Thickness Dependent Characteristics of Chemically Deposited Tin Sulfide Films

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Abstract In this study, the chemical bath deposition technique was used to produce tin sulfide thin films. The SnS films have been prepared using stannous chloride as a tin ion source and sodium thiosulphate as a sulfur ion source. Ethylenediaminetetraacetic acid disodium salt-2-hydrate was used as complexing agent in the chemical bath deposition process. The crystallographic analysis and film thickness were characterized using X-ray diffraction and profilometer, respectively. There were many deposition parameters which influenced the deposition of SnS films. Each deposition parameter influenced all the others. Based on the experimental results, the thickest films were obtained from a solution of pH 12, deposition time of 3 hours, bath temperature of 50°C, 0.15M of SnCl₂ and 0.5M of Na₂S₂O₃ solution.

Keywords Thickness, Films, Profilometer, Tin sulphide, Complexing Agent

1. Introduction

Investigation and control of film thickness are important in many applications such as semiconductor processing, thin films, optics and magnetic media. The film thickness has a strong influence on the band gap, surface roughness, optical and electrical properties. Because of these reasons, there have been many studies about the film thickness using various ways such as profilometer[1-7], ellipsometer [8], auger electron spectroscopy[9], interferometric method [10-13], weight-difference method [14-15], gravimetric method [16], stylus technique [17], Taylor-Hobson system [18], Fizzau method [19] and atomic force microscopy [20-23].

In this article, we report the influence of various deposition parameters on the properties of tin sulphide thin films using chemical bath deposition. Deposition parameters which are investigated include concentration of solutions, deposition time, bath temperature and pH value. So far, thickness of SnS films which prepared by electro deposition[24], RF sputtering technique [25] and plasma enhanced chemical vapor deposition [26] have been investigated using profilometer method by other researchers. Here, we describe for the first time, an investigation of the thickness of the chemical bath deposited SnS films using profilometer.

2. Materials and Methods

Optical microscope slide with the size of 25.4 mm x 76.2 mm and 1.2 mm thick was an important substrate used to deposit thin films of material. The substrate was prepared and cleaned by the following method. First, it was immersed into the beaker that filled with hydrochloric acid for 24 hours. After that, the microscope slide was immersed into the beaker that contained deionized water and then ultrasonically degreased for 20 minutes by using the sonicator. Later, it was immersed into the beaker that filled with ethanol and ultrasonically degreased for another 20 minutes. Then, the microscope slide was taken out and rinsed with deionized water. Finally, it was ready to be preheated in the oven for about 10 minutes at 120°C.

In this study, specified amount of stannous chloride was weighed into a 100 mL beaker in order to prepare various concentrations of SnCl₂ solution (0.05, 0.1, 0.15 & 0.2 M). Then, about 5 mL of hydrochloric acid was added to dissolve the stannous chloride. After that, 20 mL of 0.1 M ethylenediaminetetraacetic acid disodium salt-2-hydrate (Na₂EDTA) which acted as the complexing agent was added into the beaker. The mixed solutions were stirred well with a glass rod. Then, 20 mL of sodium thiosulphate according to the molarity (0.4, 0.5, 0.6 & 0.7 M) of experimental design was added into the same beaker and the mixture solutions were again stirred. Next, 1M ammonia was added to change the pH into the certain values (pH 9, 10, 11, 12) using pH meter. The preheated microscope slide was mounted in the solution and the beaker was put into the water bath at temperature required (50, 60, 70, 80°C) for a certain period of time (0.5, 1.2, 3 hours). Then, the microscope slide was taken out and dried in the oven for about 10 minutes at
120 °C. Lastly, the sample was preserved in the desiccators for 2-3 days and kept for further analysis.

In order to investigate the crystallographic properties of the tin sulphide thin films, we carried out the X-ray diffraction analysis using Philips PM 11730 diffractometer with CuKα (λ=1.5418 Å) radiation. High surface profilometer (Ambious Technology and the model was XP-200) was performed on each of the samples to measure the thickness for those samples. The surface morphology was observed by a scanning electron microscopy (JEOL, JSM-6400), at 20 kV with a 500X magnification.

3. Results and Discussion

The chemical bath deposition method is based on a chemical reaction between dissolved precursors in aqueous solution. Tin sulphide thin films were deposited on optical microscope slide from bath solution which containing stannous chloride, ethylenediaminetetraacetic acid disodium salt-2-hydrate (Na₂EDTA) and sodium thiosulphate. Stannous chloride and sodium thiosulphate were used to provide the tin ions and sulphur ions, respectively. Meanwhile, Na₂EDTA was used as the complexing agent to prolong the lifetime of the deposition bath besides enhance the adhesion of the deposition films on the optical microscope slide. The use of complexing agent is very common in the preparation of thin films through chemical bath deposition technique. Several scientists have reported the preparation of chemical bath deposited thin films in the presence of EDTA as the complexing agent[27-30].

Based on the experimental results, the chemical bath deposited SnS films could be produced in alkaline medium of pH 9-12 with different thicknesses of 555-1388 nm. Similar results have also been reported by some researchers[31-33]. We further investigated the various concentrations of tin chloride and sodium thiosulfate in all samples. Analysis of the data in the Table 1 revealed that the films deposited using 0.05M SnCl₂ produced thinner films while higher concentration of SnCl₂ solution (0.2M) produced thicker films. On the other hand, the films prepared using higher concentration (0.7M) of sodium thiosulfate produced thinner films than that prepared using 0.5M and 0.6 M of sodium thiosulfate. This indicates that higher concentration of sodium thiosulfate proved unfavorable towards the SnS films prepared using the current method.

In order to explain the influence of deposition time on the formation of SnS films, the films deposited at various deposition times such as 0.5, 1, 2 and 3 hours. It seems clear that the SnS films deposited at longer time (2 & 3 hours) produced thicker films compared with shorter deposition period. It is well known that the films are deposited through nucleation, grain growth, coalescence, filling of channel and film growth processes [34] in chemical bath deposition technique. At the shorter deposition time, a very thin layer of films could be formed which indicating films formation at this stage. As the deposition time was increased, thicker films formation was observed. This indicated that prolonged deposition time was suitable for the chemical bath deposition of SnS films.

| Table 1. The results of the film thickness of the 16 samples that were obtained in experiment |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Experiment     | PH  | Time (hour) | Temperature (°C) | Concentration of SnCl₂, M | Concentration of Na₂S₂O₃, M | Thickness (nm) |
|----------------|-----|-------------|-------------------|---------------------------|---------------------------|----------------|
| 1              | 10  | 2           | 80                | 0.05                      | 0.5                       | 815            |
| 2              | 12  | 0.5         | 80                | 0.1                       | 0.6                       | 1128           |
| 3              | 12  | 3           | 50                | 0.15                      | 0.5                       | 1388           |
| 4              | 10  | 1           | 50                | 0.2                       | 0.6                       | 1313           |
| 5              | 11  | 0.5         | 70                | 0.2                       | 0.5                       | 1061           |
| 6              | 9   | 2           | 70                | 0.15                      | 0.6                       | 863            |
| 7              | 9   | 1           | 60                | 0.1                       | 0.5                       | 1276           |
| 8              | 11  | 3           | 60                | 0.05                      | 0.6                       | 1074           |
| 9              | 9   | 3           | 80                | 0.2                       | 0.7                       | 1200           |
| 10             | 11  | 1           | 80                | 0.15                      | 0.4                       | 1104           |
| 11             | 9   | 0.5         | 50                | 0.05                      | 0.4                       | 736            |
| 12             | 10  | 3           | 70                | 0.1                       | 0.4                       | 998            |
| 13             | 11  | 2           | 50                | 0.1                       | 0.7                       | 1070           |
| 14             | 12  | 1           | 70                | 0.05                      | 0.7                       | 555            |
| 15             | 12  | 2           | 60                | 0.2                       | 0.4                       | 1115           |
| 16             | 10  | 0.5         | 60                | 0.15                      | 0.7                       | 989            |
According to Table 1, we obtained the thickest films for the sample 3 (1388 nm) if compared with other samples. This sample was prepared from a solution of pH 12, deposition time of 3 hours, bath temperature of 50 °C, 0.15M of SnCl₂ and 0.5 M of Na₂S₂O₃ solution. In order to study the structure of the films, X-ray diffraction (XRD) analysis was performed in sample 3. Table 2 shows the comparison between the experimental and standard d-spacing values for sample 3. Meanwhile, Figure 1 indicates the typical X-ray diffraction pattern of SnS films grown at mentioned deposition conditions.

| 2θ  | JCPDS data  | hkl | d-spacing (Å) |
|-----|-------------|-----|--------------|
| 29.08 | 28.37 | 111 | 3.07 | 3.14 |
| 31.69 | 32.87 | 200 | 2.82 | 2.72 |
| 45.46 | 47.17 | 220 | 1.99 | 1.93 |
| 56.51 | 55.97 | 311 | 1.63 | 1.64 |
| 75.35 | 76.14 | 331 | 1.26 | 1.25 |

From the result obtained, the strongest peak of SnS was observed at 2θ = 31.69° which corresponds to the experimental d-spacing value of 2.82 Å with (2 0 0) plane. This showed that the preferred orientation lies along (2 0 0) plane. The second highest peaks was at 2θ = 45.46° which corresponds to the experimental d-spacing value of 1.99 Å with (2 2 0) plane. The other smaller peaks were at 2θ of (29.08°, 56.51° & 75.35°) corresponding to (1 1 1), (3 1 1) and (3 3 1) plane respectively. These peaks observed from the XRD analysis were referred to the standard of Joint Committee on Powder Diffraction Standard (JCPDS) data of SnS [File No: 01-089-2755].

Figure 2 shows the scanning electron microscopy (SEM) micrograph of the sample 3. This SEM micrograph reflects that the surface of the substrate was covered completely. In addition, these obtained films are dense and non-uniform. The grains were distributed randomly over the surface of substrate. The sizes of the grains exhibit random orientation as it varies from one to another, which is in the range 10-25 µm.

4. Conclusion

Thin films of SnS with thicknesses ranging from 555 to 1388 nm have been deposited onto microscope glass
substrate by chemical bath deposition method. Tin chloride and sodium thiosulphate were used as the sources of tin and sulphur, respectively. The films deposited at pH 12 and deposition time of 3 hours could produce thicker films (1388 nm) as compared with other deposition conditions.

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REFERENCES

[1] M.S. Shinde, P.B. Ahirrao, I.J. Patil, R.S. Patil. Studies on nanocrystalline ZnS thin films prepared by modified chemical bath deposition method, Indian Journal of Pure & Applied Physics, Vol. 49, 765-768, 2011.

[2] D. Balamurugan, B.G. Jeyaprakash, R. Chandiramouli. Effect of substrate temperature on the growth of polycrystalline ZnS thin films prepared by spray pyrolysis technique, Journal of Applied Sciences, Vol. 12, 1701-1705, 2012.

[3] P. Roy, S.K. Srivastava. In situ deposition of Sn-doped CdS thin films by chemical bath deposition and their characterization, Journal of Physics D: Applied Physics, Vol. 39, 4771-4776, 2006.

[4] K.R. Murali, K. Thilakavathy, S. Vasantha, R. Oomen. Characteristics of pulse plated CdS,Se,Te thin films, Chalcogenide Letters, Vol. 5, No. 8, 165-170, 2008.

[5] X. Mathew, J.P. Enriquez. Influence of the thickness on structural, optical and electrical properties of chemical bath deposited CdS thin films, Solar Energy Materials & Solar Cells, Vol. 76, 313-322, 2003.

[6] M.A. Olopade, A.M. Awobode, O.E. Awe, T.I. Imale. Structural and optical characteristics of sol gel spin-coated nanocrystalline CdS thin film, International Journal of Research and Reviews in Applied Sciences, Vol. 15, No. 1, 120-124, 2013.

[7] S.J. Castillo, A. Apolinar-Iribe, D. Berman-Mendoza, R. Ramirez-Bon. Characterization of CdS thin films synthesized by chemical bath deposition using glycine as complexing agent, Chalcogenide Letters, Vol. 8, No. 10, 631-636, 2011.

[8] W.D. Park. Structural, optical and photocative properties of chemically deposited nanocrystalline CdS thin films, Transaction on Electrical and Electronic Materials, Vol. 12, No. 4, 164-168, 2011.

[9] A.F. El-Deeb, H.S. Metwally, H.A. Shehata. Structural and electrical properties of InSb-Se thin films. Journal of Physics D: Applied Physics, Vol. 41, No. 12, doi:10.1088/0022-3727/41/12/125305, 2008.

[10] M.E. Popa, G.I. Rusu. Structural characteristics and optical properties of zinc selenide thin films, Optoelectronics and Advanced Materials, Vol. 5, No. 8, 842-845, 2011.

[11] A.F. El-Deeb, H.S. Metwally, H.A. Shehata. Structural and
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7421-7424, 2011.

[26] L.I. Cheng, M.H. Liu, M.X. Wang, S.C. Wang, G.D. Wang, Q.Y. Zhou, Z.Q. Chen. Preparation of SnS films using solid sources deposited by the PECVD method with controllable film characters, Journal of Alloys and Compounds, Vol. 545, 122-129, 2012.

[27] A.U. Ubale, Y.S. Sakhare, S.M. Bombatkar. Influence of the complexing agent (Na$_2$EDTA) on the structural, morphological, electrical and optical properties of chemically deposited FeSe thin films, Materials Research Bulletin, Vol. 48, No. 9, 3564-3571, 2013.

[28] H. Tang, M. Yan, H. Zhang, T. Cui, L. Ni, D. Yang. Effect of different complexing agent on the properties of ZnS thin films prepared by chemical bath deposition, Acta Energiae Solaris Sinica, Vol. 27, No. 4, 373-376, 2006.

[29] A.U. Ubale. Effect of complexing agent on growth process and properties of nanostructured Bi$_2$S$_3$ thin films deposited by chemical bath deposition method, Materials Chemistry and Physics, Vol. 121, No. 3, 555-560, 2010.

[30] S.W. Shin, G.L. Agawane, M.G. Gang, A.V. Moholkar, J.H. Moon, J.H. Kim, J.Y. Lee. Preparation and characteristics of chemical bath deposited ZnS thin films: Effects of different complexing agents, Journal of Alloys and Compounds, Vol. 526, 25-30, 2012.

[31] D.L. Xia, J. Xu, W.Q. Shi, P. Lei, X.J. Zhao. Synthesis and properties of SnS thin films by chemical bath deposition, Key Engineering Materials, Vol. 509, 333-338, 2012.

[32] E. Guneri, F. Gode, C. Ulutas, F. Kirmizigul, G. Alindemir. Properties of p-type SnS thin films prepared by chemical bath deposition, Chalcogenide Letters, Vol. 7, No. 12, 685-694, 2010.

[33] Y. Jayasree, U. Chalapathi, V. Sundara Raja. Growth and characterization of tin sulphide thin films by chemical bath deposition using ethylene diamine tetra-acetic acid as the complexing agent, Thin Solid Films, Vol. 537, 149-155, 2013.

[34] C.H. Wei, C.M. Chang. Polycrystalline TiO$_2$ thin films with different thickness deposited on unheated substrates using RF Magnetron sputtering, Materials Transactions, Vol. 52, No. 3, 554-559, 2011.