STUDY OF BAND GAP AND REFRACTIVE INDEX OF ZnS THIN FILMS ON GLASS SUBSTRATE BY SPRAY PYROLYSIS METHOD

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ABSTRACT

In this study of annealed ZnS thin film prepared by spray pyrolysis method at 450 ^oC spraying solution time 10 min for optical and structural properties was studied. The XRD of the films have been carried out in the 2θ ranges from 20^0 to 100^0 using C_uK_α radiations, after annealing for 1 hour at 100 ^oC the sample the XRD is found to be polycrystalline. The spray of equimolar solution (Zn:S = 1:1) results small grain size and wide band gap value of the 2.6eV.Due to this wide band gap its use solar cells applications. Zinc sulfide used in coating in the microelectronic and optical device. Due to high refractive index it is commonly used as filter, reflector and planar waveguide. The optical properties of the thin films and its dispersion is very important when these are to be used in solar cell.

KEYWORDS: Spray pyrolysis, XRD,Thin film, Optical properties, Energy gap , ZnS

INTRODUCTION

Zinc Sulphide (ZnS) is a large band gap direct transition semiconductor compound suitable use solar cells applications[1]. It is also the most commonly used host material in thin film electroluminescence devices The wide band 2.6 eV to 3.2 eV gap of this material makes it suitable for the use of in the blue light emitting [2](1) and other optoelectronic devices such as electoluminscent display [3] and multilayer dielectrie filters[4] Zinc sulbhiste are commonly found in cubie and hexagonal crystaliograplic modification [5] . Many authers studied the structural and optical properties of Zinc Sulphide thin films by laser evaporation. According to the literature many researcher have studied ZnS thin films deposited onto glass substrates by SILAR method[6], chemical bath deposition[7].But due to low cost , a cheap technique to produce large area thin films and adehent spray pyrolysis method is best useful for thin film. ZnS.In this paper , ZnS thin film on glass substrate is studied for its optical and XRD analysis.

EXPERIMENTAL

The cleaned glass substrate were mounted on substrate holder with heating arrangement. The substrate temperature 450^0C was measured by precalibrated thermocouple ZnS thin films were deposited by spray pyrolysis technique[8]on a pre cleaned hot glass substrate at 405^oC of molar concentration 0.025M solution are used for spraying the films.

The chemicals used were of AR grade (99.9% pure) The substrate is already weighted before depositing thin film on the digital monopan balance of 0.1mg accuracy. The aqueus solutions are prepared in double distilled water. The ammonia as a complexing agent was added in the solution before spraying. The source of Zn and S are Zinc chloride ($ZnCl_2$) and thiourea (NH–CS–NH2). By applying the same technique described elsewhere for ZnS thin film were deposited[9].Then all the films are annealed for 1 hr. at 100^0C constant temperature

The band gaps of these films are found out from reflection data.[10] Absorption spectra of this material are taken at room temperature with the help of ELICO spectrophotometer. Model SL 159 in the wavelength range is 380-1000 nm. The structural characterization was carried out by taking XRD pattern of thin films of 0.025 M motor concentration with the help of phillip X-Ray Diffractometer using CuKα ($\lambda=1.5405A^0$) radiaction as X-ray source.

RESULT AND DISCUSSION

The thickness of the ZnS thin films was computed by weighting difference method using a sensitive microbalance The optical properties of ZnS annealed thin film in the wavelength range 300 to 900 nm is studied**.** . The visible wavelength light source is long life WL lamp. Energy band gap (Eg) of materials is related to absorption coefficient α as according to Tauc relation , the absorption coefficient for direct band gap material is given by

$$\alpha = \frac{A}{h\nu} \left(h\nu - E\, g\right)^{1/2} \qquad \text{--------------(1)}$$

where A is a constant, hv is the photon energy, Eg the band gap and n is an index, which assumes the values 1/2, n =1/2 is taken for an allowed direct transition[12]. After preparing the solid thin films by spray pyrolysis techniques[13] the optical absorption and percentage Transmission were measured by micro-processor based ELICO UV–VIS Spectrophotometer SL-159 in the wavelength range 380 nm to 1000 nm[14]. The substrate used in the preparation of the samples ZnS of 0.025M molar concentration is a glass substrate. Part of the position of glass substrate is used to deposit the thin films which is acts as a samples and the remaining half portion of the slide act as a reference Therefore, by plotting a graph between $(\alpha h\nu)^2$ and (hν), a straight line is obtained which gives the value of the direct band gap 2.6 eV [15], [16]

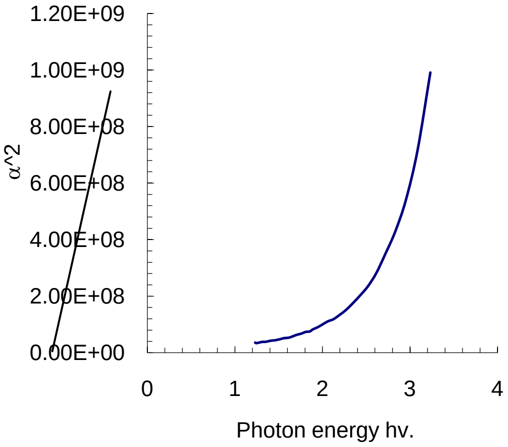

Fig.1 Energy band gap ZnS (direct)

The reflectance has been found by using the relationship R + T + A = 1. The Swanepole method was used to evaluate the refractive index of the film[17].The refractive index extinction coefficient and the thickness of the films were determined from the traces of the transmittance versus wavelength of the film on glass substrate. It was found that the dependences of refractive index and incident photon energy of the films deposited on glass substrate

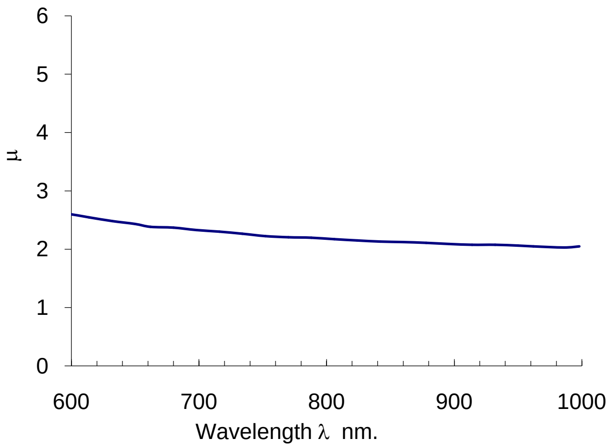

Fig.2 Refractive index verses wavelength

The X-ray diffraction patterns give the information about the nature and structure of the films. The natures and structure of as deposited thin films, have been studied by a X-ray diffractometer Philips X-pert PRO/SRC by recording XRD patterns. The XRD of the films have been carried out in the 2θ ranges from 20^0 to 100^0 using C_uK_α radiations for obtaining crystallographic structure in the form of peaks and width of the peak in XRD patterns of the films.

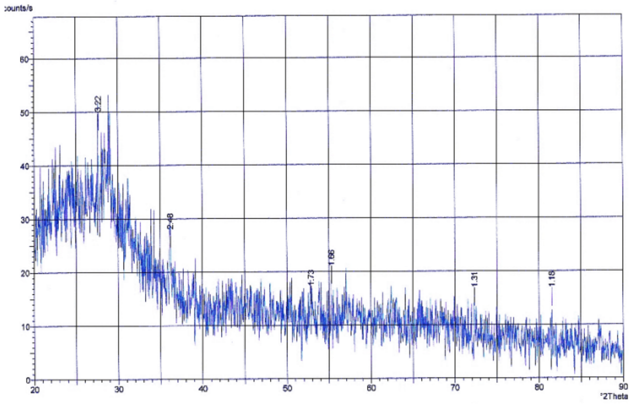

Fig 3. The XRD diffraction pattern of the samples ZnS

The patterns of XRD of ZnS indicate that films are polycrystalline and the peaks shape indicates the films are poor crystallinity in nature. The observed broad hump in XRD patterns of all samples is due to amorphous glass substrates. The XRD patterns show small crystallites. The crystallinity of the films was improved by annealing. XRD patterns of ZnS thin films shows three peaks at 20 values reang 29^0, 48^0, 47^0. This reveals that the particles exibit Zinc-blende structure [18]The three peaks corresponds to diffraction from (111), (220) and (311) planes. Due to the size effect the XRD peaks tends to broaden and their widths become larger as the crystal become smaller.

CONCLUSION

In this work, it is concluded that the band gap energy of the thin films is suitable for optoelectronic devices .The band gap of ZnS thin films lies in the range of 2.6 eV nearly to semiconductor material band gap .This shows that ZnS thin film has high transmittance and behaves as semiconducting materials The obtained films exhibit good adherence to the glass substrate . It is observed that the transmittance was constant for higher wavelength and started decreasing after particular wavelength. From the XRD analysis it was found the films was most suitable for solar cell preparation Hence spray pyrolysis is the simplest inexpensive and best method to obtain chalcopyrites semiconductor

REFERENCE

[1] C. Sabitha, I. H. Joe, K. D. A. Kumar, and S. Valanarasu, “Investigation of structural, optical and electrical properties of ZnS thin films prepared by nebulized spray pyrolysis for solar cell applications,” *Opt. Quantum Electron.*, vol. 50, no. 3, p. 153, Mar. 2018, doi: 10.1007/s11082-018-1418-z.

[2] K. Ou, L. Bai, M. Huang, L. Yi, X. Duan, and S. Wang, “Effect of Preparation Parameters on Deep-Blue Light-Emitting Diodes Based on Nanostructured ZnSe/ZnS Multilayer Films,” *ACS Omega*, vol. 5, no. 38, pp. 24567–24573, Sep. 2020, doi: 10.1021/acsomega.0c03071.

[3] Y. S. Kim and S. J. Yun, “Studies on polycrystalline ZnS thin films grown by atomic layer deposition for electroluminescent applications,” *Appl. Surf. Sci.*, vol. 229, no. 1, pp. 105–111, May 2004, doi: 10.1016/j.apsusc.2004.01.050.

[4] A. Jrad, T. Ben Nasr, and N. Turki-Kamoun, “Study of structural, optical and photoluminescence properties of indium-doped zinc sulfide thin films for optoelectronic applications,” *Opt. Mater.*, vol. 50, pp. 128–133, Dec. 2015, doi: 10.1016/j.optmat.2015.10.011.

[5] K. Alnama, B. Abdallah, and S. Kanaan, “Deposition of ZnS thin film by ultrasonic spray pyrolysis: effect of thickness on the crystallographic and electrical properties,” *Compos. Interfaces*, vol. 24, no. 5, pp. 499–513, Jun. 2017, doi: 10.1080/09276440.2017.1236538.

[6] V. K. Ashith and K. G. Rao, “Structural and Optical Properties of ZnS Thin Films by SILAR Technique obtained by acetate Precursor,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 360, no. 1, p. 012058, Sep. 2018, doi: 10.1088/1757-899X/360/1/012058.

[7] A. Karimi, B. Sohrabi, and M. R. Vaezi, “Highly transparent, flexible and hydrophilic ZnS thin films prepared by a facile and environmentally friendly chemical bath deposition method,” *Thin Solid Films*, vol. 651, pp. 97–110, Apr. 2018, doi: 10.1016/j.tsf.2018.02.021.

[8] D. L. M. Shanware, “Study of Structural Impact on Annealed CDs Thin Films by Spray Pyrolysis Method,” *Int. J. Sci. Res. Sci. Technol.*, vol. 9, no. 6, pp. 333–336, Oct. 2021, doi: 10.32628/IJSRST219658.

[9] D. L. M. Shanware, “Comparative Analysis of Optical Properties of Cdo Annealed thin Film deposited by Spray Pyrolysis Method,” *Int. J. Chem. Math. PhysicsIJCMP*, vol. 7, no. 4, Art. no. 4, Aug. 2023, Accessed: Aug. 10, 2023. [Online]. Available: http://www.journal-repository.theshillonga.com/index.php/ijcmp/article/view/6535

[10] D. L. M. Shanware, D. R. S. Meshram, and D. R. M. Thombre, “Study on Optical Properties of CDS Annealed Thin Films by Spray Pyrolysis,” *Int. J. Sci. Res. Sci. Technol.*, vol. 9, no. 4, pp. 46–48, Apr. 2021, doi: 10.32628/IJSRST219909.

[11] “Study of Structural Impact on Annealed CDs Thin Films by Spray Pyrolysis Method.□ Accessed: Feb. 15, 2025. [Online]. Available: https://scholar.google.com/citations?view_op=view_citation&hl=en&user=Bo9hRRYAAAAJ&citation_for_view=Bo9hRRYAAAAJ:IjCSPb-OGe4C

[12] I. C. Ndukwe, “Solution growth, characterization and applications of zinc sulphide thin films,” *Sol. Energy Mater. Sol. Cells*, vol. 40, no. 2, pp. 123–131, Apr. 1996, doi: 10.1016/0927-0248(95)00074-7.

[13] M. K. Rahangale and L. M. Shanware, “Effect of Annealling on Optical Band Gap of Fe2O3 Thin Films on Amorphos Transparent Glass Substrate by Spray Pyrolysis Method,” *J. Thin Films Coat. Sci. Technol. Appl.*, vol. 10, no. 2, pp. 25–29, Oct. 2023.

[14] L. M. Shanware, “INVESTGATION OF OPTICAL AND STRUCTURAL PROPERTIES OF CdZnS ANNEALED THIN FILMS BY SPRAY PYROLYSIS TECHNIQUE.□ Accessed: Aug. 10, 2023. [Online]. Available: https://scholar.google.com/citations?view_op=view_citation&hl=en&user=Bo9hRRYAAAAJ&citation_for_view=Bo9hRRYAAAAJ:qjMakFHDy7sC

[15] E. Jose and M. C. Santhosh Kumar, “Room temperature deposition of highly crystalline Cu-Zn-S thin films for solar cell applications using SILAR method,” *J. Alloys Compd.*, vol. 712, pp. 649–656, Jul. 2017, doi: 10.1016/j.jallcom.2017.04.097.

[16] “Molecules | Free Full-Text | Effect of Chemical Bath Deposition Variables on the Properties of Zinc Sulfide Thin Films: A Review.” Accessed: Aug. 14, 2023. [Online]. Available: https://www.mdpi.com/1420-3049/28/6/2780

[17] “Determining refractive index and thickness of thin films from wavelength measurements only.” Accessed: Aug. 14, 2023. [Online]. Available: https://opg.optica.org/josaa/abstract.cfm?uri=josaa-2-8-1339

[18] A. A. Faremi *et al.*, “Engineering of window layer cadmium sulphide and zinc sulphide thin films for solar cell applications,” *Results Eng.*, vol. 16, p. 100622, Dec. 2022, doi: 10.1016/j.rineng.2022.100622.