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Influence of Complexing Agents on Structural Properties of PbS Thin Films Prepared by CSD Method

In this work, the influences of complexing agents and their molar concentrations on the structural properties of lead sulfide (PbS) nanostructures prepared by chemical solution deposition (CSD) method were studied. Other experimental parameters, such as concentration of reactants, pH of solution and bath temperature, were kept constant during deposition process. The structure of the prepared samples was analyzed by x-ray diffraction (XRD). It was found that the structural form of PbS nanorods is strongly influenced by the complexing agent and its molar concentration as an improvement in the structural quality was observed with changing the concentration of the complexing agent. However, too high concentration of complexing agent could lead to the degradation in the structural quality of the prepared samples.

Keywords: Chemical solution deposition; Complexing agent; Lead sulfide; Nanorods
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1. Introduction

Lead sulfide (PbS) is a well-known IVB-VIA semiconductor compound with very good photoconductive properties in the infrared (IR) domain 800-3000nm at room temperature, where its energy band gap is approximately 0.41eV [1,2]. These materials are produced in the crystalline and polycrystalline forms and used as different devices such as light emitting diodes [3,4], solar cells [5,6] and photodetectors [7,8]. They have strong quantum-size effect in nanocrystalline form [9,10] and their advantages are attributed to the semiconductor band gap, which can be controlled by adjusting the size of the nanoparticles by adding complexing agents during deposition process [11]. Many methods have been developed to synthesize PbS thin films, including vacuum evaporation [12], electrochemical deposition [13], chemical bath (solution) deposition (CBD or CSD) [14,15], pulsed-laser deposition [16], sono-chemical [17], spray pyrolysis [18] and successive ionic layer adsorption and reaction (SILAR) method [19]. Among the various methods, CSD is one of the most popular and widespread techniques in the area of thin film technology due to its easier composition control, better homogeneity, low processing temperature, large-field production of thin films and does not require sophisticated vacuum equipment.

In the present study, we report the structural properties of PbS-NS thin films grown on glass substrates by chemical solution deposition method (CSD) at room temperature using three different reducing agent; hydrazine hydrate (N_2H_4), hydroxylamine hydrochloride ($NH_2OH\cdot HCl$) and tri-

ethanolamine (TEA). These properties were introduced by x-ray diffraction (XRD).

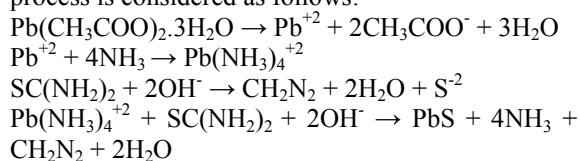
2. Experimental Part

The hydrazine hydrate (HH) supplied by Sigma-Aldrich Co. was used in this work. It is soluble in water and even hygroscopic. Lead acetate ($Pb(CH_3COO)_2$), thiourea ($SC(NH_2)_2$) and sodium hydroxide (NaOH) supplied by Fluka and Aldrich were also used directly without further purification. De-ionized water was used in all experiments.

The PbS thin films deposition were deposited on glass substrates by CSD method. Prior to deposition, the substrates were very carefully cleaned using ultrasonic bath for 15 min at 50°C in acetone, rinsed with di-ionized water and dried in clean dry air to provide better surface nucleation for growth of the films. The substrates were introduced vertically into the solution by dip coating instrument.

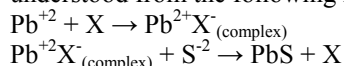
The chemical bath contained an aqueous solution of the following constituents mixed in the sequence: 0.5M $Pb(CH_3COO)_2$ was mixed with 6ml di-ionized water and stirred for several minutes to get a homogeneous solution. Thereafter, 1M NaOH was added under stirring condition for 3 min until the color of the solution became white before a 7ml of 2M thiourea was added. The hydroxylamine hydrochloride ($NH_2OH\cdot HCl$), hydrazine hydrate (N_2H_4) or tri-ethanolamine (TEA) ($C_6H_{15}NO_3$) were used as complexing agents, which are introduced in the bath in order to control the nucleation/growth process during the deposition of the PbS layer. The concentration of each complexing agent was varied (0.359, 1.439 and 1.798M). Finally, the reaction solution was placed in 50 ml beaker into the water

bath at room temperature to deposit film samples. The starting pH of the reaction of 12.4 was kept constant for all depositions. The substrates were removed from the beaker after 30 min. The reaction process is considered as follows:



The Pb^{2+} ion complexes with X initially to form $[\text{Pb}^{2+}\text{X}]$ and later this complex decomposes and releases Pb^{2+} ions to make bonds with S^{2-} ion present in the solution to form PbS. Release rate of Pb^{2+} ions can be altered by adding a complexing agent to the solution containing the Pb salt to form lead complex species, which upon dissociation, results in the release of changed concentrations of Pb^{2+} ions [20]. Metal complex and released sulfide ions migrate to the substrate surface, where they react to form PbS thin film.

The mechanism of film formation can be understood from the following reaction:



(where X is the complexing agent HH, TEA, HXAHC)

After deposition, the samples were rinsed in deionized water. Then the non-adherent PbS layer was removed by treatment for 2 min in an ultrasonic bath, and the compact inner layer was dried. The obtained layers were strongly adherent to the substrates. The resultant films were homogeneous and specularly reflecting with a varying color depending on the kind of complexing agent. Thin films with mirror-like surface were deposited on both sides of the glass slide but only the films on the side facing the wall of the beaker during deposition process were used for the measurements. In case of using hydroxylamine hydrochloride (HXAHC) as an agent, we can see – for the first 5 min of reaction time – that the solution remained transparent, indicating the occurrence of decomposition reactions. Beyond 5 min, the solution color turned brown then dark gray, indicating the formation of PbS, for tri-ethanolamine (TEA). The solution remained milk-like for 10 min then the color of the beaker's wall gradually converted into mild gold, gray to dark during the film deposition. With increasing TEA concentration, the deposition becomes slow.

In case of using hydrazine hydrate (HH), the solution remained milk-like for 3 min then turned to dark gray, which also indicates the formation of PbS. After the deposition time, each sample was removed from the solution, rinsed ultrasonically in acetone for 2 min, then the non-adherent PbS layer was removed during 10 min in distilled water and the compact inner layer was dried in air.

The structural characterization of the prepared films was carried out with PW-1840 XRD system.

3. Results and Discussion

From the XRD results, the orientations of the crystal planes were determined and the average grain size of PbS films was estimated, as in table (1). The XRD patterns of the as-deposited films for different concentrations of HH are shown in Fig (1). The structure of thin film showed a polycrystalline cubic structure as eight different peaks are observed at 2θ values of approximately 26° , 30° , 43° , 51° , 53° , 69° , 71° and 79° corresponding to the (111), (200), (220), (311), (222), (331), (420) and (422) crystal planes of cubic phase, respectively, which indicates that the PbS films are well crystalline. The intensity of (200) peak is higher than that of (111) peak indicating that there is a (200) preferred orientation during the deposition. Such result of preferred orientation has been recently reported for nanowires [21].

Table (1) The XRD parameters of PbS nanorods prepared using 1.439M HH complexing agent

$d_{\text{theor.}} (\text{\AA})$	$d_{\text{exp.}} (\text{\AA})$	$2\theta (\text{deg.})$	(hkl)
3.429	3.450	26	(111)
2.969	2.995	30	(200)
-	-	-	(210)
2.099	2.107	43	(220)
1.790	1.797	51	(311)
1.714	1.720	53	(222)
-	-	-	(400)
1.362	1.360	69	(331)
1.327	1.329	71	(420)
1.212	1.213	79	(422)

The average crystalline size of PbS nano film was determined from the (200) by using Scherrer's formula [22] as:

$$D = \frac{K \lambda}{\beta \cos(\theta)} \quad (1)$$

where K is a constant taken to be 0.94 [22], λ is the wavelength of x-ray used, which is $\text{CuK}\alpha$ radiation, and β is the full width at half maximum (FWHM) of the diffraction peak corresponding to a particular crystal plane. The crystallite size (D) as shown in Table (2), also illustrated comparative with AFM Analysis.

Table (2) The average grain size of PbS nano film prepared using 1.439M HH complexing agent as determined from XRD results

Average Grain Size (nm)	FWHM (deg.)	Position of peak 2θ (deg.)
42	0.337	29.826

The XRD patterns of the as-deposited films for different concentrations of TEA are shown in Fig (2). The structure of thin film showed a polycrystalline cubic structure and four different peaks are observed at 2θ values of approximately 26° , 30° , 43° and 51° corresponding to the (111),

(200), (220), (311) crystal planes of cubic phase, respectively, which indicates that the PbS films are well crystallized. The intensity of (200) peak is higher than that of (111) peak indicating that there is a (200) preferred orientation during the deposition (table 3).

Table (3) The XRD parameters of PbS nanorods prepared using 1.439M TEA complexing agent

$d_{theor.} (\text{Å})$	$d_{exp.} (\text{Å})$	$2\theta (\text{deg.})$	(hkl)
3.429	3.468	25.665	(111)
2.969	2.998	29.770	(200)
-	-	-	(210)
2.099	2.107	42.870	(220)
1.790	1.802	50.629	(311)
1.714	-	53.216	(222)
-	-	57.601	(400)
1.362	-	68.397	(331)
1.327	-	70.421	(420)
1.212	-	79.136	(422)

The measured broadening of grain size of PbS nanorods obeys the Scherrer's formula (Eq. 1). We found that the grain size of PbS film on glass is 15nm and 37.97nm for glass substrate. Table (4) showed the grain size for PbS films calculated from XRD.

Table (4) The average grain size of PbS nano film prepared using 1.439M TEA complexing agent as determined from XRD results

Average Grain Size (nm)	FWHM (deg.)	Position of peak 2θ (deg.)
15	0.337	29.826

The XRD patterns of the as-deposited films for different concentrations of HXAHC are shown in Fig (3). They showed a polycrystalline cubic structure and eight different peaks are observed at 2θ values of approximately 26° , 30° , 43° , 51° , 53° , 58° , 69° , 71° and 79° corresponding to the (111), (2 00), (220), (311), (222), (331), (400) (420) and (422) crystalline planes of cubic phase, respectively, which indicates that PbS films are well crystalline.

Table (5) The XRD parameters of PbS nanorods prepared using 1.439M TEA complexing agent

$d_{theor.} (\text{Å})$	$d_{exp.} (\text{Å})$	$2\theta (\text{deg.})$	(hkl)
3.429	3.476	25.665	(111)
-	-	-	(210)
2.099	2.111	42.758	(220)
1.790	1.795	50.742	(311)
1.714	1.720	53.216	(222)
-	1.598	57.601	(400)
1.362	1.370	68.397	(331)
1.327	1.335	70.421	(420)
1.212	1.208	79.136	(422)

The intensity of (200) peak is higher than that of (111) peak indicating that there is a (200) preferred orientation during the deposition. Table (5) shows the XRD parameters of PbS nanorods prepared using

1.439M TEA complexing agent and table (6) shows the average grain size of these structures.

Table (6) The average grain size of PbS nano film prepared using 1.439M HXAHC complexing agent as determined from XRD results

Average Grain Size (nm)	FWHM (deg.)	Position of peak 2θ (deg.)
33.6	0.370	29.713

The presence of HH, TEA and HXAHC complexing agents in bath can affect the rate of deposition and the microstructure and nanostructure of deposited PbS films. Meanwhile, the orientation growth of the film is (200). These results confirm that the film has been formed from nanometer grains.

4. Conclusion

In concluding remarks, PbS nano films were successfully deposited on glass substrate by CSD technique. The XRD patterns of these films showed that nanocrystalline structures were formed using different complexing agents with different molarities (0.359, 1.439, 1.798M). The effects of complexing agents on structural properties were confirmed as the kind of complexing agent besides its molarity are the conditional parameters that strongly influence the nanocrystalline structure of the prepared PbS films. The presence of complexing agents in bath can affect the rate of deposition and the microstructure and nanostructure of deposited PbS films. Further studies may extend this method for the preparation of other nanocrystalline sulfide semiconductors.

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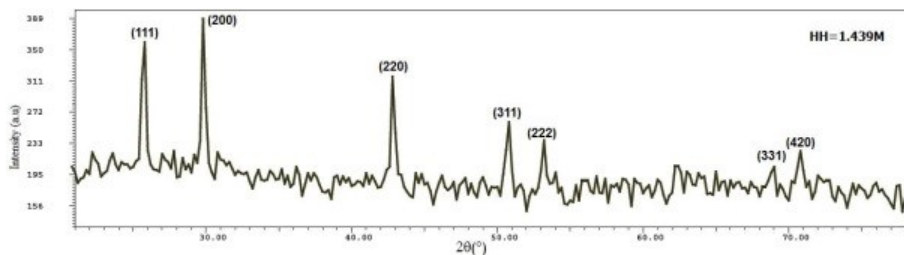


Fig. (1) The XRD patterns of PbS films prepared using 1.439M HH complexing agent

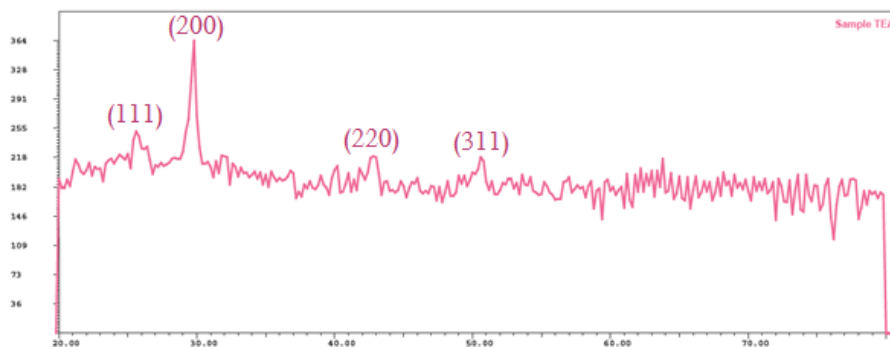


Fig. (2) The XRD patterns of PbS films prepared using 1.439M TEA complexing agent

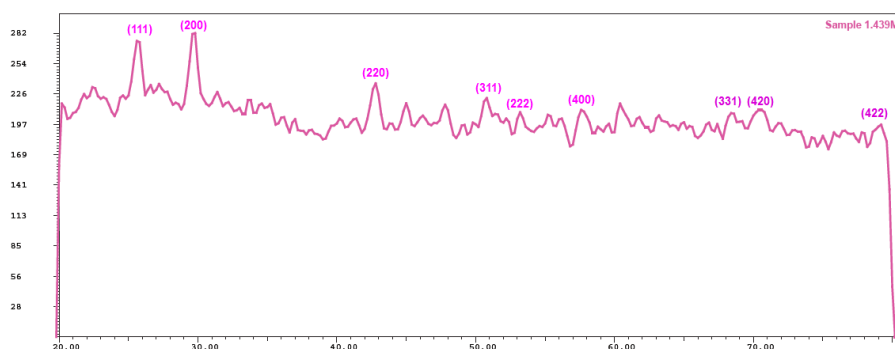


Fig. (3) The XRD patterns of PbS films prepared using 1.439M HXAHC complexing agent