Research article Available online www.ijsrr.org ISSN: 2279–0543

International Journal of Scientific Research and Reviews

Effect of Post annealing on CBD deposited ZnS thin films

R. P. Khatri[1]*, A. J. Patel[2]

[1]Governmnet Engineering College, Modasa, Aravalli, Gujarat 383315, India
[2]Government Engineering College, Godhra, Panchmahal, Gujarat 389001, India
*Email: rajukhatri_222@yahoo.co.in

ABSTRACT

The growth of zinc sulphide (ZnS) thin films onto glass substrate by chemical bath deposition method has been reported. These films were deposited onto glass substrates by using zinc chloride, triethanolamine (TEA), thiourea and 25% ammonia at bath temperature 70 °C. The effect of annealing at 350 °C temperature for 1 hr onto properties of the ZnS thin films was investigated. X-ray diffraction confirms the wrutzite, hexagonal phase of ZnS. Average crystallite size calculated by Debye-Scherrer equation was 331 nm for as-grown and 643 nm for annealed ZnS thin films, respectively. The ZnS thin films have transmittance of about 5-35% in the range of 350 -1200 nm. The transmittance of annealed ZnS thin film is higher than that of as-deposited ZnS thin film in the range 350-800 nm. The band gap values were calculated in the range of 3.80-4.18 eV.

KEYWORDS: Chemical bath deposition, Thin film, Zinc Sulphide

***Corresponding Author**

Rajesh P. Khatri

Government Engineering College Modasa

Aravalli, Gujarat 383315, INDIA

Email: rajukhatri_222@yahoo.co.in

INTRODUCTION

CIGS based solar cells have been recognized as the most promising technology [1-3]. Although the theoretical conversion efficiency of CIGS based solar cells is ~30%, the best efficiency achieved thus far has been approximately 20% (for small area cells) [4]. Recently, CdS is most widely used materials as buffer layer in CIGS based solar cells. But CdS is toxic material and it pollute environment in the process of production. ZnS thin films with large band gap and II-VI semiconductors are promising candidate for Cd-free buffer layer [5]. The wide band gap and the presence of large number of point defects present within band gap make ZnS most needed member of optoelectronics industry [6] such as light emitting diodes in the blue to ultraviolet spectral region. In area of optics, ZnS can be used as reflector and dielectric filter of high refractive index (2.35) and its high transmittance in the visible range, respectively [7, 8]. It can be used in photoluminescence and electroluminescence [9, 10].

ZnS thin films can be synthesized by different method such as thermal evaporation[11], Spray Pyrolysis[12], MOCVD [13], SILAR [14], Chemical bath deposition [15-23]. Out of all above deposition methods CBD is highly attentive because it has number of merits than other deposition methods. Like all other deposition methods, CBD does not requiring high temperature as well as sophisticated and expensive equipments. The starting precursors are easily available and cost-effective [24]. However, the films obtained by using the CBD method are either amorphous or poorly crystallized. Therefore, an annealing process is needed to improve the crystallinity of films [25].

In the present work, attempts have been made to deposit well-adherent and homogeneous ZnS thin films onto glass substrate by optimizing deposition parameter. The effect of post annealing on structural and optical properties were investigated.

EXPERIMENTAL SECTION

All reagent viz. zinc chloride ($ZnCl_2$), triethanolamine ($C_6H_{15}NO_3$), ammonia solution (NH_4OH), thiourea ($SC(NH_2)_2$) were purchased from merck chemicals and used without further purification. Deionized water used as solvent. Here zinc chloride and thiourea are the sources of Zn^{2+} and S^{2-} ions, respectively. Triehanolamine works as complexing agent, where as ammonia solution was used for adjusting pH of the solution to achieve the alkaline medium.

Microscope glass slide (76 mm ×26 mm × 1.35 mm) used as substrates for the deposition of ZnS thin film. The cleaning of glass substrate was done by keeping it in HCl overnight. Next day the glass substrate was washed twice with mild detergent and finally ultrasonically cleaned in deionized water and methanol sequentially, then dried in oven for 2 hr at 50 ^{0}C.

The zinc sulphide (ZnS) thin film deposition was done on glass substrate by chemical bath deposition (CBD) method. Various precursors, complexing agent, temperature and pH were tried to optimize bath parameter to obtain good quality ZnS thin films. The best ZnS thin films by CBD method was obtained by using below synthesis process:

In a typical synthesis process, 50 ml of reaction solution was obtained by mixing 10 ml of 0.1 M zinc chloride, 1 ml of 25% ammonia, 5 drop of triethanolamine (TEA), 10 ml of 1 M thiouea and 27 ml of deionized water. Initial zinc chloride solution was milky and turbid due to formation of $Zn(OH)_2$ suspension. Under continuous stirring addition of ammonia led to dissolution of turbidity and made solution clear and transparent. Now 5 drop of TEA was added and kept 5 min for stirring. 10 ml thiourea was then added with constant stirring. Finally 27 ml of deionized water was added to make total 50 ml reaction solution. The pH was found to be 10.5. The pre-cleaned glass substrates were immersed vertically into reaction solution. The CBD process was carried out at 70 ^{0}C for 2 hr. After 2 hr substrates were removed from the solution and rinsed with deionized water to remove the loosely adherent ZnS particles from surfaces before air-drying. One of ZnS thin films was annealed at 350 ^{0}C for 1 hr.

The samples were analyzed by X-ray diffraction (PANalytical Empyrean XRD), Thermogravimetry (METTLER TOLEDO) and UV/VIS/NIR spectrometry (LAMBDA 19). X-ray diffraction (XRD) spectra were recorded with an automated PANalytical X-ray diffractometer with CuK_α radiations for 2θ values over 10-90°. Measurements for thin films were taken using a glancing angle detector at an angle of 5°, in the steps of 0.01° with a collection time of 7 s. The optical transmission measurements were performed using UV/VIS/NIR spectrometer at room temperature in the wavelength range 200 nm to 1200 nm. TGA analysis was made from room temperature to 900 ^{0}C.

RESULT AND DISCUSSION

Thermal analysis of dried ZnS gel

The reaction solution was allowed to dry at room temperature; forms dry ZnS gel. The thermal behaviours of ZnS gel have been investigated by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The TGA results shown in fig. 1.

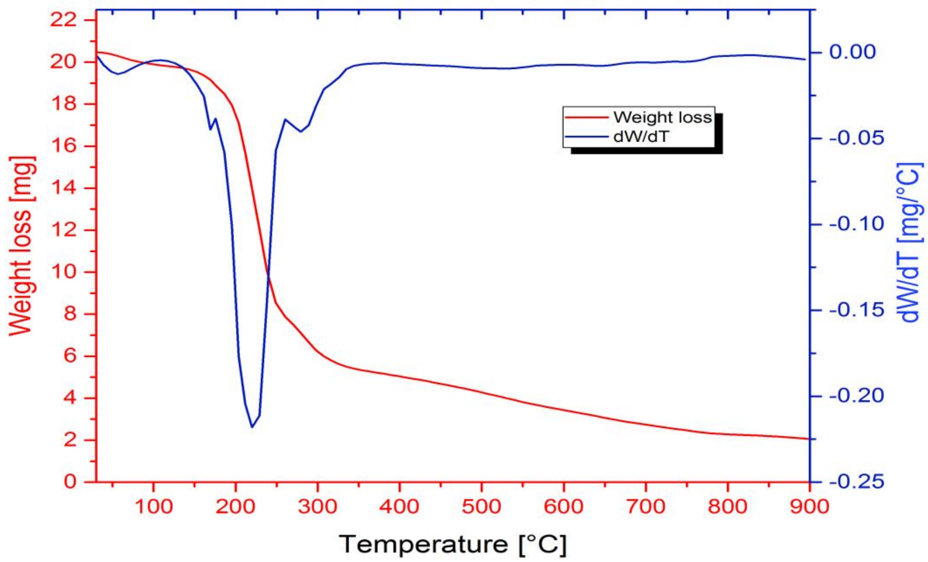

Fig. 1 : DTA and TGA curves of ZnS gel formed at room temperature.

Two weight losses were observed at 50-100 ^{0}C and 150-350 ^{0}C in TG curve. The first weight loss is due to evaporation of water. The second weight loss is caused by the decomposition of residual organic and thiourea. Two endothermic peaks were found at 70 ^{0}C and 220 ^{0}C, respectively. These peaks were accompanied by the weight loss mentioned above. It is observed that there is no weight loss after 350 ^{0}C. So, the annealing temperature was selected 350 ^{0}C.

Structural Analysis

Generally Zinc sulphide has two crystal structure namely, sphalerite and wrutzite. Among these structures, sphalerite occurs at room temperature and wrutzite occurs at temperature above 1020 °C [26]. However, some authors have reported hexagonal structure for ZnS thin films by CBD methods [27, 28]. The structural properties of the ZnS thin films are investigated by X-ray diffraction (XRD) with CuK_α radiation and they were scanned in the range 2θ range of 10-90° with step size 0.01° and glancing angle 5°.

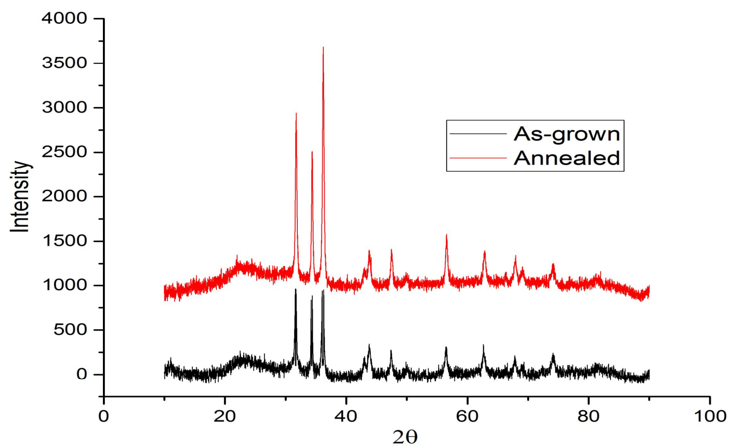

Fig. 2 : XRD patterns of as-grown and annealed ZnS thin films

Fig. 2 depict X-ray diffraction pattern (XRD) for as-grown and annealed zinc sulphide thin films. The sharp peak at 31.623°, 34.386° and 36.282° corresponds to the lattice planes (1 0 4), (1 0 6) and (0 0 10) represents hexagonal phase of ZnS (JCPDS: 39-1363). This result is well matched with earlier results [29]. The sharpness of peak increase with annealing at 350 °C for 1 hr. This result shows the crystallinity of film increase with annealing. It is possible to roughly estimate the crystallite size using debye-scherrer formula by full width at half maximum of diffraction peak for plane (h k l) [30].

$$D = \frac{0.94\lambda}{\beta \mathrm{Cos}\theta} \qquad (1)$$

Where D is the mean particle size, λ is the wavelength of the target used in XRD instrument and 0.15406 nm for CuK_{α} target, β is the FWHM of the peak of (h k l) plane and θ is the diffraction angle. From debye-scherrer formula, estimated crystallite size for as-grown film was 331 nm and for annealed film was 643 nm, respectively.

Optical Properties

The surface states strongly influence the optical properties (transmittance and absorbance) of the ZnS thin films. The optical properties of these ZnS thin films were determined from transmission and absorption measurements taken between wavelength range 200 nm and 1200 nm. The transmission spectra of as-grown and annealed ZnS thin films were taken with UV/VIS/NIR spectrophotometer and result shown in fig. 3. The observed transmittances were 5 % and 35 % for as-grown and annealed ZnS thin films, respectively. This difference in optical performance between 350 nm and 1200 nm is caused by improvement in crystallinity of ZnS thin films annealed at 350 °C for 1 hr. Low transmittance of as-grown ZnS film is due to rough surface that promote scattering of incident light and compactness of film increase with annealing. Fig. 4 depicts absorption spectra for as-grown and annealed zinc sulphide film grown by CBD technique. The sharp absorption edge values of ZnS thin a film annealed at 350 °C gets shifted to lower wavelength and sharp absorption edge is near to 300 nm which is also consistent with earlier reports [19].

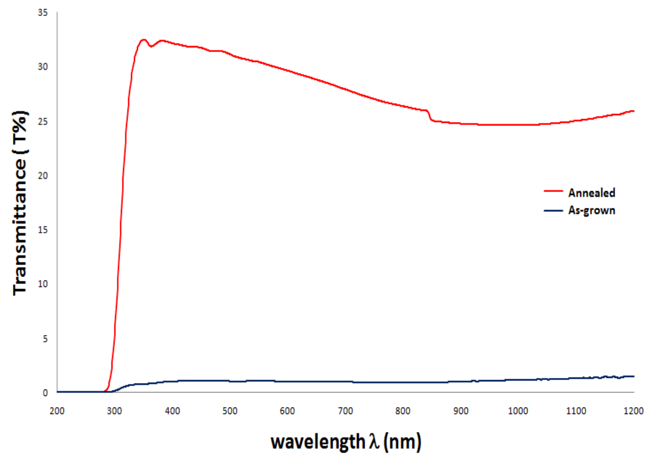

Fig. 3 : Transmission spectra of as-grown and annealed ZnS thin films.

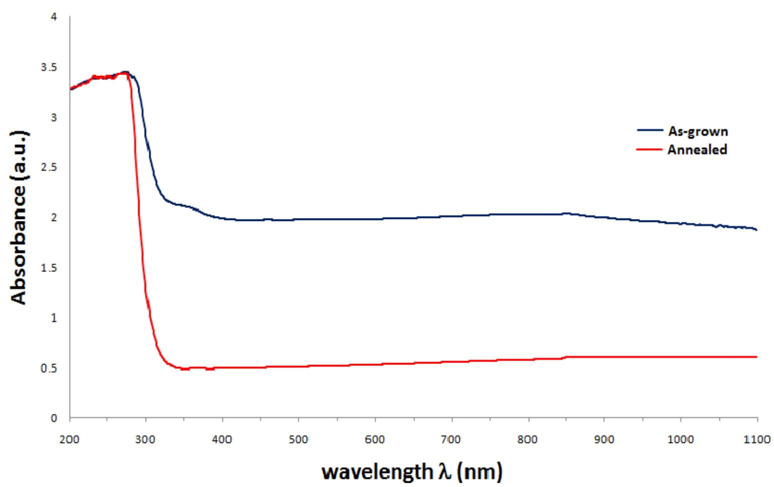

Fig. 4 : Plot of absorbance, A with wavelength, λ(nm) of as-grown and annealed ZnS thin films.

The energy band gaps were calculated with the help of the optical absorption spectra. To determine the energy band gap, we plotted $(\alpha h\nu)^2$ against $h\nu$. The absorption coefficient (α) of thin film can be calculated using formula;

$$\alpha = \frac{2.303A}{t} \qquad (2)$$

Where A is absorbance and t is thickness of film. The theory of inter-band absorption shows that the optical absorption edge, the absorption coefficient α varies with the photon energy $h\nu$ according to

$$\alpha(h\nu) = K(h\nu - Eg)^n \qquad (3)$$

Where E_g is the optical band gap, K is a constant and the exponent n = ½, 1, 2, 3 in k-space. For determination of the optical band gap of ZnS thin film, taking n =1/2 gives the best fit for the films.

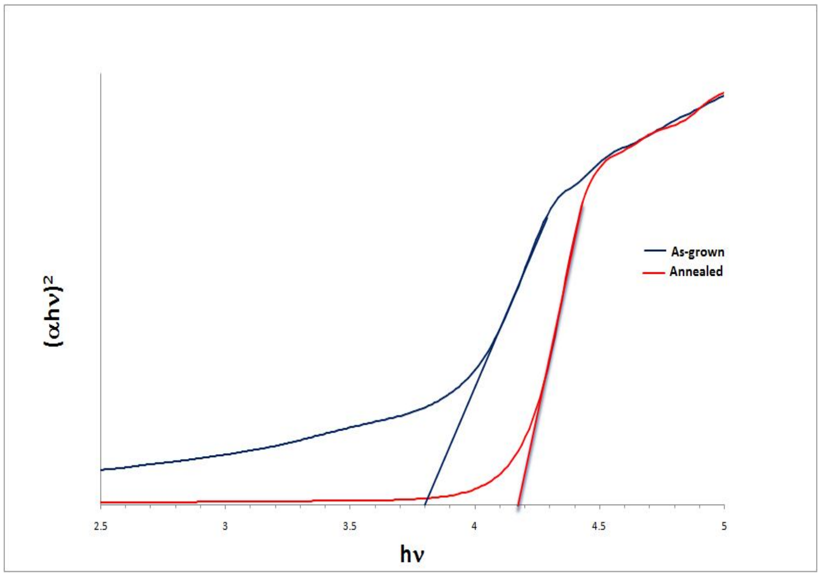

Fig. 5 : Plot of $(\alpha h\nu)^2$ versus photon energy hν of as-grown and annealed ZnS thin films.

Fig. 5 depict curve of $(\alpha h\nu)^2$ against $h\nu$. The band gap energy can be calculated by elongating straight line portion of curve at $\alpha h\nu = 0$. The calculated band gap is summarized in table. 1. From fig. 5, the calculated energy band gap increased upon annealing at 350 °C for 1 hr. These increases in band gap values can be attributed to agglomeration of small particles into large particles. These band gap values (which are good agreement with those that of earlier reports) are higher than that of bulk ZnS which is likely due to quantum size effect [31]. This is the reason the film annealed at 350 °C for 1 hr shows sharp XRD peaks, suggest improved crystallinity for that film.

Table No. 1 : "Tabulation of average crystallite size, Transmittance and band gap of as-grown and annealed ZnS thin films"

Film	Average crystallite size (nm)	Transmittance (T%)	Band gap (eV)
As-grown	331	5	3.80
Annealed	643	35	4.18

CONCLUSION

In present article uniform and well-adherent zinc sulphide thin film were successfully deposited onto glass substrates using chemical bath deposition method and influence of post annealing at 350 °C for 1 hr was studied. The XRD confirms hexagonal phase for both as-grown and annealed ZnS thin films. The average crystallite size was calculated to be 331 nm for as-grown and 643 nm for annealed ZnS thin films, respectively. TGA analysis showed 350 °C is suitable for annealing. Optical measurement showed that the transmittance were 5-35% in the visible region. Also, all of the films have direct band gap, which increased from 3.80 eV to 4.18 eV with annealing at 350 °C for hr. The materials have potential for use in electroluminescence devices and photovoltaic cells.

ACKNOWLEDGEMENT

The authors are grateful to Prof. M. P. Deshpande, Prof. G.K. Solanki and Prof. S.H. Chaki, Department of Physics, Sardar Patel University, Vallabh Vidhayanagar, Gujarat, India for providing their kind support and guidance.

REFERENCES

1. J. A. Frantz, R.Y. Bekele, V.Q. Nguyen et al. Cu(In,Ga)Se_2 thin films and devices sputtered from a single target without additional selenization. Thin Solid Films 2011; 519(22): 7763.
2. Shogo Ishizuka, Akimasa Yamada. Development of high-efficiency flexible Cu(In,Ga)Se_2 solar cells: A study of alkali doping effects on CIS, CIGS, and CGS using alkali-silicate glass thin layers. Curr. Appl. Phys. 2010; 10(2): 154-156.
3. Yanfa Yan, R. Nou, M.M. Al-Jaasim. Grain-Boundary Physics in Poly- crystalline $CuInSe_2$ Revisited: Experiment and Theory. Phys. Rev. Lett. 2006; 96: 2055501.

4. S. N. Kundu, S. Johnston and L. C. Olsen. Traps identification in Copper-Indium-Gallium-Sulfur-Selenide solar cells completed with various buffer layers by deep level transient spectroscopy. Thin Solid Films. 2006; 515(4): 2625-2631.
5. Limei Zhou, Nan Tang, Sumei Wu et al. Influence of Deposition Time on ZnS Thin Films Performance with Chemical Bath Deposition. Physics Procedia. 2011; 22: 354-359.
6. P. F. Smet, I. Moreeels, Z. Hens et al. Luminescence in sulfides: a rich history and a bright future. Materials. 2010; 3: 2834-2883.
7. J. A. Ruffner, M.D. Hilmel, V. Mizrahi et al. Effects of low substrate temperature and ion assisted deposition on composition, optical properties, and stress of ZnS thin films. J. Appl. Opt. 1989; 28(24): 5209-2514.
8. K. Ahn, J. H. Jeon, S.Y. Jeong et al. Chemical bonding states and atomic distribution within Zn(S,O) film prepared on CIGS/Mo/glass substrates by chemical bath deposition. Curr. Appl. Phys. 2012; 12(6):1465-1469.
9. M.S. Akhtar, Y.G. Alghamdi, M.A. Malik et al. Structural, optical, magnetic and half-metallic studies of cobalt doped ZnS thin films deposited via chemical bath deposition. J. Mater. Chem. 2015; C 3: 6755-6763.
10. X. Xu, L. Hu, N. Gao etal. Controlled growth from ZnS nanoparticles to ZnS–CdS nanoparticle hybrids with enhanced photoactivity. Adv. Funct. Mater. 2015; 25(3): 445-454.
11. V. Dimitrova and J. Tate. Synthesis and characterization of some ZnS-based thin film phosphors for electroluminescent device applications. Thin Solid Films. 2000; 365(1): 134-138.
12. O.Mustafa, M. Bedir, S. Ocak et al. The role of growth parameters on structural, morphology and optical properties of sprayed ZnS thin films. J. Mater. Electron. 2007; 18(5): 505-512.
13. Young-Gui Yoon, and In-Hwan CHOI. Preparation of ZnS thin films by using photo assisted MOCVD. Journal of Korean Physical Society. 2013; 63(8): 1609-1614.
14. R. Nomura, T. Murai, T. Toyosaki et al. Single-source MOVPE growth of zinc sulfide thin films using zinc dithiocarbamate complexes. Thin Solid Films. 1995; 271(1-2): 4-7.
15. Z.Y. Zhong, E.S. Cho, S.J. Know. Characterization of the ZnS thin film buffer layer for Cu(In, Ga)Se_2 solar cells deposited by chemical bath deposition process with different solution. Mater. Chem. Phys. 2012; 135(2-3): 287-292.
16. T. Iwashita, S.Ando.Preparation and characterization of ZnS thin films by the chemical bath deposition method. Thin Solid Films. 2012; 520(24): 7076-7082.

17. P.U. Bhaskar, G.S. Babu, Y.B.K. Kumar et al. Effect of bath concentration, temperature on the growth and properties of chemical bath deposited ZnS films. Mater. Chem. Phys. 2012; 134: 53.
18. G.L. Agawane, Seung Wook Shin, M.S. Kim et al. Green route fast synthesis and characterization of chemical bath deposited nanocrystalline ZnS buffer layers. Current Appl. Phys. 2013; 13(5): 850-856.
19. G.L. Agawane, Seung Wook Shin, A.V. Moholkar et al. Non-toxic complexing agent Tri-sodium citrate's effect on chemical bath deposited ZnS thin films and its growth mechanism. J. of Alloys Compound. 2012; 535(15): 53-61.
20. J. McAleese, P. O'Brien. Nucleation Studies of ZnS And ZnO Growth By Chemical Bath Deposition (CBD) On The Surface Of Glass And Tin Oxide Coated Glass. Thin-Film Structures for Photovoltaics. 1997; 485: 255.
21. I.O.Oladeji, L. Chow. A study of the effects of ammonium salts on chemical bath deposited zinc sulfide thin films. Thin Solid Films. 1999; 339(1-2): 148-153.
22. P. O'Brien, M.R. Heinrich, D.J. Otway et al. New Approaches to Chemical Bath Deposition of Chalcogenides. Chemical Processing of Dielectrics, Insulators and Electronic Ceramics. 2000; 606: 199-204.
23. A. Bayer, D.S. Boyle, P. O'Brien. In situ kinetic studies of the chemical bath deposition of zinc sulfide from acidic solutions. J. Mater. Chem. 2002; 12(10): 2940.
24. R.S. Mane and C. D. Lokhande. Chemical deposition method for metal chalcogenide thin films. Materials Chemistry and Physics. 2000; 65: 1-31.
25. J. Vidal, O. Vigil, O. D. Melo. et al. Influence of NH_3 concentration and annealing in the properties of chemical bath deposited ZnS films. Mater. Chem. Phys.1999; 61(2): 139.
26. L.I. Berger. Semiconductor Materials. CRC Press. Boca Raton. FL 1997. 198-203.
27. D. A. Johnston, M.H. Carletto, K.T.R. Reddy et al. Chemical bath deposition of zinc sulfide based buffer layers using low toxicity materials. Thin Solid Films. 2002; 403: 102-106.
28. J. Cheng, D.B. Fan, H. Wang et al. Chemical bath deposition of crystalline ZnS thin films. Semicond. Sci. Technol. 2003; 18(7): 676.
29. Kumar V, Saroja M, Venkatachalam M et al. Synthesis and characterization of ZnS thin films by sol-gel dip and spin coating methods. International Journal of Recent Scientific Research. 2015; 6(11): 7377-7379.
30. B.D. Cullity, S.R. Stock. Elements of X-ray diffraction. Prentice-Hall. Pearson. New york. 2001.

31. L. V. Makhova, I. Konovalov, R. Szargan et al. Composition and properties of ZnS thin films prepared by chemical bath deposition from acidic and basic solutions. Phys. Stat. Sol (c). 2005; 2(3): 1206-1211.