Pak. J. Sci. Ind. Res. Ser. A: Phy. Sci. 2011 **54** (1) 1-5

Deposition and Characterization of ZnS Thin Films Using Chemical Bath Deposition Method in the Presence of Sodium Tartrate as Complexing Agent

Anuar Kassim*[a], Tan Wee Tee[a], Ho Soon Min[a] and Saravanan Nagalingam[b]
[a]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[b]Department of Bioscience and Chemistry, Faculty of Engineering and Science,
Universiti Tunku Abdul Rahman, 53300 Kuala Lumpur, Malaysia

(received October 21, 2010; revised January 21, 2011; accepted January 22, 2011)

Abstract. ZnS thin films were deposited on indium tin oxide glass substrate using the chemical bath deposition method. The deposited films were characterized by X-ray diffraction and atomic force microscopy. The influence of bath temperature on the structure and morphology of the thin films was investigated at three different bath temperatures of 60, 70 and 80 °C in the presence of sodium tartrate as a complexing agent. The XRD results indicated that the deposited ZnS thin films exhibited a polycrystalline cubic structure. The number of ZnS peaks increased from three to four peaks as the bath temperature was increased from 60 to 80 °C based on the XRD patterns. From the AFM measurements, the film thickness and surface roughness were found to be dependent on the bath temperature. The grain size increased as the bath temperature was increased from 60 to 80 °C.

Keywords: chemical bath deposition, thin films, zinc sulphide, atomic force microscopy

Introduction

Zinc sulphide thin films are wide band gap semiconductors which have been used in phosphors, catalysts, solar cells, electro-luminescent devices and many other optoelectronic devices. The ZnS thin films have been deposited using various methods such as RF reactive sputtering (Shao *et al*., 2003), chemical bath deposition (Goudarzi *et al*., 2008; Noikaew *et al*., 2008; Antony *et al*., 2005), atomic layer epitaxy (Oikkonen *et al*., 1998), pulsed-laser deposition (Yano *et al*., 2003) and electrodeposition (Lokhande *et al*., 1998). Chemical bath deposition method is considered a cheap method for producing large area thin films. Up-to-date, chemical bath deposition method has been successfully used to deposit various thin films including FeS_2 (Anuar *et al*., 2010), PbS (Raniero *et al*., 2010), CdTe (Garadkar *et al*., 2010), CdS (Li *et al*., 2005) and As_2S_3 (Mane *et al*., 2004). Chemical bath deposition method is based on controlled precipitation from solution of a compound on a suitable substrate. The substrate is immersed in either alkaline or acidic solution containing the metal ion, chalcogenide source and a complexing agent. Several complexing agents have been utilized in the deposition of thin films such as ammonium sulphate (Soundeswaran *et al*., 2004), sodium citrate (Esparza-Ponce *et al*., 2009), triethanolamine (Gumus *et al*., 2005), disodium ethylene diamine tetra-acetate (Anuar *et al*., 2009), nitrilotriacetic acid (Khallaf *et al*., 2008) and sodium tartrate (Anuar *et al*., 2004).

The present work reports preparation and physical characterization of ZnS thin films onto indium tin oxide glass substrates using chemical bath deposition method. The chemical bath contains zinc sulphate and sodium thiosulphate which provide Zn^{2+} and S^{2-} ions, respectively. It is the first time that the influence of bath temperature ranging from 60 to 80 °C on the ZnS thin film in the presence of sodium tartrate solution is reported. Thin films were analyzed by X-ray diffraction and atomic force microscopy.

Materials and Methods

All the chemicals used for the deposition were analytical grade reagents and all the solutions were prepared in deionised water (Alpha-Q Millipore). Zinc sulphide thin films were prepared from an acidic bath using aqueous solutions of zinc sulphate ($ZnSO_4$) and sodium thiosulphate ($Na_2S_2O_3$) as a source of Zn^{2+} and S^{2-} ions, respectively. Sodium tartrate ($Na_2C_4H_4O_6$) was used as complexing agent to chelate with Zn^{2+} for obtaining Zn-tartrate complex solution. Indium tin oxide (ITO) glass was used as the substrate for deposition of ZnS thin films. Before deposition, indium tin

*Author for correspondence; E-mail: soonminho@yahoo.com

oxide glass was degreased with ethanol for 10 min. Then, ultrasonically cleaned with distilled water for another 10 min and finally dried in desiccator. Deposition of ZnS thin films was carried out using the following procedure: 25 mL of zinc sulphate (0.3 M) was complexed with 25 mL of sodium tartrate (0.5 M) solution. To this, 25 mL of sodium thiosulfate (0.3 M) was added slowly. pH was adjusted to 3 by addition of hydrochloric acid with constant stirring. Hydrochloric acid also prevents the formation of hydroxyl species and insoluble compounds. The cleaned indium tin oxide glass was immersed vertically into a beaker. The deposition process was carried out at different bath temperatures (60, 70 and 80 °C) in order to determine the optimum conditions for deposition of ZnS thin films. During deposition, the beaker was kept undisturbed. After completion of deposition (120 min), the indium tin oxide glass was removed, washed several times with distilled water and dried naturally in desiccator.

The structural characterization of films was carried out using a Philips PM 11730 diffractometer with $CuK_{á}$ radiation (λ=0.15418 nm) in the scanning angle from 25° to 70°. The surface morphology of films was investigated by atomic force microscopy (Quesant Instrument Corporation, Q-Scope 250). It was operated in a contact mode with Si_3N_4 cantilever. The value of root mean square (RMS) roughness was calculated from the height in the atomic force microscopy images using commercial software.

Results and Discussion

Figure 1 shows X-ray diffraction (XRD) patterns of ZnS thin films deposited on indium tin oxide glass substrate at various bath temperatures. The XRD patterns were found to be polycrystalline with cubic structure. Films deposited at 60 and 70 °C show three peaks at 2θ =28.5°, 33.3° and 56.6° corresponding to (111), (200) and (311) planes, respectively. The observed *d*-spacing values and the standard values are in good agreement with the Joint Committee on Powder Diffraction Standard (JCPDS) values (Reference code: 00-065-0309) (Dubrovin *et al*., 1983) which confirms the deposition of ZnS thin films under the proposed deposition conditions. The lattice parameter values are a=b=c=5.4 Å. XRD results confirm that the films deposited at higher bath temperature proved more favourable as the peak intensity corresponding to ZnS increased. Furthermore, the number of peaks assigned to ZnS also increased. As the bath temperature was increased to 80 °C, additional peak corresponding to (220) plane was obtained. Meanwhile, as the bath temperature was increased from 60 to 80 °C, the intensity of the peak corresponding to (111) plane increased. The (111) plane seems dominant at this stage of experiment. Similar (111) plane was found to be prominent for zinc sulphide thin films reported elsewhere (Hoa *et al*., 2009; Laukaitis *et al*., 2000; Tran *et al*., 2000).

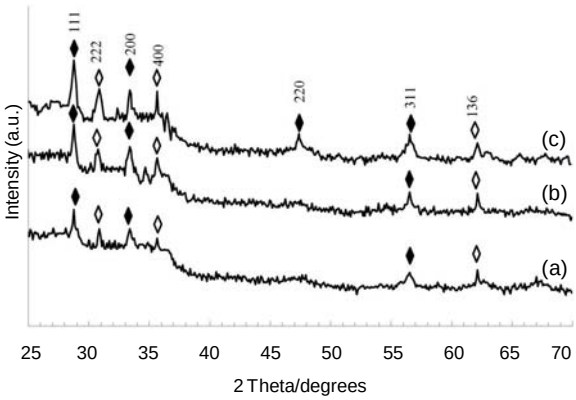

Fig. 1. X-ray diffraction patterns of ZnS thin films deposited at different bath temperatures (a) 60 °C (b) 70 °C (c) 80 °C (◊ $In_{1.875}O_3Sn_{0.125}$; ♦ ZnS)

From the X-ray diffraction results, it can be seen that the presence of indium tin oxide peaks (Reference code: 01-089-4597) in the X-ray diffraction patterns are due to the glass substrate used in the analysis. All three peaks, corresponding to (222), (400) and (136) reflection, were observed. The peaks marked with solid diamonds are associated with reflections of ZnS and those marked with open diamonds can be ascribed to indium tin oxide (Nadaud *et al*., 1998).

The surface morphology of zinc sulphide thin films deposited on indium tin oxide glass substrate was investigated by atomic force microscopy (AFM). Figures 2(a), 3(a) and 4(a) show two-dimensional while Fig. 2(b), 3(b) and 4(b) display three-dimensional AFM images of ZnS thin films deposited at 60, 70 and 80 °C, respectively. The AFM images (Fig. 2a and 2b) indicate that the films deposited at 60 °C have smaller grain sizes (0.5-0.8 μm) and the substrate surfaces are well covered with spherical grains. It is seen that the films deposited at 70 °C (Fig. 3a and 3b) are more homogeneous and more uniform compared to the films

deposited at other bath temperatures. Also, the grain sizes are larger (1.5 and 2 μm) as compared to the films deposited at 60 °C. The ZnS grains are formed on the substrate in an irregular distribution pattern at 80 °C. This observation suggests irregular growth rate of grains. As a result, the films consist of majority of larger grains and a few smaller grain sizes. The size distribution of grains seems to be very broad with the maximum size reaching 3 μm.

Root mean square (RMS) roughness is defined as the standard deviation of the surface height profile from the average height and is the most commonly reported measurement of surface roughness (Jiang *et al.* 2005). The surface roughness values of 63, 124 and 205 nm were observed for the films prepared at 60, 70 and 80 °C, respectively, indicating that the surface roughness increased with the increasing bath temperatures. That means the films deposited at lower bath tempera-

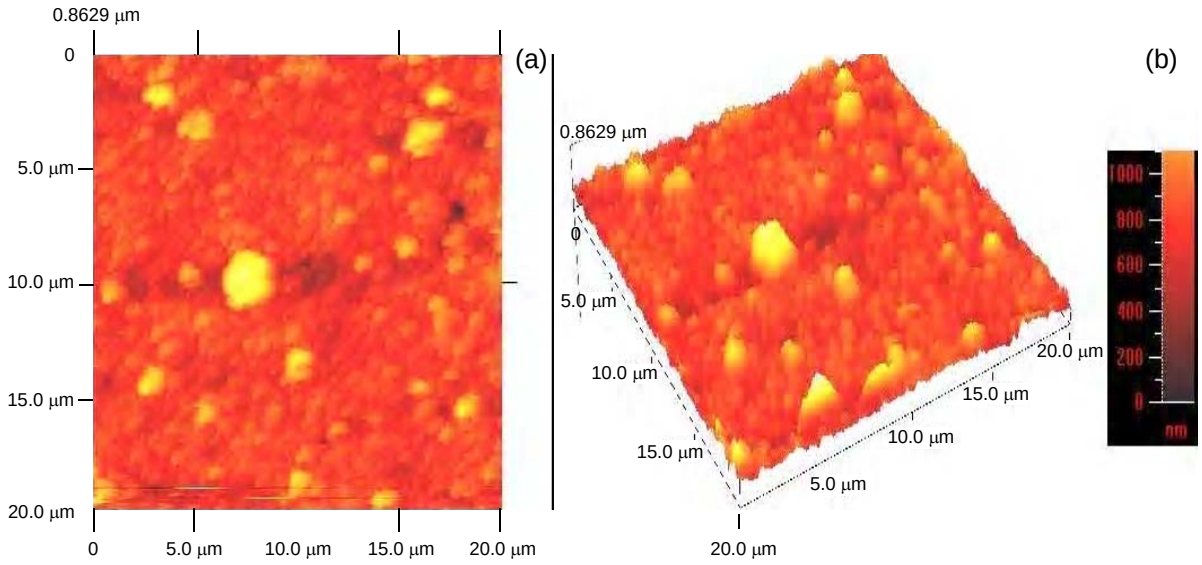

Fig. 2. Two-dimensional (a) and three-dimensional (b) atomic force microscopy images of ZnS thin films deposited at 60 °C.

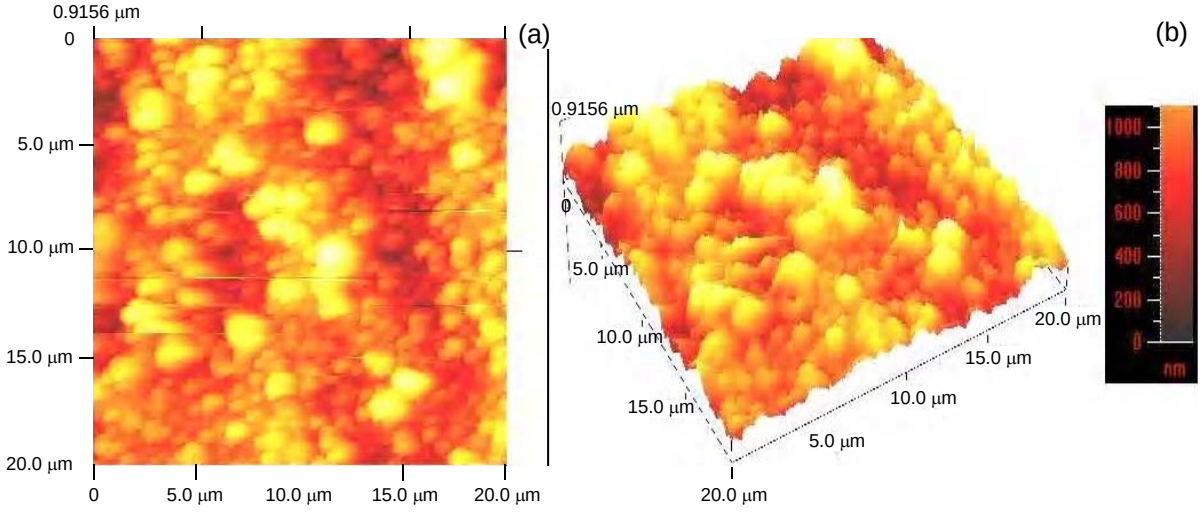

Fig. 3. Two-dimensional (a) and three-dimensional (b) atomic force microscopy images of ZnS thin films deposited at 70 °C.

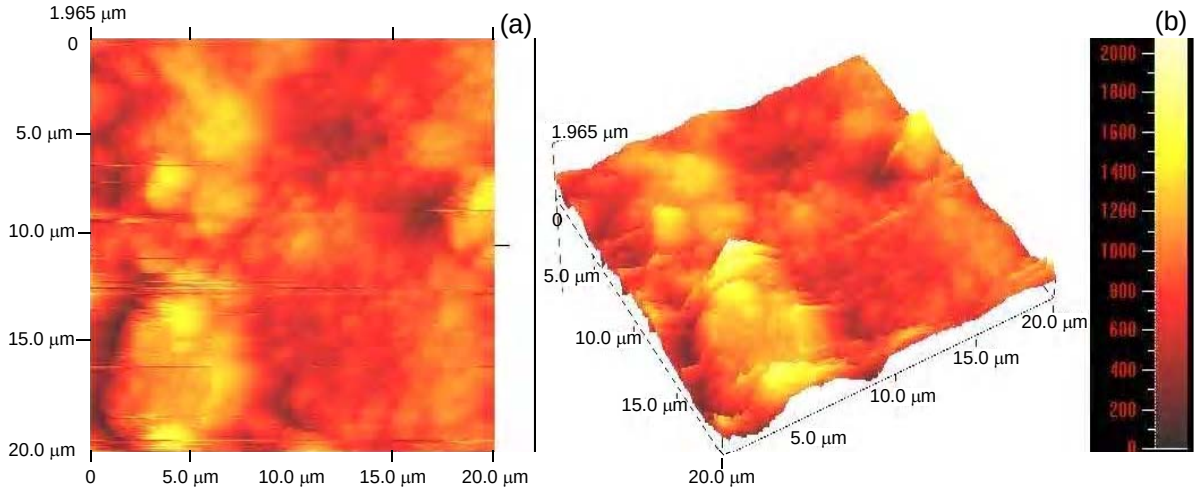

Fig. 4. Two-dimensional (a) and three-dimensional (b) atomic force microscopy images of ZnS thin films deposited at 80 °C.

ture have smoother surface (smaller grain sizes) while the films prepared at higher bath temperature have rougher surface (larger grain sizes). Similarly, the corresponding values of thickness are 863, 916 and 1965 nm, respectively. We can conclude that more materials deposited onto the substrates and thicker films are formed for the films prepared at the higher bath temperature.

Conclusion

The zinc sulphide thin films could be deposited on indium tin oxide glass substrate using zinc sulphate, sodium thiosulphate and sodium tartrate solutions. Based on the X-ray diffraction results, the thin films produced were polycrystalline in nature. The X-ray diffraction patterns showed that the most intense peak corresponded to (111) plane of ZnS. The number of ZnS peaks increased from three to four peaks as the bath temperature was increased from 60 to 80 °C. From the AFM measurements, the grain size, film thickness and surface roughness were found to be dependent on the bath temperature. The films deposited at 60 °C have smaller grain sizes. However, at higher bath temperature (80 °C), larger grain sizes and thicker films are be formed.

Acknowledgement

The authors would like to thank the Department of Chemistry, Universiti Putra Malaysia for provision of laboratory facilities and MOSTI for the National Science Fellowship.

References

Antony, A., Murali, K.V., Manoj, R., Jayaraj, M.K. 2005. The effect of the pH value on the growth and properties of chemical-bath-deposited ZnS thin films. *Materials Chemistry and Physics*, **90:** 106-110.

Anuar, K., Tan, W.T., Dzulkefly, K.A., Atan, M.S., Ho, S.M., Gwee, S.Y., Saravanan, N. 2010. Preparation and characterization of iron sulphide thin films by chemical bath deposition method. *Indonesian Journal of Chemistry*, **10:** 8-11.

Anuar, K., Saravanan, N., Tan, W.T., Atan, M.H., Dzulkefly, K.A., Elas, M.J., Ho, S.M. 2009. Effect of deposition period and pH on chemical bath deposited Cu_4SnS_4 thin films. *Philippine Journal of Science*, **138:** 161-168.

Anuar, K., Zulkarnain, Z., Saravanan, N., Zuriyatina, A., Sharin, R. 2004. Preparation and studies of nickel sulfide thin films in the presence of sodium tartrate as a complexing agent. *Materials Science, (Medziagotyra)*, **10:** 157-161.

Dubrovin, I.V. Budennaya, L.D., Mizetskaya, I.B., Sharkina, E.V. 1983. Phase equilibria in the Sn Te-ZnS system. *Inorganic Materials*, **19:** 1603-1608.

Esparza-Ponce, H.E., Hernandez-Borja, J., Reyes-Rojas, A., Cervantes-Sanchez, M., Vorobiev, Y.V.,

Ramirez-Bon, R., Perez-Robles, J.F., Gonzalez-Hernandez, J. 2009. Growth technology, X-ray and optical properties of CdSe thin films. *Materials Chemistry and Physics*, **113:** 824-828.

Garadkar, K.M., Pawar, S.J., Hankare, P.P., Patil, A.A. 2010. Effect of annealing on chemically deposited polycrystalline CdTe thin films. *Journal of Alloys and Compounds*, **491:** 77-80.

Goudarzi, A., Aval, G.M., Sahraei, R., Ahmadpoor, H. 2008. Ammonia-free chemical bath deposition of nanocrystalline ZnS thin film buffer layer for solar cells. *Thin Solid Films*, **516:** 4953-4957.

Gumus, C., Ulutas, C., Esen, R., Ozkendir, O.M., Ufuktepe, Y. 2005. Preparation and characterization of crystalline MnS thin films by chemical bath deposition. *Thin Solid Films*, **492:** 1-5.

Hoa, T.T.Q., Vu, L.V., Canh, T.D., Long, N.N. 2009. Preparation of ZnS nanoparticles by hydrothermal method. *Journal of Physics Conference Series*, **187:** 1-6.

Jiang, T., Hall, N., Ho, A., Morin, S. 2005. Quantitative analysis of electrodeposited tin film morphologies by atomic force microscopy. *Thin Solid Films*, **417:** 76-85.

Khallaf, H., Oladeji, I.O., Chow, L. 2008. Optimization of chemical bath deposited CdS thin films using nitrilotriacetic acid as a complexing agent. *Thin Solid Films*, **516:** 5967-5973.

Laukaitis, G., Lindroos, S., Tamulevicius, S., Leskela, M., Rackaitis, M. 2000. Stress and surface studies of SILAR grown ZnS thin films on (100) GaAs substrates. *Material Science and Engineering*, **A288:** 223-230.

Li, W.Y., Cai, X., Chen, Q.L., Zhou, Z.B. 2005. Influence of growth process on the structural, optical and electrical properties of CBD-CdS films. *Materials Letters*, **59:** 1-5.

Lokhande, C.D., Yermune, V.S., Pawar, S.H. 1998. Electrodepositions of CdS, ZnS and $Cd_{1-x}Zn_xS$ films. *Materials Chemistry and Physics*, **20:** 283-292.

Mane, R.S., Todkar, V.V., Lokhande, C.D. 2004. Low temperature synthesis of nanocrystalline As_2S_3 thin films using novel chemical bath deposition route. *Applied Surface Science*, **227:** 48-55.

Nadaud, N., Lequeux, N., Nanot, M., Jove, J., Roisnel, T. 1998. Structural studies of tin-doped indium oxide (ITO) and $In_4Sn_3O_{12}$. *Journal of Solid State Chemistry*, **135:** 140-148.

Noikaew, B., Chinvetkitvanich, P., Sripichai, I., Chityuttkan, C. 2008. The influence of growth conditions on the chemical bath deposited ZnS thin films. *Journal of Metals Materials and Minerals*, **18:** 49-52.

Oikkonen, M., Tuomi, T., Luomajarvi, M. 1998. Density of ZnS thin films grown by atomic layer epitaxy. *Journal of Applied Physics*, **63:** 1070-1072.

Raniero, L., Ferreira, C.L., Cruz, L.R., Pinto, A.L., Alves, R.M.P. 2010. Photoconductivity activation in PbS thin films grown at room temperature by chemical bath deposition. *Physica, B: Condensed Matter*, **405:** 1283-1286.

Shao, L.X., Chang, K.H., Hwang, H.L. 2003. Zinc sulfide thin films deposited by RF reactive sputtering for photovoltaic applications. *Applied Surface Science*, **212-213:** 305-310.

Soundeswaran, S., Kumar, O.S., Dhanasekaran, R. 2004. Effect of ammonium sulphate on chemical bath depsoition of CdS thin films. *Materials Letters*, **58:** 2381-2385.

Tran, N.H., Hartmann, A.J., Lamb, R.N. 2000. Epitaxial ZnS thin films grown by single source chemical vapour deposition. *Journal of Physics and Chemistry B*, **104:** 1150-1152.

Yano, S., Schroeder, R., Ullrich, B., Sakai, H. 2003. Absorption and photocurrent properties of thin ZnS films formed by pulsed-laser deposition on quartz. *Thin Solid Films*, **423:** 273-276.