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Study of Optical Properties of Chalcogenide Metal Thin Films by Means of UV-Visible Spectrophotometer: A Review

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Abstract: In this work, UV-visible spectrophotometer was used to investigate the band gap energy and optical properties of obtained thin films prepared by using various deposition methods in the range of 200 to 800 nm. This tool was selected due to its quick analysis ability and easy to use by many researchers. Nowadays, thin films characterization technology is in high demand in all engineering and material science areas. This is because of the properties of thin films can vary dramatically under various deposition conditions.

Key words: UV-visible spectrophotometer · Band gap · Absorption · Transmittance · Thin films

INTRODUCTION

UV-Visible spectrophotometer could be used to analyze substance rapidly in the field of medicine, material science, pharmacy, forensic and food industry. It is consisted of few parts such as sources, wavelength selector, sample containers, detector and signal processor. Generally, this tool is not difficult to use, therefore is widely used as described by many researchers[1-12]. Basically, there are two types of UV-visible spectrophotometer, namely single beam and double beam spectrophotometer. Single beam tool requires scientist to measure a baseline sample before analyzing other sample. However, double beam spectrophotometer was used to monitor the reference sample while researchers can observe the one they wish to analyze during the experiment. Researchers have found that double beam spectrophotometer is more accurate and beneficial than single beam spectrophotometer.

UV-visible spectrophotometer uses light in the visible portion (400-800 nm) and ultraviolet region (200-400 nm). Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. Spectroscopic analysis can be presented as transmittance and absorbance and is generally carried out in solutions, but solids and gases may also be investigated. In this work, UV-visible spectrophotometer was employed in the chalcogenide metal semiconductor industry to measure the band gap and optical properties of films deposited onto substrate.

Literature Survey: Photochemical deposition has been developed to deposit zinc sulphide thin films from an aqueous solution by Gunasekaran *et al*. [13]. During the experiment, sulphur atoms have to be released from thiosulphate ions in the acidic medium and finally react with zinc ions. The optical transmission spectra have been recorded before and after deposition as reported by them. By measuring transmission of solutions, they claim that the absorption edge near 300 nm was because of thiosulphate ions. At the same time, they observe that the absorption by other species is negligible within the spectral range of the mercury lamp. Finally, they point out that reduces in the transmission are due to the release of sulphur.

Manganese sulphide thin films have been prepared and characterized using UV-Visible spectrophotometer by Agbo *et al.* [14]. The films indicate high transmittance in the ultraviolet region. The results make the films good materials for antireflection coatings and for solar thermal applications in flat plate collectors, house heating for solar chick brooding and other uses.

Chemical bath deposition method was adopted for the preparation of CdSe films by Eya [15]. The variation of transmittance as functions of wavelength ranging from

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200-800 nm was investigated. The obtained results show that the transmittance is proportional to the wavelength. He found that the transmittance is almost zero in the UV region but suddenly increases within the visible portion of the spectrum.

The copper sulphide and zinc sulphide thin films were prepared by Ilenikhena[16]using chemical bath deposition method under various pH values. The transmittance spectra analysis reveal that both films have low transmittance for wavelength less than 300 nm and high transmittance for wavelength range 300 to 900 nm. For example, transmittance data of the copper sulphide films were varies from 0.313-0.926 and 0.515-0.995 for wavelength lower than 300 nm and greater than 300 nm, respectively. He also claims that the films prepared at pH 7 has the highest transmittance value, however, the films prepared at pH 12 has the lowest value. Meanwhile, in other case (zinc sulphide thin films), transmittance values were varies from 0.289-0.964 and 0.847-0.995 for the wavelength lower than 300 and greater than 300 nm, respectively. He concludes that the films prepared at pH 9 and 12 display the highest transmittance of 1.033 at 350 nm. Based on the findings obtained, he points out that the CuS and ZnS films could be used in antireflection coatings for solar thermal devices and eyeglass coatings to reduce solar reflectance and increase the transmittance of glass.

On the other hand, optical absorption spectra of the different thin films prepared at various deposition conditions were recorded using dual beam spectrophotometer. $CuInS_2$ films have been deposited on glass substrates using simple chemical bath deposition technique. The effect of the change in volume of copper precursor on the optical properties was investigated by Mahanubhav *et al.* [17]. The absorption spectra were recorded using UV-Visible spectrophotometer. It is clear that the absorption edge move towards the lower wavelength portion when the copper to indium ratio is reduced from 23.928 to 1.47. This is because of reducing in grain size of nanocrystalline structure of the material from 61.3 to 31.6 nm. In other case, optical absorption measurements of CdS films prepared at various bath temperatures were carried out by Wagh&Bhagat[18]. It is interesting to suggest that the absorption edge is sharp for the sample prepared at room temperature. However, the slight move in the absorption edge could be found for the films prepared at higher bath temperature such as 45, 65 and 85 °C. The optical properties of chemical bath deposited silver aluminum sulphide films have been analyzed by Ezeobele&Ezenwa [19]. The obtain results reflect that absorbance value reduce with increasing in deposition time from 26, 36 to 48 hours. In the other case, the influence of solution concentration on the CuS films in the presence of tartaric acid as complexing agent was studied using UV-Visible spectrophotometer. The optical studies reveal that the films prepared using 0.2 M of copper sulphate thiourea and tartaric acid showed the largest absorption value if compared to other concentrations such as 0.05 M and 0.1 M. This is due to the formation of regular grain sizes with higher surface area as reported by Anuar *et al.* [20]. Lastly, there are many studies reveal that the deposited films have high absorbance in the UV region and low absorbance in the visible portion. These materials could be used for coating windscreens, driving mirrors, solar cell and in the production of blue and green emitting devices.

The optical absorbance data could be used to determine band gap of the semiconductor material. The relation between band gap (E_g), constant value (A), absorption coefficient (α) and the photon energy (hv) can be represented as the following equation.

$$\alpha = \frac{A(hv-E_g)^2}{hv} \quad \{E1\}$$

According to this equation, the optical absorption data could be used to plot a graph of $(\alpha hv)^2$ versus hv. Furthermore, extrapolation of the linear line of the curve to $(\alpha hv)^2=0$ determines the band gap. Based on the obtained band gap during the experiments, semiconductor materials can be classified into several groups. The first group thin films such as PbS [21, 22], PbSe [23] and $Cu_2Sn_{1-x}Ge_xSe_3$ [24] have the band gap value less than 1 eV. These materials can be used in ion-selective sensor, photodetectors, photoresistors and photoemitters in the infrared. Meanwhile, ZnS[25-27], MnS [28], MnS_2 [29] and CdZnS [30] films are categorized as wide band gap semiconductor. They have the band gap value ofmore than 3 eVwith a range of potential applications in optoelectronic devices including blue light emitting diodes and solar cells. It is also an excellent host material for electroluminescent phosphors. In other case, some semiconductor materials such as $CdS_{0.5}Se_{0.5}$ [31], $CdIn_2S_4$ [32], CdSe [33], CdTe [34], SnSe [35], $FeSe_2$ [36], ZnTe[37], $Sn_4Sb_6S_{13}$ [38], CuS [39], Cu_2ZnSnS_4 [40], CdZnS [41], Cu_2SnS_3[42], FeS_2[43], $In_2Se_{2.5}Te_{0.5}$[44], InSe [45], SnS [46, 47], NiSe[48], $CuInSe_2$ [49], MnTe [50], Cu_4SnS_4 [51], $Ni_3Pb_2S_2$ [52], CdS [53], $CuInS_2$[54], $CuInTe_2$[55] and

$Ag_2Se_{0.2}Te_{0.8}$ [56]have band gap within 1-3 eV. These materials have received great attention in the field of filters, holography, optical waveguides, gas sensor, solar cells, thin film transistor and temperature sensor.

There are some disadvantages of UV-visible spectrophotometer as revealed by many researchers. The UV-visible spectrophotometer's performance degrades as the dust costs mirrors in these types of equipment. At this moment, repair costs double due to technician cannot replace one mirror if it needs fixing if compared to single beam spectrophotometer. In other words, technician must replace both mirrors because of theseparts work as a pair. Sometimes, sample source may produce noise that reduces measurement accuracy and decreases the device's sensitivity as well. Lastly, the stray light could influence the accuracy of the absorption. The stray light will reduce linearity range and decrease the absorbency of substance.

CONCLUSION

Thin films have been prepared by many deposition methods and could be applied in several optoelectronic and semiconductor industry. UV-visible spectrophotometer is a valuable tool to analyze the optical properties of thin films. During the experiment, the absorption data will be collected and the band gap value could be calculated from absorption spectra.

REFERENCE

1. Thirumavalavan, S., K. Mani and S. Sagadevan, 2015. Studies on structural, surface morphology and optical properties of zinc sulphide thin films prepared by chemical bath deposition. Int. J. Phys. Sci., 10: 2014-209.
2. Ersin, Y. and K. Suleyman, 2015. The effects of coumarin additive on the properties of CdS thin films grown by chemical bath deposition. Ceram. Int., 41: 4726-4734.
3. Ramesh, K., S. Thanikaikarasan and B. Bharathi, 2014. Structural, morphological and optical properties of copper selenide thin films. Int. J. ChemTech Res., 6: 5408-5411.
4. Li, J., C. Xue, Y. Wang, G. Jiang, W. Liuand C. Zhu, 2016. Cu_2SnS_3 solar cells fabricated by chemical bath deposition–annealing of SnS/Cu stacked layers. Sol. Energy Mater. Sol. Cells,144: 281-288.
5. Pitchaiman, K., L. Amalrajand S. Muthukumaran, 2016. Microstructure, optical and structural characterization of $Cd_{0.98}Fe_{0.02}S$ thin films co-doped with Zn by chemical bath deposition method. Physica E, 78: 56-64.
6. Mochahari, P.K. and K.C. Sarma, 2016. Study of structural and optical properties of chemically synthesized nanostructured cadmium zinc sulphide films for band gap tenability. Indian J. Phys., 90: 21-27.
7. Muthukannan, A., J. Henry, G. Sivakumar and K. Mohanraj, 2016. Fabrication and characterization of vacuum evaporated Al:$CuSe_2$ thin films. Superlattices Microstruct., 89: 83-88.
8. Li, L., Y. Ma, G. Gao, W. Wang, S. Guo, J. You and J. Xie, 2016. Fabrication and characterization of copper indium diselenide ($CuInSe_2$) thin film using one step electrodeposition process. J. Alloys Compd., 658: 774-779.
9. Kim, S., K. Kim, H. Tampo, H. Shibata, K. Matsubara and S. Niki, 2016. Ge-incorporated $Cu_2ZnSnSe_4$ thin film solar cells with efficiency greater than 10%. Sol. Energy Mater. Sol. Cells, 144: 488-492.
10. Anuar, K., S.M. Ho, K.S. Limand N. Saravanan, 2011, SEM, EDAX and UV-visible studies on the properties of Cu_2S thin films, Chalcogenide Lett., 8: 405-410.
11. Anuar, K., S.M. Ho, S. Atan, H. Jelasand N. Saravanan, 2011. Chemical bath deposition of SnS thin films: AFM, EDAX and UV-Visible characterization.Oriental J. Chem., 27: 1375-1381.
12. Anuar, K., K. Zulkefly, S. Atan, W.T. Tan, S.M. Ho, N. Saravanan, 2010. Preparation and studies of chemically deposited Cu_4SnS_4 thin films in the presence of complexing agent Na_2EDTA. Indian J. Eng. Mater. Sci., 17: 295-298.
13. Gunasekaran, M., R. Gopalakrishnan and P. Ramasamy, 2003. Deposition of ZnS thin films by photochemical deposition technique, Mater. Lett., 58: 67-70.
14. Agbo, S.N.F.I. Ezema, 2007.Analysis of chemically deposited MnS thin films, Pacific J. Sci. Technol., 8: 150-154.
15. Eya, D.D.O., 2006. Optical properties and applications of cadmium selenide (CdSe) thin films prepared by chemical bath deposition technique. Pacific J. Sci. Technol., 7: 64-68.
16. Ilenikhena, P.A., 2008. Comparative studies of improved chemical bath deposited copper sulphide (CuS) and zinc sulphide (ZnS) thin films at 320 K and possible applications. Afr. Phys. Rev., 2, 59-67.

17. Mahanubhav, M.D., L.A. Patil, P.S. Sonawane, R.H. Bari and V.R., 2006. Structural and optical properties of chemically deposited nanocrystalline thin films of non-stoichiometric $CuInS_2$. Sens. Transducers J., 73: 826-833.
18. Wagh, B.G. and D.M. Bhagat, 2004. Some studies on preparation and characterization of cadmium sulphide films.Curr. Appl. Phys., 4: 259-262.
19. Ezeobele, E.E. and I.A. Ezenwa, 2015. Optical properties of silver aluminum sulphide ternary thin films deposited by chemical bath method.Int. J. Sci. Technol., 4: 45-57.
20. Anuar, K., S.M. Ho, J.H. Mohd and N. Saravanan, 2011. Preparation of thin films of copper sulfide by chemical bath deposition. Int. J. Pharm. Life Sci., 2: 1190-1194.
21. Beddek, L., M. Messaoudi, S. Guitouni, N. Attafand M.S. Aida, 2015. Structural, optical and electrical properties of PbS thin films deposited by CBD at different bath pH.Int. J. Sci. Res. Eng. Technol., 3: 138-142.
22. More, P.D., 2012. Synthesis and characterization of hydrophobic PbS thin films. Adv. Appl. Sci. Res., 3: 2508-2513.
23. Suriyanarayanan, N., S. Prabahar, S. Srikanth, V. Balasubramanian and D. Kathirvel, 2010. Optical and AFM studies on lead selenide thin films.Arch. Phys. Res., 1: 81-88.
24. Kang, M.K., K. Shinho, T. Hitoshi, S. Hajjime, M. Koji and N. Shigeru, 2015. Narrow band gap $Cu_2Sn_{1-x}Ge_xSe_3$ thin film solar cells. Mater. Lett., 158: 205-207.
25. Long, F., W. Wang, Z. Cui, L. Fan, Z. Zouand T. Jia, 2008. An improved method for chemical bath deposition of ZnS thin films. Chem. Phys. Lett., 462: 84-87.
26. Manjulavalli, T.E. and A.G. Kannan, 2015. Structural and optical properties of ZnS thin films prepared by chemical bath deposition method. Int. J. Chem Tech Res., 8: 396-402.
27. Alexander, B., S.B. David and O. Paul, 2002. In situ kinetic studies of the chemical bath deposition of zinc sulfide from acidic solutions. J. Mater. Chem., 12: 2940-2944.
28. Gumus, C., C. Ulutas, R. Esen, O.M. Ozkendirand Y. Ufuktepe, 2005. Preparation and characterization of crystalline MnS thin films by chemical bath deposition. Thin Solid Films, 492: 1-5.
29. Anuar, K., H.A. Abdul, S.M. Ho and N. Saravanan, 2010. Influence of deposition time on the properties of chemical bath deposited manganese sulfide thin films.Av. Quim., 5: 141-145.
30. Jana, S., R. Maity, S. Das, M.K. Mitra and K.K. Chattopadhyay, 2007. Synthesis, structural and optical characterization of nanocrystalline ternary $Cd_{1-x}Zn_xS$ thin films by chemical process. Physica E, 39: 109-114.
31. Khomane, A.S., 2013. Crystallographic and microscopic properties of ternary $CdS_{0.5}Se_{0.5}$ thin films. Optik, 124: 2432-2435.
32. 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. J. Phys. Chem. Solids, 67: 2331-2336.
33. Rajni, K.S., 2014. Studies on the structural and conduction mechanism (ac) in thermally evaporated CdSe thin films. Int. J. Chem Tech Res., 7: 1509-1515.
34. Fathy, M., S. Elyamny, S. Mahmoud and A.E.B. Kashyout, 2015. Effect of thermal and chemical treatment on electrodeposited CdTe thin films for solar cell applications. Int. J. Electrochem. Sci., 10: 6030-6043.
35. Escobar, D., M. Ramachandran, A.S. Juarez and J.S.N. Rios, 2013. Optical and electrical properties of $SnSe_2$ and SnSe thin films prepared by spray pyrolysis.Thin Solid Films, 535: 390-393.
36. Mahalingam, T., S. Thanikaikarasan, R. Chandramohan, M. Raja, C. Sanjeeviraja, J. Kim and Y. Kim, 2007. Effects of bath temperature in electrodeposited $FeSe_2$ thin films. Mater. Chem. Phys., 106: 369-374.
37. Ikhioya, I.L., 2015. Optical and electrical properties of ZnTe thin films using electrodeposition technique. Int. J. Innovation Appl. Stud., 12: 369-373.
38. Harizi, A., A. Sinaoui, F.C. Akkari and M. Kanzari, 2016. Physical properties of $Sn_4Sb\,S_{13}$ thin films prepared by a glancing angle deposition method. Mater. Sci. Semicond. Processing, 41: 450-456.
39. Mani, P., K. Manikandan, A.J. Ramya, A.I. Seelan, S.S. Zahirullah, M.S. Hameed and J.J. Prince, 2014. Influence of molar concentrations on optical properties of copper sulphide thin films by Silar method. Int. J. ChemTech Res., 6: 3573-3578.
40. Rana, T.R., N.M. Shinde and J.H. Kim, 2016. Novel chemical route for chemical bath deposition of Cu_2ZnSnS_4 thin films with stacked precursor thin films. Mater. Lett., 162: 40-43.

41. Carreon-Moncada, I., L.A. Gonzalez, M.I. Pech-Canul and R. Ramirez-Bon, 2013. $Cd_{1-x}Zn_xS$ thin films with low Zn content obtained by an ammonia free chemical bath deposition process. Thin Solid Films, 548: 270-274.
42. Reddy, T.S., R. Amiruddin and M.C.S. Kumar, 2015. Deposition and characterization of Cu_2SnS_3 thin films by co-evaporation for photovoltaic application. Sol. Energy Mater. Sol. Cells, 143: 128-134.
43. Anuar, K., W.T. Tan, K.A. Dzulkefly, M.S. Atan, S.M. Ho, S.Y. Gwee and N. Saravanan, 2010. Preparation and characterization of iron sulphide thin films by chemical bath deposition method.Indo. J. Chem, 10: 8-11.
44. Emziane, M. and R.L. Ny, 2000. Photoconductivity of textured γ-$In_2Se_{3-x}Te_x$($0<x<0.5$) thin films. Thin Solid Films, 366: 191-195.
45. Sanjay, B.B. and G.W. Vasant, 2015. Structural and morphological properties of indium selenide thin films deposited by chemical bath deposition, Int. J. Pharm. Res. Dev., 6: 5-7.
46. Anuar, K., W.T. Tan, S.M. Ho and X.Y. The, 2011. Deposition and characterization of tin sulphide thin films by chemical bath deposition technique, Int. J. Appl. Chem., 7: 175-182.
47. Hedge, S.S., A.G. Kunjomana, K.A. Chandrasekharan, K. Ramesh and M. Prashnantha, 2011. Optical and electrical proeprties of SnS semiconductor crystals grown by physical vapor deposition technique. Physica B, 406: 1143-1148.
48. Anuar, K., Y.R. Mohd and S.M. Ho, 2011. UV-Visible studies of chemical bath deposited NiSe thin films. Int. J. Chem. Res., 3: 21-26.
49. Meglali, O., A. Bouraiou and N. Attaf, 2008. Characterization of $CuInSe_2$ thin films elaborated by electrochemical deposition. Rev. Energies Renouvelables, 11: 19-24.
50. Sharma, R.K., A.C. Rastogi and G. Singh, 2004. Electrochemical growth and characterization of manganese telluride thin films. Mater. Chem. Phys., 84: 46-51.
51. 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 J. Chem., 22: 222-232.
52. Ho, S.M., 2015. UV-visible studies of chemical bath deposited $Ni_3Pb_2S_2$ films. J. Chem. Pharm. Res., 7: 50-55.
53. Pushpalatha, H.L. and R. Ganesha, 2014. Growth and characterization of CdS thin films by photochemical and chemical bath deposition, Int. J. ChemTech Res., 7: 185-189.
54. Cliff, O.M., 2015. Optical properties of $CuInS_2$ films produced by spray pyrolysis method. Rift Vally J. Sci. Technol., 1: 18-27.
55. Wasim, S.M. and J.G. Albornoz, 1988. Electrical and optical properties of n- and p-type $CuInTe_2$. Phys. Status Solidi, 110: 575-583.
56. Vijayan, C., M. Pandiaraman, N. Soundararajan, P. Gnanadurai and R. Chandramohan, 2014. Photoluminacence studies on $Ag_2Se_{0.2}Te_{0.8}$ thin films.Int. J. ChemTech. Res., 6: 3343-3345.