Effect of Deposition Time on Surface Topography of Chemical Bath Deposited PbSe Thin Films Observed by Atomic Force Microscopy.

K. Anuar, Ph.D.*[1]; H.A. Abdul, Ph.D.[1]; S.M. Ho, M.Sc.*[1]; and N. Saravanan, Ph.D.[2]

[1]Department of Chemistry, Faculty of Science, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia.
[2]Department of Bioscience and Chemistry, Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, 53300 Kuala Lumpur, Malaysia.

*E-mail: anuar@science.upm.edu.my

ABSTRACT

Lead selenide thin films were deposited onto microscope glass slides by the chemical bath deposition method at various deposition periods ranging from 20 to 150 min. Atomic force microscopy was used to study the topographic characteristics of thin films including grain size, film thickness, and surface roughness. The thickness values as well as surface roughness values were increased when the deposition time was increased from 20 to 150 min. Film thickness ranged from 156 to 1186 nm while roughness ranged from 11 to 184 nm. The AFM images confirmed that the grain size of the films increased with the increased of deposition time. The AFM images indicated that optimum properties were obtained for the films deposited for 60 min. These thin films were uniform and the substrate surface was well covered with spherical grains that were uniformly distributed over the surface.

(Keywords: chemical bath deposition, lead selenide, thin films, atomic force microscopy)

INTRODUCTION

PbSe is an important semiconducting material and has been extensively investigated for infrared detectors, photographic plates, solar cells, and photo resisters. Various processing routes, both physical and chemical deposition techniques have been utilized to prepare lead selenide thin films, including electrodeposition (Molin and Dikusar, 1995), chemical bath deposition (Grozdanov et al., 1999), electrochemical atomic layer epitaxy (Vaidyanathan et al., 2004), photochemical (Zhu et al., 2001), molecular beam epitaxy (Gautier et al., 1998), and pulsed laser deposition method (Rumianowski et al., 2003). Among these, the chemical bath deposition method was chosen as an ideal preparation method for preparing lead selenide thin films basically due to its low deposition temperature, simple, no requirement of sophisticated instruments and minimum material. Up-to-date, chemical bath deposition method has been successfully used to deposit many different thin films including FeS_2 (Anuar et al., 2009), PbS (Larramendi et al., 2001), Cu_2S (Lu et al., 2008), SnS (Avellaneda et al., 2009), Cu_4SnS_4 (Anuar et al., 2010), and $CuInS_2$ (Cui et al., 2009).

The present work reports the preparation and physical characterization of PbSe thin films onto microscope glass slides using the chemical bath deposition method. The chemical bath contains lead nitrate and sodium selenate which provide Pb^{2+} and Se^{2-} ions, respectively, while triethanolamine acted as a complexing agent. We report the influence of deposition time ranging from 20-150 min on the surface topography of PbSe thin films at 80 °C at pH 6 for the first time.

MATERIALS AND METHODS

Preparation of Thin Films

All the chemicals used for the deposition were analytical grade and all the solutions were prepared in deionized water (Alpha-Q Millipore). The lead selenide thin films were prepared from an acidic bath using aqueous solutions of lead nitrate [$Pb(NO_3)_2$] and sodium selenate [Na_2O_4Se] acted as a source of Pb^{2+} and Se^{2-} ions, respectively. The microscope glass slide was used as the substrate for chemical bath deposition of lead selenide thin films. Before deposition, the glass slide was degreased with ethanol for 10 min., then, ultrasonically cleaned with distilled water for another 10 min and dried in desiccator. Deposition of PbSe thin films was carried out by using following procedure: 25 ml of 0.15 M lead nitrate was taken in a 100 mL beaker. Then, 5 mL of concentrated triethanolamine was added to the beaker. Following that, 25 mL of 0.15 M sodium selenate was mixed into the above mentioned mixture. The pH was adjusted to 6 by hydrochloric acid. The beaker was kept in water bath. The temperature of the water bath was then allowed to increase slowly up to 80 °C. The clean microscope glass slide was placed in the beaker, supported vertically on the wall of the beaker. The deposition process was carried out at different deposition periods (20, 40, 60 and 150 min) in order to determine the optimum condition for the deposition of thin films. After the completion of deposition, the films were washed with distilled water and dried naturally in desiccator for further characterization.

<u>Characterization of Thin Films</u>

The surface morphology, thickness, and roughness were examined by recording atomic force microscopy images with a Q-Scope 250 in contact mode with a commercial Si_3N_4 cantilever. Values of root mean square (RMS) roughness were calculated from the height values in the atomic force microscopy images using the commercial software.

RESULTS AND DISCUSSION

The surface morphology of PbSe thin films was studied using atomic force microscopy (AFM). Figures 1a and 1b show two-dimensional and three dimensional AFM images of PbSe thin films deposited for 20 min, respectively. At shorter deposition periods, there are only few grains (with grain size of 0.2-0.3 µm) that could be observed over the substrate. The low density of these grains implies that the nucleation has occurred only on some specific sites.

Figure 2 shows AFM images of PbSe thin films deposited for 40 min, measured over an area of 20 x 20 µm. From the 2-dimensional (Figure 2a) and 3-dimensional AFM images (Figure 2b), it was found that the small spherical grains of different shapes and sizes (0.5-0.6 µm) were distributed in thin films. The films revealed an incomplete coverage of the substrate surface and the grains are not distributed uniformly over substrate. However, the number of grains has increased as compared with the films deposited for 20 min indicating more nucleation sites has formed.

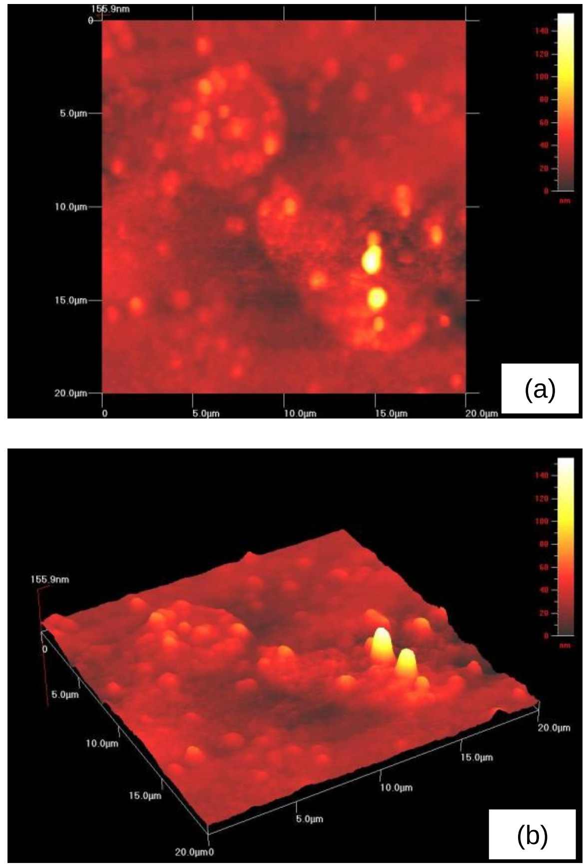

Figure 1: Atomic Force Microscopy Images of PbSe Thin Films Deposited for 20 min (a) 2-dimensional (b) 3-dimensional image.

Figure 3a and 3b show two-dimensional and three dimensional AFM images of PbSe thin films deposited for 60 min, respectively. Figures show that the lead selenide thin films are uniform and the substrate surface is well covered with spherical grains that are uniformly distributed over the surface. These films show grain size of 0.8-1 µm.

Figure 4 represents AFM images of PbSe thin films deposited for 150 min. The AFM images reveal the granular nature of the films. There was agglomeration of grains in most of the cases as evident from the 2-dimensional image (Figure 4a). Figure 4b indicates the formation of islands that shows the three dimensional growth of the thin films. The grain size was found to be increased for the films deposited at longer deposition period which due to coalesce of smaller grains into larger grains. The AFM images show that the films have irregular grains on the surface and the grain size varied in the range 1.2-1.4 µm.

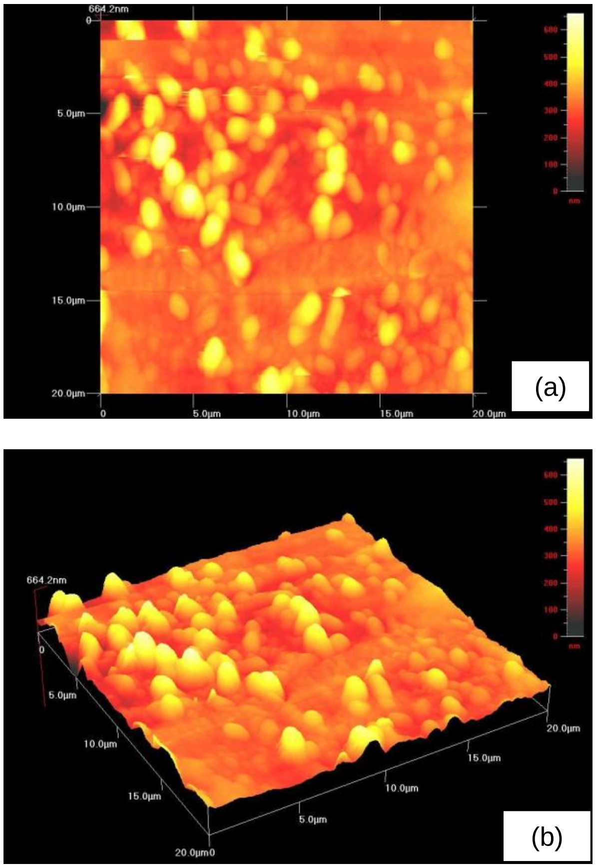

Figure 2: Atomic Force Microscopy Images of PbSe Thin Films Deposited for 40 min (a) 2-dimensional (b) 3-dimensional image.

The thickness of the thin films was investigated using AFM images. At the right side of the AFM images, an intensity strip is shown, which indicates the depth and height along the *z*-axis. Figure 5 shows the thickness variation of PbSe thin films as a function of deposition time. It shows that the thickness of the films increased from 156 to 1181 nm when the deposition period was increased from 20 to 150 min. This indicates the thickness of the thin films grown onto glass slides is dependent on deposition period.

In the chemical bath deposition process, there are two different stages could be distinguished, namely initial linear region and saturation stage. For example in our case, initially, the growth rate increases (7.8, 16.6, and 19.5 nm/min) with an increase of deposition time from 20 to 60 min. However, with further increase in the deposition time, the growth rate decreases (7.9 nm/min). This is a feature well known in chemically deposited semiconductor thin films.

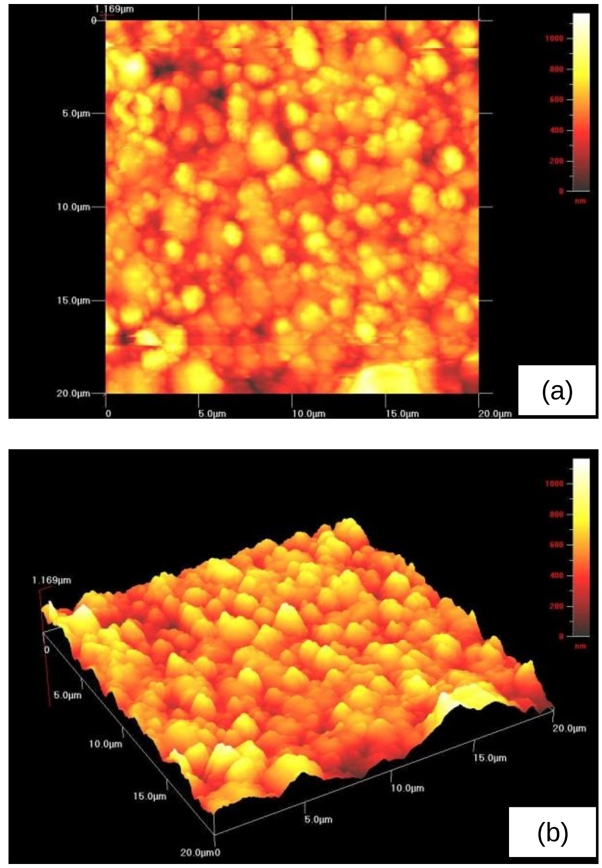

Figure 3: Atomic Force Microscopy Images of PbSe Thin Films Deposited for 60 min (a) 2-dimensional (b) 3-dimensional image.

The root mean square (RMS) roughness of the thin films was also studied from AFM images (Figure 6). Root mean square roughness is defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness [Jiang et al., 2005]. The roughness values of 11, 63, 138 and 184 nm have been observed for the films prepared for 20, 40, 60 and 150 min, respectively. The surface roughness of the thin films is unavoidable since grains were grown with different sizes and spherical in shapes. Following this tendency, it can be concluded that the surface roughness increases with the deposition time.

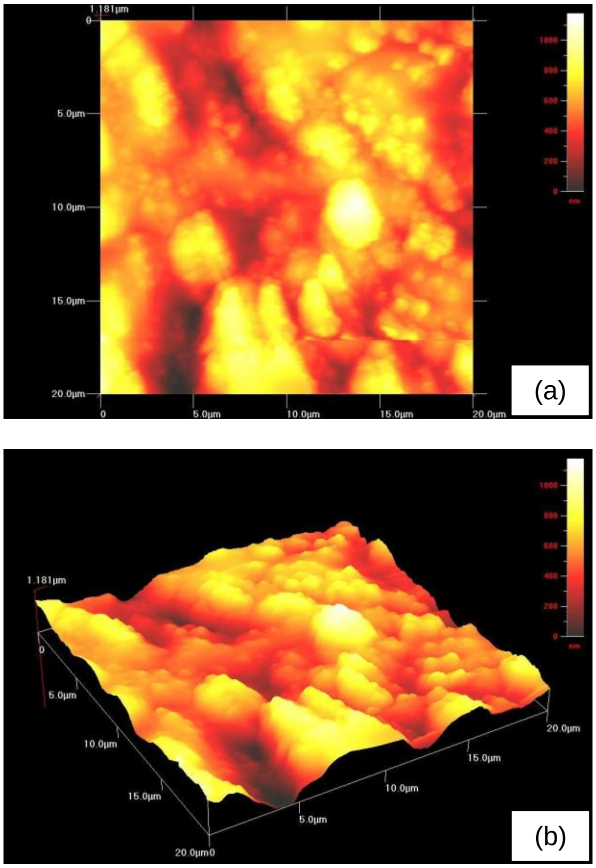

Figure 4: Atomic Force Microscopy Images of PbSe Thin Films Deposited for 150 min (a) 2-dimensional (b) 3-dimensional image.

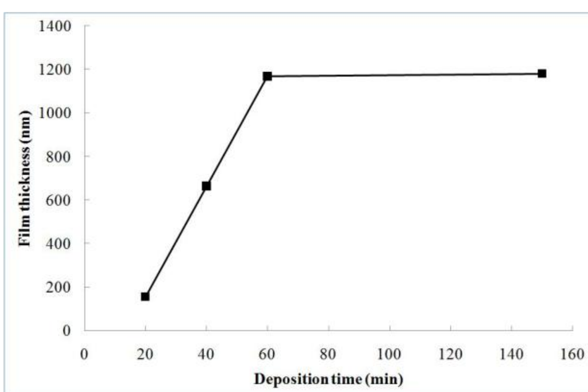

Figure 5: A Plot of Film Thickness versus Deposition Time for PbSe Thin Films.

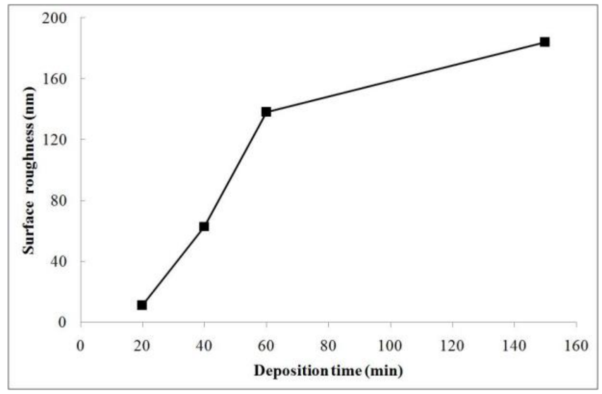

Figure 6: A Plot of Surface Roughness versus Deposition Time for PbSe Thin Films.

CONCLUSION

The chemical bath deposition method has proven to be an ideal method to produce thin films with low cost and simplicity. By using atomic force microscopy, we have studied the surface topography of thin films deposited under various deposition periods. The grain size, surface roughness, as well as thickness values, were increased when the deposition time was increased from 20 to 150 min. The AFM images indicated that the films deposited for 60 min. were uniform and the substrate surface was well covered with spherical grains. Therefore, we concluded that the growth of PbSe thin films could be optimized in terms of the modifications of the surface topography by properly controlling the deposition time.

REFERENCES

1. Anuar, K., W.T. Tan, N. Saravanan, S.M. Ho, and S.Y. Gwee. 2009. "Influence of pH Values on Chemical Bath Deposited FeS_2 Thin Films". *Pacific Journal of Science and Technology*. 10(2): 801-805.

2. Anuar, K., W.T. Tan, S. Atan, Z. Kuang, M.J. Haron, S.M. Ho, and N. Saravanan. 2010. "Effects of Electrolytes Concentration on the Chemically Deposited Cu_4SnS_4 Thin Films". *Asian Journal of Chemistry*. 22: 222-232.

3. Avellaneda, D., M.T.S. Nair, and P.K. Nair. 2009. "Photovoltaic Structures using Chemically Deposited Tin Sulfide Thin Films". *Thin Solid Films*. 517: 2500-2502.

4. Cui, F., L. Wang, Z. Xi, Y. Sun, and D. Yang. 2009. "Fabrication and Characterization of $CuInS_2$ Films by Chemical Bath Deposition in Acid Conditions". *Journal of Materials Science: Materials in Electronics*. 20: 609-613.

5. Gautier, C., G. Breton, M. Nouaoura, M. Cambon, S. Charar, and M. Averous. 1998. "Sulfide Films on PbSe Thin Layer Grown by MBE". *Thin Solid Films.* 315: 118-122.

6. Grozdanov, I., M. Najdoski, and S.K. Dey. 1999. "A Simple Solution Growth Technique for PbSe Thin Films". *Materials Letters.* 38: 28-32.

7. Jiang, T., N. Hall, A. Ho, and S. Morin. 2005. "Quantitative Analysis of Electrodeposited Tin Film Morphologies by Atomic Force Microscopy". *Thin Solid Films.* 417: 76-85.

8. Larramendi, E.M., O. Calzadilla, A.G. Arias, E. Hernandez, and J.R. Garcia. 2001. "Effect of Surface Structure on Photosensitivity in Chemically Deposited PbS Thin Films". *Thin Solid Films.* 389: 301-306.

9. Lu, Y.J., S. Liang, M. Chen, and J.H. Jia. 2008. "Preparation of Nano-Crystal Cu_2S Films by Chemical Bath Deposition and its Optical Properties". *Journal of Functional Materials,* 39: 1894-1896.

10. Molin, A.N., and A.I. Dikusar. 1995. "Electrochemical Deposition of PbSe Thin Films form Aqueous Solutions". *Thin Solid Films.* 265: 3-9.

11. Rumianowski, R.T., R.S. Dygdala, W. Jung, and W. Bala. 2003. "Growth of PbSe Thin Films on Si Substrates by Pulsed Laser Deposition Method". *Journal of Crystal Growth*. 252: 230-235.

12. Vaidyanathan, R., J.L. Stickney, and U. Happek. 2004. "Quantum Confinement in PbSe Thin Films Electrodeposited by Electrochemical Atomic Layer Epitaxy (EC-ALE)". *Electrochimica Acta.* 49: 1321-1326.

13. Zhu, J.J., X.H. Liao, J. Wang, and H.Y. Chen. 2001. "Photochemical Synthesis and Characterization of PbSe Nanoparticles". *Materials Research Bulletin.* 36: 1169 -1176.

ABOUT THE AUTHORS

Anuar Kassim is a Professor at the Department of Chemistry, Faculty of Science, Universiti Putra Malaysia. He holds a Ph.D. in chemistry from the University of Salford. His research interests are in thin films, conducting polymers, and activated carbon.

Abdul Halim Abdullah is an Associate Professor at the Department of Chemistry, Faculty of Science, Universiti Putra Malaysia. He holds a Ph.D. in chemistry from the University of Dundee. His research interests are in thin films, nanomaterials, and activated carbon.

Saravanan Nagalingam is an Assistant Professor at the Department of Bioscience and Chemistry, Faculty of Engineering and Science, Universiti Tunku Abdul Rahman. He holds a Ph.D. in chemistry from the Universiti Putra Malaysia. His research interests are in thin films, nanomaterials, and electrochemistry.

Ho Soon Min is a researcher at the Department of Chemistry, Faculty of Science, Universiti Putra Malaysia. He holds an M.Sc. in chemistry from the Universiti Putra Malaysia. His research interests are in thin films and nanomaterials.

SUGGESTED CITATION

Anuar, K., H.A. Abdul, S.M. Ho, and N. Saravanan. 2010. "Effect of Deposition Time on Surface Topography of Chemical Bath Deposited PbSe Thin Films Observed by Atomic Force Microscopy". Pacific Journal of Science and Technology. 11(1):399-403.

Pacific Journal of Science and Technology