

POLYCRYSTALLINE ZnS THIN FILMS BY SCREEN PRINTING METHOD AND ITS CHARACTERIZATION

VIPIN KUMAR^{a,*}, M.K. SHARMA^a, J. GAUR^a, T. P.SHARMA^b

^a*Department of Physics, Krishna Institute Of Engg. & Technology, Ghaziabad, India*

^b*Department of Physics, University of Rajasthan, India*

The II-VI compound semiconductors are of great importance due to their application in various electro-optic devices. Several methods have been used to prepare ZnS thin films. We have deposited ZnS films on ultra-clean glass substrate by Screen-printing method followed by sintering process. ZnS having wide band gap of 3.50-3.70 eV is a promising material to be used in photovoltaic devices, solar cells. The optical, structural and electrical properties of ZnS thin films have been examined. The optical band gap of these films is studied by reflection spectra in wavelength range 325-600nm using Tauc relation. The band gap does not show noticeable change with sintering temperature. The Wurtzite structure of ZnS films is confirmed by X-ray diffraction analysis. The electrical resistivities of the films were measured in vacuum by two-probe technique. Sintering is a very simple and viable method compared to other intensive methods. The results of the present investigation will be useful in characterizing the material ZnS for its applications in electro-optic devices, photovoltaic.

(Received October 29, 2008; accepted November 3, 2008)

Keywords: Thin films; Semiconductors; Sintering; Optical properties; X-ray diffraction.

1. Introduction

Zinc Sulphide is an important II-VI group semiconductor with a large direct band gap of 3.50-3.70 eV in the UV range. It is used as a key material for light emitting diodes [1, 2] and other optoelectronic devices such as electroluminescent displays [3], Cathodoluminescent displays and multilayer dielectric filters [4,5]. ZnS is highly suitable as a window layer in heterojunction photovoltaic solar cells; because the wide band decreases the window absorption losses and improves the short circuit current of the cell [6]. In the area of optics, ZnS can be used as a reflector, because of its high refractive index (2.35), and a dielectric filter because of its high transmittance, in the visible range [6].

The research on renewable energies includes the photovoltaic conversion of solar energy and important investigations of novel materials and structures. Photovoltaics are the most fascinating ways of direct solar energy conversion. Thin film solar cells give hope to meet the cost goals, which are necessary to provide the needs for energy production by photovoltaics.

It is generally recognized that any large-scale application must rely on cheap polycrystalline materials. The use of thin film polycrystalline semiconductors has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices. The technological interest in polycrystalline-based devices is mainly due to their very low production costs.

Several techniques have been used to produce ZnS thin film such as thermal evaporation [7,8], spray pyrolysis [9-12], molecular beam epitaxy [13], RF reactive sputtering [14], chemical bath deposition [15-22], photochemical deposition technique [23], atomic layer deposition [24].

* Corresponding author: vipinkumar28@yahoo.co.in

The technique of screen-printing followed by sintering offers interesting possibilities for preparing ZnS thin films [25,26].

Our intention is to use this material for the fabrication of photovoltaic devices and to study the optical, structural and electrical properties of ZnS films. Screen-printing followed by sintering is one of the best techniques for the preparation of polycrystalline films with ease, at low costs and large area applications. It is extremely simple and viable as compared to the other cost intensive methods [26-32]. In present investigation optical, structural and electrical characterization of polycrystalline ZnS films has been carried out. It is easy to incorporate screen-printing technique in the industrial production line.

2. Experimental details

In present investigation ZnS films were prepared by Screen printing followed by sintering process [26-32]. A Commercially available ZnS powder with 99.999% purity was used as the starting material. Slurry consisting of ZnS powder, 10% weight of ZnCl₂ and an appropriate amount of ethylene glycol were thoroughly mixed. ZnCl₂ was used as an adhesive and ethylene glycol as a binder. The paste thus prepared was screen printed on ultra-clean glass substrates. It was then cleaned by embryo powder, acetone and finally washed with distilled water. The samples thus prepared were dried at 120°C for 4 hours in the open air. The reason of drying the sample at lower temperature was to avoid the cracks in the samples. The removal of organic materials takes place at about 400°C. So sintering temperature could not be less than 400°C. Zinc chloride is hygroscopic and its melting point is 283°C. To get stable film, zinc chloride and ethylene glycol should not remain in the samples. The sintering temperature and sintering time was optimized by performing the experimental process for different values of these two parameters and concluded that the samples should be sintered at 500°C for 10 min in a temperature controlled furnace in air atmosphere. All the films were synthesized under the same experimental conditions. The thickness of prepared films is of the order of a micron.

3. Techniques of characterization

The optical reflectance versus wavelength traces of all the films were recorded in 325-600nm wavelength range using a double beam spectrophotometer (Hitachi U-3400). The XRD traces were recorded using Philips X-ray diffractometer using CuK α radiation. The electrical resistivity of the films was measured in vacuum by two-probe technique.

4. Results and discussion

4.1. Optical properties

Reflection spectra of sintered ZnS films is taken at room temperature with the help of a Hitachi Spectrophotometer model U-3400. In this model the prism/grating double monochromatic system is used, the lenses used in conventional monochromator are replaced with mirrors. So, the image deviation due to chromatic aberration is eliminated. Its wavelength range is 187-2600nm. The lead sulphide detector (PbS) is used for the detection of infrared rays. The visible wavelength light source is long life WL lamp. The optical band gaps of these films are determined with the help of reflection spectra [32]. Almost all the II-VI Compounds are direct band gap semiconductors. According to Tauc relation [33], the absorption coefficient for direct band gap material is given by $\alpha_{hv} = A (hv - E_g)^n$,

Where hv is photon energy, A is constant, E_g is the band gap, and n is equal $\frac{1}{2}$ for direct band gap material.

To measure energy band gap from reflection spectra, a graph between $(\alpha h\nu)^2$ Vs. $(h\nu)$ is plotted. Absorption coefficient α is proportional to $\text{Ln} [(R_{\text{max}} - R_{\text{min}}) / (R - R_{\text{min}})]$ [32] where reflectance falls from R_{max} to R_{min} due to absorption by the material and R is the reflectance for any intermediate energy photons. So α is used in terms of reflectance as $\text{Ln} [h\nu (R_{\text{max}} - R_{\text{min}}) / (R - R_{\text{min}})]$ and extrapolation of straight line to $(\alpha h\nu)^2 = 0$ axis give the value of energy band gap of film material. Fig. 1 shows the reflection spectra of sintered ZnS by above described Hitachi spectrophotometer model U-3400.

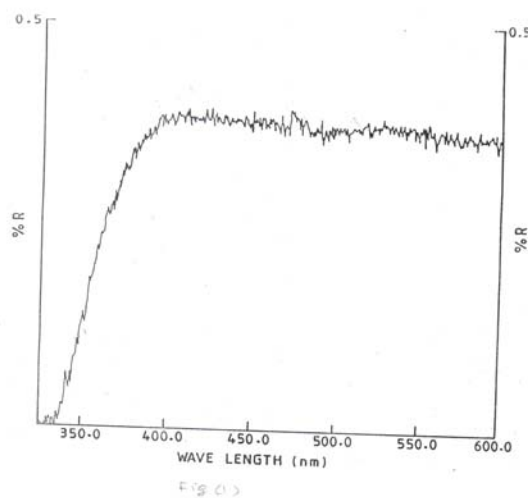


Fig.1. Reflection spectra of ZnS sintered film.

The mode of optical transition in these films is of band to band direct type. This has also been confirmed by plotting $\text{Ln}(\alpha h\nu)$ Vs $[\text{Ln}(h\nu - E_g)]$ for direct allowed type transitions, therefore we are using here the Tauc relation[33] for direct band gap material in which we plot a graph between $(\alpha h\nu)^2$ Vs. $(h\nu)$. Fig. 2 shows a plot between $[h\nu \text{Ln} \{ (R_{\text{max}} - R_{\text{min}}) / (R - R_{\text{min}}) \}]^2$ Vs $h\nu$ for sintered ZnS film. The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ gives the value of direct band gap. From this graph the value of energy band gap comes out to be 3.50eV. The band gap does not show noticeable change with sintering temperature. **M.E Rincon et.al** have reported the band gap of 3.70eV of ZnS film prepared by screen printing technique and **Y.S.Seol et.al** have reported the band gap 3.54 eV of ZnS films sintered at 650°C for 10 min in nitrogen atmosphere .

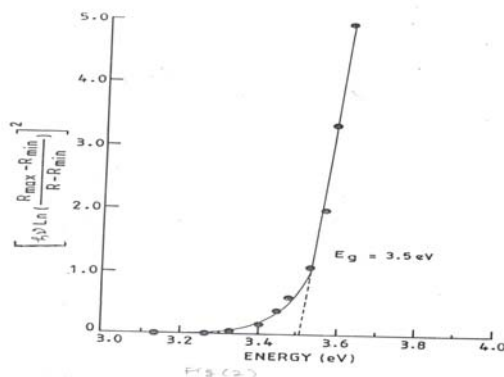


Fig. 2. Energy Band gap determination of ZnS sintered from Reflectance measurement

4.2. Structural properties

In literature Zinc sulphide films have been found to grow in sphalerite, cubic (zinc blende) and hexagonal wurtzite forms depending upon the deposition process. In present investigation we report hexagonal wurtzite structure of ZnS material prepared by screen-printing technique. **M.E Rincon et.al** has also reported the hexagonal wurtzite structure with some low intensity peaks of ZnO (zincite) for ZnS films prepared by same method.

The deposited ZnS thin films were analysed by X-ray diffraction pattern for structural analysis by using CuK α radiation with the help of Philip X-ray diffractometer. The d-values were calculated by calculating θ values from the peaks of the X-ray spectrum by using Bragg's relation $2d\sin\theta = n\lambda$ ($n=1$ in present study and $\lambda= 1.54045$ for CuK α). These d values were compared with the standard ASTM data to confirm the structure of ZnS (See table 1). Fig.3 is the X-ray diffraction pattern of sintered ZnS film with CuK α radiation.

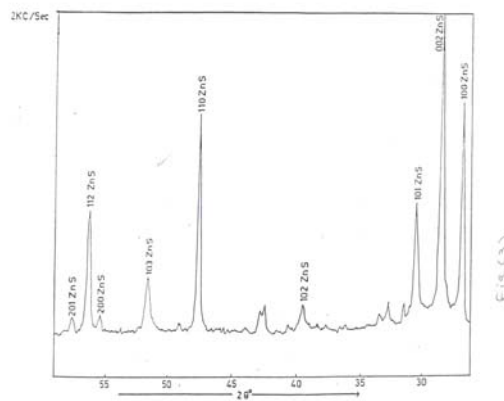


Fig. 3. X-ray diffraction pattern of ZnS sintered film.

Table.1 is the X-ray analysis of sintered ZnS film. All the peaks were in well agreement with the standard ASTM data except three peaks at 33° , 43° & 48° which may be attributed to the presence of ZnCl $_2$ as ZnCl $_2$ is used as an adhesive in ZnS sintered films. The X-ray analysis of ZnS film confirms the hexagonal wurtzite structure of ZnS material. The presence of sharp structural peaks in this XRD confirmed the polycrystalline nature of ZnS films.

SEM of these films revealed homogeneous, uniform grains and average grain size of about 2.0 μm . It has been observed that that grain sizes of prepared films do not show noticeable change with sintering temperature.

Table 1.

No.	$2\theta^\circ$	d (exp) \AA	d (ASTM) \AA	Plane (hkl)
1.	26.9	3.314	3.309	100
2.	28.5	3.132	3.128	002
3.	30.5	2.931	2.925	101
4.	39.6	2.276	2.273	102
5.	47.4	1.918	1.911	110
6.	51.8	1.765	1.764	103
7.	55.4	1.659	1.654	200
8.	56.3	1.634	1.630	112
9.	57.6	1.600	1.599	201

4.3. Electrical properties

The electrical transport properties of the materials are of great importance in determining the congruency of the material with our necessities. The electrical properties are dependent on various films and growth parameters such as film composition, thickness, and substrate temperature and deposition rate. For photovoltaic applications, important characterization includes electrical resistivity.

4.3.1 Electrical resistivity

The electrical resistivity of ZnS films was measured using the D.C two point probe method in vacuum. Fig (4) shows the variation of log of resistivity ($\log \rho$) with reciprocal of temperature ($1/T$) $\times 10^3$. For all films resistivity follows the relation

$$\rho = \rho_0 \exp (E_0/ kT) \quad (1)$$

Where ρ is resistivity at temperature T , ρ_0 is a constant, k is the Boltzman, s constant and E_0 is activation energy required for the conduction. From the resistivity plot, the thermal activation energy was calculated using Eq (1). The electrical resistivity of the samples were measured at 500K.

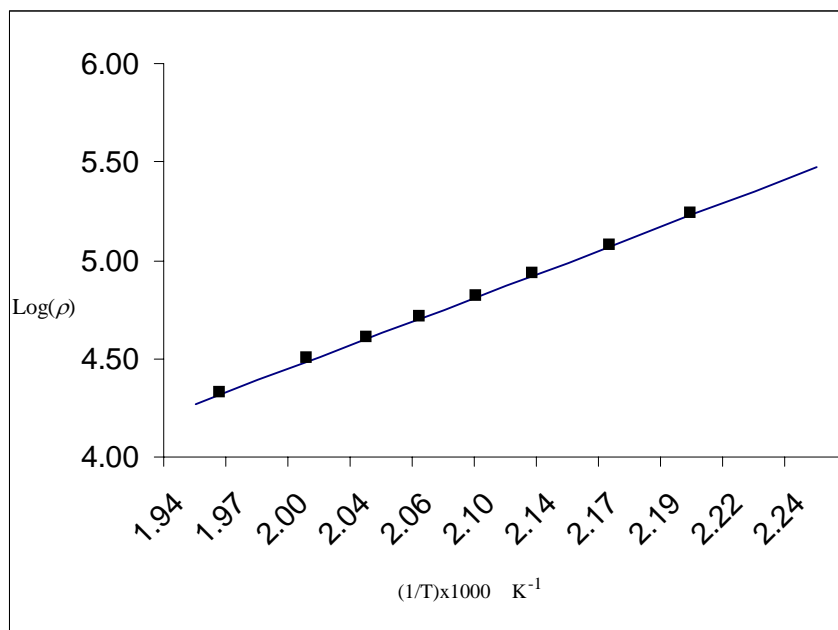


Fig. 4. Temperature dependence of Electrical resistivity of ZnS sintered film.

From fig (4) it is clear the resistivity of ZnS samples decrease with temperature indicating semi-conducting nature of the films. The plot of $\log \rho$ against $1000/T$ for ZnS films is a straight line indicating that conduction in ZnS film is through thermally activated process. A similar behavior of polycrystalline materials prepared by different methods was reported by several workers [34-36]. Obviously, the straight-line nature of this plot suggests that grain boundary limited conduction is the dominant conduction mechanism. We would like to state that the grain boundaries are the consequence of the imperfections associated with the polycrystalline films. Seto

[37] explained the high temperature conduction mechanism in semiconductors. In present investigation the electrical resistivity and activation energy of ZnS film comes out to be $0.37 \times 10^5 \text{ohm cm}$ and 0.80eV respectively.

5. Conclusions

The optical, structural and electrical properties of ZnS sintered films were investigated. The band gap of ZnS sintered film comes out to be 3.50 eV . The films of ZnS are found to be polycrystalline in nature and have hexagonal wurtzite structure. It has been observed that the electrical resistivity and activation energy of ZnS comes out to be $0.37 \times 10^5 \text{ohm cm}$ and 0.80eV respectively. The conduction in ZnS film is through thermally activated process. Due to optimum band gap, large absorption coefficient, polycrystalline nature, stable material, fairly high activation energy, ZnS sintered film may be suitable for solar cells, Wide band gap window material and other photovoltaic devices. The sintering technique is simple, inexpensive, viable and attractive means of obtaining films of II-VI semiconductors.

Acknowledgements

The Authors are thankful to Dr. Ajay Sharma (Director General, KIET, Gzb) and Prof. Prabal K. Chakravorty (Director, KIET, Gzb) and Prof. C.M. Batra (Head, Deptt. of B.S., KIET, Gzb) for constant support and encouragement to carry out this work.

References

- [1] H. Katayama, S. Oda, H. Kukimoto, *Appl. Phys. Lett.*, **27**, 657 (1975).
- [2] A. Antony, K.V. Mirali, R. Manoj, M.K. Jayaraj, *Mater.Chem.Phys.*, **90**, 106 (2005).
- [3] G.O.R. Mach, *Physics Status Solidi.*, **69**, 11 (1982).
- [4] A.M. Ledger, *Appl. Opt.*, **18**, 2979 (1979).
- [5] P.L. Jones, D.M. Moore and D.C. Smith, *J. Phys. E.*, **9**, 312 (1976).
- [6] N. Fathy, R. Kobayashi, M. Ichimura, *Mater.Sci.Eng.B.*, **107**, 271 (2004).
- [7] S.M.A. Durrani, A.M. Al-shukri, A. Iob, E.E. Khawaja, *Thin Solid Films*, **379**, 199 (2000).
- [8] V. Dimitrova, J. Tate, *Thin Solid films.*, **365**, 134 (2000).
- [9] H.H. Afifi, S.A. Mahmoud, A. Ashour, *Thin Solid films*, **263**, 248 (1995).
- [10] B. Elidrissi, M. Addou, M. Regragui, A. Bougrine, A. Kachouane, J.C. Bernede, *Mater.Chem.Phys.* **68**, 175 (2001).
- [11] M. C. Lopez, J. P. Espinos, F. Martin, D. Leinen, J.R. Ramos-Barrado, *J. of Cryst Growth.*, **285**, 66 (2005).
- [12] M.A. Hernandez-Fenollosa, M.C. Lopez, V. Donderis, M. Gonzalez, B. Mari, J.R. Ramos-Barrado, *Thin Solid Films*, **516**, 1622 (2008).
- [13] M. Yoneta, M. Ohishi, H. Saito, *J. Cryst. Growth.*, **127**, 314 (1993).
- [14] L.-Z. Shaoi, K.-H. Chang, H.-L. Hwang, *Appl. Surf. Sci.*, **212-213**, 305 (2003).
- [15] I.O. Oldaji, L. Chow, *Thin Solid Films*, **339**, 148 (1999).
- [16] P.O. Brien, D.J. Otway, D.S. Boyle, *Thin Solid Films*, **361-362**, 17 (2000).
- [17] J. Cheng, D.B. Fan, H. Wang, B.W. Liu, Y.C. Zhang, H. Yan, *Semicond. Sci. Tech.* **18**, 676 (2003).
- [18] S.D. Sartale, B.R. Sankapal, M. Luxsteiner, E. Ennaoui, *Thin Solid Films* **480-481**, 168 (2005).
- [19] Pulomi Roy, Jyoti R. Ota, S.K. Srivastava, *Thin Solid Films*, **515**, 1912 (2006).
- [20] Alireza Goudarzi, Ghaffar Motedayen, Reza Sahraei, Hiva Ahmadpoor, *Thin Solid Films* **516**, 5953 (2008).
- [21] Maria Ladar, E.J. Popovici, J. Baldea, R. Green, E. Indrea, *J. of Alloys & Comp.* **434-435**, 697 (2007).

- [22] P.O. Brien, J.Mcaleese, J.Mat.Chem.Phys., **8**, 2309 (1998).
- [23] M. Gunasekaran, R, Gopala Krishnan, P. Ramasamy. Mat.Lett., **58**, 67 (2003).
- [24] Y.S. Kim, S.J. Yun, Appl. Surf. Sci., **229**, 105 (2004).
- [25] M.E. Rincon, M.W. Martinez, M. Miranda-Hernandez, Sol. Energy Mater. Sol. Cells. **77**, 25 (2003).
- [26] Y.S. Seol , H.B. Im , J. of Mater .Sci., **22**, 3533 (1987).
- [27] S. Kumar, S.K. Sharma, T.P. Sharma, M. Husain, J. Phys. Chem. Solids., **61**, 1809 (2000).
- [28] Vipin Kumar, T.P, Sharma, J. Phys. Chem. Solids., **59**, 1321 (1998).
- [29] Vipin Kumar, T.P. Sharma, J. Opt. Mater., **10**, 253 (1998).
- [30] Vipin Kumar , K.L.A. Khan ,G. Singh and T.P. Sharma , Appl .Surf. Sci. **253**, No.7, 2543 (2007).
- [31] M. Husain , B.P. Singh , S. Kumar ,T.P. Sharma , P.J. Sebastian ,Sol. energy Mater. Sol. Cells **76**, 399(2003).
- [32] Vipin Kumar, S.K. Sharma, T.P. Sharma, V. Singh, J. Opt. Mater., **12**, 115 (1999).
- [33] J. Tauc (Ed.), Amorphous & Liquid Semiconductors , Plenum press, New York, 159 (1974).
- [34] A.U. Ubale and D.K. Kulkarni , Bull.Mater.Sci., **28**, 43 (2005).
- [35] S.S. Kale , U.S. Jahav and C.D. Lokhande , Ind.J.of Pure & Appl . Phys., **34**, 324 (1996).
- [36] Y.Z. Wang , G.W. Qioa , X.D. Lia , B.Z. Ding , and Z.Q. Hu , Mater. Lett., **17**, 152 (1993).
- [37] J.Y.W. Seto. J. Appl.Phys., **46**, 5247 (1975).