Structural Properties of Vacuum Evaporated ZnS Thin Films

D Kathirvel 1, R Jeyachitra2

1 Department of Physics, Chikkanada Government Arts College, Tirupur, India.
2 Department of Physics, Kalaigann Karunanidhi Institute of Technology, Coimbatore, India.

ABSTRACT

Thin films of zinc sulphide was deposited on to a glass substrate which is well rinsed in a $10^{-6}$ Torr vacuum. Quartz crystal monitor method was used to determine the film thickness. ZnS films and a typical diffraction pattern of the as-grown ZnS thin films were subjected to X-Ray Power Diffraction (XRD) analysis. A ZnS thin film of lower and higher thicknesses has an amorphous structure and polycrystalline nature with cubic structure respectively. Evaluation of the structural parameters such as micro strain, lattice constant (a), inter-planar distance (d), dislocation density and grain size (D) have been carried out. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) was employed to find the grain size of the particles and to study about the surface smoothness. Films with different thicknesses and their grain sizes were calculated. The resolution and magnification was kept at 20µm and 5000x respectively and the SEM micrographs of different thicknesses were analyzed. It is clearly observed that the tiny Nano sized grains are engaged in a fibrous-like structure. This clearly points towards the glassy nature and amorphous phase of ZnS thin films. The AFM micrograph indicates that as the thickness increases, the particle size and the surface roughness of ZnS thin films also increases. The Energy-dispersive X-ray spectroscopy (EDAX) confirms the presence of sulphur, zinc and oxygen in all the films.

Keywords: ZnS, Structural properties, SEM, AFM, Vacuum deposition.

1. INTRODUCTION

The ZnS semiconductor has very unique electronic properties. These properties are essential for fabrication of devices like solar cells, photo diodes, light emitting devices, thin film resistors and photo detectors [1, 2]. There are various methods available to synthesize ZnS thin films. Vacuum evaporation technique is considered to be cost effective, simple and reliable. The development of low cost solar cells depends highly on the exploitation of the thin films. Thus ZnS films got under different experimental conditions require broad optical characterization [3, 4, 5]. The preparation of ZnS thin films with controlled properties needs an operating environment which possesses considerably less interface with the film formation process. To reduce the interaction between the surface of the growing films and the residual gases, extensive works has been performed on the very high vacuum attachment [6, 7, 8]. Currently the studies on film structures are performed using a sophisticated signal channel pulse height analyzer and Philips X-ray diffractometer proportional counter. One of the main advantages of the scanning electron microscope micrographs is that they possess a large field depth. This results in a characteristic three-dimensional appearance which is useful to understand the sample surface structure [9, 10, 11, 12]. AFM enables imaging, measuring and manipulating matter at the nanoscale [13, 14, 15] and is regarded as one of the major tools for facilitating such operations. Cantilevers are used to scan electric potentials. The Energy-Dispersive X-ray spectroscopy (EDAX) was used as an x-ray detector in order to calculate the plentiness of emitted x-rays and their energy levels [16, 17]. The energy calculated from the measurement of voltage...
corresponding to each incident x-ray was propagated to a computer for display and further evaluation of data [18, 19]. The spectrum of x-ray energy versus counts was assessed to find the elemental composition of the sampled volume.

2. MATERIALS AND TECHNIQUES

The 99% pure ZnS powder was made to evaporate by means of a Tungsten conical basket (200 amps) under 2 x 10⁻⁵ Torr pressure on a pre-cleaned glass substrate (3.25 x 2.75 x 0.1 cm dimension). The pressure was measured by a Pirani and Penning gauge. In the coating unit the diffusion pump was supported by rotary pump. The evaporation rate was maintained at a constant rate of 1 Å / sec right through the process of film fabrication. The function of the rotary equipment is to maintain consistency in film thickness. As mentioned earlier a quartz crystal monitor was used to measure and control the thicknesses of the film. The thickness monitor consisted of a flat circular plate which is approximately 0.05 inch (1.4cm) in diameter and 0.011 inch (0.28 cm) thick. For growing the thin films at various substrate temperatures a substrate heater arrangement was used. The temperature inside the chamber was measured using a thermocouple and copper–constant. Digital thickness monitor was used to measure the vacuum evaporated ZnS thin films of varying thicknesses ranging from 550 Å to 1850 Å. The assessment of X-ray diffraction outcomes was done using Cu-Kα, radiation enabled Rigaku Miniflex system. The mean wavelength associated with the system is 1.54059 Å. The SEM is represented by the pollen micrograph shown at the right. SEM enables huge magnifications in the range of 10 to 500,000 times. This equals to 250 times the magnification limit of the world’s best light microscopes available [20, 21, 22]. Atomic Force Microscope (AFM) instruments (N9410S-5500) has a very high-resolution and is a subdivision of scanning probe microscopy. The resolutions are established in the range of Nano metric fractions, 1000 times better than the limit of optical diffraction. A significant technique used for separating the x-ray characteristics of multi-various elements and grouping them into energy spectrums is the Elemental Composition Analysis (ECA). This energy spectrum is then analysed by EDAX system software to find the abundance of particular elements [23, 24, 25].

3. RESULT AND DISCUSSION

3.1. XRD analysis

ZnS films were exposed to XRD analysis. The diffraction pattern of the synthesized ZnS thin films from the technique of vacuum evaporation on glass surface substrates with varying thicknesses of 550 Å, 1150 Å and 1850 Å are depicted in figures B1, B2 and B3 respectively.

The grazing angle was kept at 1.5°. 2θ was scanned in the range 0°-60° to obtain the necessary spectra. The diffraction pattern indicates the sharpness and definition of the peak. From them the polycrystalline nature of the film was concluded.

The existence of the diffraction peak was observed at 2θ = 26.6°. It corresponds to either the (002) hexagonal or the (111) cubic planes. Occurrence of a very small difference (0.021°) between the position of the peak (111) of the cubic structure and the peak (002) of the more stable hexagonal structure makes it difficult to elucidate the crystalline structure of the samples. Furthermore, the missing of other peaks make it impossible to differentiate between the phases under consideration.

It is obvious from the diagrams that as the film thickness increases the peak intensity in the case of diffraction patterns also increases which is contributed by the material growth associated with the diffraction process denoting a progress in the film’s degree of crystallinity. There is an intense peak along the (002) plane in all the films. It notifies the orientation of films with respect to the ‘c’ axis.

The plane-spacing equation of cubic crystals shown in equation (3.1) was used to calculate the lattice parameter (a) and inter planar distance (d),

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

(3.1)

where d=inter-planar distance
a=lattice parameter and
h,k,l=parameters

Scherer’s formula shown in equation (3.2) was used to calculate the grain size,
\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

(3.2)

where  
\[ D = \text{grain size} \]  
\[ \beta = \text{full width half maximum of the peaks}. \]  
\[ K = \text{Shape factor} \]  
\[ \Theta = \text{Bragg angle} \]  
\[ \lambda = \text{X-ray wavelength} \]

The size and structure of the unit cell greatly affects diffraction direction and is a deciding factor in determining it. There is a fair amount of coincidence between the calculated ‘d’ values of ZnS sample and bulk material available in the ASTM tables. All these information results depict that there is a clear presence of cubic ZnS. The lattice parameter (a), inter-planar distance (d), dislocation density (p), grain size (D) and micro strain (\( \varepsilon \)) are depicted in table A1.

Table A1 clearly explains that with the increase in film thickness the grain size of the film also increases. However the micro strain and dislocation density is found to decrease proportionally. This can be considered as an after effect of dislocations and imperfections of the films.

3.2. Scanning Electron Microscope (SEM)

SEM is one of the prominent tools used in the study of material surface topology. The functioning is carried out in vacuum. A beam of high energy coefficient (Probably in the range of 5 to 20eV) is focused on to a spot of diameter in the multiples of nanometers. Figure B4, B5 and B6 depicts the thickness variant SEM images of ZnS thin films. The analysis of SEM micrographs of different thicknesses were carried out at a magnification of 5000x with a 20\( \mu \)m resolution. The SEM micrographs of 550 Å thicknesses reveal that the grain distribution is non-uniform throughout the areas. On the contrary the films are non-void without cracks or pinholes. They conceal the entire substrate well. The Nano sized grains are involved in a fibrous structure, indicating the amorphous phase and glassy nature of ZnS thin films [26, 27]. The grains are thickly packed and spacing between the grains is reduced for a film thickness of 1150 Å as shown in figure B5.

From figure B6, it is concluded that for the films of higher thickness (say 1850 Å) the crystals grow in size. This size difference could be attributed to the existence of an amorphous phase in the films in addition to the crystalline phase which is predominant [27, 28, 29]. The surface morphological study also indicates that the decrease in the Zn content improves the surface smoothness.

3.3. Atomic Force Microscope (AFM)

Depending upon the application, the AFM can operate under many modes. The modes which are possible are sub-divided into static and dynamic modes. The static mode is also called contact mode and the dynamic mode is also known as non-contact mode. In the latter mode the cantilever gets vibrated. The static tip deflection acts as a feedback signal in static mode. Since noise and drift plays an important role in the static signal measurement, cantilevers of low stiffness are employed to amplify the deflection signal. The static mode AFM is used when the overall force is repulsive. Considering static mode, while scanning, the force between the surface and the tip is kept constant such that a constant deflection is maintained. In the dynamic mode, there is no contact between the tip of the cantilever and the sample surface. Instead, the cantilever is made to oscillate at a frequency marginally above the resonant frequency. Here the oscillation amplitude is found in the range of a few nanometers (<10 nm). The sample distance measurement at each data point permits the scanning software to build a sample surface topographic image.

Figures B7, B8 and B9 depicts a two dimensional AFM micrograph corresponding to ZnS thin films having thickness 550 Å, 1150 Å and 1850 Å respectively. The scanning is performed on an 1\( \mu \)m x 1\( \mu \)m area. The AFM images reveal the large uniformity of the spherical shape films. It also shows the films with beta phase with a grain size ranging from 50 to 200 nm.

The mean particle size is calculated from the Debye-Scherrer formula. Table A2 shows the average size and the root mean square of the roughness (rms) at the ZnS films surface with thicknesses of 550 Å, 1150 Å and 1850 Å.

It is obvious from table A2 that the size of the particle and the roughness of the surface pertaining to ZnS thin films rises as the thickness increases.

3.4. Energy Dispersive X-ray Spectrometer (EDAX)
An energy-dispersive spectrometer can be used to detect the energy and amount of X-rays emitted from a specimen. As X-ray energy is characterized by the energy difference among the two shells and the atomic structure of the component from which they were produced, the elemental composition of the specimen can be measured. Figure B10, B11 and B12 shows the energy dispersive X-ray spectra of ZnS thin films of with respective thicknesses of 550 Å, 1150 Å & 1850 Å.

From table A3, the presence of Zinc, Sulphur and Oxygen is confirmed in all the films. The oxygen presence is due to the usage of octylamine. Variations in the concentrations of Zn, S and O are observed to be varying with film thickness. However a uniform variation is not found in any case.

4. CONCLUSION
ZnS thin films are developed as a result of vacuum evaporation and deposition. From the diffraction patterns, it is clear that the film is polycrystalline and exhibits cubic structure. The intensity increases proportionally with the thickness of the films. It indicates the improvement of crystallinity with increase in film thickness. The SEM micrographs reveal that, the grain distributions are uneven throughout the regions. Thus the glassy nature and amorphous phase of ZnS thin films are once again revealed. The AFM studies emphasizes that the particle size increases with increase in film thickness. The compositions of constituents in the ZnS thin films are confirmed by the energy dispersive x-ray analysis.

ACKNOWLEDGEMENT
The authors are grateful to the Algappa Institute of Technology, Karaikudi for aiding the research by providing some of the equipments for the research work.

REFERENCES
[1] Jeffrey M.Pieryga, Richard D.Schaller, DonaldWerder, Michael H.Stewart, Victor I.Klimov and Jennifer A.Hollingsworth, Pushing the Band Gap Envelope: Mid-Infrared Emitting Colloidal PbSe Quantum Dots, Journal of the American Chemical Society, Vol. 126, No. 38, 2004, pp. 11752–11753, http://dx.doi.org/10.1021/ja047659f.
[2] P.N.Gibson, M.E.Ozsan, D.Lincot, P.Cowache and D.Summa, Modelling of the Structure of CdS Thin Films, Thin Solid Films, Vol. 361–362, 2000, pp. 34–40, http://dx.doi.org/10.1016/S0040–6090(99)00833–0.
[3] R.B.Kale, S.D.Sartale, V.Ganesan, C. D.Lokhande, Yi–Feng Lin and Shih–Yuan Lu, Room Temperature Chemical Synthesis of Lead Selenide Thin Films with Preferred Orientation, Applied Surface Science, Vol. 253, No. 2, 2006, pp. 930–936, http://dx.doi.org/10.1016/j.apsusc.2006.01.050.
[4] S.Prabahar, N.Suryanarayanan, S.Srikanth and D.Kathirvel, Photoluminescence Analysis of Chemical Bath Deposited Cadmium Sulphide Thin Films, Chalcogenide Letters, Vol. 6, No. 7, 2009, pp. 309 – 313.
[5] S.H.Jeong, S.Kho, D.Jung, S.B.Lee and J.H.Boo, Deposition of Aluminum–Doped Zinc Oxide Films by RF Magnetron Sputtering and Study of their Surface Characteristics, Proceedings of the Eight International Conference on Plasma Surface Engineering, Garmisch-Partenkirchen, Germany, 2003, pp. 187–192 http://dx.doi.org/10.1016/S0257–8972(03)00600-5.
[6] S.J.Castillo, A.Mendoza-Galvan, R.Ramirez-Bon, F.J.Espinoza-Beltran, M.Sotelo-Lerma, J.Gonzalez-Hernandez and G.Martinez, Structural, Optical and Electrical Characterization of In/CdS/Glass Thermally Annealed System, Proceedings of the 11th International Conference on Thin Films, Cancun, Mexico, 2000, pp. 10–14, http://dx.doi.org/10.1016/S0040–6090(00)01080–4.
[7] Shailaja Kolhe, S.K.Kulkarni, M.G.Takwale and V.G.Bhide, The Electrical Conduction Insprayed CdS Films, Solar Energy Materials, Vol. 13, No. 3, 1986, pp. 203–211, http://dx.doi.org/10.1016/0165–1633(86)90019–5.
[8] Sushil Kumar, Zishan H.Khan, M.A.Majeed Khan and M.Husain,
Studies on Thin Films of Lead Chalcogenides, Current Applied Physics, Vol. 5, No. 6, 2005, pp. 561–566, http://dx.doi.org/10.1016/j.cap.2004.07.001.

[9] T.L.Chu, S.S.Chu, C.Ferekides, C.Q. Wu, J.Britt and C.Wang, 13.4% Efficient Thin-Film CdS/CdTe Solar Cells, Journal of Applied Physics, Vol. 70, No.12, 1991, pp. 7608, http://dx.doi.org/10.1063/1.349717.

[10] T.Mahalingam, M.Radakrishnan, C.P.alasubramanian, Dielectric behaviour of lanthanum oxide thin film capacitors, Thin Solid Films, Vol. 78, No. 3, 1981, pp. 229-233, http://dx.doi.org/10.1016/0040-6090(89)90588-9.

[11] T.L.Chu, S.S.Chu, J.Britt, C.Ferekides and C.Q.Wu, Cadmium Zinc Sulfide Films and Heterojunctions, Journal of Applied Physics, Vol. 70, No. 5, 1991, pp. 2688, http://dx.doi.org/10.1063/1.349384.

[12] V.Das Damodara and K.Seetharama Bhat, Temperature Variation of Thermoelectric Power of Vacuum Deposited PbSe Thin Films and its Thickness Dependence, Journal of Materials Science: Materials in Electronics, 1990, Vol. 1, No. 4, pp. 169-174, http://dx.doi.org/10.1007/BF00696071.

[13] A.N.Molin and A.I.Dikusar, Electrochemical Deposition of PbSe Thin Films from Aqueous Solutions, Thin Solid Films, Vol. 265, No. 1–2, 1995, pp. 3–9, http://dx.doi.org/10.1016/0040-6090(95)06548-2.

[14] H.Metin and R.Esen, Annealing effects on optical and crystallographic properties of CBD grown CdS films, Semiconductor Science and Technology, Vol.18, No. 7, 2003.

[15] Sunny Mathew, P.S.Mukerjee and K.P.Vijayakumar, Optical and Surface Properties of Spray-Pyrolysed CdS Thin Films, Thin Solid Films, Vol. 254, No. 1–2, 1995, Pages 278–284, http://dx.doi.org/10.1016/0040-6090(94)06257-L.

[16] G.C.Morris, R.Vanderveen, Cadmium Suphide Films Prepared by Pulsed Electrodeposition, Solar Energy Materials and Solar Cells, Vol. 27, No. 4, 1992, pp. 305–319, http://dx.doi.org/10.1016/0927-0248(92)90092-4.

[17] M.S.Ali, K.A.Khan and M.S.R.Khan, Temperature Effect on the Electrical Properties of Lead Selenide Thin Films, Physica Status Solidi (a), Vol. 149, No. 2, 1995, pp. 611–618, http://dx.doi.org/10.1002/pssa.2211490211.

[18] V. Damodara Das and K. Seetharama Bhat, Electrical Conductivity of Air-Exposed and Unexposed Lead Selenide Thin Films: Temperature and Size Effects, Physical Review B, Vol. 40, No.11—15, 1989, http://dx.doi.org/10.1103/PhysRevB.40.7696.

[19] H.Ashour and F.El Akkad, Trap Levels in RF Sputtered CdS Thin Films, Physica Status Solidi (a), Vol. 184, No. 1, pp. 175–178, 2001, http://dx.doi.org/10.1002/1521-396X(200103)184:1<175::AID-PSSA175>3.0.CO;2-M.

[20] B.O.Dabbousi, M.G.Bawendi, O.Onitsuka and M.F.Rubner, Electroluminescence from CdSe Quantum-Dot/Polymer Composites, Applied Physics Letters, Vol. 66, No. 11, pp. 1316 http://dx.doi.org/10.1063/1.113227.

[21] T.Ben Nasr, N.Kamoun and C.Guasch, Physical Properties of ZnS Thin Films Prepared by Chemical Bath Deposition, Applied Surface Science, Vol. 254, No. 16, 2008, pp 5039–5043, http://dx.doi.org/10.1016/j.apsusc.2008.01.173.

[22] J.W.Li, Y.K.Su, M.Yokoyama, M.Takahashi, T.Nakata and Y.Hashimoto, The Crystallinity of ZnS Thin Films Prepared by MOCVD, Applied Surface Science, Vol. 65–66, 1993, pp. 433–436, http://dx.doi.org/10.1016/0169-4332(93)90697-A.

[23] M.Ruhul Amin Bhuiyan, M.Monjarul Alam, M.Abdul Momin, Effect of Substrate Temperature on the Optical Properties of Thermally Evaporated
ZnS thin films, Turkish Journal of Physics, Vol. 34, 2010, pp. 43–49, http://dx.doi.org/10.3906/fiz-0902-9.

[24] K.Sarmah, R.Sarma, H.L.Das, Structural Characterization of Thermally Evaporated CdSe Thin Films, Chalcogenide Letters Vol. 5, No. 8, 2008, pp. 153 – 163.

[25] R.Mariappan, V.Ponnuswamy, M.Ravrandar, D.Krishnamoorthi and C.Sankara, The Effect Of Annealing Temperature on Structural and Optical Properties of Undoped and Cu doped CdS thin films, Optik - International Journal for Light and Electron Optics, Vol. 123, No. 12, 2012, pp. 1098–1102, http://dx.doi.org/10.1016/j.ijleo.2011.07.038.

[26] J.M. Blackmore, A.G. Cullis, The structure of ZnS thin films deposited by r.f. sputtering, Thin Solid Films, Vol. 199, No. 2, 1991, pp. 321–334, http://dx.doi.org/10.1016/0040-6090(91)90014-0.

[27] Heini Saloniemi, Tapio Kanniainen, Mikko Ritala, Markku Leskelä and Reijo Lappalainen, Electrodeposition of Lead Selenide Thin Films, Journal of Materials Chemistry, Vol. 8, No. 3, 1998, pp. 651-654.

[28] Sze, S. M., Physics of Semiconductor Devices, Ed John Wiley (1981).

[29] A.Divya, K.Siva Kumar and P.Sreedhara Reddy, Investigations on Structural and Optical Properties of Zn1−xGdxS Nanoparticles, Applied Surface Science, Vol. 258, No. 2, 2011, pp. 839–842, http://dx.doi.org/10.1016/j.apsusc.2011.09.001.
APPENDIX A

Table A1. Structural parameters of ZnS thin films

| Thickness  | (h k l) | d (Å)  | d (Å) ASTM | 2θ  | a (Å) | Grain size (D) Å | Dislocation density (ρ) cm² | Strain (ε) 10⁻³ |
|------------|--------|--------|------------|-----|-------|-----------------|----------------------------|-----------------|
| 550 Å      | 002    | 1.65   | 1.72       | 34  | 5.4709| 5.0206          | 3.6374                    | 6.4709          |
|            | 110    | 3.32   | 3.46       | 20  | 5.0658| 5.1911          | 3.5819                    | 6.4816          |
|            | 101    | 2.00   | 2.01       | 33  | 5.3625| 2.5711          | 14.582                    | 13.5751         |
|            | 111    | 3.42   | 3.40       | 16  | 5.3711| 4.2461          | 8.6862                    | 7.6406          |
| 1150 Å     | 002    | 1.76   | 1.62       | 36  | 5.5706| 5.0521          | 3.4673                    | 6.3706          |
|            | 110    | 3.54   | 3.60       | 23  | 5.692 | 5.2511          | 3.4709                    | 6.292           |
|            | 101    | 1.54   | 1.89       | 36  | 5.8761| 2.5918          | 14.3545                   | 13.4866         |
|            | 111    | 3.81   | 3.72       | 19  | 5.4819| 4.3416          | 8.3921                    | 7.582           |
|            | 002    | 1.72   | 1.68       | 30  | 5.4419| 5.0658          | 3.2342                    | 6.2539          |
|            | 110    | 3.26   | 3.20       | 19  | 5.5106| 5.2911          | 3.3757                    | 6.1543          |
|            | 101    | 1.97   | 1.97       | 28  | 5.3625| 2.6219          | 14.1194                   | 13.2433         |
|            | 111    | 3.32   | 3.22       | 16  | 5.5261| 4.5662          | 8.8176                    | 7.3972          |

Table A2. Variation of particle size with thickness

| SL No. | Film thickness (Å) | Particle size (nm) | Roughness of the surface (nm) |
|--------|--------------------|--------------------|-------------------------------|
| 1      | 550                | 62.48              | 11.60                         |
| 2      | 1150               | 74.52              | 12.48                         |
| 3      | 1850               | 193.80             | 21.56                         |

Table A3. Elemental composition of ZnS thin films

| Element | Wt %     | At %     |
|---------|----------|----------|
|         | 550 Å    | 1150 Å   | 1850 Å | 550 Å    | 1150 Å   | 1850 Å |
| Zn L    | 72.38    | 72.96    | 72.96  | 21.35    | 25.94    | 25.94  |
| S K     | 12.87    | 20.8     | 20.8   | 10.08    | 17.84    | 17.84  |
| O K     | 30.44    | 21.93    | 21.93  | 84.26    | 71.91    | 71.91  |
APPENDIX B

Figure B1. X-ray diffractogram of ZnS thin film of thickness 550 Å

Figure B2. X-ray diffractogram of ZnS thin film of thickness 1150 Å

Figure B3. X-ray diffractogram of ZnS thin film of thickness 1850 Å
Figure B4. SEM Micrographs of ZnS thin film of thickness 550 Å

Figure B5. SEM micrographs of ZnS thin film of thickness 1150 Å
Figure B6. SEM micrographs of ZnS thin film of thickness 1850 Å

Figure B7. Two dimensional AFM micrograph of the ZnS thin film of thickness 550 Å
Figure B8. Two dimensional AFM micrograph of the ZnS thin film of thickness 1150 Å

Figure B9. Two dimensional AFM micrograph of the ZnS thin film of thickness 1850 Å
Figure B10. EDAX spectrum of ZnS thin film of thickness 550 Å

Figure B11. EDAX spectrum of ZnS thin film of thickness 1150 Å
Figure B12. EDAX spectrum of ZnS thin film of thickness 1850 Å