM; XRD was utilized to chemically identify the compound and its structure; XPS was used to assure the chemical composition; and electrical measurements were performed to evaluate the resistivity. The morphology varies greatly from a smooth granulate amorphous phase to a polycrystalline clustered surface. All polycrystalline films are cubic Lead Sulfide. The clusters in these layers have crystallite sizes between 9 and 22 nm ranges. The obtained values for resistivity were 35.62 Ω·cm, and 13.50 Ω·cm for the samples with deposition time of 20 and 40 minutes, respectively.

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1. Introduction

The lead sulfide that is found as Galena in nature is a semiconductor with a broad bandgap (0.41 eV) [1- 3] with p-type conductivity in thin films and a high dielectric constant. The quantum confinement from holes and electrons is due to its large excitation Bohr radius (18nm)[3, 4] and therefore a strong electrostatic projection which results in a long lifetime of 63 μs for Intrinsic PbS [5].

Since the 1950's there has been great interest on PbS due to its detection properties in the infrared range of the electromagnetic spectrum.

The determination of the superficial interfacial layer composition and structural is critical for the understanding of the fundamental properties and the electric and adhesive behaviors.

The thin films are widely used in semiconductors with applications like infrared emission sensors [6, 7], Thin Films Transistors [TFT], gas sensors [8], and solar cells [9, 10]. The main advantage of PbS thin films produced by CBD is its low cost since they are deposited with few resources in large areas.

It is found that the substrates have great influence on the morphology and microstructure of the resultant film affecting the physical properties of the material.

There are several methods to obtain PbS thin films including electrodeposition [11], atomic layer epitaxy [17], chemical vapor deposition [18], sonochemistry [19], supercritical fluid

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deposition [20], electrodeposition [11] and [12], and successive ionic layer adsorption and reaction (SILAR) method [14] and [15]., spray pyrolysis [13], and chemical bath deposition [14- 16], RF sputtering deposition [5], Atomic Layer deposition [17], chemical vapor deposition [18], sonochemistry [19], supercritical fluid deposition [20] among others.

Several works have considered the CBD method to improve the symmetric structure through temperature control, application of magnetic fields, and growth with reduced stretching layers.

2. Experimental

Our main goal is to produce an active layer in Thin Film Transistors (TFT's). We controlled the thickness and the homogeneity of PbS thin films through the following formulation:

1. - 5 ml of Lead acetate (0.5 M)
2. - 5 ml of Sodium Hydroxide (2 M)
3. - 6 ml of Thiourea (1 M)
4. - 2 ml of Triethanolamine (1 M)
5. - 82 ml of deionized water

Let us start explaining that six Lead Sulfide thin films were grown on a glass substrate in order to evaluate their surface morphologies, thicknesses and crystallite sizes. Two more samples were deposited on different substrates.

Table1 shows the eight designed samples labeled as it is indicated, the asterisk located in labels 5, 7 and 8, stands for the samples with the same deposition time but with different substrates: glass, SiO_2/Si and HfO_2/Si. It is important to note that the last two substrates have been used as gates in TFT´s technology.

Table 1, Deposition time of the complete set of PbS thin films at 70^0C for different substrates

Labels	Substrate	Deposition time (minutes)
1	Glass	4
2	Glass	5
3	Glass	10
4	Glass	12
5*	Glass	20
6	Glass	40
7*	SiO_2/Si	20
8*	HfO_2/Si	20

The surface morphology and thickness by cross section were carried on SEM, using a Zeiss SUPRA 40 with operating voltage of 5 kV. The material was identified through XRD, data from were estimated the crystallite sizes, using a Rigaku Ultima III X-ray diffractometer with Cu Kα (λ)=1.54 Å, operated at 40 kV and 44 mA. The 2θ scan rate was $=0.5^0$/min. An X-Ray photoelectron spectrometer PHI5600 was used to measure the chemical content. And a 4200 Keithley semiconductor characterization system under dark conditions to measure indirectly resistivity.

Fig. 1 shows the morphology evolution of the sequence of PbS thin films, Image (1) is a granular homogenous surface with grainsizes around 60 nm, seen from the image scale with a deposition time of 4 minutes; Image (2) shows a fragmentation of the previous granular conformation, which was deposited for 5 minutes and its crystallinities are reviewed in XRD patterns; nevertheless, for the next sample, Image (3) that had a deposition time of 10 minutes shows a kind of intertwined pellets of sizes up to around 110 nm, which surely are clusters and a certain crystallinity can be predicted. After this growth time the sizes of the clusters tend to be bigger and homogenize, images (4, 5* and 6) for deposition times of 12, 20 and 40 minutes. For

devices design reasons we proposed to choose the samples (4) or (5*) to be considered. Further on, we present the concerning electrical resistances measured upon these samples where the correlation is evident.

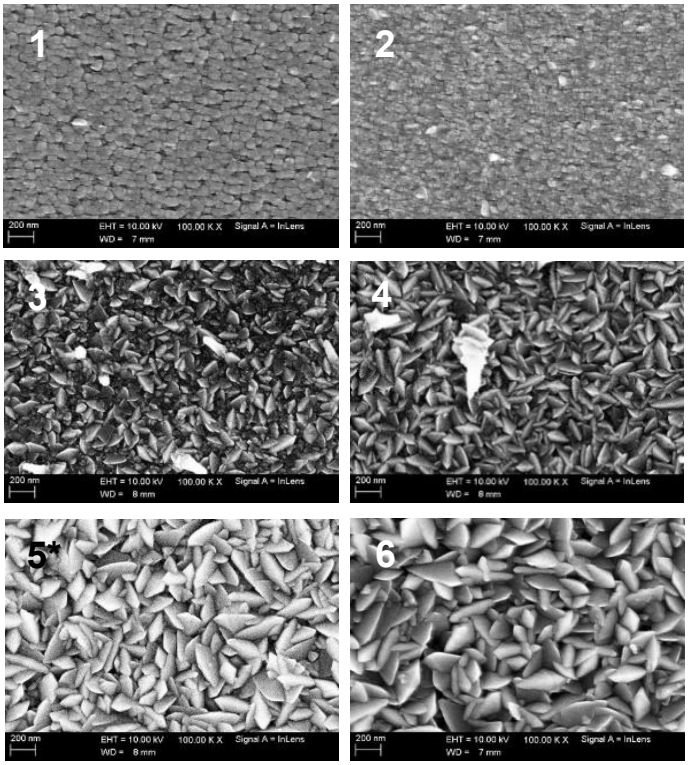

Fig.1. Morphology variations when the reaction time parameter increases from 4, 5, 10, 12, 20, to 40 minutes, which corresponds to labels 1,2,3,4,5 and 6, respectively.*

Fig. 2, presents three comparative morphological images of PbS thin films. The lower image (5*) is grown on a glass substrate for 20 minutes, while the upper left image (7*) is grown on a SiO_2/Si substrate for 20 minutes and the upper right (8*) is grown on a HfO_2/Si substrate also during 20 minutes. As it can be observed, the thin film grown on SiO_2/Si, is porous, meanwhile the one grown on HfO_2/Si, seems to be more compact, and such substrate is a high K material.

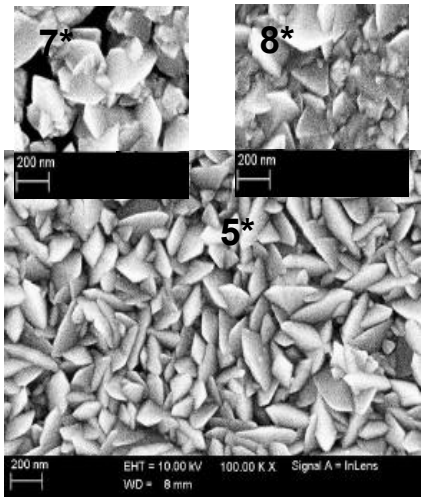

Fig. 2. Comparative morphologies of the three PbS thin films, 7 and 8* are deposits on SiO_2 and HfO_2, respectively, meanwhile 5* is upon glass substrate.*

Figure 3 shows the SEM images that were used to determine the thickness, taking as examples the samples grown during 4 minutes (labeled with 1) and 40 minutes (labeled with 6). These measurements were carried on by scanning electron microscopy. Their thicknesses were of 53.58 and 297.52 nm, respectively. The complete set of values of the projected samples in the experimental section, are plotted in Figure 4.

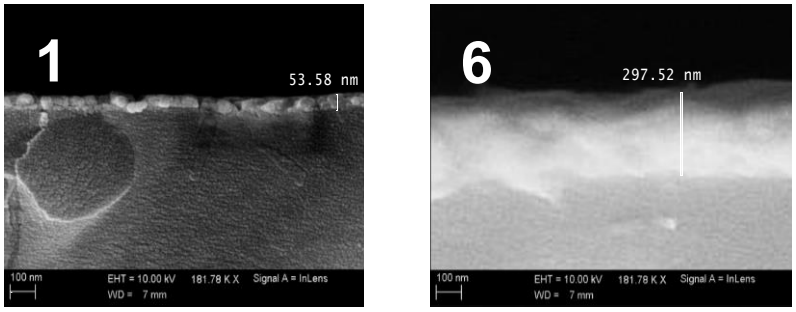

Fig. 3. Schematic representation of thickness determination from cross section by SEM images; values corresponding to samples 1 and 6.

The plot containing the thickness for all the samples grown. The typical saturation behavior is observed since it is known that those grown on CBD are thicker on glass than those grown on other substrates. Samples 7* and 8* were grown for 20 minutes, based on the magnitude order needed to build an active-semiconductor/gate bilayer for TFT's purposes (see Fig. 2).

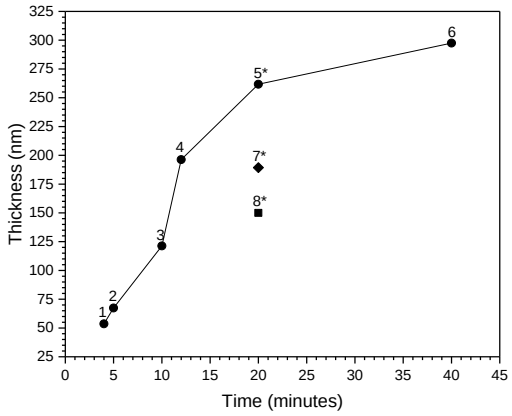

Fig. 4. Plot representing the growth kinetics of grown CBD PbS thin films on the following substrates: glass (1,2,3,4,5,6), SiO_2 (7*) and HfO_2 (8*).*

As it can be observed, for all the considered deposition times PbS thin films were formed. However, for the smallest considered deposition time (4 minutes), the material behave as amorphous, while for times between 5 to 40 minutes it was identified as cubic lead sulfide, matching the crystallographic code PDF # 65-9496, see Figure 5 of XRD patterns. Also from this data the crystallite sizes were calculated, using the Debye-Scherer method upon the (200) orientation peak. Those values are compiled in Table 2.

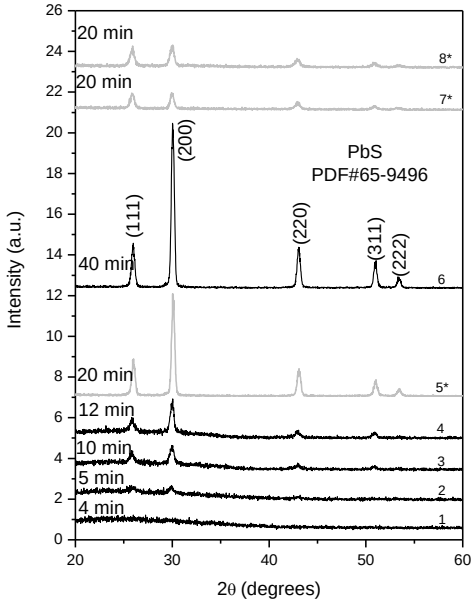

Fig. 5. Complete set of X ray patterns, 1,2,3,4,5,6 correspond to PbS layers on glass substrate; 7* and 8* are PbS layers deposited on SiO_2 and HfO_2 substrates, respectively.*

Table 2. Calculated values of crystallite sizes for all the samples presenting the crystalline phase, while sample 1 is amorphous.

Sample label	1	2	3	4	5*	6	7*	8*
Crystallite Size (nm)	-	15.1	15.3	16.54	21.1	22.8	15.1	15.3

Fig. 6 corresponds to High Resolution XPS spectra for sample (5*). The partial images are labeled by the chemical symbols in consideration. For each case we present two plots, the lower plot is for the introduced sample without etching and the upper plot is under some conditions of Argon etching.

The plots with circle symbols are the measured data from the XPS equipment. Each one has an adjusted plot. In addition we included some deconvolution signals for the as ground and the etched samples. There is a drastic diminish of the counts of Carbon and Oxygen after etching. Anyhow, that for the Lead and Sulfur elements, the etching implies a shift and the appearing of oxidation states.

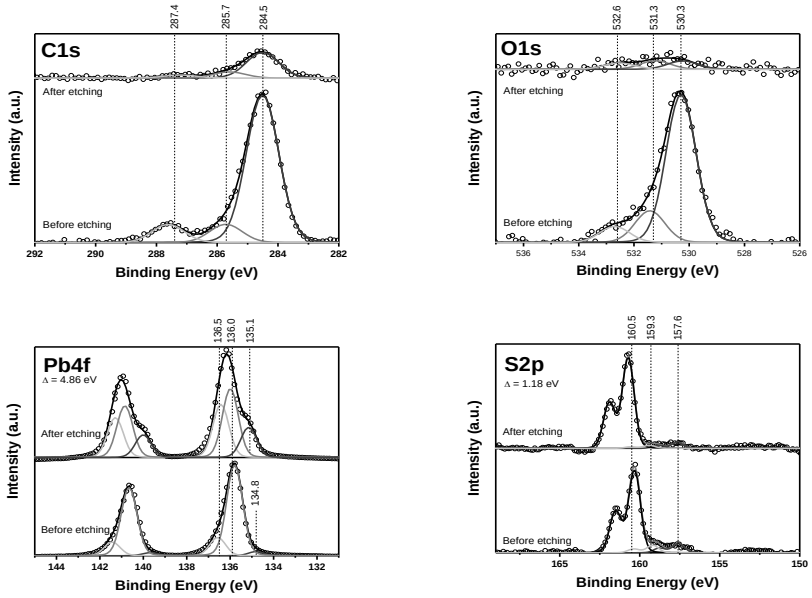

Fig. 6. HR-XPS show the main signals for the elements Lead, Sulfur, Carbon and Oxygen, contained in the 20 minutes of reaction time sample.

Were carried out electrical resistance measurements by the 4 dots technique. According to the results, the PbS thin films behave as an open circuit for the samples corresponding to 4, 5, 10 and 12 minutes; while the samples of 20 and 40 minutes give 300 and 100 KΩ □□□respectively.

Then from $R = \rho \frac{l}{A}$ or $\rho = \frac{RA}{l}$, where R and ρ are the electrical resistance and the resistivity, l is the distance between probes and A is the transverse area of the film, respectively, see Fig. 7. The obtained values for resistivity were 13.50 Ω·cm, and 35.62 Ω·cm for the films of 40 and 20 minutes, respectively.

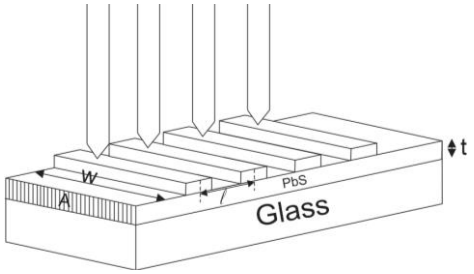

Fig. 7. Schematic diagram of the used configuration to measure the resistance values to evaluate the resistivity.

3. Conclusions

This study enabled us to estimate the resistivity of the PbS layers, involving 3 different kind of substrates, monitoring surface morphology, thickness, structure and somehow chemical purity. From this analysis it is possible to sustain the proposal of the use of PbS layers deposited upon SiO_2 or HfO_2 layers as gates in the TFTs technology, or like complementary p-type semiconductor layer in tandem solar cell designs.

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