Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Applied Science Research, 2011, 3 (2):311-317

(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

"Structural, Optical and Electrical Properties of Nanocrystalline ZnS thin films Deposited by Novel Chemical Route"

M. S. Shinde[1], P. B. Ahirrao[2], R. S. Patil[1,*]

[1]Dept. of Physics, P. S. G. V. P. M'S Arts, Science & Commerce College Shahada, Dist- Nandurbar
[2]Department of Physics, S.V.S.'s Arts and Science College Dondaicha, Dist- Dhule

---

ABSTRACT

Semiconducting Zinc sulphide (ZnS) thin films were deposited on glass substrate using relatively simple, quick chemical bath deposition method (CBD) using the mixed aqueous solution of zinc sulphate, thiourea and ammonia. The ammonia was used as the complexing agents. The preparative parameters such as concentration, temperature, deposition time, pH of solution have been optimized. Thin film of ZnS with different thickness were prepared by changing the deposition time at 85^0c. The characterization of thin films was carried out for the structural, surface morphological, optical and electrical properties. The thin films we characterized by using X-ray diffraction (XRD), Scanning electron microscopy (SEM), UV-VIS Spectra and d.c. two point probe method. The effect of thin film thickness on optical and electrical properties has been studied.

Keywords: Nanocyrstalline**,** ZnS Thin film, XRD, SEM.

INTRODUCTION

Zinc Sulphide belongs to II-VI group compound material with large direct band gap between 3.4 to 3.70 eV depending upon composition. It is potentially important material to be used as an antireflection coating for heterojunction solar cells[1], for light emitting diode[2,3] and other optoelectronic devices such as blue light emitting diode[4], electro luminescence devices and photovoltaic cells which enable wide application in the field of displays[5,6], sensors and lasers[7] in recent years nanocrystalline ZnS attracted much attention because the properties in nano form differ significantly from those of their bulk counter parts. Therefore much effort has been made to control the size, morphology and crystallinity of ZnS thin film. There has been growing interest in developing techniques for preparing semiconductor nano particles and films.

Several techniques have been employed to prepare ZnS thin films such as Thermal evaporation [8,9], Spray pyrolysis [10-13], Molecular beam epitaxy [14], RF reactive sputtering [15],

Chemical bath deposition technique[16-23], Photo chemical deposition technique[24], Atomic layer deposition [25], Screen printing technique[26].

In present investigation ZnS thin films have been deposited using chemical bath deposition method. The structural, surface morphological, optical and electrical properties of the as deposited ZnS thin films were studied.

MATERIALS AND METHODS

The deposition of film was carried out by using Corning glass slides (25 mm X 75 mm X 1 mm) as substrate which were initially boiled in concentrated chromic acid for 30 min. rinsed in acetone, double deionised water and finally ultrasonically cleaned. All analytical grade (A.R) reagents were used as it is without further purification for the deposition of ZnS thin films. For deposition of ZnS thin films aqueous solution of 0.1M Zinc Sulphate, 0.1M thiourea and complexing agent 20% aqueous ammonia were used. Initially 10 ml of $ZnSo_4$ solution and 3.5 ml ammonia were placed in 100 ml beaker, after stirring for several minutes solution becomes colorless and homogeneous under continuous stirring , 10 ml thiourea solution was introduced then pretreated substrate were vertically immersed into the prepared bath at 85^0C temperature. Preparative parameters are optimized for best quality ZnS film. The variation of film thickness with concentration of Zinc Sulphate is as shown in **fig.1** keeping concentration of thiourea 0.1M. The ZnS film formation was started at concentration of 0.025M of Zinc Sulphate but it optimize for maximum thickness at 0.1M concentration.

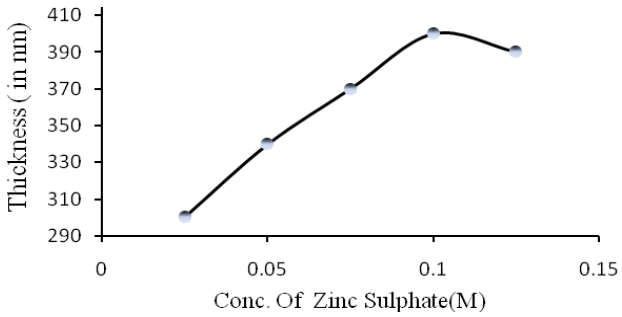

Fig.1 Variation of ZnS film thickness as function of concentration of Zinc Sulphate for fixed concentration of Thiourea (0.1M)

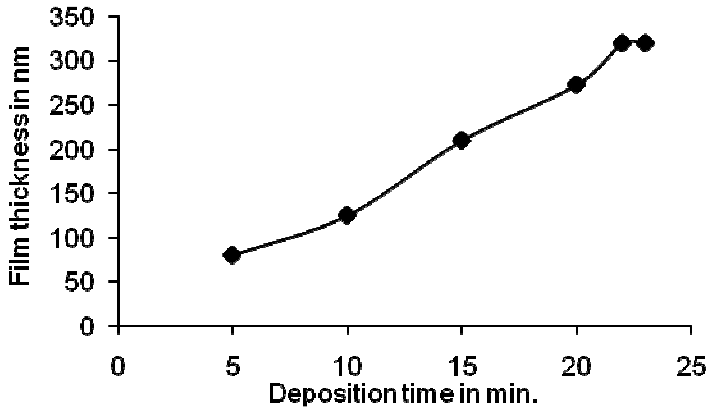

Fig. 2. Graph of as deposited ZnS film thickness as a function of deposition time.

After this ZnS film thickness was decreased due to formation of outer porous layer and peeling off from glass substrate [27].The thickness of ZnS thin film was measured by profilometer. **Fig. 2** shows the variation of film thickness with deposition time. Initially film thickness increases with deposition time.

This ZnS film had maximum terminal thickness of 320 nm for deposition time 22min. after this film thickness starts to decrease due to peeling of the material from the substrate [27].

Characterization Techniques

The thickness of the thin film was measured by a surfcom 480^{o}A profilometer. The structural characterization of the film was carried out using Philips (PW-3710) X-ray diffractometer with CuKα radiation (α= 1.5404^{o}A) in 2θ range from 20-80$^{o.}$ The surface morphological study of ZnS film was carried out by scanning electron microscopy using Cambridge steriscan 250 microscopy MK-3 model. The electrical resistivity of the film was measured by two probe technique. The optical absorption spectra of the film was recorded on Systronic spectrophotometer in the wavelength range of 350-850 nm.

RESULT AND DISCUSSION

4.1 structural studies

Fig. 3 shows XRD pattern onto glass substrate showing amorphous structure with some sharp diffraction lines with wurtzite hexagonal ZnS phase.

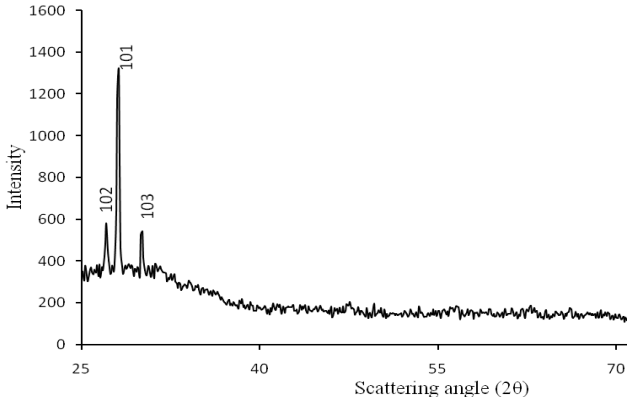

Fig. 3: The X-ray diffraction pattern of as-deposited ZnS on glass substrate at 85^{0}C temperature

In order to determine average grain size of ZnS film particles slow scan between 27^{o} and 31^{o} was carried out with a step 0.02^{o}/min. using the scherrer's formula the crystalline size (d) was calculated as

$$d = 0.9\lambda / \beta \text{Cos } \theta \qquad \textbf{(1)}$$

where β is the broadening of diffraction line measured at full width of half maximum intensity (rad.) and λ= 1.5406^{o}A is the wavelength of CuKα radiation [28] the average grain size of ZnS thin films was found to be about 100 nm.

4.2 Surface morphological studies

Scanning electron microscopy (SEM) is a versatile technique for studying microstructure of thin films. The ZnS thin film of 320 nm thickness was used to study the surface morphology using a scanning electron microscopy.

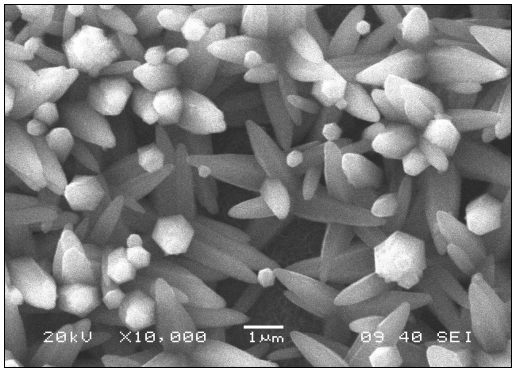

Fig.4: The surface morphology of as-deposited ZnS on glass substrate at 85^{0}C temperature by scanning electron microscopy studies

Fig. 4 shows a scanning electron microscope of ZnS thin films at X 10000 magnification the scale bar length is 1µm the average grain size of ZnS thin films was estimated using Cotrells methods [29]. The estimated average grain size is 100 nm of ZnS thin film. It is observed that the film is uniform whitish and well substrate covered.

4.3 Optical properties

The optical properties of ZnS thin film is determined from absorbance measurement in the range 350-800 nm **Fig. 5** shows the absorbance spectra of ZnS thin film.

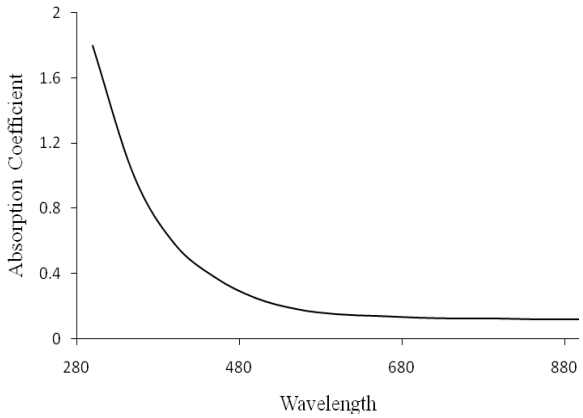

Fig.5: The absorbance spectra of as-deposited ZnS on glass substrate.

Absorbance coefficient α associated the strong absorption region of the film was calculated from absorbance (A) and the film thickness (t) using relation [29,30]

$$\alpha = 2.3026\ A/t \qquad \textbf{(2)}$$

The absorption coefficient α was analyzed using the following expression for optical absorption of semiconductors [31]

$$(\alpha h\upsilon) = K\ (h\upsilon - E_g)^{n/2} \qquad \textbf{(3)}$$

where k is Boltzmann's constant, E_g is separation between valence and conduction bands and n is constant that is equal to 1 for direct band gap semiconductor.

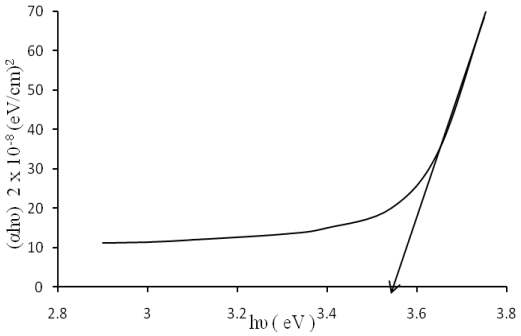

Fig. 6: Plot shows the variation of $(\alpha h\upsilon)^2$ verses hυ of as-deposited ZnS thin film on glass substrate at room temperature.

The band gap was determined from the intersect of straight line portion of $(\alpha h\upsilon)^2$ versus hυ graph shown in **fig. 6** The observed band gap value of the film was 3.45 eV.

4.4 Electrical resistivity

The electrical resistivity of ZnS thin film was measured using d.c.. two point probe method **Fig. 7** shows the variation of log of resistivity (log ρ) with 1/T X 10^{-3}K for film. The resistivity follows the relation

$$\rho = \rho_0 \exp (Ea/kT) \qquad \textbf{(4)}$$

where ρ is resistivity at temperature T, ρ_0 is a constant , k is Boltzmann constant , E_a is activation energy for conduction. From **fig. 8** resistivity of ZnS sample decreases with temperature indicating semiconducting nature of thin film,

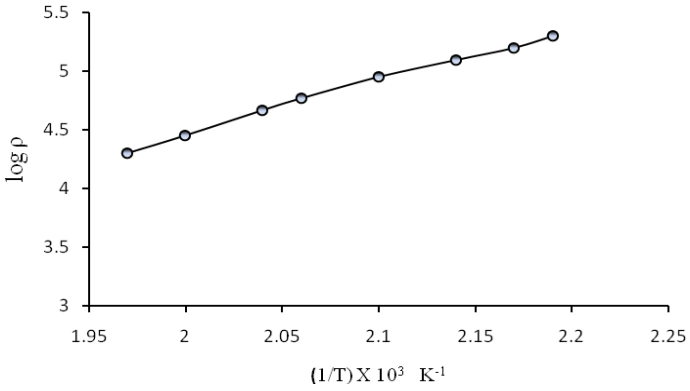

Fig. 7: The graph shows the variation of log *ρ* with 1000/T for as-deposited ZnS on glass substrate at room temperature.

from this plot thermal activation energy was calculated using relation **(4)** [32-34]. Resistivity of the sample was measured at 500^o K and it found to be 0.36 X 10^5 Ω-cm with activation energy 0.82 eV.

CONCLUSION

A simple chemical bath deposition method was used for preparation of ZnS thin films on glass substrate . The XRD study showed the Wurtzite (Hexagonal) structure of ZnS thin film. The SEM micrographs reveals that substrate is well covered and average grain size is 100 nm .The

Optical bandgap was found to be 3.45eV. It has been observed that the electrical resistivity of ZnS thin film comes out to be 0.36 X 10^5 Ω-cm with activation energy 0.82 eV.

REFERENCES

[1]W.H. Bloss, F. Pfisterer, H.W.Schock " *Advances in solar energy , an Annual review of research & development* ",**1988** ,Vol.4 , P-275
[2] H. Katayama, S. Oda, H. Kukimoto, *Appl. Phys. Lett.*, **1975**, 27, 657.
[3] A. Antony, K.V. Mirali, R. Manoj, M.K. Jayaraj, *Mater.Chem.Phys.*,**2005**, 90, 106.
[4] S. Coe, W.K. Woo, M.G. Bawendi, V. Bulovic, *Nature*,**2002**, 420, 800.
[5] M.C. Beard, G.M. Turner, C.A. Schmuttenmaer, *Nano Lett.* , **2002**, 2, 983.
[6] R.P. Raffaelle, S..L. Castro, A.F. Hepp, S.G. Bailey, *Prog. Photovoltaics* , **2002,** 10, 433.
[7] V.I. Klimov, A.A. Mikhailovsky, S. Xu, A. Malko, J.A. Hollingsworth, C.A. Leatherdale, H.J. Eisler, M.G. Bavendi, *Science*, **2000,** 290, 314.
[8] S.M.A Durrani, A.M. Al-shukri, A. Iob, E.E.Khawaja, *Thin Solid Films*, **2000**, 199,379.
[9] V. Dimitrova, J. Tate, *Thin Solid films*, **2000,** 134, 365.
[10] H.H. Afifi, S.A. Mahmoud, A. Ashour, *Thin Solid films*, **1995**, 263,248.
[11] B. Elidrissi, M. Addou, M. Regragui, A. Bougrine, A. Kachouane, J.C.Bernede,*Mater.Chem.Phys*., **2001,** 68, 175.
[12] M. C. Lopez, J. P. Espinos, F. Martin, D. Leinen, J.R. Ramos-Barrado, *J.of Cryst Growth*., **2005**, 66, 285.
[13] M.A. Hernandez-Fenollosa, M.C. Lopez, V. Donderis, M. Gonalez, B. Mari, J.R. Ramos-Barrado, *Thin Solid Films*, **2008,** 516, 1622.
[14] M. Yoneta, M. Ohishi, H. Saito, *J.Cryst.Growth.*, **1993**,127, 314.
[15] L.-Z. Shaoi, K.-H. Chang, H.-L. Hwang, *Appl.Surf.Sci.*, **2003** , 305, 212-213.
[17] I.O. Oldaji, L. Chow, *Thin Solid Films*, **1999,** 339, 148.
[18] P.O. Brien, D.J. Otway, D.S. Boyle, *Thin Solid Films*, **2000,** 17,361-362.
[19] J. Cheng, D.B. Fan, H. Wang, B.W. Liu, Y.C. Zhang, H. Yan, *Semicond.Sci.Tech.* **2003**,18, 676.
[20] S.D. Sartale, B.R. Sankapal, M. Luxsteiner, E. Ennaoui, *Thin Solid Films* **2005**,168 ,480-481
[21] Pulomi Roy, Jyoti R. Ota, S.K. Srivastava, *Thin Solid Films*, **2006**, 515, 1912
[22] Alireza Goudarzi, Ghaffar Motedayen, Reza Sahraei, Hiva Ahmadpoor, *Thin Solid Films* **2008**,516, 5953.
[23] Maria Ladar, E.J. Popovici, J. Baldea, R. Green, E. Indrea, *J.of Alloys & Comp*. **2007,**295, 434-435.
[24] P.O. Brien, J.Mcaleese, *J.Mat.Chem.Phys*., **1998** ,8, 2309.
[25] M. Gunasekaran, R, Gopala Krishnan, P. Ramasamy. *Mat.Lett.*, **2003** ,58, 67.
[26] Y.S. Kim, S.J. Yun, *Appl. Surf. Sci*., **2004**, 105, 229.
[27] R. S. Patil , C .D .Lokhande , R. S. Mane , H. M. Pathan ,Oh-Shim Joo ,Sung-Hwan Han, *material science and engineering,* **2006** , B129,59-63
[28] Y.S. Seol , H.B. Im , *J. of Mater .Sci*., **1987**, 22, 3533.
[29] A.cottrell, *Intorduction to Mettallurgy ,Arnold, Londan*, **1975,** P.173
[30] R.S.Longhurst, *Geometrical & physical optics ,Longmans green,Londan* **1957.**
[31] Vipin Kumar , K.L.A. Khan ,G. Singh and T.P. Sharma , *Appl .Surf. Sci*., **2007**, 7, 253.
[32] R. S. Patil , C .D .Lokhande , R. S. Mane , H. M. Pathan ,Oh-Shim Joo ,Sung-Hwan Han, *material science and engineering,* **2006** , B129,59-63
[33] R. S. Patil, T.P. Gujar, C.D. Lokhande, R.S.Mane, Sung-Hwan Han, *Solar Energy* **2007**, 81,648-652.

[34] R. S. Patil, T.P. Gujar, C.D. Lokhande, R.S.Mane, Sung-Hwan Han, *Journal of non-crystalline Solids* , **2007,** 353,1645-1649.