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COMPARISON OF PROPERTIES OF CADMIUM, COPPER AND LEAD SULFIDES THIN FILMS GROWN BY CBD

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In this work we are presenting a comparative study of Cd, Cu and Pb sulfides thin films grown by Chemical Bath Deposition technique, the as ground films were polycrystalline for the Cd and Pb Sulfides while the Cu sulfide was amorphous. The Atomic Force Microscopy images gave us information about the representative surface morphology and roughness, being RMS_{PbS}=15.3nm, RMS_{CdS}=3.2nm, RMS_{CuS}=30.4nm. We used UV-Vis Spectroscopy to determine simple optical responses, getting the biggest transmittances of 45% for PbS, 72% for CdS and 80% for CuS, and direct energy band gaps of 2.37 eV for CdS and 1.26 eV for CuS. We use X-rays Photoelectrons Spectroscopy to formalize the chemical composition analysis, from this analysis we could to proof the high purity of the chemical bath deposition method in the materials preparation.

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1.Introduction

Thin films have attracted the attention of researchers for their potential optoelectronic applications. Especially the PbS, and CdS have a direct narrow gap semiconductor. In the case of PbS, it is very suitable for infrared detection applications due to have a energy band gap of approximately 0.37–0.4 eV at room temperature [1,2]. This material has also been used in many fields such as photography [3], Pb2+ ion selective sensors [4] and solar absorption [5-7].

The CdS has been used in the manufacture of solar cells because it has an energy band gap in the 2.42 to 2.45 eV, interval, it is one promising II-VI compound materials because of its wide range of applications in various optoelectronics, piezo electronic and semi conducting devices. It is used in CdTe devices as an optical window. However, poor conductivity as low as $(10.8\ \Omega m)^{-1}$ have been reported. CuS thin films of the present case have been found to be of poor crystallinity or even amorphous. It may, however be possible to bring in crystallinity and to convert these films into the more desirable chalcocite phase by introducing copper ions/atoms into them [8]. In [9] it is showed a amorphous nature of thin film and indirect transition with a bandgap of 1.28 eV.

CuS is a well-known material because of its opto-electronic properties. Precipitate-based copper sensitive ion-selective electrodes use a membrane prepared by pressing a disk of

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coprecipitated copper and silver sulfides [9,10]. Copper sulfide films have been used in photothermal conversion applications [11, 12], photovoltaic applications [13, 14], solar control coatings [15] and other electronic devices [16].

2. Experimental

The deposition of PbS films was done on glass slide substrates, immersed in a reactive solution prepared into a 100 ml beaker by the subsequent addition of 5 ml of 2M lead acetate, 6 ml of 1 M sodium hydroxide, 5ml of 1M thiourea and 2ml of 1M triethanolamine. The solution was diluted adding deionized water to complete a total volume of 100 ml, we use 30 min. and 54 ^{o}C as condition to grown the films.

The CdS films were deposited on glass slide substrates in a 100 ml beaker containing the reaction prepared by the subsequent addition of the 31 ml of deionized water, 4 ml of 0.1 M cadmium nitrate tetrahydrated ($Cd(NO_3)_2$ $4H_2O$), 5ml of 0.5 M glycine (NH_2CH_2COOH), 2 ml of pH 11 buffer, 5 ml of 1 M thiourea ($(NH_2)_2CS$) and deionized water to complete 60 ml. The mixture was initially stirred to homogenize and then its temperature was choose at 70 ^{o}C in a thermal water bath. The substrates were immersed in the solution at this temperature and removed after 22 min when the reaction finished, according to its appearance. The direct energy band gap of the films was 2.37 eV.

CuS thin films were deposited on glass slides substrates by means of the chemical bath method. Chemical bath used for the deposition of CuS thin films was: 31 ml of H_2O, 2 ml of 0.1 M copper nitrate, 2 ml of 0.01 M barium hydroxide, 2 ml of 1M t riethanolamine , 4 ml of 1 M thiourea and other 19 ml of H_2O. The films were deposited in the substrate into solution to 54^{o}C; they were kept into solution for 25 min. The obtained CuS films were flat homogeneous, green-gray transparent and weak adherence to the substrate. The direct energy band gap of the films was 1.26 eV similar to [9]. Their thickness was approximately 150 nm and had a amorphous structure. There was not stirring during the deposition processes.

The X-ray diffraction measurements were performed using a Rigaku Ultima III diffractometer. Optical transmission spectra of the bilayer were recorded by an Ocean Optics USB4000-UV-VIS spectrometer in the 280- 850 wavelength range. The morphology of the samples surface was investigated by Atomic force microscopy (AFM) using a JSPM-4210 scanning probe microscope (JEOL Ltd), and a XPS (Perkin-Elmer Phi-5000) model used to the chemical composition of the thin films compared.

3. Results and discussion

All our obtained films PbS, CuS and CdS were homogeneous. The CdS and PbS are very adherent and CuS while not. In Fig. 1 are shown the XRD spectra corresponding of to PbS, CdS and CuS, the PbS and CdS are polycrystalline while the CuS is amorphous

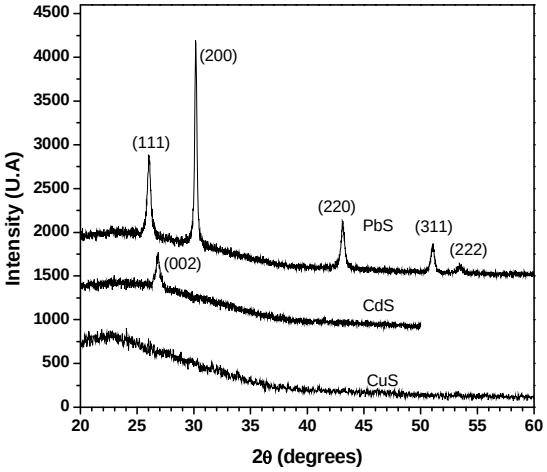


Fig1. XRD spectra for our three compounds, PbS, CdS, and CuS thin films.

The indices in the diffraction peaks, for the PbS thin film, fit with the well known cubic PbS crystalline phase, while the CdS thin film fit with the also well known hexagonal CdS crystalline phase, this film was highly oriented, see table I.

Table 1. Association of label crystallographic planes of the database of the used XRD equipment.

X-ray peaks of PbS (cubic structure)	
1	(111)
2	(200)
3	(220)
4	(311)
5	(222)
X-ray peaks of CdS (hexagonal structure or wurtzite type)	
6	(002)
X-ray peaks of CuS	
-	amorphous

The comparative optical response was done for wavelengths between the 240 to 840 nm range, this set of materials behaved as follow : for the PbS films grown during 30 min. at 54^{o}C of temperature, the transmittance is relatively low, arising until 45% between the 360 to 640 nm range. It is observed in the left graph of the figure 2. For the same film the reflectance response have a increase behavior starting in 420 nm. The CdS film grown during 22 min at 70^{o}C, is shown in the middle graph of figure 2. There can be observed a high transmittance of around 72% while the reflectance is low and both behave almost constant between the 640 and 840 nm ranges.
Finally in the right graph of the figure 2 it is represented the optical response for CuS thin films grown during 25 min at 54^{o}C had thickness of 150 nm, and physically looked very transparent what corresponds with the very high transmittance showed in the right graph of the figure 2. So, we get this kind of the semiconductor thin films.

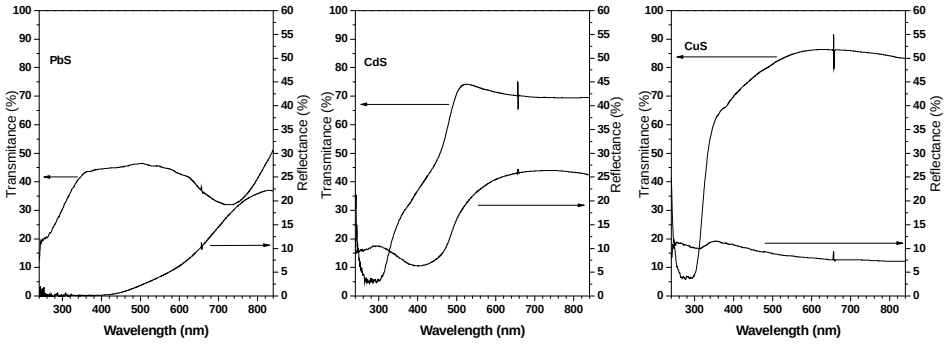


Fig2. UV-VIS spectra showing Transmittance and reflectance for our three compounds, PbS, CdS, and CuS like thin films.

The figure 3 corresponds to the surface morphology of our set of films, CdS, PbS and CuS. The Atomic Force Microscopy images gave us information about the representative surface morphology and roughness for the case of the PbS, in figure 3 a) and b) and CdS in the figure 3 c) and d) the clusters size is about the same magnitude while the high of the PbS compared with CdS is approximately three times bigger, but in the case of CuS the scale is different because the film is more dense while the high result around of 6 times bigger than CdS.

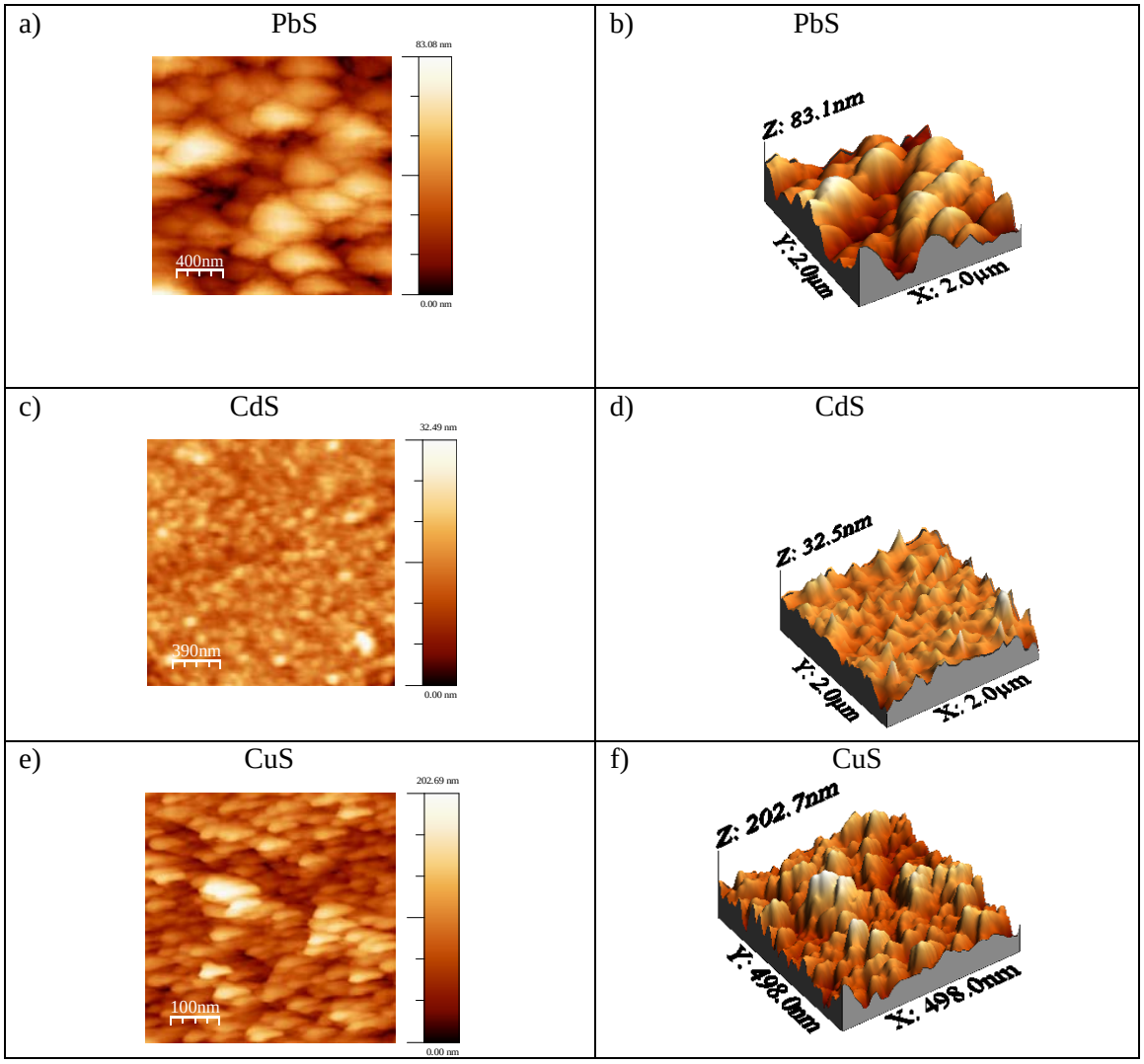


Fig.3 AFM images for our three compounds, PbS, CdS, and CuS thin films. a), c) and e) are top views, while b), d), and f) are 3D perspective views [17].

In the Figure 4 it is shown the measurements of X-Ray Photoelectron Spectroscopy this gave us the elemental composition of the CdS, CuS and PbS films.

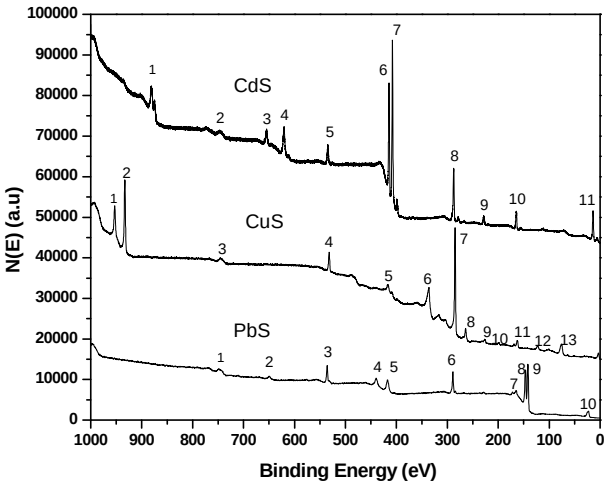


Fig. 4. XPS spectra for our three compounds, PbS, CdS, and CuS thin films. These plots confirm the chemical composition the obtained materials.

Table 2 shows the peaks associated to binding energies of the different sublevels and present elements into the CdS, CuS and PbS films. Returning to figure 4, the CdS had 11 contributions, the peaks 1,3,4,6,7,11 are corresponding to the Cadmium element, the peaks 9 and 10 are of Sulfur, the peaks 2 and 5 are Oxygen, and the peak 8 is Carbone. The CuS had 13 contributions, the peaks ; 1,2,6,11,13 are Copper element, the peak 9 is Sulfur, the peaks 3 and 4 are Oxygen, the peak 7 is Carbone, the peak 8 is Chloride, the peaks 10 and 12 are Silice, and we need identify the peak 5. The PbS had 11 contributions, the peaks 2,4,5,8,9,10 are corresponding to the Lead element, the peak 7 is Sulfur, the peaks 1 and 3 are Oxygen, and the peak 6 is Carbone.

Table 2. Association of level binding energies for elements PbS, CdS and CuS thin films.

XPS			
Label	PbS	CdS	CuS
1	O KLL (Auger)	Cd MNN (Auger)	Cu 2p1
2	Pb 4p3	O KLL (Auger)	Cu 2p3
3	O 1s	Cd 3p1	O KLL (Auger)
4	Pb 4d3	Cd 3p3	O 1s
5	Pb 4d5	O 1s	-
6	C 1s	Cd 3d3	Cu LMM (Auger)
7	S 2p3	Cd 3d5	C 1s
8	Pb 4f5	C 1s	Cl 2s
9	Pb 4f7	S 2s	S 2p
10	Pb 5d5	S 2p	Si 2s
11	-	Cd 4d5	Cu 3s
12	-	-	Si 2p
13	-	-	Cu 3p3

5. Conclusions

We conclude that from XPS analysis that the CBD technique is inexpensive, clean and easy to grow this kind of useful films that are been used recently in order to produce microelectronic devices. For the PbS and CdS films, nanocrystal clusters were observed of comparable width for both cases. Nevertheless, CuS showed a kind of structure formed may be of irregular atomic networks, the width of such formations is much smaller than those mentioned clusters, however, the heights of the clusters are approximately three times lower than the amorphous CuS film. The RMS roughness for the CuS is higher and it is congruent with the amorphous configuration. The CuS thin film present the maximums transmittance between the three thin films and it is coincidental with the high of the corresponding AFM graph and by this it is used like a window cover in devices.

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