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Morphological Characteristics of Lead Sulfide Thin Films Prepared by Chemical Solution Deposition

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Abstract
Lead sulfide nanostructures (PbS-NS) thin films were prepared using chemical solution deposition (CSD) method by varying of the complexing agent. The influence of the complex agents and the different molar concentration of these reducing agents on the morphology and structure properties of PbS nanostructures were 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 nanostructures were analyzed by atomic force microscope AFM. It appears that the complexing agent at which the PbS crystals were prepared had a strong influence on their form and morphology. Studies revealed that there is an improvement in the structural quality with changing the concentration in some range. However, too high concentration of complexing agent could lead to the degradation in structural quality of thin film.

***Keywords*:** Chemical solution deposition (CSD); Complexing agent; Lead sulfide; Nanocube
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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 (800–3000 nm at room temperature). At room temperature, its energy band gap is approximately 0.41 ev [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], photo detectors [7,8] and a strong quantum-size effect in nanocrystalline form [9,10]. The advantages of these nanostructure films are regarding to the size of the semiconductor band gap, which can be controlled by adjusting the size of the nanoparticles by adding complexing agents during deposition [11]. Many methods have been developed to synthesize PbS thin films, including vacuum deposition [12], electrochemical deposition [13], chemical bath (solution) deposition (CBD or CSD) [14,15], pulsed laser deposition [16], sonochemical [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, does not require sophisticated vacuum equipment, large-field production of thin films. In the present study, we report the structure properties of PbS-NS thin films grown on glass substrates using chemical solution deposition method (CSD) at room temperature. The remainder of this paper is organized as follows. Experimental details are given in Section 2 with particular emphasis on the compounds involved in the reactions and the deposition parameters. In Section 3, we present structure properties of the grown films, and comparative preliminary results between many types of PbS films Prepared by used different reducing agent (hydrazine hydrate (N_2H4) – hydroxylamine hydrochloride (NH_2OH-HCl) and (TEA). The morphology and roughness of the films was investigated by atomic force microscopy (AFM). AFM imaging is performed on the Nanosurf system (easyScan2) operating in a tapping mode in air at room temperature.

2. Experimental materials and methods

2.1 Reaction mechanism and deposition of PbS films

The PbS-NS thin film deposition was performed on glass substrate (microscope slides with dimensions of (75×25×1mm) 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 were used. The cleaning of the substrate surface is extremely important for the quality of the thin film that will be obtained later. 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 lead acetate ($Pb(CH_3COO)_2$) were mixed with 6ml di-ionized water and stirred for several minutes to get a homogeneous solution. Thereafter 1M sodium hydroxide (NaOH) added under stirring condition for 3 min the color of the solution become whiten then added 7ml of 2M thiourea SC $(NH_2)_2$, and in which hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), hydrazine hydrate (N_2H_4) or tri-ethanolamine (TEA) ($C_6H_{15}NO_3$) is used as a complexing agent. The complexing agent is introduced in the bath in order to control the nucleation/growth process during the deposition of the PbS layer. the concentration of complexing agents for the films was varied to (0.359M, 1.439 M, and 1,798M), Lastly, the reaction solution was placed in 50 ml beaker into the water bath, The deposited film was carried out water bath temperature at room temperature, The starting pH of the reaction (pH 12.4) was kept constant for all depositions. That was selected to study the characteristics of PbS thin films. The substrates were retired from the beaker at 30 min. The reaction process is considered as follows:

$Pb(CH_3COO)_2.3H_2O \rightarrow Pb^{+2} + 2CH_3COO^- + 3H_2O$

$Pb^{+2} + 4NH_3 \rightarrow Pb(NH_3)_4^{+2}$

$SC(NH_2)_2 + 2OH^- \rightarrow CH_2N_2 + 2H_2O + S^{-2}$

$Pb(NH_3)_4^{+2} + SC(NH_2)_2 + 2OH^- \rightarrow PbS + 4NH_3 + CH_2N_2 + 2H_2O$

After deposition, the samples were rinsed in deionized water. Then the non-adherent PbS layer was removed during 2 min treatment in an ultrasonic bath, and the compact inner layer was dried. The layers obtained were strongly adherents 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 slides. The thin films on the side that faced the wall of the beaker during the deposition were used for all measurements. In case of used the hydroxylamine hydrochloride (HXAHC) a agent, we can see for the first 5 min of reaction time, the solution remained transparent, indicating the occurrence of decomposition reactions. Beyond 5 min, the solution turned brown color then dark gray, indicating the formation of PbS, for tri-ethanolamine (TEA), the solution remained milk likely for 10 min then the color of the wall of the beaker graduate to mild gold, gray to dark during the deposition film. With increasing of concentration (TEA) the deposition becomes slow, and for hydrazine hydrate (HH) the solution remained milk likely for 3 min then the solution turned then dark gray, also indicating the formation of PbS. After completion of 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 for 10 min and the compact inner layer was dried in air. The layer obtained were strongly adherents 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 slides. The thin films on the side that faced the wall of the beaker during the deposition were used for all measurements. The obtained samples were studied by AFM images.

2.2 Characterizations

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 (Tap190 Al-G, NanoSensors) in air at room temperature. This study focuses on the synthesis, structural characterization of thin films of PbS deposited with various complexing agent.

3. Results and Discussion

Typically, PbS films were obtained from the reaction between a lead salt and thiourea in an alkaline solution. The slow release of Pb^{+2} ions is achieved by adding a complexing agent (ligand) to the Pb salt to form some lead complex species, which, upon dissociation, results in the release of small concentrations of Pb^{+2} ions. The S^{-2} ions are supplied by the decomposition of thiourea. AFM studies reveal that the there is a dramatic change in the morphologies of the deposited films with the growth techniques. In this work, determine the contribution of the complexing agent (hydroxylamine hydrochloride (HXAHC), hydrazine hydrate (HH), tri-ethanolamine (TEA) at different molar

concentrations) to the quantity and quality of the thin film. A very adherent film with gray-black color and metallic aspect as mirror was obtained for all samples.

a) hydrazine hydrate (HH):

AFM results (Fig. 1) showed discontinuous films in the PbS films' grownwithNH4OH–N2H4 free solution. AFM images of the surface morphology recorded on samples of the PbS thin films deposited with different concentration hydrazine hydrate 0.359M (a), 1.439M (b) and 1.798M(c) are shown in Fig. (1). Hydrazine hydrate(HH) in bath can affect the rate of deposition and the nanostructure of deposited lead sulfide film. The PbS nanocrystallite have the cubic (rock-salt type) structure. The prepared thin films have excellent quality, uniform morphology and covered the entire substrate surface. The mean surface roughness determined from AFM images for three different concentrations.

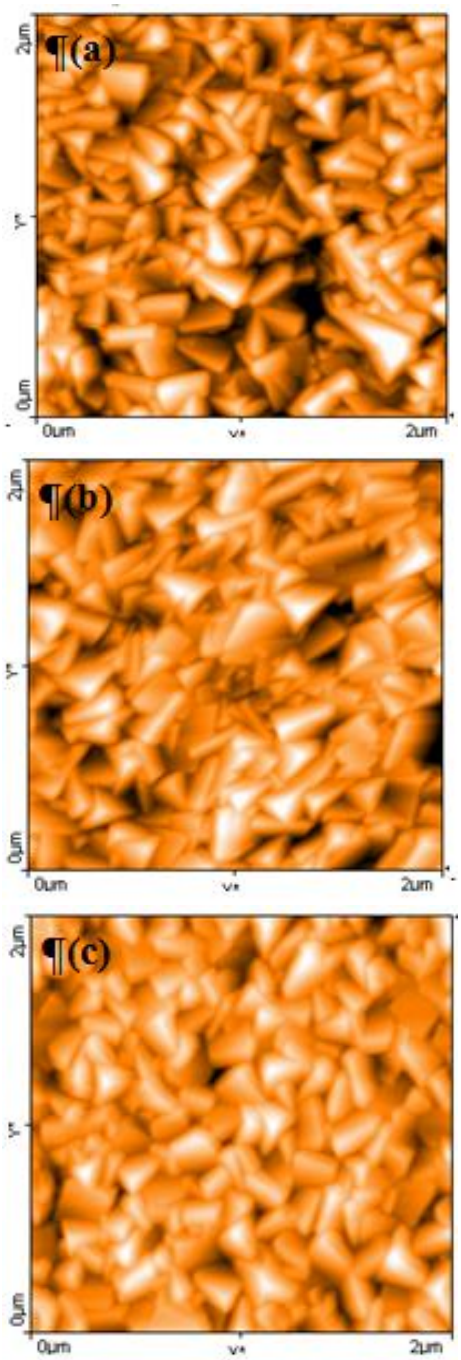

Fig. (1) 2x2µm AFM images for PbS thin films/glass for three different concentrations of hydrazine hydrate (a) 0.359M , (b) 1.439M, (c) 1.798M

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Fig. 2 shows the mean height and mean roughness of PbS-NPs in function of deposition time, it appears that decreasing of mean height by increasing molarities of hydrazine hydrate (HH) but the roughness increasing by increasing molarities (at 1.439 M) then decreasing and that because The introduction of hydrazine hydrate reduced the grain size of the PbS nanoparticles. Atomic force microscopy results show that the roughness of the samples obtained from 1.798 M hydrazine hydrate were smaller than those of 0.359M concentration samples with ascription (~89%).

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.

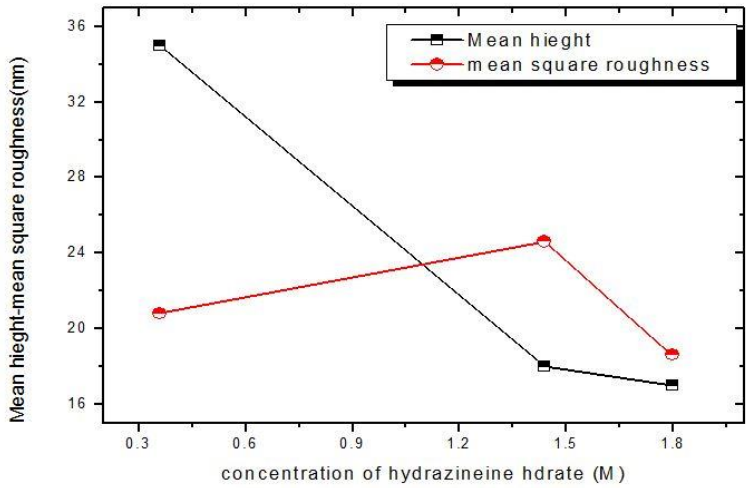

Fig. (2) PbS film mean height, mean roughness as a function of hydrazine hydrate concentration

Figure (3) shows The mean grain diameter of the films are found to vary from 72 to 90 nm.

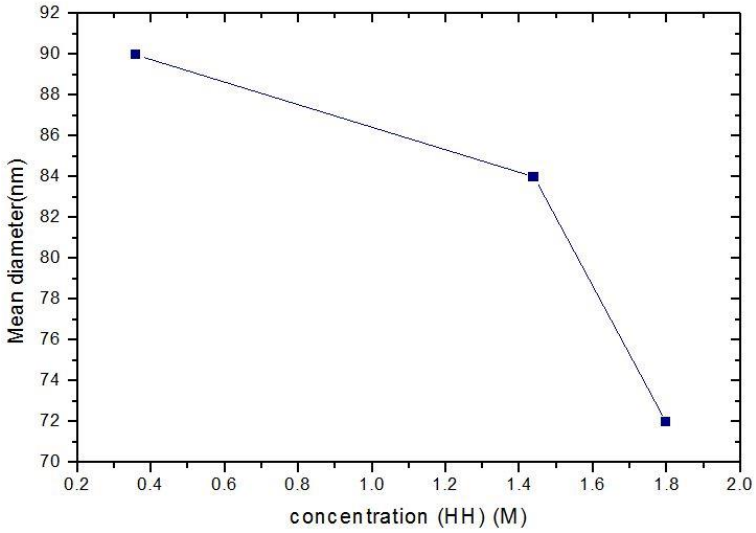

Fig. (3) PbS film mean grain diameter as a function of hydrazine hydrate concentration

b) tri-ethanolamine (TEA):

In Fig. (4), all cases the prepared thin films have good quality, uniform morphology and covered the entire substrate surface, the PbS-NPs carpet the substrate with uniformly spherical shape. In Fig. (4a) at lower molarities the particles start to aggregate and made clusters. In the case of PbS layers grown at 1.439M of (TEA, Fig. 4b) the grain size decrease with increase molarities without aggregate of the particles. We can expect this result due to the preferable concentration of (TEA) is 1.439M.

As we note from Figs. (5) and (6), the smallest mean diameter, mean height and mean roughness were at 1.439M of (TEA) (67, 5 and 3.5 nm, respectively). Atomic force microscopy results show that the roughness of the samples obtained from at concentration for (TEA) 1.439 M were smaller than those of 0.359M concentration samples with ascription (~31%) shown in Fig. (6).

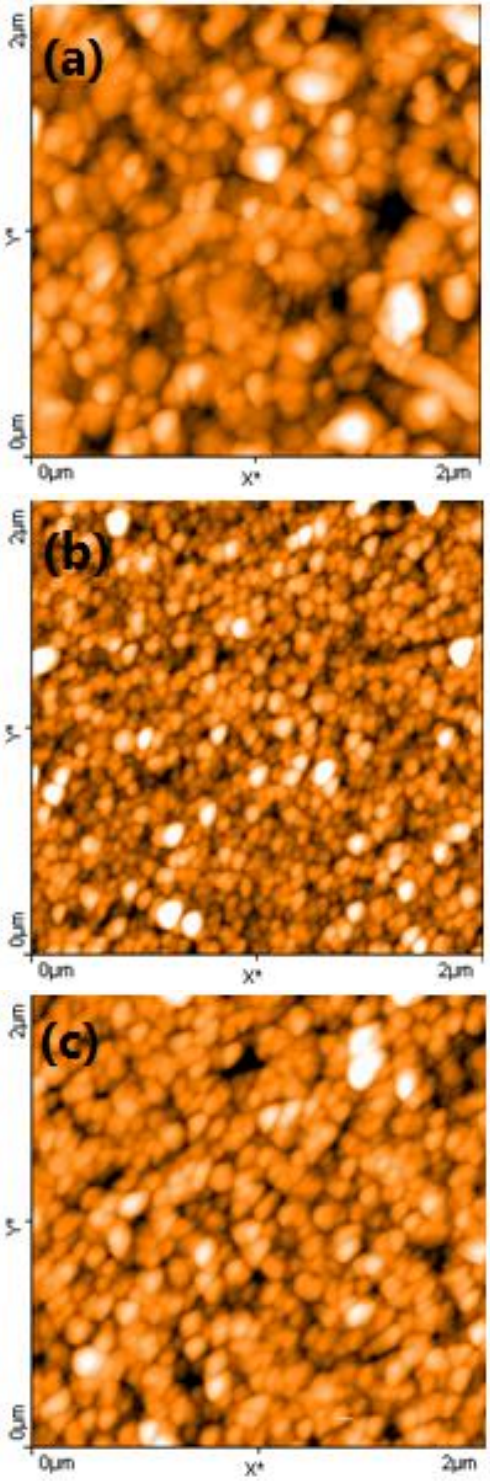

Fig. (4) 2x2µm AFM images for PbS thin films/glass for three different concentrations of Triethanolamin (TEA) (a) 0.359M, (b) 1.439M, (c) 1.798M

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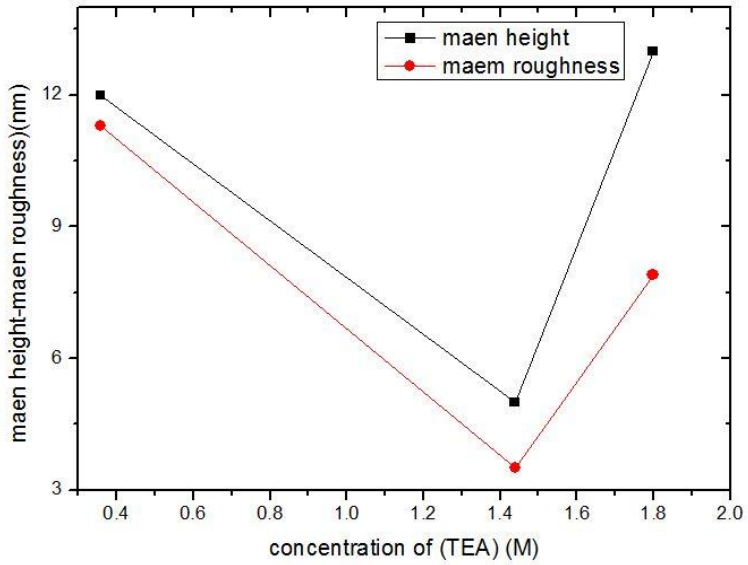

Fig. (5) PbS film mean height, mean roughness as a function of Triethanolamin (TEA) concentration

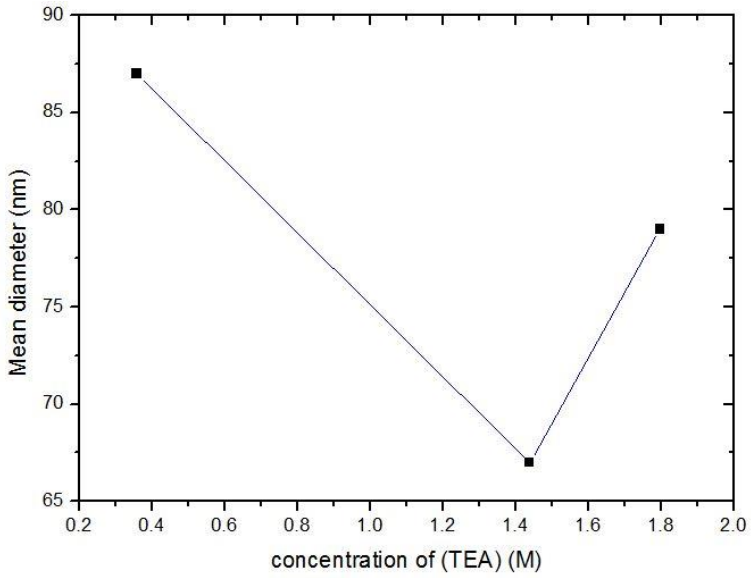

Fig. (6) PbS film mean diameter as a function of Triethanolamin (TEA) concentration

c) hydroxylamine hydrochloride (HXAHC)

In Fig. (7), all cases the prepared thin films have excellent quality, uniform morphology and covered the entire substrate surface, the PbS-NPs carpet the substrate with uniformly spherical shape. In Fig. (7a) at lower molarities the particles start to aggregate and made clusters. In the case of PbS layers grown at 1.439M of (HXAHC, Fig. 7b) the grain size decrease with increase molarities without aggregate of the particles.

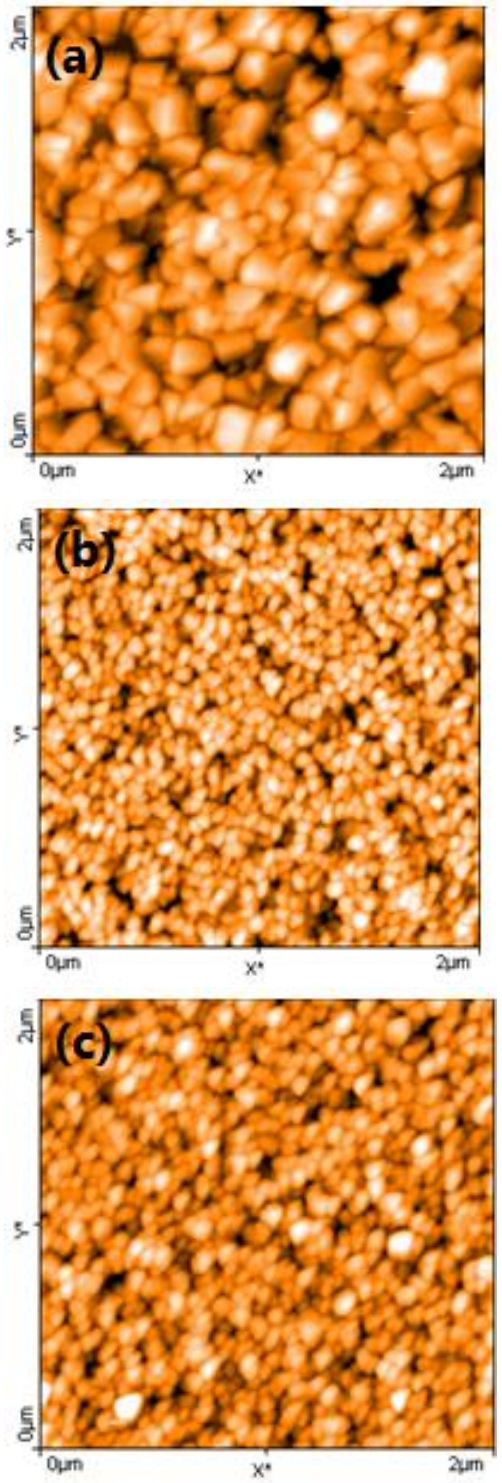

Fig. (7) 2x2µm AFM images for PbS thin films/glass for three different concentration of (HXAHC) (a) 0.359M, (b) 1.439M, (c) 1.798M

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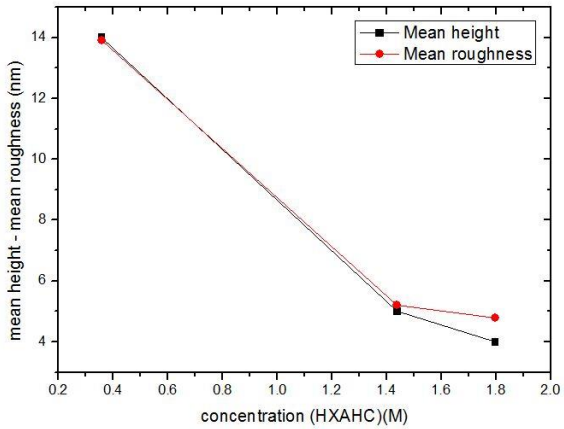

Fig. (8) PbS film mean height, mean roughness as a function of hydroxylamine hydrochloride (HXAHC) concentration

Figure (9) shows the mean grain diameter of the films are found to vary from 85 to 62 nm

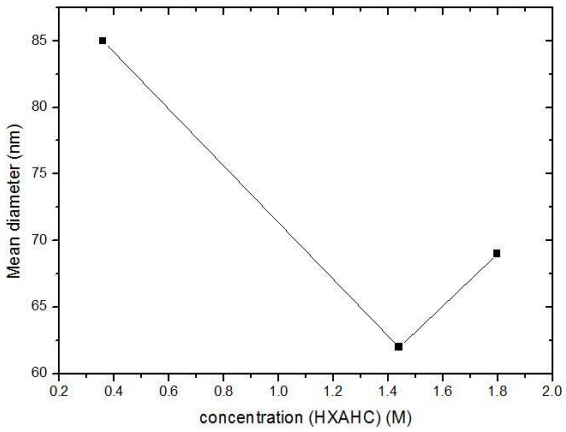

Fig. (9) PbS film mean diameter as a function of hydroxylamine hydrochloride (HXAHC) concentration

d) comparative between three complexing agent:

Figure (11) shows that mean diameter of (HXAHC) the smallest comparative with all complexing agent

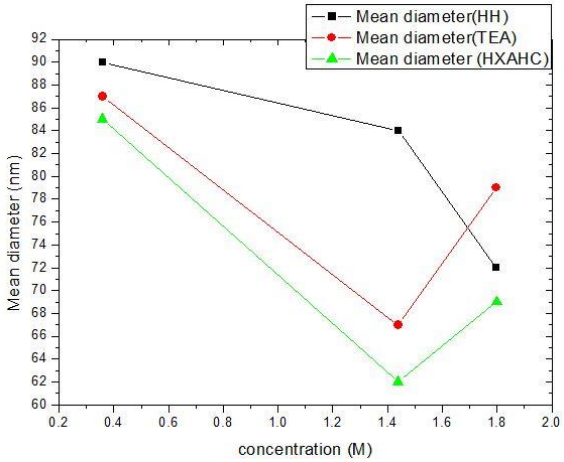

Fig. (11) PbS film mean diameter of (HH, TEA, HXAHC) as a function of concentration

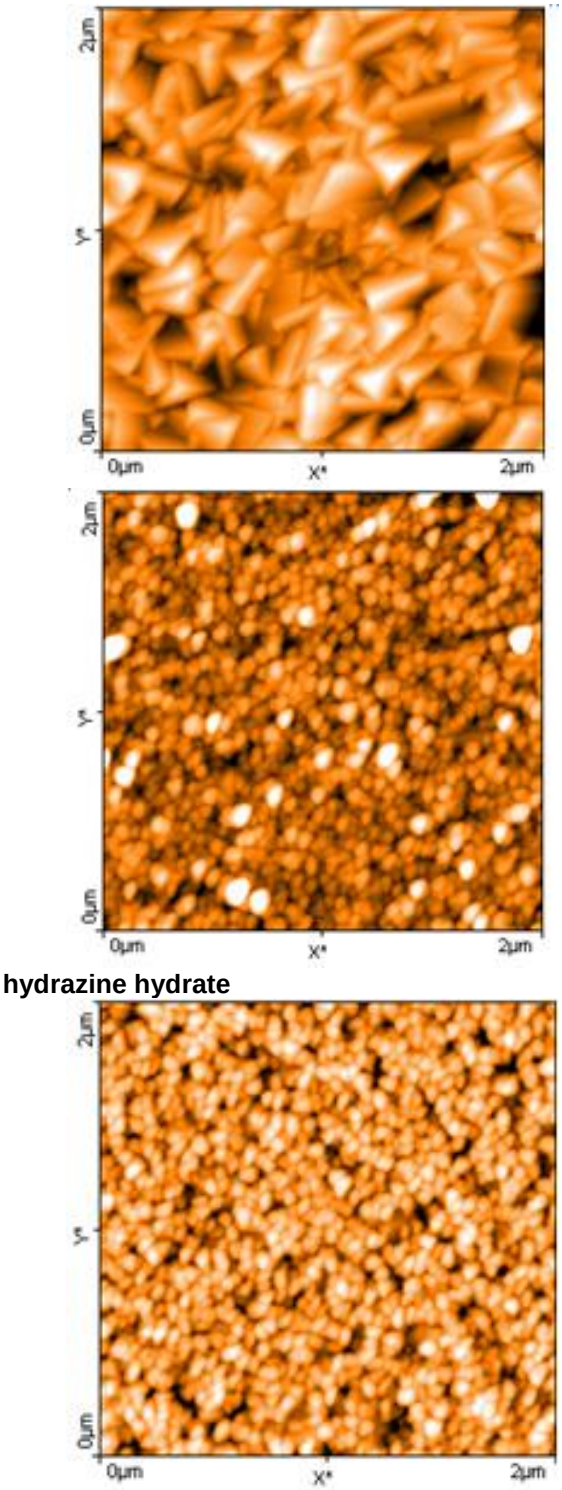

Fig. (10) 2x2µm AFM images for PbS thin films/glass for three different complexing agent

4. Conclusion

In summary, PbS nanoparticles thin films were successfully deposited on glass substrate by CSD technique. AFM image of PbS thin film showed nanocrystalline PbS thin films with different molarities of complexing agent (0.359, 1.439, 1.798M) have been prepared and characterized. The effects of complexing agent on structural properties were discussed. This study confirmed that kind of complexing agent besides molarities, are the conditional parameters that strongly influence the nanocrystallite structure of the films and consequently the optical properties of PbS thin films. The presence of complexing agent in bath can affect the rate of deposition and the nanostructure of

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deposited lead sulfide film. Further studies may extend this method for the preparation of other nanocrystalline sulfide semiconductors.

References

[1] J.I. Pankove, “Optical Processes in Semiconductors”, Dover Publications Inc., New York, 1971.
[2] H. Kanazawa and S. Adachi, J. Appl. Phys. 83 (1998) 5997.
[3] L. Bakuevaa et al., Appl. Phys. Lett., 82 (2003) 2895.
[4] J.S. Steckel et al., Adv. Mater., 15 (2003) 1862.
[5] S. Zhang et al., Appl. Phys. Lett., 87 (2005) 233.
[6] K.W. Johnston et al., Appl. Phys. Lett., 92 (2008) 151.
[7] M. Böberl et al., Adv. Mater., 19 (2007) 3574.
[8] G. Konstantatos et al., Nature, 442 (2006) 180.
[9] G.H. Blount, P.J. Schreiber and D. Smith, J. Appl. Phys., 44 (1973) 978.
[10] S. Espevik, C. Wu and R.H. Bube, J. Appl. Phys., 42 (1971) 3513.
[11] G.P. Kothiyal, B. Ghosh and R.Y. Deshpande, J. Phys. D: Appl. Phys., 13 (1980) 869.
[12] N.I. Fainer et al., Thin Solid Films, 280 (1996) 16.
[13] A. Mondal and N. Mukherjee, Mater. Lett., 60 (2006) 2672.
[14] R.K. Joshi, A. Kanjilalb and H.K. Sehgala, Appl. Surf. Sci., 221 (2004) 43.
[15] E.M. Larramendi et al., Thin Solid Films, 389 (2001) 301.
[16] J. Vaitkus et al., Mater. Res. Bull., 33 (1998) 711.
[17] R. Xie et al., J. Mater. Sci., 42 (2007) 1376.
[18] B. Thangaraju and P. Kaliannan, Semicond. Sci. Technol., 15 (2000) 849.
[19] R. Resch et al., Appl. Surf. Sci., 120 (1997) 51.

