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Application of Energy Dispersive X-Ray Analysis Technique in Chalcogenide Metal Thin Films: Review

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Abstract: Thin films have been synthesized in the presence of different precursors using various deposition methods such as chemical bath deposition, electrodeposition and successive ionic layer adsorption and reaction. The obtained thin films could be investigated using energy dispersive X-ray (EDX) technique in terms of compositional characterization. Generally, EDX analyzer was equipped with the scanning electron microscopy as described by many researchers. In this work, the EDX analysis has been carried out in order to improved quality control and rapid identification of source.

Key words: Compositional analysis · Atomic percentage · Energy dispersive x-ray technique · Thin films · Scanning electron microscopy

INTRODUCTION

Nowadays, there are many analytical techniques could be used to characterize samples by researchers. For example, X-ray diffraction [1-6] was used to investigate the structure of the samples. The morphology and topography of films were studied using scanning electron microscopy [7-14] and atomic force microscopy[15-26], respectively. One of the common analytical techniques is called energy dispersive X-ray analysis (EDX). EDX is employed to investigate the compositional of samples by many researchers. As a briefly introduce the EDX, there are four main components namely excitation source, X-ray detector, pulse processor and analyzer. EDX is emerged as an important analytical technique due to some advantages including rapid identification of source, improved quality control, reduced sample damaged, high count rates and processing. As a result, there are several industries such as aerospace, automotive, semiconductors, electronics and materials are using EDX facility.

In this work, the compositional of samples was investigated using EDX will be discussed and reported. EDX when combined with scanning electron microscopy can provide elemental analysis on areas as small as nanometers in diameter. The data generated by EDX analysis could be interpreted in spectra and atomic percentage of elemental.

Literature Survey: Generally speaking, the compositional analysis of the films could be carried out by the energy dispersive x-ray (EDX) technique. There are some of the examples have been reported by many researchers as shown in literature review.

Electro deposition of cadmium indium sulfide thin films was carried out at -580 mV versus SCE (saturated calomel electrode) for 2 hours was reported by Kokate *et al*. [27]. They produced 1-2 μmthick layers at the pH of 3 at the bath temperature of 45 °C. They suggest that the formation of good quality films is possible from acidic aqueous bath containing 0.1 M $InCl_3$, 0.1 M $CdSO_4$ and 0.01 M $Na_2S_2O_3$. EDX results show that the In:Cd ratio is almost 2 and Cd:S ratio is almost 4. Therefore, the sample was confirmed as $CdIn_2S_4$.

Chemical bath deposited cadmium selenide films have been prepared by Kale and Lokhande[28]in the presence of cadmium acetate and sodium selenosulfate. The obtained films are red in colour and specularly reflective. The EDX analysis indicated that the average atomic percentage of Cd:Se was 50.5:49.5. It means that the samples contain slightly Se^{2-} deficient. On the other hand, CdSe films were prepared using electrodeposition method

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for 30 minutes at pH 2.75 by Pawar *et al.* [29]. The EDX analysis reflects that the sample was slightly selenium rich. The average atomic percentage of Cd:Se was 44.64: 55.36 as indicated in EDX pattern.

Soliman *et al.* [30] have reported the preparation of CdS films using electrodeposition method. The chemicals such as $CdCl_2$ and $Na_2S_2O_4$ were used in order to produce thin films under various deposition potentials. They conclude that the CdS films prepared at -0.6V (SCE) have an excess of tellurium (48.44%) if compared to cadmium (46.97%). Meanwhile, the films displayed a nearly stoichiometric cadmium(49.21%)/tellurium (49.49%) at the deposition potential of -0.65 V (SCE). On the other hand, the CdS films were deposited on soda lime glass using chemical bath deposition method by Pushpalatha *et al.* [31]. The obtained films were characterized using EDX before and after air annealing at 300 °Cin furnace for 1hour. They observe that the stoichiometric thin films with ratio Cd:S = 19.01: 17.88 was obtained for the annealed films. However, the average atomic percentage ratio was Cd:S = 60.45%: 29.13% (2:1) for the as-deposited films as reported by them.

Anuar *et al.* [32] have proposed that the preparation of nickel selenide thin films using simple chemical bath deposition method. The films were successfully deposited onto microscope glass slides from aqueous solution containing nickel sulphate, sodium selenite and ethylenediaminetetraacetic acid disodium salt (Na_2EDTA). Deposition of films was carried out for 150 minutes at pH 2.5 under unstirred conditions. They claim that the atomic ratio of Ni:Se was 1:1 for the films prepared at bath temperature of 65 °C. The EDX results reflect that the atomic percentage obtained was51.36% and 48.64% for the nickel and sulfur, respectively.

Mali *et al.* [33] have reported the synthesis of Cu_2ZnSnS_4 (CZTS) using successive ionic layer adsorption and reaction (SILAR) method. The formation of films could be occurred from the bath containing cationic (Cu^{2+}, Zn^{2+} and Sn^{2+}) and anionic (S^{2-}) precursors, respectively. The compositional of films was investigated using EDX. They observe that the elemental ratios for Cu:Zn:Sn:S were consistent with the 2:1:1:4 stoichiometry. Furthermore, they suggest that the EDAX spectrum showed copper poor and zinc rich, Cu/(Zn+Sn)=0.47 and Zn/Sn=2.15, to improve the conversion efficiency. On the other hand, EDX method was employed by Subramaniam *et al.* [34] in order to produce thin films on indium tin oxide substrate. They found that the composition of the films is Cu (18.15 %), zinc (17.54 %), Sn (16.03 %) and sulphur (48.28 %). Additionally, they found that the ratios for Cu/(Zn+Sn) was 0.54, Zn/Sn was 1.09 and S/(Cu+Zn+Sn) was 0.93.

Zinc acetate, thiourea, triethanolamine and tri-sodium citrate were used to prepare zinc sulfide thin films onto glass substrate by Gode *et al.* [35]. The influence of deposition times on the compositional was investigated by using EDX technique. They found that the average atomic ratio of sulfur:zinc provides the value of 0.51, 0.56, 0.57 and 0.58 for the deposition periods such as 3, 3.5, 4 and 4.5 hours, respectively. In other words, they claim that the average atomic ratio of S:Zn increases with increasing deposition period and also the surface of the films was rich in zinc content.

Seghaier *et al.* [36] have presented a chemical bath deposition method to prepare PbS films at room temperature for 1 hour. The chemical bath contains lead nitrate, sodium hydroxide and thiourea. The EDX pattern indicated that the stoichiometric compound (Pb:S equal to 1) was confirmed.

Bi_2S_3 thin films were deposited on glass substrate using chemicals such as bismuth nitrate, EDTA and sodium thiosulphate as reported by Balasubramanian *et al.* [37]. The compositional of chemical bath deposited films was investigated using EDX technique. They pointed out that the composition was found stoichiometric. This confirmed that the formation of Bi_2S_2 with the atomic percentage of Bi (52.09%):S (47.91%).

MnS films were deposited onto soda lime glass substrate at room temperature by Gumus *et al.* [38] using inexpensive chemical bath deposition method. Manganese acetate and thioacetamide were used as manganese and sulphur source, respectively. The films obtained show that in good stoichiometric ratio (Mn:S was 1:0.82) as indicated in EDX spectrum.

Iron selenide films have been deposited onto stainless steel substrates using electrodeposition method in the presence of ferric chloride and selenium dioxide. During the experiment, the electrodeposition was carried out on the unit area (1cm^2) of substrates at the deposition potential of 0.244V/SHE (standard hydrogen electrode) in an unstirred bath as proposed by Pawar *et al*. [39]. The EDX results pointed out that the atomic percentage of Fe:Se was 60:40. In other words, the obtained films were rich in iron.

The deposition of zinc cadmium selenide thin films from aqueous acidic bath was conducted by Chandramohan *et al.* [40]. During experiment, a platinum mesh, saturated calomel electrode and tin oxide coated glass substrate was used as counter, reference and working electrode. They found that a small percentage of excess selenium in all the electrodeposited films before annealing as indicated in EDX studies.However, the reduction in the selenium content was observed to be reduced after annealing process.

Lead selenide thin films were prepared from the solutions containing lead acetate, selenium oxide and complexing agent. The composition of the electrodeposited films prepared under various deposition potentials was reported by Li *et al.* [41], The reddish selenium films (Pb:Se was 10 %:90 %) and silvery lead films (Pb:Se was 85 %: 15 %) were obtained for the films prepared at the potential of -0.7V and -0.9V (SCE), respectively. They suggest that nearly stoichiometric films (Pb:Se was 49%:51%) could be found at the deposition potential of -0.8 V, at 50 °C for 10 minutes.

The synthesis of zinc mercury selenide thin films was reported by Mahalingam *et al.* [42] using electro deposition method. The films were deposited onto conducting glass from aqueous solution bath containing $ZnSO_4$, $HgCl_2$ and SeO_2 The films were characterized using EDAX in order to study the compositional of films. They conclude that the mercury rich and zinc rich could be detected for the films prepared at more positive (>-0.6 V versus SCE) and more negative (<-0.8 V versus SCE), respectively.

Copper sulphide thin films were prepared using chemical bath deposition method as described by Anuar *et al.* [43]. The chemical bath contained thiourea, copper sulfate, tartaric acid in order to form thin films onto microscope glass substrates. The compositional of films was studied using EDX method. The results indicate that the average atomic ratio of copper to sulfur was 1.89, 1.95 and 2.25 for the films prepared at 55, 65 and 75 °C, respectively. In other words, they conclude that the average atomic ratio of Cu/S increases with increasing bath temperature.

The obtained EDX results showing that it is often necessary to identify the different elements associated with the sample. Nowadays, the EDX instrument is operated using very sophisticated software. Furthermore, today EDX systems are much less expensive and much more user friendly.

CONCLUSION

Binary, ternary and quaternary thin films have been synthesized by using various deposition techniques onto substrate in the presence of different precursors. The compositional of thin films was studied using EDX technique. The stoichiometric composition of sample could be determined using the data generated by EDX analyzer.

REFERENCES

1. Patidar, D., K.S. Rathore, N.S. Saxena, K. Sharma and T.P. Sharma, 2008. Energy band gap and conductivity measurement of CdSe thin films. Chalcogenide Letters, 5: 21-25.
2. Anuar, K., W.T. Tan, H.A. Abdul, N. Saravanan and S.M. Ho, 2010. Deposition and characterization of Cu_4SnS_4 thin films by chemical bath deposition method. Macedonian Journal of Chemistry and Chemical Engineering, 29: 97-103.
3. Kang, S.H., Y. Kim, D. Choi and Y. Sung, 2006. Characterization of electrodeposited $CuInSe_2$ film. ElectrochimicaActa, 51: 4433-4438.
4. Anuar, K., S.M. Ho, M. Shanthi and N. Saravanan, 2010. Synthesis of PbSe thin film by chemical bath deposition and its characterization using XRD, SEM and UV-Vis spectrophotometer. Makara Sains, 14: 117-120.
5. Poulomi, R. and K.S. Suneel, 2006. In situ deposition of Sn doped CDs thin films by chemical bath deposition and their characterization. Journal of Physics D: Applied Physics, 39: 4771-4776.
6. Anuar, K., S.M. Ho, S. Atan and N. Saravanan, 2010. X-ray diffraction and atomic force microscopy studies of chemical bath deposited FeS thin films. Studia Universitatis Babes-Bolyai Chemia, 55: 5-11.
7. Ho, S.M., 2015. Scanning electron microscopy study of surface morphology of $Ni_3Pb_2S_2$ thin films. Asian Journal of Chemistry, 27: 3851-3853.
8. Kostoglou, M., N. Andritsos and A.J. Karabelas, 2003. Incipient CdS thin film formation. Journal of Colloid and Interface Science, 263: 177-189.
9. Anuar, K., S.M. Ho, K.S. Lim and N. Saravanan, 2011. SEM, EDAX and UV-Visible studies on the properties of Cu_2S thin films. Chalcogenide Letters, 8: 405-410.

10. Mahalingam, T., S. Thanikaikarasan, R. Chandramohan, M. Raja, C. Sanjeeviraja, J. Kim and Y.D. Kim, 2007. Effects of bath temperature in electrodeposited $FeSe_2$ thin films. Materials Chemistry and Physics, 106: 369-374.
11. Ho, S.M., 2015. Morphological studies of $Ni_3Pb_2S_2$ thin films by means of scanning electron microscopy technique. International Journal of Applied Chemistry, 11: 363-369.
12. Cheng, S., Y. He and G. Chen, 2008. Structure and properties of SnS films prepared by electrodeposition in presence of EDTA. Materials Chemistry and Physics, 110: 449-453.
13. Ho, S.M., 2015. Chemical bath deposition of Nickel lead sulphide films: sem studies. Journal of Chemistry and Chemical Research, 1: 14-19.
14. Baban, C. and G.I. Rusu, 2003. On the structural and optical characteristics of CdSe thin films. Applied Surface Science, 211: 6-12.
15. Anuar, K., S.M. Ho, K.S. Lim and N. Saravanan, 2013. Investigation of morphological properties of the copper sulfide films in acidic media based on atomic force microscopy. International Research Journal of Chemistry, 3: 62-68.
16. Anuar, K., S.M. Ho, W.T. Tan, S.M. Ho and N. Saravanan, 2012. Temperature-dependent surface topography analysis of SnSe thin films using atomic force microscopy. Asian Journal of Research in Chemistry, 5: 291-294.
17. Anuar, K., S.M. Ho, K.S. Lim and N. Saravanan, 2011. Surface morphology of CuS thin films observed by atomic force microscopy. SQU Journal for Science, 16: 24-33.
18. Pathan, H.M. and C.D. Lokhande, 2005. Chemical deposition and characterization of copper indium diselenide thin films. Applied Surface Science, 245: 328-334.
19. Anuar, K., S.M. Ho, W.T. Tee, K.S. Lim and N. Saravanan, 2011. Morphological characterization of CuS thin films by atomic force microscopy. Research Journal of Applied Sciences, Engineering and Technology, 3: 513-518.
20. Cortes, A., H. Gomez, R.E. Marotti, G. Riveros and E.A. Dalchiele, 2004. Grain size dependence of the band gap in chemical bath deposited CdS thin films. Solar Energy Materials and Solar Cells, 82: 21-34.
21. Anuar, K., S.M. Ho, Kelvin, W.T. Tan and N. Saravanan, 2011. Influence of pH on the morphology properties of ZnSe thin films studied by atomic force microscopy. European Journal of Scientific Research, 66: 592-599.
22. Rabchynski, S.M., D.K. Ivanou and E.A. Streltsov, 2004. Photoelectrochemical formation of indium and cadmium selenide nanoparticles through Se electrode precursor. Electrochemistry Communications, 6: 1051-1056.
23. Ho, S.M., 2014. Atomic force microscopy investigation of the surface morphology of $Ni_3Pb_2S_2$ thin films. European Journal of Scientific Research, 125: 475-480.
24. Anuar, K., N. Saravanan, K. Zulkefly, S. Atan, W.T. Tan and S.M. Ho, 2010. Influence of complexing agent (Na_2EDTA) on chemical bath deposited Cu_4SnS_4 thin films.Bulletin of the Chemical Society of Ethiopia, 24: 259-266.
25. Anuar, K., S.M. Ho, W.T. Tan, S. Atan, K. Zulkefly, H. Jelas and N. Saravanan, 2008. Cathodic electrodeposition of chalcogenide thin films $Cu_4 SnS_4$ for solar cells. CMU. J. Nat. Sci., 7(2): 317-326.
26. Anuar, K., S.M. Ho, S. Atan, H. Jelas and N. Saravanan, 2011. Chemical bath deposition of SnS thin films: AFM, EDAX and UV-Visible characterization. Oriental Journal of Chemistry, 27: 1375-1381.
27. Kokate, A.V., M.R. Asabe, S.D. Delekar, L.V. Gavali, I.S. Mulla, P.P. Hankare and B.K. Chougule, 2006. Photoelectrochemical properties of electrochemically deposited $CdIn_2S_4$ thin films. Journal of Physics and Chemistry of Solids, 67: 2331-2336.
28. Kale, R.B. and C.D. Lokhande, 2005. Band gap shift, structural characterization and phase transformation of CdSE thin films from nanocrystalline cubic to nanorod hexagonal on air annealing. Semiconductor Science and Technology, 20: 1-9.
29. Pawar, S.M., A.V. Moholkar and C.H. Bhosale, 2007. Influence of pH on electrochemically deposited CdSe thin films. Materials Letters, 61: 1034-1038.
30. Soliman, M., A.B. Kashyout, M. Shabana and M. Elgamal, 2001. Preparation and characterization of thin films of electrodeposited CdTe semiconductors. Renewable Energy, 23: 471-481.

31. Pushpalatha, H.L., S. Bellappa, T.N. Narayanaswamy and R. Ganesha, 2014. Structural and optical properties of CdS thin film obtained by chemical bath deposition and effect of annealing. Indian Journal of Pure and Applied Physics, 52: 545-549.
32. Anuar, K., S.M. Ho, W.T. Tan and R. Yazid, 2011. Preparation and characterization of chemical bath deposited NiSe thin films. Ozean Journal of Applied Sciences, 4: 363-372.
33. Mali, S.S., P.S. Shinde, C.A. Betty, P.N. Bhosale, Y.W. Oh and P.S. Patil, 2012. Synthesis and characterization of Cu_2ZnSnS_4 thin films by SILAR method. Journal of Physics and Chemistry of Solids, 73: 735-740.
34. Subramaniam, E.P., G. Rajesh, N. Muthukumarasamy, M. Thambidurai, V. Asokan and D. Velauthapillai, 2014. Solar cells of Cu_2ZnSnS_4 thin films prepared by chemical bath deposition method. Indian Journal of Pure and Applied Physics, 52: 620-624.
35. Gode, F., C. Gumus and M. Zor, 2007. Investigations on the physical properties of the polycrystalline ZnS thin films deposited by the chemical bath deposition method. Journal of Crystal Growth, 299: 136-141.
36. Seghaier, S., N. Kamoun, R. Brini and A.B. Amara, 2006. Structural and optical properties of PbS thin films deposited by chemical bath deposition. Materials Chemistry and Physics, 97: 71-80.
37. Balasubramanian, V., N. Suriyanarayanan and R. Kannan, 2012. Optimization of chemical bath deposited bismuth sulphide thin films on glass substrate. Archives of Applied Science Research, 4: 1864-1868.
38. Gumus, C., C. Ulutas, R. Esen, O.M. Ozkendir and Y. Ufuktepe, 2005. Preparation and characterization of crystalline MnS thin films by chemical bath deposition. Thin Solid Films, 492: 1-5.
39. Pawar, S.M., A.V. Moholkar, U.B. Suryavanshi, K.Y. Rajpure and C.H. Bhosale, 2007. Electrosynthesis and characterization of iron selenide thin films. Solar energy Materials and Solar Cells, pp: 560-565.
40. Chandramohan, R., T. Mahalingam, J.P. Chu and P.J. Sebastian, 2004. Preparation and characterization of semiconducting $Zn_{1-x}Cd_xSe$ thin films. Solar Energy Materials and Solar Cells, 81: 371-378.
41. Li, K., X. Meng, X. Liang, H. Wang and H. Yan, 2006. Electrodeposition and characterization of PbSe films on indium tin oxide glass substrates. Journal of Solid State Electrochemistry, 10: 48-53.
42. Mahalingam, T., A. Kathalingam, S. Velumani, S. Lee, K.S. Lew and Y.D. Kim, 2005. Characterization of electrodeposited $Zn_{1-x}Hg_xSe$ thin films, Semiconductor Science and Technology, 20: 749-754.
43. Anuar, K., S.M. Ho, K.S. Lim and N. Saravanan, 2011. SEM, EDAX and UV-Visible studies on the properties of Cu_2S thin films. Chalcogenide Letters, 8: 405-410.