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Effect of Deposition Time on the Nanocrystalline PbS Thin Films Synthesized by Chemical Solution Deposition Method: Structural Characterization

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Abstract: Lead sulfide nanocubes and nanocrystallines (PbS-NCs) thin films were deposited on glass substrates prepared from lead nitrate, ammonia and thiourea solution using Chemical Solution Deposition (CSD) technique. The influence of the deposition time on the properties of PbS film is investigated. The other parameters: concentration of the reactants, pH of solution, and temperature of bath were kept constant for the all depositions. The structure and morphology of prepared PbS nanocrystalline were analyzed by atomic force microscope and X-ray diffraction. The AFM images confirmed that the surface roughness and cubical grain size of PbS increased with increasing dipping time. The x-ray results indicated that the obtained materials were cubic nanocrystalline PbSe with an average grain size of 60 nm.
Key Words: Chemical solution Deposition (CSD), PbS nanocube, PbS nanocrystallin, chalcogenides, Atomic Force Microscopy (AFM), X-ray diffraction.

1. Introduction

Lead sulfide (PbS) is an important semiconductor material with interesting properties such as narrow direct band gap of ~ 0.37- 0.41eV[1] and exceptionally large excitation Bohr of ~20 nm at room temperature [2, 3], and abundance in nature. Thus, PbS nanocrystals are of considerable interest since their optical gap can be tuned from mid-infrared to near-infrared by adjusting their size. PbS thin films have been widely used in a variety of fields such as light-emitting diode, solar energy panels[4], gas sensors and pollution monitor[5], infrared detector and mid-infrared lasers[6] ect. For these reasons, many researches groups have an increasing interesting in the development and study of this material. For synthesize of PbS nanocrystals, different methods are used at present, namely, solution growth technique[7], hydrothermal synthesis[8], sputtering, sol-gel technique[9], Spin coating[10], vacuum evaporation[11], pulsed laser deposition[2], photochemical deposition[13], electrochemical deposition[14], Microwave heating[15,17], sonochemical preparation[16,17], ultrasonic irradiation[5], Spray pyrolysis[18], Green synthesis[19], Solid-Vapor Deposition[20], ect. Among these methods, chemical solution deposition processing is a very comfortable and most convenient method for deposition polycrystalline lead sulfide (PbS) thin films with a good specification properties, CSD is relatively inexpensive, simple and it does not require complicated equipment or the initial high purity chemical materials as is the case of organic or physical evaporation and offers many advantages which include low processing temperature, high purity, convenient for large area deposits on substrates of different materials. Due to its advantages, the CSD approach was used in this study. By CSD method, the dimensions of the crystallites can be varied controlling deposition parameters: concentration of the reactants, reaction time deposition, temperature, pH of solution, solution composition, number of layer deposition, ect [21, 22, 23]. The morphological structure characteristic of chemically deposited PbS films evidenced in surface images measured by Atomic Force Microscopy(AFM) and X-ray diffraction (XRD).

2. Experimental materials and methods

2-1. Reaction mechanism

To prepare PbS we used CSD and it's need to require ions of lead and ions of sulfide, so used lead nitrate $Pb(NO_3)_2$ source of lead ions Pb^{+2} and thauoria SC- $(NH_3)_2$ source of sulfide ions S^{-2} and require a base medium so used sodium hydroxide [NaOH] that is used also as complexing agent to vary the pH of the reaction bath and to control the Pb^{+2} ions concentration. The chemical process can be described through the following chemical reactions:

$Pb(NO_3)_2 + 2NaOH \rightarrow Pb(OH)_2$ (white solution)$+2NaNO_3$
$Pb(OH)_2 + 4NaOH \rightarrow Na_4Pb(OH)_6$ (hydroxocomplex ions)
$Na_4Pb(OH)_6 \rightarrow 4Na^+ + HPbO_2^- + 3OH^- + H_2O$
$SC(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + SH^-$

$HpbO_2^- + SH^- \rightarrow PbS$ (black)$+2OH^-$

The amount of Pb^{+2} and S^{-2} ions released in the solution depends on the concentration of the reactants (lead salt, thiourea, NaOH). When the ionic product of Pb^{+2} and S^{-2} ions exceed the solubility product of PbS, the insoluble particles of PbS precipitate.

2-2. Deposition of ZnS films :

PbS films were deposited on commercial glass substrates (75mm × 25mm × 1mm) by chemical solution deposition technique. Prior to deposition, the substrate was degreased in ethanol for 10 min, followed by ultrasonically cleaned with double distilled water for another 10 min, rinsed in de-ionized water and finally dried in the air. The cleaning of the substrate surface is very important for the quality of the film formation. In a typical deposition set up of PbS, the CSD was achieved by mixing 11 ml of 0.175M $Pb(NO_3)_2$ solution, 28.3 ml of 0.15M $SC(NH_2)_2$ solution, and 8.7 ml of 0.57 M NaOH solution. The de-ionized water was added to the solution to achieve a total volume of 50 ml. Firstly, sodium hydroxide solution was added slowly to the required quantity of lead sulfate, after stirring for several minutes the solution becomes colorless, there after thiourea solution was added under stirring the color of the solution becomes black. The glass substrates were then immersed vertically inside this beaker without disturbing it. The resulting films were homogeneous, well adhered to the substrate with darker surface like mirror. Fig. 1 shows an experimental setup of presently used chemical solution deposition unit.

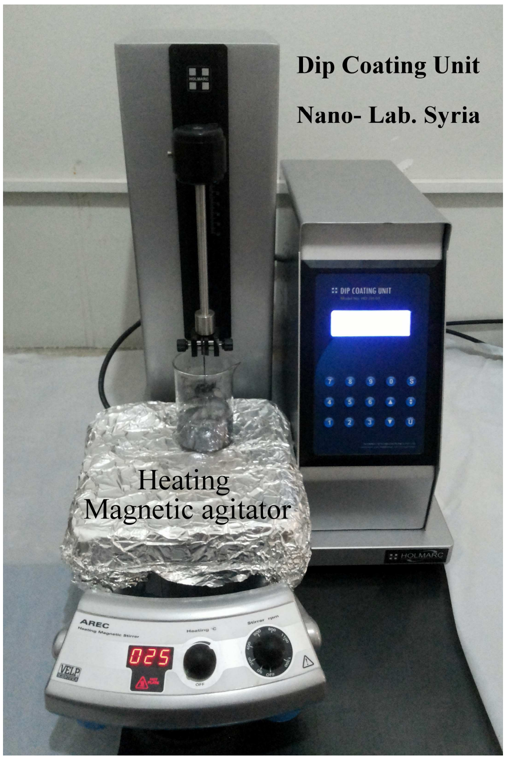

Figure 1. Photograph of the dip-coating apparatus (Model HO-TH-01, India) used in this work.

The deposited PbS film was carried out at constant temperature (25°C) and pH of the depositing solution is 9, for various dipping times, (10, 20, 30, 40 min) that were selected to study the structural characteristic of PbS thin films. After completion of film deposition, each sample was removed from the beaker and was cleaned with de-ionized water to remove the black, loosely, adherent powders precipitate in the solution during the deposition.

2-3. Characterizations:

The structural properties of PbS were investigated by X-ray diffraction (XRD, Philips, PW 1840) that was operated at a voltage of 40 kV and a current of 30 mA with an excitation source of CuK_{α} radiation (1.54060A°), in the range of scanning angle 20-80°. The surface morphology and surface roughness were determined from the Atomic Force Microscopy measurements (AFM, Nanosurf easyScan2, Switzerland). The AFM measurements were performed in a tapping mode in air at room temperature. Silicon cantilevers (Tap190 Al-G, NanoSensors) with 30 nm thick aluminum reflex coating are used. According to the producer's datasheet, the cantilever spring constant is in the range of 1.5-015 N/m and the resonance frequency is 15- 500 kHz. The tip radius is less than 10 nm. The scan rate is set at 0.7 Hz and the images are captured in the medium mode with 256x256 pixels in a JPEG format. This study focuses on the synthesis, structural characterization of thin films of PbSe deposited with different deposition times.

3 Results and discussion:

3.1 AFM analysis:

AFM studies reveal that the there is a dramatic change in the morphologies of the deposited films with the growth techniques. In this work, we have used this technique to visualize the surface morphology and determine the contribution of dipping times (d_t) to the quantity and quality of the film. A very adherent film with gray-black color and metallic aspect was obtained for all samples. AFM images of the surface morphology recorded on samples of the PbS-NCs thin films deposited with various deposition time periods for (d_t = 10, 20, 30, 40 min) are shown in Fig. 2. The AFM images showed existence of a continuous compact polycrystalline film with grain size around 250-580 nm. In Fig. 2(S1, S2) at lower deposition time (10, 20 min) the PbS-NCs carpet the substrate with uniformly cubical shape and have relatively low and narrow size distributions. In the case of PbS layers grown at 30 and 40 min Fig. 2 (S3, S4) the grain size increase more and more. We can expect this result due to the increase of the film thickness and the changes in nucleation and growth rate with the extension of the reaction time. Figure. 3 shows the mean grain diameter of PbS-NCs in function of deposition time, it appears that the particle size increased with increasing of the deposition time. The same relation between the mean height of PbS-NCs and the deposition time has been observed.

The mean surface roughness determined from AFM images for four deposition time 10, 20, 30, 40 min were found to be 39, 44, 54, and 70 nm, respectively. As it can be seen the increasing of roughness by increasing deposition time and that because of formation of new bigger domed cubic grains form.

It is important to note that these obtained values are averaged and there is a statistical variation associated with them which depends on the location of the measurement that is performed on the samples. To minimize these errors, we have performed many measurements of each parameter in different locations on the surface of samples. The parameters of experiments and the data of results observed in these experiments were collected in Table 1.

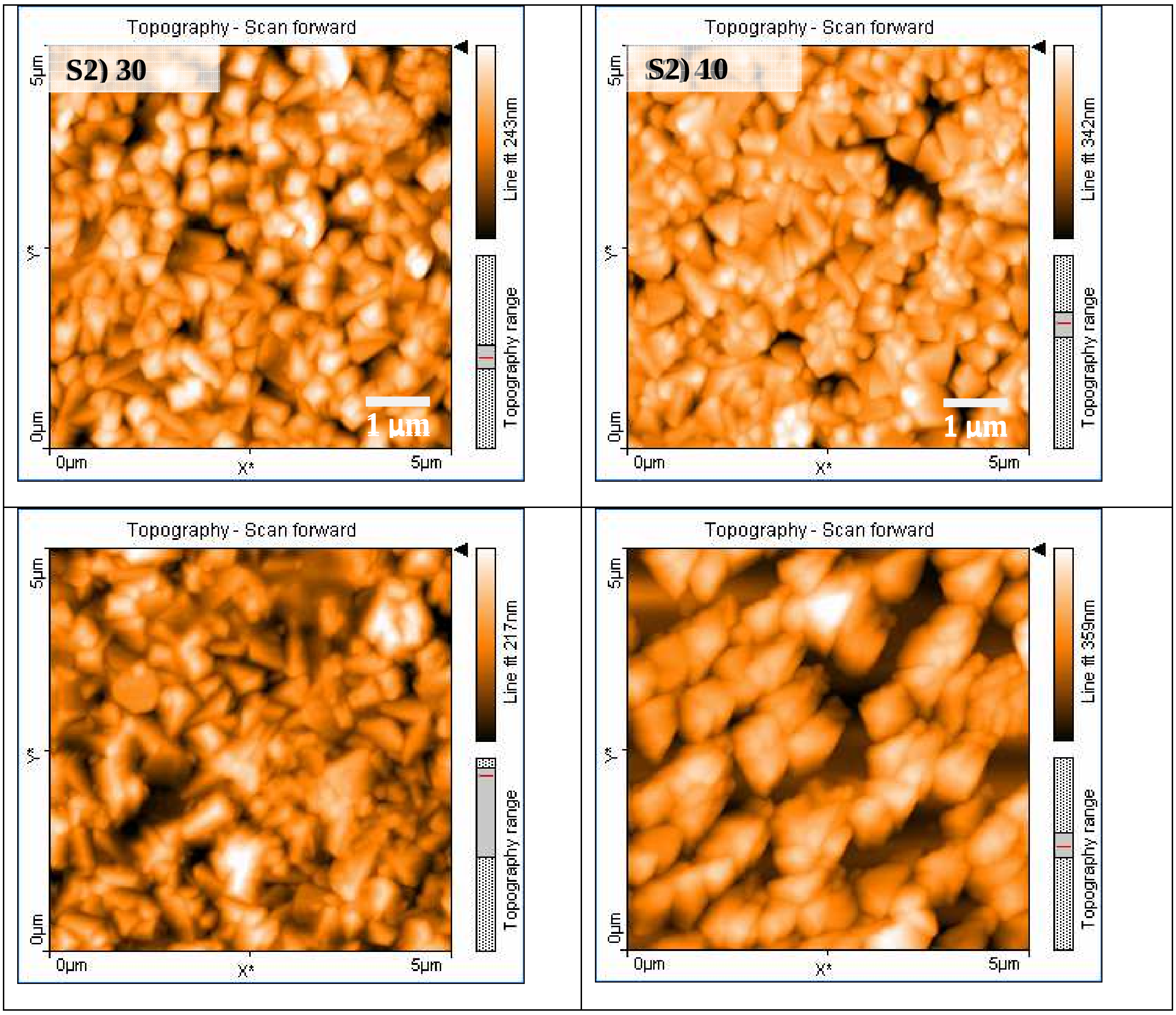

Fig. 2: 5x5µm AFM images for PbS thin films/glass for four different deposition time : ***(S1) 10 min, S2) 20 min, (S3) 30 min, (S4) 400 min***.

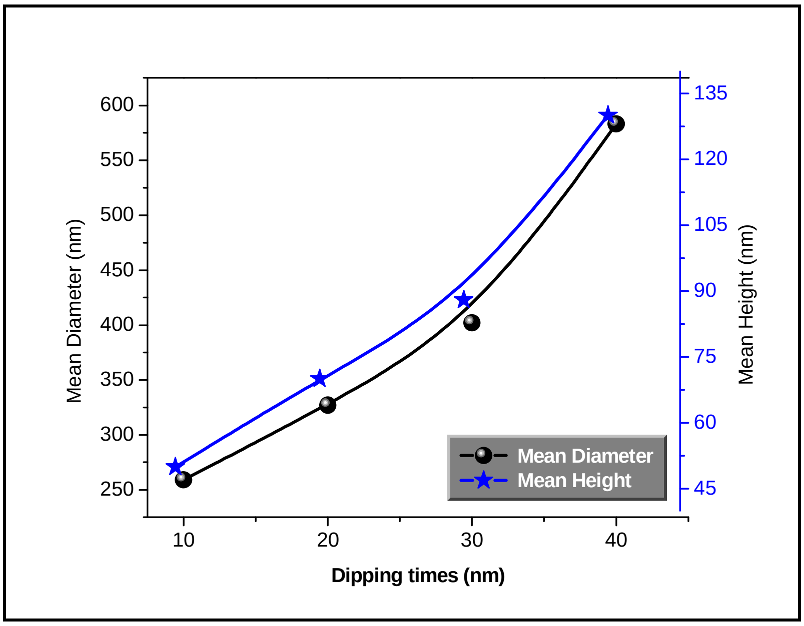

Fig. 3: Changes of mean diameter (circle symbols), mean height (star symbols) of PbS-NCs thin film versus dipping times.

Table.1: Morphological characteristics of PbS-NCs for four different deposition time.

No. Sample	Mean NCs diameter	Mean NCs height	Mean roughness
(S1) dt=10 min	259 nm	50 nm	39 nm
(S2) dt=20 min	327 nm	70 nm	44 nm
(S3) dt=30 min	402 nm	88 nm	54 nm
(S4) dt=40 min	583 nm	130 nm	70 nm

3.2 X-ray studies:

Figure 4 shows the X-Ray Diffraction (XRD) patterns of the as-prepared lead sulfide thin films deposited various deposition periods ranging from 10 to 40 min. The X-ray diffraction spectrum shows a polycrystalline structure and display nine diffraction peaks at 2θ values of approximately 26°, 30°, 43°, 51°, 53°, 62°, 69°, 71° and 79°, correspond to the crystal planes of (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (4 2 0) and (4 2 2) planes of PbS cubic crystalline, respectively.

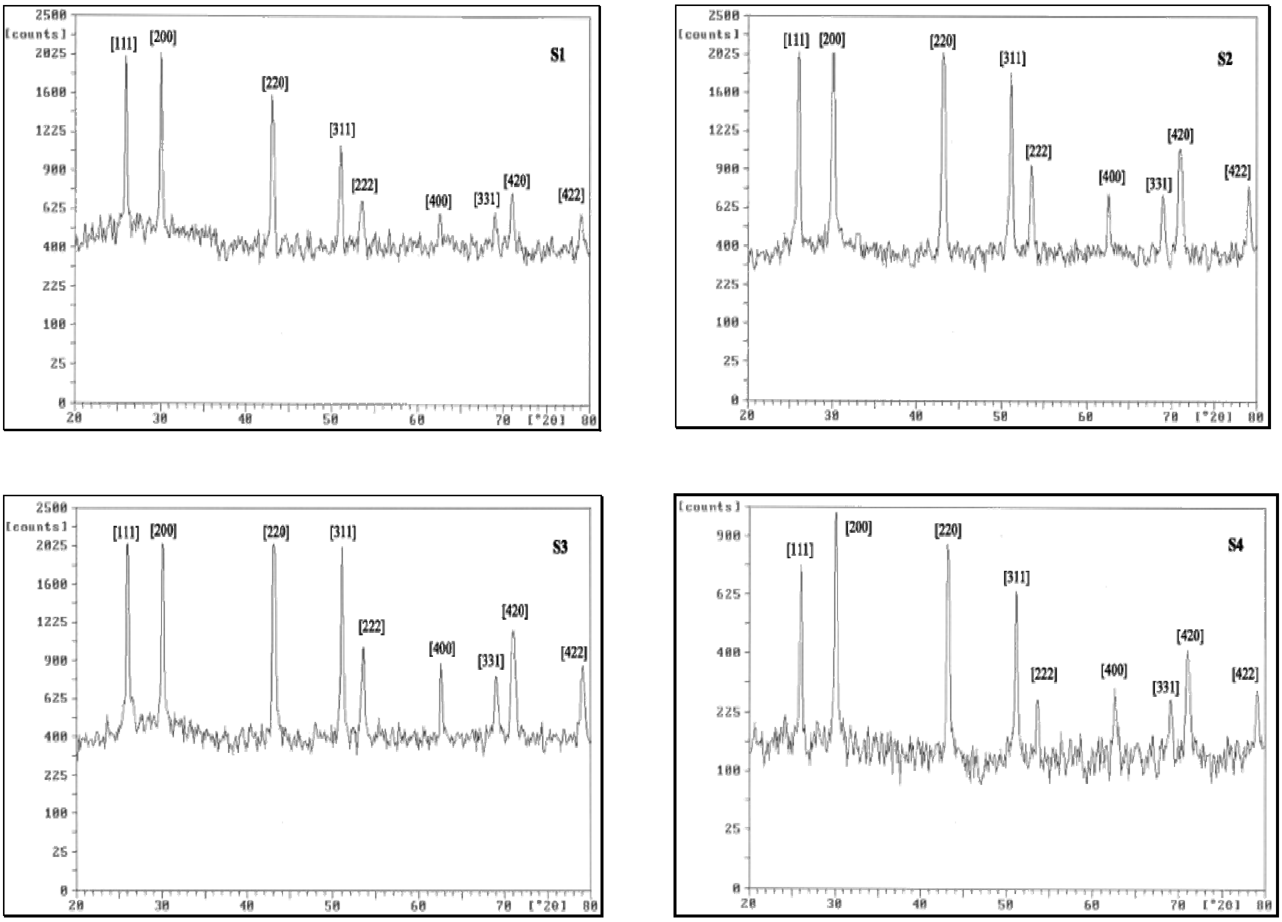

Fig.4. X-ray diffraction pattern of nanocrystalline PbS thin films for different deposition time: (S1) 10 min, (S2) 20 min, (S3) 30 min, (S4) 40 min.

The dominant and sharp peaks indicate that PbS nanocrystals are highly crystalline [24]. The XRD pattern is identical to pure PbS without signals for oxides and precursor compounds, demonstrates the formation of high purity PbS. Its observed a preferred orientation grows along (200) direction. The positions and intensities of the peaks are in good agreement with the literature [25, 26]. The intensity of the films increases with increasing dipping time (see table. 2) and there is an increase in the crystallite size of the deposited films for higher periods of deposition. The broadening of the peaks indicates that the crystal sizes are very small. The average size of the as-prepared PbS nanocrystals are estimated to be in the order 59 nm according to the Scherrer's formula. It observed that the average grain sizes determined from the AFM images are comparatively larger than measured by X-ray. This larger value of grain sizes may be due to the agglomeration of grain. on the surface during extension of the deposition. The X-ray diffraction parameters are tabulated in table. 2.

Table.2: X-ray diffraction parameter of nanocrystalline PbS thin films for different deposition time: (S1) 10 min, (S2) 20 min, (S3) 30 min, (S4) 40 min.

2Θ (deg)	d_{hkl} (A°) Practically	d_{hkl} (A°) Theoretically	hkl	INT	No. S
26.25	3.392	3.429	(111)	87.71	S1
30.00	2.947	2.969	(200)	100.0	
43.00	2.085	2.099	(220)	75.43	
51.00	1.786	1.790	(311)	49.12	
53.50	1.719	1.714	(222)	24.56	
62.50	1.464	1.484	(400)	14.03	
69.00	1.351	1.362	(331)	17.54	
71.00	1.326	1.327	(420)	24.56	
79.00	1.208	1.212	(422)	19.29	
26.23	3.395	3.429	(111)	96.92	S2
30.00	2.976	2.969	(200)	93.84	
43.20	2.092	2.099	(220)	100.0	
51.05	1.788	1.790	(311)	89.23	
53.60	1.708	1.714	(222)	40.00	
62.73	1.480	1.484	(400)	27.69	
69.12	1.358	1.362	(331)	27.69	
71.03	1.326	1.327	(420)	50.76	
79.26	1.201	1.212	(422)	29.23	
26.22	3.396	3.429	(111)	92.06	S3
30.27	2.951	2.969	(200)	93.65	
43.40	2.083	2.099	(220)	98.41	
51.10	1.786	1.790	(311)	100.0	
53.30	1.717	1.714	(222)	42.85	
62.80	1.478	1.484	(400)	36.50	
69.60	1.350	1.362	(331)	28.57	
71.30	1.322	1.327	(420)	55.55	
79.35	1.207	1.212	(422)	41.26	
26.24	3.394	3.429	(111)	71.42	S4
30.45	2.933	2.969	(200)	100.0	
43.50	2.079	2.099	(220)	87.01	
51.35	1.778	1.790	(311)	68.83	
53.91	1.699	1.714	(222)	22.07	
62.85	1.477	1.484	(400)	38.96	
68.95	1.361	1.362	(331)	24.67	
71.30	1.322	1.327	(420)	44.15	
79.80	1.201	1.212	(422)	22.07	

4 Conclusion

Good quality nanocrystallines PbS/glass thin films with different deposition time (10- 40 min) have been prepared and characterized. The homogeneous formation of crystalline grains was observed from AFM images, it is apparent that the as-prepared PbS nanocrystals present uniform cubical morphologies and their diameter ranged between 250 to 580 nm and it is increases with increase in the deposition time. A cubic phase PbS polycrystalline thin films have been prepared. The X-ray diffraction spectrum showed preferred orientation at (200) plane. From the observation, it is concluded that the low deposition time is the best condition to prepare good quality lead sulfide thin films and the surface morphology study revealed that the grains have cubic shape crystal.

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