



Morphology control of chemically deposited nanostructured PbS thin films

Scientific research paper

Hajar Farshidi^{1*}, Alimorad Rashidi¹, Amir Ali Youzbashi², and Mehdi Heidari Saani³

¹Nanotechnology Research Center, Research Institute of Petroleum Industry, Tehran 14857-33111, Iran

²Department of Semiconductors, Materials and Energy Research Center (MERC), Karaj 31787-316, Iran

³Department of Physics, Malek-Ashtar University of Technology, Shahin shahr, Esfahan 83145-115, Iran

ARTICLE INFO

Article history:

Received 24 April 2019

Revised 4 September 2019

Accepted 17 May 2020

Available online 20 May 2020

Keywords:

PbS thin films

Chemical bath deposition

Deposition mechanism

Deposition time

ABSTRACT

PbS thin films were grown on glass substrates by chemical bath deposition (CBD) using lead nitrate, thiourea, and sodium hydroxide in aqueous solutions during different deposition times (30-150 min.). The microstructure and morphology of the films were investigated using X-ray diffraction, field emission scanning electron microscopy, and atomic force microscopy. The results indicate that deposition time is an important parameter in determining the dominant mechanism of deposition and consequently the characteristics of the film. The active deposition mechanism changes from cluster to ion-by-ion mechanism during the deposition reaction. Therefore, the film properties such as shape, size, roughness, and preferred orientation change completely.

1 Introduction

PbS is a significant binary IV-VI semiconductor with a relatively small band gap (0.41 eV at 300 K) and rather large excitation Bohr radius (18-20 nm) [1], which provides good quantum confinement of both holes and electrons in nanostructures [2]. These inherent characteristics make PbS one of the most important functional materials used as thin films for such applications as in IR detectors [3], photovoltaic cells [4-6], thin film transistors [7,8], LED [9], gas and biosensors [10-16] and photonic crystals [17]. Different methods including microwave assisted chemical bath deposition [2], pulse electrodeposition [18], spray pyrolysis [19], successive ionic layer adsorption and reaction (SILAR) [20], atomic layer

deposition [21], pulse laser deposition [22], and chemical bath deposition have recently been applied for deposition of PbS thin films.

The chemical bath deposition method, which is also referred to as chemical solution deposition, has turned into an advantageous technique because of its low cost, simple equipment, freedom of deposition of materials, suitability for large areas and deposition of various substances, and capability of tuning thin film properties via adjustment and control of the experimental parameters of deposition [23]. Changing CBD parameters such as temperature and solution composition reportedly leads to nanoparticles with different sizes and shapes [24], which change the band gap value with respect to the effective mass model. In

*Corresponding author.

Email address: Farshidih@Ripi.ir

DOI: 10.22051/jitl.2020.25675.1028

Archive of SID

the CBD process, the elimination of spontaneous precipitation via controlled chemical reaction is necessary for the formation of a thin film [25].

Chemical deposition of films on solid substrates occurs by two main mechanisms. The first mechanism, in which subsequent ionic reactions form the film, is the ion-by-ion mechanism. In this mechanism a complexing agent is needed to prevent the formation of hydroxide precipitate when the reaction is carried out under basic conditions [26].

The cluster mechanism occurs when the complex concentration is not enough for complete prevention of metal hydroxide formation. Under these circumstances, a small amount of colloidal hydroxide forms, which subsequently reacts with the anions generated in the bath to give the final product. The processes for the synthesis of lead sulfide films through ion by ion and cluster mechanisms have been previously reported [27, 28]. It has experimentally been shown that the dominant deposition mechanism depends on the reaction conditions where the change of the dominant mechanism is possible during the deposition [26].

Different particle sizes and morphologies are obtained through each mechanism. The film properties are influenced by the mechanism by which it is formed. Thus, impact of the deposition parameters on the reaction mechanism should be predicted to synthesize a film with specific properties. To the best of our knowledge, few researchers have studied impact of the deposition mechanism on the film properties [29]. The role of deposition temperature in the determination of the dominant deposition mechanism has been previously reported [30].

2 Materials and methods

In order to evaluate the effect of deposition time on the film characteristics, thin layers of lead sulfide with different deposition times (30 to 150 min.) were deposited on the glass substrate. The glass substrates were washed according to the instructions reported by Obeid et al. [2] respectively with hot distilled water, 20% hydrochloric acid, acetone. Finally, the substrates were thoroughly cleaned ultrasonically with deionized water in ultrasonic bath.

Details of the synthesis reaction solution have been reported before [30]. Briefly, Lead sulfide thin films are prepared from reaction solution containing 8.9 mM lead nitrate (PbNO_3), 0.146 M sodium hydroxide (NaOH), and 51.2 mM thiourea ($\text{CS}(\text{NH}_2)_2$) at room temperature with deposition time between 30 and 150 minutes. Thirty minutes after placing the cleaned substrates in the reaction bath, the first sample is removed from the bath and washed with DI water and air dried. Next, samples are taken out of the bath at 60, 90, 120, and 150 minutes after launch of deposition.

X-ray diffraction patterns were obtained using an X-ray diffractometer (Philips PW3710) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$, time/step=0.5 S, step size=0.02). In order to eliminate the effect of glass substrate on the XRD patterns of thin films, X'Pert HighScore Plus software was used. The microstructure and thickness of the prepared PbS films was characterized by plane and cross section view of field emission scanning electron microscopy (FE-SEM, Hitachi S-4160, Japan). Atomic force microscopy (AFM) Auto probe CP (Park Scientific Instruments) was used in non-contact mode for morphological studies using commercial Si_3N_4 cantilevers under ambient conditions.

3 Results and discussion

Deposited films are grayish, homogenous and well adherent to the substrate. Figure 1 shows the XRD pattern of a PbS film deposited on a glass substrate at room temperature for 30 to 150 min. As shown in Figure 1, with increasing the deposition time, the intensity of the peaks and the crystallinity of the films was improved. This can be attributed to the enlarged thickness and particle size obtained with increasing reaction time.

According to the identification with X'pert HighScore plus software, all reflections correspond to the rock salt phase of PbS (JCPDS powder diffraction file #5-0592). No other crystalline phases with detectable concentrations such as lead oxides or carbonates are present within the layers, as indicated by the absence of other diffraction peaks.

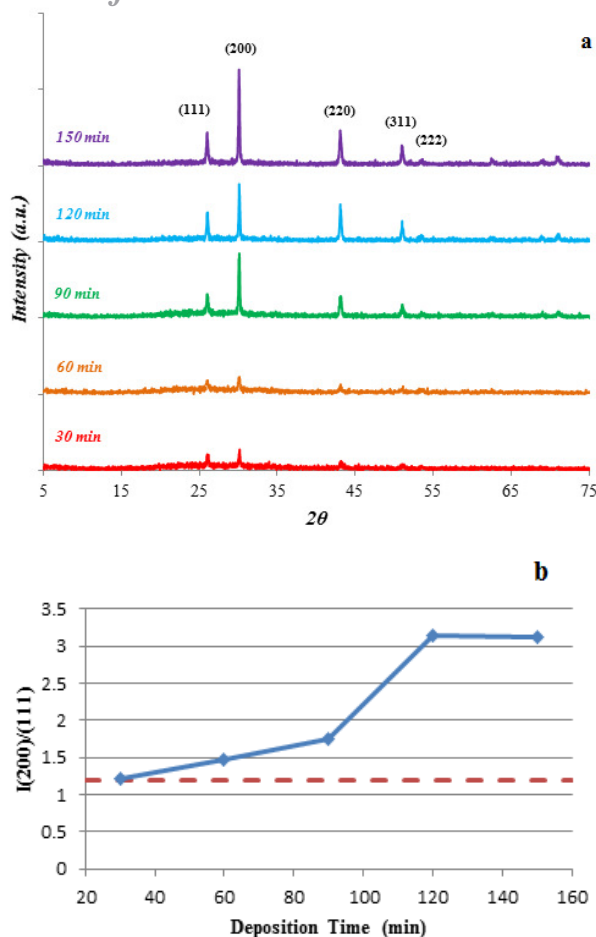


Figure 1:(a) XRD pattern of film PbS deposited on glass substrate at room temperature during different deposition times (b)I(200)/I(111) X-ray diffraction intensity ratio vs. deposition time. The dashed line denotes the intensity ratio expected for powder PbS according to JCPDS file #5-592.

Figure 1b shows the average intensity ratio of the 200 and the 111 Bragg reflections plotted vs. the deposition time. The dashed horizontal line represents the expected intensity ratio I(200):I(111) for PbS powder. The ratio started from 1.20 for the sample deposited in 30 min., steadily increasing to 1.75 for film deposited in 90 min. The ratio rocketed to 3.14 for the sample synthesized in 120 min. The ratio did not change significantly upon further increase in the deposition time. This chart indicates that (200) preferred orientation has been boosted with increasing deposition time.

The AFM surface plot images show the evolution of the film topography with deposition time (Figure 2). The initial nucleation stage is shown in Figure 2a.

Figures 2b–2e show films slowly developed with increasing deposition time. Figure 2f shows the plot of the surface roughness vs. deposition time for layers deposited at room temperature, indicating that coarse islands form and the roughness value of the film sharply increases from 20 to 65 nm. The surface roughness falls back to around 30 nm as the thickness increases. Samples deposited at lower deposition temperatures (10 °C) on the GaAs (100) substrate have been reported to behave similarly [31]. Nevertheless, these changes take place over longer time periods because of the lower deposition temperature.

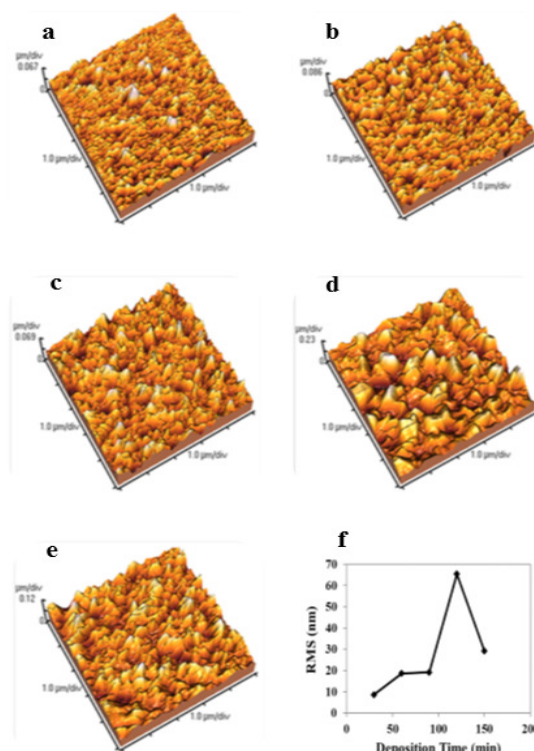


Figure 2: AFM surface plot images of PbS films deposited at room temperature for (a) 30 min., (b) 60 min., (c) 90 min., (d) 120 min., (e) 150 min., (f) surface RMS roughness as a function of deposition time.

In the period from 90 to 120 min., the surface roughness of the film has significantly increased due to island growth. However, over the range of 120–150 min., the growth process has progressed through layer by layer growth (Frank–van der Merwe), resulting in a significant reduction in RMS.

A discontinuous nano crystalline film consisting of round particles with typical size of 100 nm was shown by the sample deposited for 30 min. (Figure 3a). A

Archive of SID

relatively continuous, dense film was formed by increasing the deposition time to 60 min. (Figure 3b). Moreover, nuclei with typical 20-30 nm have appeared on the primary film. A well adherent, dense compact layer covering the entire substrate surface was obtained within 90 min. (Figure 3c), during which the first signs of change in particle shape appeared. Distinguishing of the particle boundaries and determination of particle size are difficult considering the film compactness. Increasing the deposition time further to 120 min. (Figure 3d), led to complete transition to faceted cubic particles with typical size of 500 nm. The boundaries of particles are quite distinguished, which can be attributed to the dominance of columnar growth (*vs.* layer by layer growth) at this stage. Further increase in deposition time to 150 min. did not significantly change the film morphology.

Figure 3f shows the film thickness as a function of the deposition time. The change in the growth rate with the reaction time is illustrated by this curve. The different slopes of the graph represent the different stages of the reaction. The initial slope can be attributed to the nucleation stage or incubation time, at which the thickness slightly increases as the time increases because the primary nuclei are forming. The formation of these nuclei provides the fast growth rate of the film during the next stage. In the third stage, due to the depletion of the reaction solution from the reactants, the deposition rate is less than that in the second stage.

It is known that the characteristic growth rate, grain size and shape, which directly influence the nature and properties of the films, are associated with each deposition mechanism [29]. Hence, it can be concluded that the changes in the deposition rate and particle shape are due to the transition in the deposition mechanism. On the other hand, it is well understood that cluster mechanism is associated with a higher growth rate. Therefore, the high rate of deposition in the second stage (60-90 min.) can be attributed to the dominance of cluster mechanism.

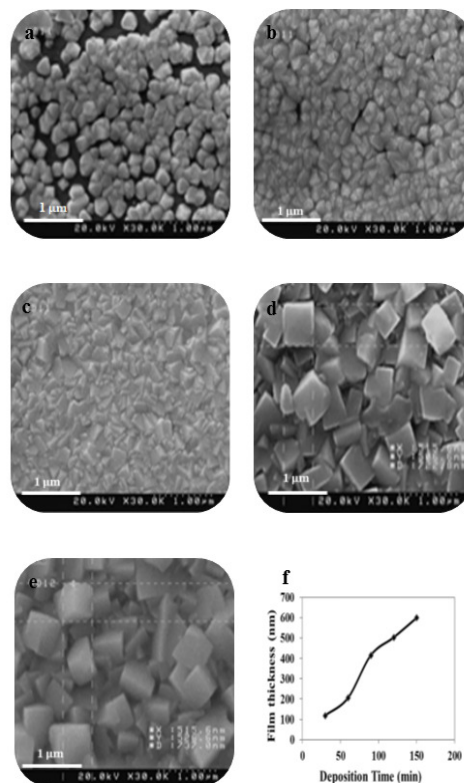


Figure 3: Field Emission Scanning Electron Microscopy (FE-SEM) Images of PbS films deposited on glass at room temperature for (a) 30 min., (b) 60 min., (c) 90 min., (d) 120 min. (e) 150 min., (f) film thickness as a function of deposition time.

The reduction in the deposition rate together with tendency to form larger particles and columnar growth in the third stage of deposition are evidence for the transition from the cluster growth mechanism in the initial growth stages to ion-by-ion growth. This time dependent transition from cluster to ion-by-ion mechanism is in fact expected considering the depletion of lead ions in the solution (i.e. increased complex-to-metal ion concentration ratio) as the reaction progresses. This observation is consistent with the AFM results obtained by increasing the deposition time from 90 to 120 min. The roughness of the samples increases sharply from about 20 to about 65 nm, which can be attributed to the columnar growth, whereas the columnar growth is characteristic of the ion-by-ion mechanism. It is proposed that the active mechanism has altered to ion-by-ion after 90 min. from the beginning of the reaction. The deposition mechanism depends on the reaction conditions and specifies the product characteristics. Previous studies on the PbS films deposited *via* CBD, revealed that the texture development observed with increasing

Archive of SID

thickness is also related to the change of the dominant mechanism [32].

4 Conclusions

Thin films of lead sulfide were deposited on a glass substrate using CBD method at different deposition times. It was observed that the morphology of the samples was dependent on the deposition time. As the deposition time increases, the shape of the particles changes from round to cubic and the texture (200) develops. The roughness of the film also changes during the deposition. These changes are attributed to the change in the dominant deposition mechanism. This study showed that deposition time is an important parameter in the determination of the dominant mechanism of deposition and consequently the characteristics of the film.

References

- [1] D. Kumar, G. Agarwal, B. Tripathi, D. Vyas, V. Kulshrestha, "Characterization of PbS nanoparticles synthesized by chemical bath deposition." *Journal of Alloys and Compounds*, **484** (2009) 463.
- [2] A. Obaid, M. Mahdi, Z. Hassan, M. Bououdina, "Characterization of nanocrystalline PbS thin films prepared using microwave-assisted chemical bath deposition." *Materials Science in Semiconductor Processing*, **15** (2012) 564.
- [3] Z. Sun, Z. Liu, J. Li, G.-a. Tai, S.-P. Lau, F. Yan, "Infrared Photodetectors Based on CVD-Grown Graphene and PbS Quantum Dots with Ultrahigh Responsivity." *Advanced Materials*, **24** (2012) 5878.
- [4] R. Gertman, A. Osherov, Y. Golan, I. Visoly-Fisher, "Chemical bath deposited PbS thin films on ZnO nanowires for photovoltaic applications." *Thin Solid Films*, **550** (2014) 149.
- [5] D. Saikia, P. Phukan, "Fabrication and evaluation of CdS/PbS thin film solar cell by chemical bath deposition technique." *Thin Solid Films*, **562** (2014) 239.
- [6] D.H. Yeon, S.M. Lee, Y.H. Jo, J. Moon, Y.S. Cho, "Origin of the enhanced photovoltaic characteristics of PbS thin film solar cells processed at near room temperature." *Journal of Materials Chemistry A*, **2** (2014) 20112.
- [7] A. Carrillo-Castillo, A. Salas-Villasenor, I. Mejia, S. Aguirre-Tostado, B. Gnade, M. Quevedo-López, "P-type thin films transistors with solution-deposited lead sulfide films as semiconductor." *Thin Solid Films*, **520** (2012) 3107.
- [8] C.H. Jo, J.H. Kim, J. Kim, J. Kim, M.S. Oh, M.S. Kang, M.-G. Kim, Y.-H. Kim, B.-K. Ju, S.K. Park, "Low-temperature annealed PbS quantum dot films for scalable and flexible ambipolar thin-film-transistors and circuits." *Journal of Materials Chemistry C*, **2** (2014) 10305.
- [9] S. Kaci, A. Keffous, S. Hakoum, N. Makrani, M. Kechouane, L. Guerbous, "Investigation of nc-PbS/a-Si 1- xCx: H/pSi (100) heterostructures for LED applications." *Optical Materials*, **35** (2012) 1.
- [10] T. Fu, "Research on gas-sensing properties of lead sulfide-based sensor for detection of NO and NH₃ at room temperature." *Sensors and Actuators B: Chemical*, **140** (2009) 116.
- [11] N. Sonawane, K. Gurav, R. Ahire, J. Kim, B. Sankapal, "CdS nanowires with PbS nanoparticles surface coating as room temperature liquefied petroleum gas sensor." *Sensors and Actuators A: Physical*, **216** (2014) 78.
- [12] S. Kaci, A. Keffous, S. Hakoum, M. Trari, O. Mansri, H. Menari, "Preparation of nanostructured PbS thin films as sensing element for NO₂ gas." *Applied Surface Science*, **305** (2014) 740.
- [13] D. Dhawale, D. Dubal, A. More, T. Gujar, C. Lokhande, "Room temperature liquefied petroleum gas (LPG) sensor." *Sensors and Actuators B: Chemical*, **147** (2010) 488.
- [14] S. Patil, P. Deshmukh, C. Lokhande, "Fabrication and liquefied petroleum gas (LPG) sensing performance of p-polyaniline/n-PbS heterojunction at room temperature." *Sensors and Actuators B: Chemical*, **156** (2011) 450.
- [15] H. Fan, K. Zhao, Y. Lin, X. Wang, B. Wu, Q. Li, L. Cheng, "A new electrochemical biosensor for DNA detection based on molecular recognition and lead sulfide nanoparticles." *Analytical Biochemistry*, **419** (2011) 168.
- [16] S. Navale, D. Bandgar, M. Chougule, V. Patil, "Facile method of preparation of PbS films for NO₂ detection." *RSC Advances*, **5** (2015) 6518.

- [17] N. Gutman, A. Armon, A. Osherov, Y. Golan, A. Sa'Ar, "Two-and three-dimensional composite photonic crystals of macroporous silicon and lead sulfide semiconductor nanostructures." *Physica status solidi (a)*, **206** (2009) 1290.
- [18] A. Aghassi, M. Jafarian, I. Danaee, F. Gobal, M. Mahjani, "AC impedance and cyclic voltammetry studies on PbS semiconducting film prepared by electrodeposition." *Journal of Electroanalytical Chemistry*, **661** (2011) 265.
- [19] S. RaviShankar, A. Balu, M. Anbarasi, V. Nagarethinam, "Influence of precursor molar concentration on the structural, morphological, optical and electrical properties of PbS thin films deposited by spray pyrolysis technique using perfume atomizer." *Optik-International Journal for Light and Electron Optics*, **126** (2015) 2550.
- [20] E. Güneri, F. Göde, S. Çevik, "Influence of grain size on structural and optic properties of PbS thin films produced by SILAR method, *Thin Solid Films*, **589** (2015) 578.
- [21] N.P. Dasgupta, H.J. Jung, O. Trejo, M.T. McDowell, A. Hryciw, M. Brongersma, R. Sinclair, F.B. Prinz, "Atomic Layer Deposition of Lead Sulfide Quantum Dots on Nanowire Surfaces." *Nano Letters*, **11** (2011) 934.
- [22] K.A. Aadim, A.M.E. Ibrahim, J.M. Marie, "Structural and Optical Properties of PbS Thin Films Deposited by Pulsed Laser Deposited (PLD) Technique at Different Annealing Temperature." *International Journal of Physics*, **5** (2017) 1.
- [23] A. Osherov, J.P. Makai, J. Balazs, Z.J. Horvath, N. Gutman, A. Sa'ar, Y. Golan, "Tunability of the optical band edge in thin PbS films chemically deposited on GaAs (100)." *Journal of Physics: Condensed Matter*, **22** (2010) 262002.
- [24] F. Göde, E. Güneri, F. Emen, V.E. Kafadar, S. Ünlü, "Synthesis, structural, optical, electrical and thermoluminescence properties of chemically deposited PbS thin films." *Journal of Luminescence*, **147** (2014) 41.
- [25] K. Preetha, K. Deepa, A. Dhanya, T. Remadevi, "Role of complexing agents on chemicalbath deposited PbS thin film characterization." *IOP Conference Series: Materials Science and Engineering*, **73** (2015) 012086.
- [26] G. Hodes, "Semiconductor and ceramic nanoparticle films deposited by chemical bath deposition." *Physical Chemistry Chemical Physics*, **9** (2007) 2181.
- [27] A. Osherov, V. Ezersky, Y. Golan, "The role of solution composition in chemical bath deposition of epitaxial thin films of PbS on GaAs (100)." *Journal of Crystal Growth*, **308** (2007) 334.
- [28] S. Seghaier, N. Kamoun, R. Brini, A.B. Amara, "Structural and optical properties of PbS thin films deposited by chemical bath deposition." *Materials Chemistry and Physics*, **97** (2006) 71.
- [29] M. Shandalov, Y. Golan, "Microstructure and morphology evolution in chemical solution deposited semiconductor films: 2. PbSe on As face of GaAs (111)." *The European Physical Journal Applied Physics*, **28** (2004) 51.
- [30] H. Farshidi, A.A. Youzbashi, M. Heidari Saani, A. Rashidi, A. Kazem Zadeh, "Control of morphology and optical properties of PbS nanostructured thin films by deposition parameters: study of mechanism." *Journal of Experimental Nanoscience*, **11** (2016) 1416.
- [31] A. Osherov, V. Ezersky, Y. Golan, "Microstructure and morphology evolution in chemically deposited semiconductor films: 4. From isolated nanoparticles to monocrystalline PbS thin films on GaAs (100) substrates, *The European Physical Journal Applied Physics*, **37** (2007) 39.
- [32] A. Osherov, M. Shandalov, V. Ezersky, Y. Golan, "EPITAXY and orientation control in chemical solution deposited PbS and PbSe monocrystalline films, *Journal of Crystal Growth*." **304** (2007) 169.