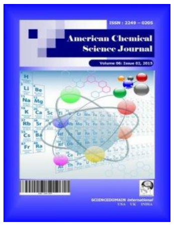

American Chemical Science Journal
14(4): 1-6, 2016, Article no.ACSJ.23356
ISSN: 2249-0205

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Chemical Bath Deposition of ZnSe Thin Films: Investigations of the Growth Conditions

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

Article Information

DOI: 10.9734/ACSJ/2016/23356
Editor(s):
(1) T. P. West, Department of Chemistry, Texas A&M University-Commerce, USA.
Reviewers:
(1) A. Ayeshamariam, Khadir Mohideen College, India.
(2) Hilda Esparza, CIMAV, Mexico.
(3) Anonymous, Indiana University, USA.
(4) Lung-Chien Chen, National Taipei University of Technology, Taiwan.
Complete Peer review History: http://sciencedomain.org/review-history/14545

Original Research Article

Received 27th November 2015
Accepted 2nd January 2016
Published 9th May 2016

ABSTRACT

The main objective of this work was to deposit zinc selenide thin films onto glass substrate by using chemical bath deposition technique. ZnSe films could be used in solar cell applications. The chemical bath deposition method was chosen due to have many advantages if compared to other deposition techniques. Zinc acetate and sodium selenosulphate were used to provide the zinc and selenide ions, respectively. In this work, energy dispersive X-ray analysis (EDAX) and UV-Visible spectrophotometer technique were applied in order to study the properties of obtained ZnSe films which prepared under various pH values ranged from 10.2 to 11.2. The zinc rich content could be observed at these pH values as indicated in EDX results. The band gap was determined by using absorption spectra. The band gap was increased from 2.7 to 2.85 eV as the pH was increased from 10.2 to 11.2.

Keywords: Thin films; zinc selenide; chemical bath deposition; band gap.

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1. INTRODUCTION

The preparation and deposition of chalcogenide thin films are considered as interesting research activities in material chemistry since few decades ago. Because of they have a wide range of applications for solar cells, optoelectronic devices, electronic devices, thin films transistors, and laser devices. Zinc selenide is an example of II-VI compound semiconductor with a direct band gap material. Literature reviews indicated that several methods have been used to prepare zinc selenide thin films such as thermal evaporation [1], atomic layer deposition [2], electrodeposition [3], electron beam evaporation [4], reactive evaporation method [5], pulsed laser deposition [6], successive ionic layer adsorption and reaction [7] and chemical bath deposition [8-12].

In this work, the chemical bath deposition of ZnSe films from an alkaline bath was reported and discussed. This method is chosen because of many advantages such as simple, cheaper and can produce large area of deposition if compared with other deposition techniques. Therefore, many researchers have prepared various types of chalcogenide metal thin films using this method [13-30]. Here, chemical bath deposition method is used to deposit materials onto substrate. During the deposition process, selenide ions will combine to zinc ions to form zinc selenide films. In other words, the formation of a solid phase from a solution could be observed. It is spontaneous reaction. Generally, researcher can describe this method involves two major steps, namely nucleation and growth process. Eventually, the chemical bath deposition method uses a controlled chemical reaction to achieve desired binary, ternary or quaternary compound. In this work, ion by ion and cluster by cluster in metal chalcogenide films were briefly discussed.

The influence of pH which ranged from 10.2 to 11.2 was studied. To our knowledge, there is no report on the investigation of composition of ZnSe films by using EDX technique in the presence of zinc acetate and sodium selenosulphate solutions.

2. MATERIALS AND METHODS

All chemicals such as zinc acetate, hydrazine hydrate, ammonia and hydrochloric acid were of analytical grade and were applied in this experiment without further purification. Microscope glass slide was used as substrates. These substrates were rinsed with ethanol, distilled water and dried in oven as described previously [31] before use. Zinc selenide thin films were prepared from a bath containing 20 mL of zinc acetate (0.1 M) and 2 mL of hydrazine hydrate (55%). The pH of the solution was adjusted to pH 10.2, 10.5, 10.8 & 11.2 by addition of fresh and concentrated ammonia using the pH meter in order to establish the influence of the pH on the properties of the deposits. Following that, 0.01 M of sodium selenosulphate (20 mL) was added before the substrate was immersed in bath. The deposition was conducted at 70°C for 100 min. After completion of deposition process, the deposited films were removed from beaker, washed with distilled water and dried in air.

Energy Dispersive X-ray analysis was used to analyze the elemental composition of the films under scanning electron microscope (JEOL, JSM-6400). Perkin Elmer UV/Vis Lambda 20 Spectrophotometer was used to study the optical absorption in ZnSe thin films. In this experiment, the film-coated microscope glass slide was placed across the sample radiation pathway while the uncoated microscope glass slide was put across the reference path.

3. RESULTS AND DISCUSSION

The obtained chemical bath deposited ZnSe films were analyzed in the range from 300-800 nm using UV-Visible spectrophotometer. The absorption spectra indicate that all the films could be used in solar cell applications because of gradually increasing of absorbance value as shown in Fig. 1. In other words, these results point out that the growth of ZnSe films could be carried out in basic media. However, the highest absorption behavior could be seen in the films prepared in pH 10.2. These data supported the literature review which reported by Ezema et al. [32].

On the other hand, band gap could be calculated by using the Tauc equation as described in equation 1.

$$A = \frac{[k(hv - E_g)^{\frac{n}{2}}]}{hv} \quad (1)$$

The symbols such as v, h, E_g and k could be defined as frequency, Planck's constant value, band gap value and constant value, respectively. The band gap energy could be determined by using absorption data. The band gap such as

2.7, 2.75, 2.85 and 2.8, could be obtained for the films prepared at pH 10.2, 10.5, 10.8 and 11.2, respectively (Table 1). The obtained band gap values match with other researchers which the ZnSe thin films prepared using various deposition methods such as thermal evaporation, spray pyrolysis, vacuum evaporation, electro deposition and chemical bath deposition (Table 2).

Table 1. Band gap of ZnSe films prepared at various pH values

pH	Band gap (eV)
10.2	2.7
10.5	2.75
10.8	2.85
11.2	2.8

The compositional of zinc selenide thin films was studied using energy dispersive X-ray analysis (EDX) as shown in Figs. 2, 3, 4 and 5. These samples were confirmed contain zinc and selenium ions based on the EDX data as presented in Table 3. However, the content of zinc and selenium depends on the pH values. In other words, the accuracy of the spectra can be affected by the nature of the sample. The data produced by EDX analysis consist of spectra indicating peaks corresponding to the elements making up the true composition of the sample being analyzed. The EDX results indicate that the zinc content increases from 50.11% to 50.77 % as the pH was increased from 10.2 to 11.2. Among these samples, the films prepared at pH 10.2 are nearer to stoichiometry.

Table 2. Band gap of ZnSe films reported in the literature which prepared using different deposition methods

Deposition method	Band gap (eV)
Thermal evaporation	2.76 [1]
Chemical bath deposition	2.6-2.69 [9]
Spray pyrolysis	2.65-2.7 [33]
Electro deposition	2.66 [34]
Vacuum evaporation	2.63 [35]
Thermal evaporation	2.14-2.58 [36]
Chemical bath deposition	1.6-1.75 [37]
Chemical bath deposition	2.9 [38]
Chemical bath deposition	2.85 [39]
Successive ionic layer adsorption and reaction	2.8 [40]
Electrodeposition	2.6-2.7 [41]
Thermal evaporation	2.799-2.803 [42]

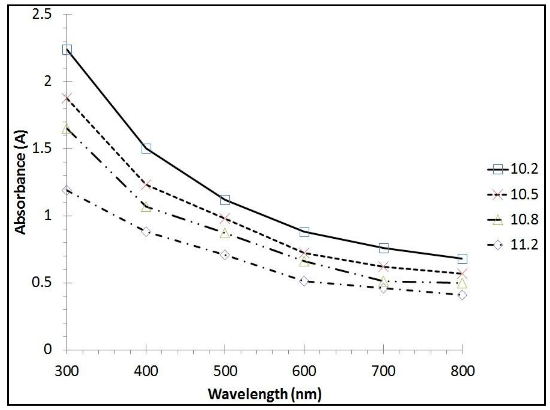

Fig. 1. Optical absorbance versus wavelength of ZnSe films obtained at various pH values

Generally speaking, the formation of zinc selenide films involved two growth mechanisms, namely ion-by-ion and cluster by cluster processes. Firstly, the release of zinc ions and selenide ions in the solutions could be occurred during the deposition process. Secondly, condense on an ion by ion basic on the substrates. The deposition of ZnSe occurs when the ionic product of Zn^{2+} and Se^{2-} exceeds the solubility product of the ZnSe. The ion-by-ion growth results in the thin, uniform and adherent films. Meanwhile, the cluster-by-cluster growth results in the thick and powdery films. Scanning electron microscopy and atomic force microscopy could be used to investigate the morphology and topography in the future works.

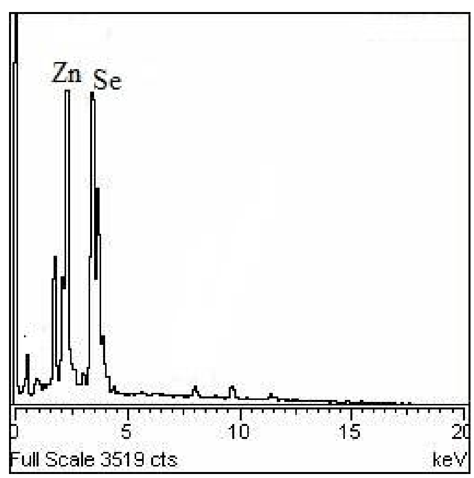

Fig. 2. EDX spectrum of zinc selenide films prepared at pH of 10.2

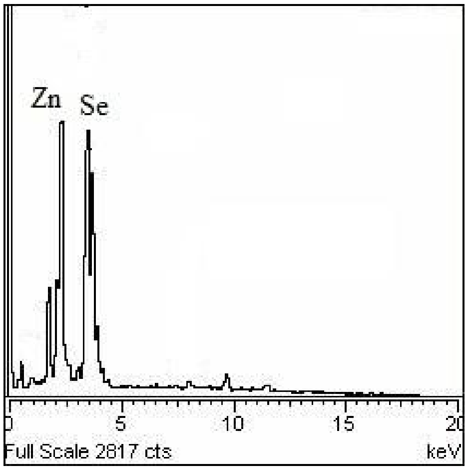

Fig. 3. EDX spectrum of zinc selenide films prepared at pH of 10.5

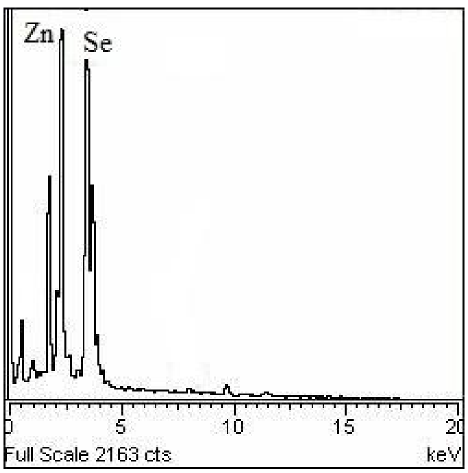

Fig. 4. EDX spectrum of zinc selenide films prepared at pH of 10.8

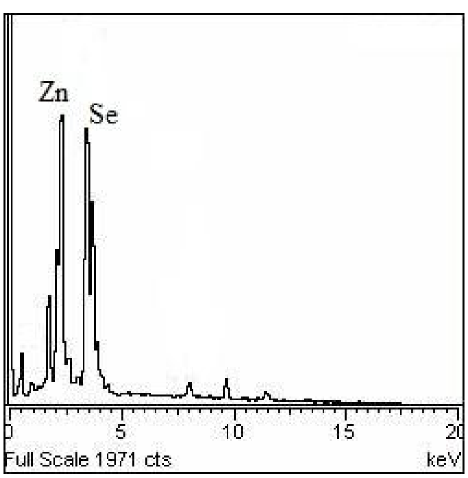

Fig. 5. EDX spectrum of zinc selenide films prepared at pH of 11.2

Table 3. Atomic composition obtained by EDX of ZnSe films deposited at various pH values

pH	Zinc content (%)	Selenium content (%)
10.2	50.11	49.89
10.5	50.34	49.66
10.8	50.66	49.34
11.2	50.77	49.23

4. CONCLUSIONS

ZnSe thin films have been successfully deposited onto glass substrate using chemical bath deposition technique. The band gap was measured from the absorption spectra and its value was keep increasing with the pH value. The ZnSe films prepared at the pH 10.2 show the highest absorption characteristics if compared to the pH values.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Khan TM, Mehmood MF, Mahmood A, Shah A, Raza Q, Iqbal A, Aziz U. Synthesis of thermally evaporated ZnSe thin film at room temperature. Thin Solid Films. 2011;519:5971-5977.
2. Guziewicz E, Godlewski M, Kopalko K, Lusakowska E, Dynowska E, Guziewicz M, Godlewski MM, Philips M. Atomic layer deposition of thin films of ZnSe – Structural and optical characterization. Thin Solid Films. 2004;446:172-177.
3. Kowalik R, Zabinski P, Fitzner K. Electrodeposition of ZnSe. Electrochim. Acta. 2008;53:6184-6190.
4. Kissinger NJS, Velmurugan N, Perumal K. Substrate-temperature-dependent structural and optical properties of ZnSe thin films fabricated by using an electron beam evaporation technique. J. Korean Phys. Soc. 2009;55:1577-1582.
5. Ali Z, Aqili AKS, Maqsood A, Akhtar SMJ. Properties of cu-doped low resistive ZnSe films deposited by two sourced evaporation. Vacuum. 2005;80:302-309.
6. Ryu YR, Zhu S, Han SW, White HW, Miceli PF, Chandrasekhar HR. ZnSe and ZnO film growth by pulsed-laser deposition. Appl. Surf. Sci. 1998;127-129:496-499.

7. Kale RB, Lokhande CD. Room temperature deposition of ZnSe thin films by successive ionic layer adsorption and reaction (SILAR) method. Mater. Res. Bull. 2004;39:1829-1839.
8. Hankare PP, Chate PA, Delekar SD, Asabe MR, Mulla IS. Novel chemical synthetic route and characterization of zinc selenide thin films. J. Phys. Chem. Solids. 2006;67:2310-2315.
9. Deshmukh P, Pingale PC, Kamble SS, Lendave SA, Mane ST, Pirgonde BR, Sharon M. Role of reducing environment in the chemical growth of zinc selenide thin films. Mater. Lett. 2013;92:308-312.
10. Kale RB, Lokhande CD, Mane RS, Han SH. Use of modified chemical route for ZnSe nanocrystalline thin films growth: Study on surface morphology and physical properties. Appl. Surf. Sci. 2006;252:5768-5775.
11. Hankare PP, Chate PA, Chavan PA, Sathe DJ. Chemical deposition of ZnSe thin films: Photoelectrochemical applications. J. Alloy Compd. 2008;461:623-627.
12. Wei AX, Zhao XH, Liu J, Zhao Y. Investigation on the structure and optical properties of chemically deposited ZnSe nanocrystalline thin films. Physica B. 2013;410:120-125.
13. Anuar K, Ho SM, Saravanan N. Preparation of lead selenide thin films by chemical bath deposition method in the presence of complexing agent (tartaric acid). Turk. J. Sci. Technol. 2011;6:17-23.
14. Ezema FI, Ekwealor ABC, Asogwa PU, Ugwuoke PE, Chigbo C, Osuji RU. Optical properties and structural characterizations of Sb_2S_3 thin films deposited by chemical bath deposition technique. Turk. J. Phys. 2007;31:205-210.
15. Anuar K, Ho SM, Atan S, Haron MJ. The effect of the pH value on the growth and properties of chemical bath deposited SnS thin films. Res. J. Chem. Environ. 2011;15: 45-48.
16. Raniero L, Ferreira CL, Cruz LR, Pinto AL, Alves RM. Photoconductivity activation in PbS thin films grown at room temperature by chemical bath deposition. Physica B: Condensed Matter. 2010;405:1283-1286.
17. Anuar K, Ho SM, Tan WT, Ngai CF. Influence of triethanolamine on the chemical bath deposited NiS thin films. Am. J. Appl. Sci. 2011;8:359-361.
18. Anuar K, Ho SM. Deposition and characterization of MnS thin films by chemical bath deposition method. Int. J. Chem. Res. 2010;1:1-5.
19. Anuar K, Ho SM, Atan S, Saravanan N. X-ray diffraction and atomic force microscopy studies of chemical bath deposited FeS thin films. Stud. U. Babes Bol. Chem. 2010;55:5-11.
20. Song WC, Lee JH. Growth and characterization of $Zn_xCd_{1-x}S$ films prepared by using chemical bath deposition for photovoltaic devices. J. Korean Phys. Soc. 2009;54:1660-1665.
21. Anuar K, Zulkefly K, Atan S, Tan WT, Ho SM, Saravanan N. Preparation and studies of chemically deposited Cu_4SnS_4 thin films in the presence of complexing agent Na_2EDTA. Indian J. Eng. Mater. Sci. 2010;17:295-298.
22. Anuar K, Nani R, Ho SM. Atomic force microscopy studies of zinc sulfide thin films. Int. J. Adv. Eng. Sci. Technol. 2011;7:169-172.
23. Ubale AU. Effect of complexing agent on growth process and properties of nanostructured Bi_2S_3 thin films deposited by chemical bath deposition method. Mater. Chem. Phys. 2010;121:555-560.
24. Anuar K, Ho SM, Tan WT, Kelvin, Saravanan N. Composition, morphology and optical characterization of chemical bath deposited ZnSe thin films. Eur. J. Appl. Sci. 2011;3:75-80.
25. Asenjo B, Guilln C, Chaparro AM, Saucedo E, Bermudez V, Lincot D, Herrero J, Gutirrez MT. Properties of In_2S_3 thin films deposited onto ITO/glass substrates by chemical bath deposition. J. Phys. Chem. Solids. 2010;71:1629-1633.
26. Anuar K, Ho SM, Tee WT, Lim KS, Saravanan N. Morphological characterization of CuS thin films by atomic force microscopy. Res. J. Appl. Sci. Eng. Technol. 2011;3:513-518.
27. Gopakumar N, Anjana P, Vidyadharan PP. Chemical bath deposition and characterization of CdSe thin films for optoelectronic applications. J. Mater. Sci. 2010;45:6653-6656.
28. Ho SM. Influence of complexing agent on the growth of chemically deposited $Ni_3Pb_2S_2$ thin films. Oriental J. Chem. 2014;30:1009-1012.
29. Khallaf H, Oladeji IO, Chow L. Optimization of chemical bath deposited CdS thin films using nitrilotriacetic acid as a complexing agent. Thin Solid Films. 2008;516:5967-5973.

30. Raniero L, Ferreira CL, Cruz LR, Pinto AL, Alves RMP. Photoconductivity activation in PbS thin films grown at room temperature by chemical bath deposition. Phys. B: Condens. Matter. 2010;405:1283-1286.
31. Anuar K, Ho SM, Kelvin, Tan WT, Saravanan N. Influence of pH on the morphology properties of ZnSe thin films studied by atomic force microscopy. Eur. J. Sci. Res. 2011;66:592-599.
32. Ezema FI, Ekwealor ABC, Osuji RU. Effect of thermal annealing on the band GAP and optical properties of chemical bath deposited ZnSe thin films. Turk. J. Phys. 2006;30:157-163.
33. Oztas M, Bedir M, Bakkaloglu OF, Ormanci R. Effect of Zn:Se ratio on the properties of sprayed ZnSe thin films. Acta Phys. Pol., A. 2005;107:525-534.
34. Mahalingam T, Kathalingam A, Lee SN, Moon SW, Kim YD. Studies of electrosynthesized zinc selenide thin films. J. New Mater. Electrochem. Syst. 2005;10: 15-19.
35. Venkatachalam S, Soundararajan D, Peranantham P, Mangalaraj D, Narayandass SK, Velumani S, Schabes-Retchkiman P. Spectroscopic ellipsometry (SE) studies on vacuum-evaporated ZnSe thin films. Mater. Charact. 2007;58:715-720.
36. Al-Kuhaili MF, Kayani A, Durrani SMA, Bakhtiari IA, Haider MB. Band gap engineering of zinc selenide thin films through alloying with cadmium telluride. ACS Appl. Mater. Interfaces. 2013;5:5366-5372.
37. Ezema FI, Ekwealor ABC, Osuji RU. Effect of thermal annealing on the band gap and optical properties of chemical bath deposited ZnSe thin films. Turk. J. Phys. 2006;30:157-163.
38. Lokhande CD, Patil PS, Tributsch H, Ennaoui A. ZnSe thin films by chemical bath deposition method. Sol. Energy Mater. Sol. Cells. 1998;55:379-393.
39. Kale RB, Lokhande CD. Influence of air annealing on the structural, morphological, optical and electrical properties of chemically deposited ZnSe thin films. Appl. Surf. Sci. 2005;252:929-938.
40. Kale RB, Lokhande CD. Room temperature deposition of ZnSe thin films by successive ionic layer adsorption and reaction (SILAR) method. Mater. Res. Bull. 2004;39:1829-1839.
41. Riveros G, Gomez H, Henriquez R, Schrebler R, Marotti RE, Dalchiele EA. Electrodeposition and characterization of ZnSe semiconductor thin films. Sol. Energy Mater. Sol. Cells. 2001;70:255-268.
42. Bhuiyan MRA, Miah MAH, Begum J. Substrate temperature effect on the structural and optical properties of ZnSe thin films. J. Bangladesh Acad. Sci. 2012;36:233-240.

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