Morphological, structural, optical and electrical properties of nebulizer sprayed Zns thin films

[1]A.Nirmala Shirley, [2]J.Jebaraj Devadason, [3]K.Jeyadheepan, [4]C.Sanjeeviraja

[1]Research Scholar, PG & Research Department of Physics, Pope's College, Sawyerpuram- 628 251, Tamil Nadu, India, Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli - 627 012, Tamilnadu, India

[2]Associate Professor, PG & Research Department of Physics, Pope's College, Sawyerpuram - 628 251, Tamil Nadu, India, Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli - 627 012, Tamilnadu, India

[3]ASK-II, 107-Multifunctional Materials & Devices Lab, School of Electrical and Electronics Engineering, SASTRA Deemed to be University, Tirumalaisamudram, Thanjavur - 613 401, India,

[4]Emeritus Scientist, Alagappa College of Technology, Karaikudi - 630 004, Tamilnadu, India

Abstract: In the present work, investigations on morphological and structural properties was done over the ZnS thin films grown on glass substrates using the nebulized spray pyrolysis technique. The X-ray diffraction was performed to identify the crystal structure and grain size of the particles, whereas the morphological properties was studied using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The fabricated films were then annealed at 300ºC, 400ºC and 500ºC under vacuum, nitrogen at 500ºC and sulphur atmosphere at 500ºC for one hour. This process permits us to obtain peaks crystallized under mixture of hexagonal (H) and cubic (C) phase. Moreover, the crystallites exhibit preferential orientation along the (101) and (016) direction. In addition, the variation of grain size and roughness was studied and observed that when the annealing temperature increases the grain size of the ZnS film increases.

Keywords **- Spray technique; ZnS thin films; Characterization; XRD; AFM; SEM; UV-VIS.**

1. INTRODUCTION

In the recent decades, ZnS belonging to II-VI compound semiconductors has been under extensive research because of its world-wide technological applications. ZnS is optically transparent in the visible region, whereas its band gap energy is relatively wide in nature [1]. Recently, ZnS has attracted more interest in the application of opto-electronic devices, since it is a transparent semiconductor, non-toxic and is abundantly available on the earth [2, 3]. Moreover, it has piezoelectric properties, high transparency and good conductivity, as well as chemical and mechanical stability. ZnS and ZnS doped films are mostly being used as transparent conducting coatings in liquid crystal displays and solar cells [4]. ZnS thin films can be produced by several techniques such as chemical vapor deposition [5], spray pyrolysis [1] and sputtering techniques [6]. Among them, the spray pyrolysis technique offers interesting possibilities owing to its large area technique, with a relatively low cost and a capacity to deposit optically smooth, uniform and homogeneous layers. Research report on structural and optical characteristics of ZnS thin films have been reported by many investigators. Nevertheless, their physico-chemical properties have not yet been widely studied in order to reach the bulk and surface composition. Hence, in the present work the main objective is to study the structural and morphological properties of ZnS films deposited by spray pyrolysis technique for implementing it as an alternative for antireflective coating in solar cells. Moreover, in the present investigation ZnS thin films have been deposited using nebulized spray pyrolysis techniques and the structural, morphological, optical and electrical properties for the fabricated ZnS thin films was characterized and the obtained outcomes are reported in the proceeding sections.

2. EXPERIMENTAL DETAILS

ZnS thin films were deposited using chemical spray technique and two different solutions were used in this work as precursors for making thin films of ZnS: zinc chloride (10^{-2} M) and thiourea (10^{-2} M) in distilled water. The glass substrates were cleaned with hydrochloric acid and the acetone is boiled in an ultrasonic bath for about 15 min and later then dried in a stream of nitrogen atmosphere. The deposition time was maintained at 30 min for each samples and the layers were sprayed at different temperatures of substrate from 250ºC to 450ºC. Moreover, the deposition parameters such as the molar ratio r = [Zn]/[S] is 1:3, the deposition time (td) and the spray rate are 30 to 60 sec and 0.6 mL per min respectively with a carrier gas pressure maintained at 1.6kg/cm^2.

The XRD patterns of all the thin films were performed under copper source in an Analytical X Pert PROMPD diffractometer. The morphological and surface topography of the films were analyzed by atomic force microscopy (AFM) at Park Scientific Instrument under contact mode and scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

3.1. STRUCTURAL PROPERTIES

X-ray diffraction analysis was carried out to study the crystal structure and crystallinity of deposited ZnS thin films. It was found that ZnS may have either cubic or hexagonal structure, depending on the synthesis conditions such as deposition temperature and precursor concentration [8-10]. The purity of the phase and crystal structure of the samples were analyzed using CuKα radiations source in the 2θ degree range from 20o to 60o with a step size of 0.0170 using XPERT-PRO diffractometer. Figure 1 shows the XRD Pattern of the synthesized ZnS film. The obtained diffraction data were in agreement with the JCPDS (JCPDS 89-2144) data for the produced ZnS film. Two main peaks at (101) and (016) recommend hexagonal wurtzite structure with a lattice parameter value, α = 3.820 A˚[11, 12].

From the X-ray diffraction peaks as shown in figure 1 the particle size are determined from the full-width half-maximum [FHWM] of the XRD peaks [8,9]. Using the Debye- Scherrer's formula [7]

$$D = 0.89\ \lambda / \beta\cos\theta \qquad (1)$$

Where D, λ, β and θ are the average particle size, wavelength of the CuKα radiation, full width at half-maximum of the diffraction plane and diffraction angle respectively. The average calculated particle size of the synthesized ZnS nano particles is about 99 nm.

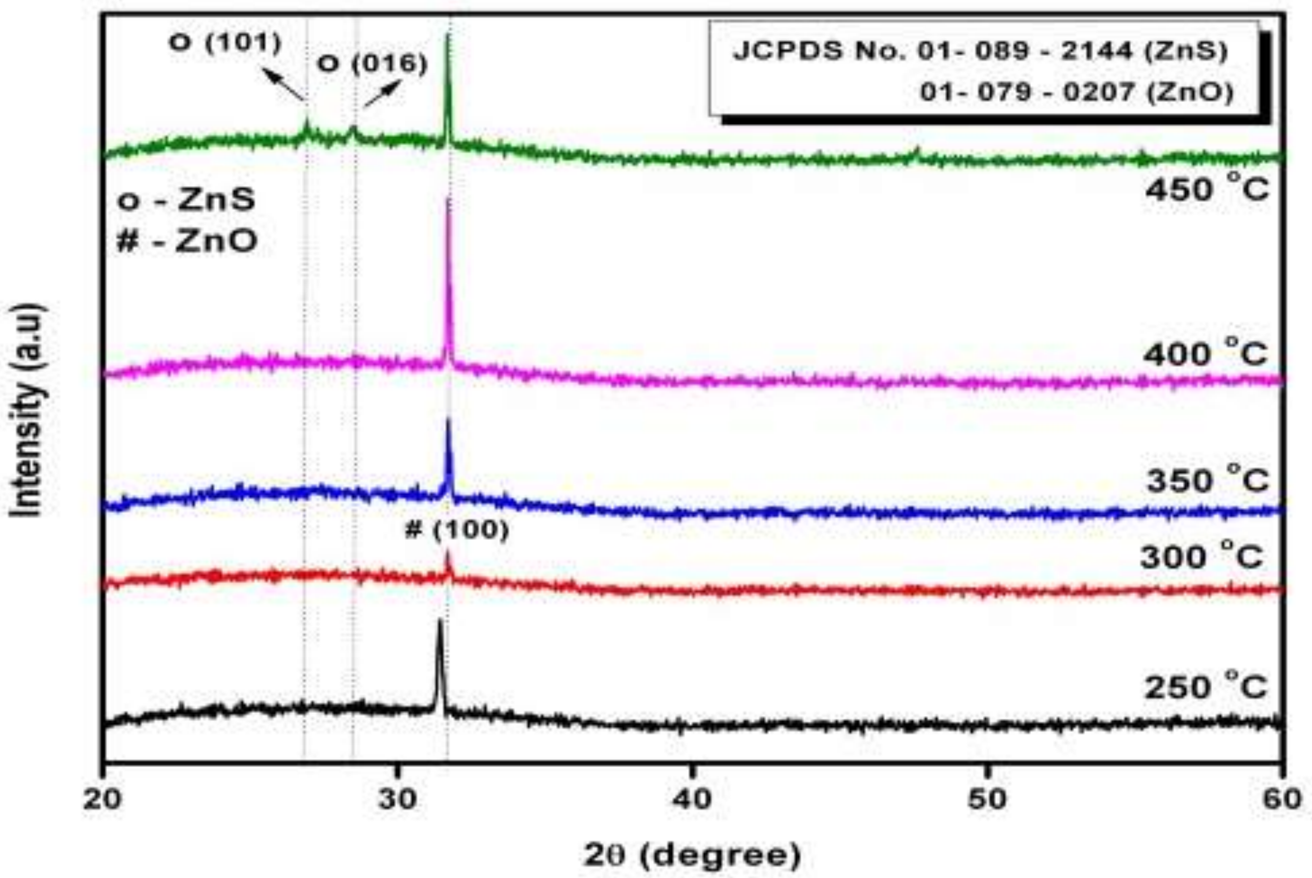

Fig 1. XRD pattern of ZnS thin film

3.2. MORPHOLOGICAL PROPERTIES

3.2.1. SEM ANALYSIS

SEM is the most prominent technique used to inspect the microstructure of the thin films. Figure 2 shows the surface morphology of ZnS thin films as deposited at room temperature captured by SEM [11]. From the micrographs, it is observed that the deposited films are uniform throughout the regions but the films are free from void, pinhole or cracks and they cover the substrates very well. Figure 2 (a-j), shows the deposition of ZnS thin films at 250ºC, 300ºC, 350ºC, 400ºC and 450ºC with corresponding energy dispersive X-ray (EDAX) image, which was performed to determine the percentage of zinc and sulfur present in the layered ZnS film.

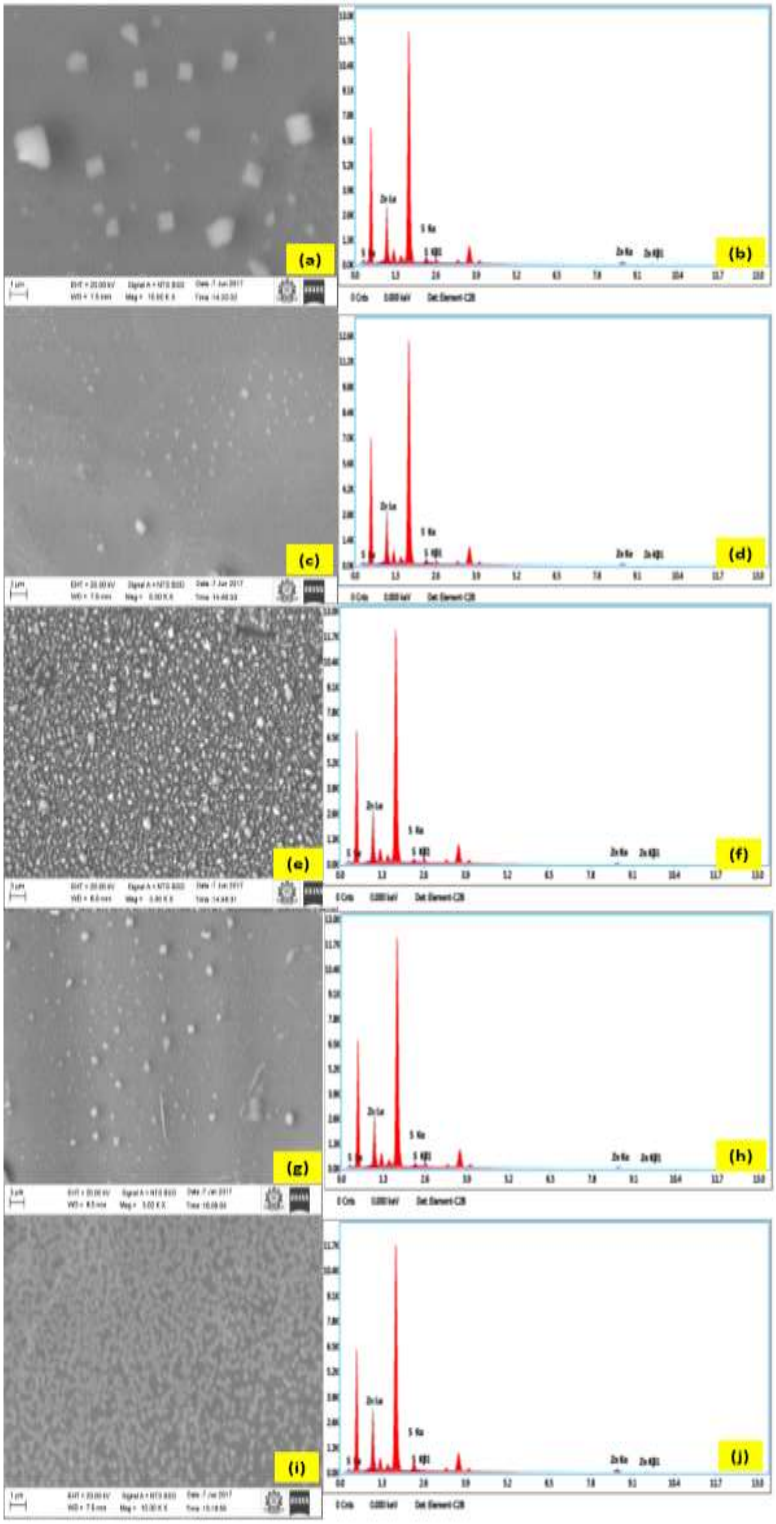

Fig 2. SEM with EDAX image at (a,b) 250°C, (c,d) 300°C, (e,f) 350°C, (g,h) 400°C and (i,j) 450°C

3.2.2. ATOMIC FORCE MICROSCOPY (AFM)

Atomic force microscopy (AFM) technique is an useful method to examine the surface topography of the thin films. Figure 3 shows the two and three dimensional AFM images for the ZnS thin films deposited on glass substrate with temperature varied from 250ºC to 450ºC along with variation in surface roughness and layer thickness over a scanning area of $2 \times 2\ \mu m^2$. By the below figure, it can be noticed that the nanoparticles coated ZnS thin films have high degree of homogeneity and even the small grains have uniform distribution on the substrate. Moreover, from the AFM studies the Root Mean Square (RMS) and Surface Roughness (RS) can be determined [10].

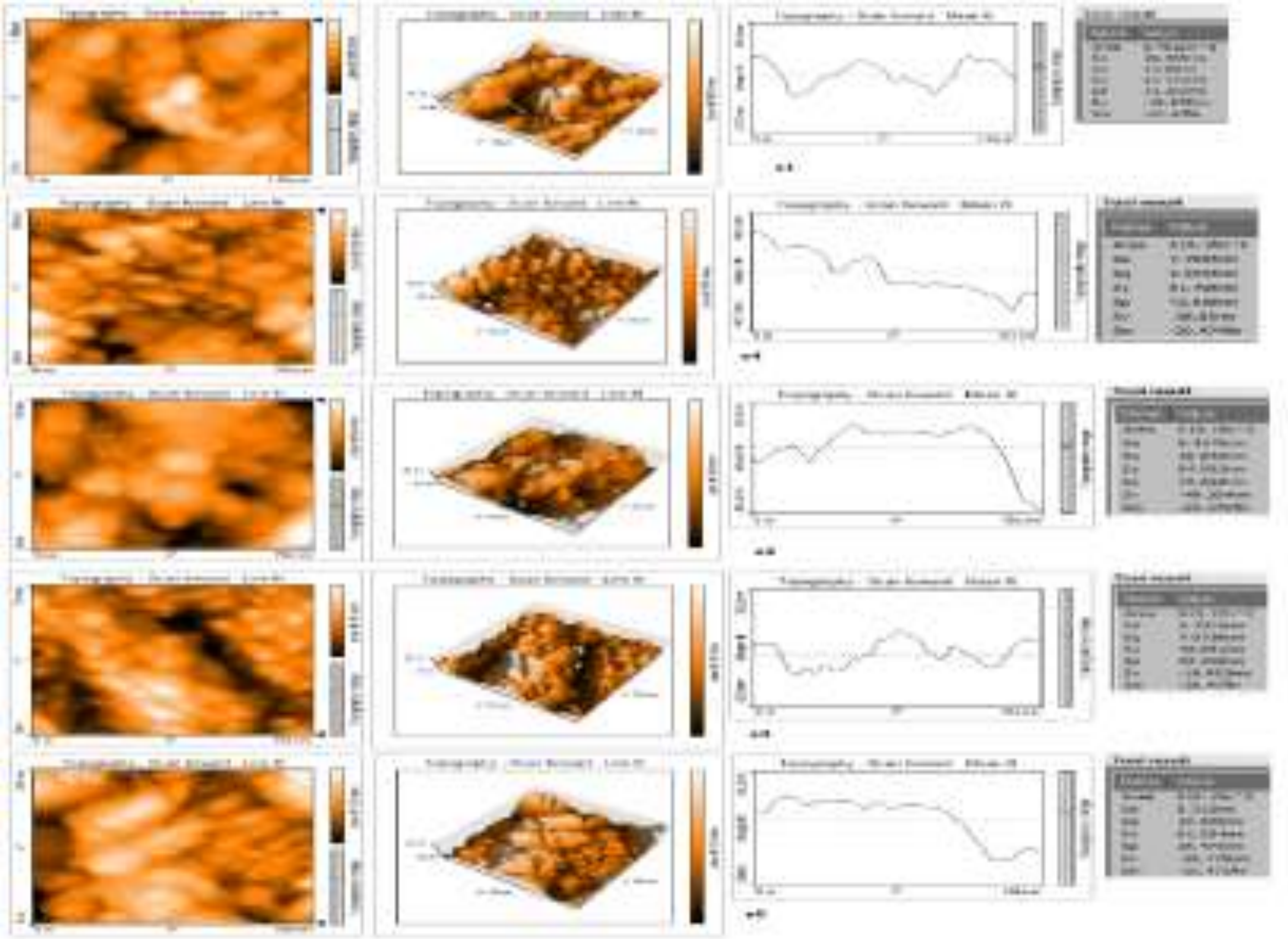

Fig 3. AFM images of ZnS at 250ºC to 450ºC

3.3. OPTICAL PROPERTIES

The optical properties were studied using a UV-Visible spectrophotometer of make JASCO Corp., V - 570. The optical properties of the thin film deposited on glass substrates were determined from the absorbance measurement in the range of 300-700 nm. Figure 4 depicts the absorption spectra of the ZnS thin films and it was observed that the transmission of the film is greater than ~ 64% for the wavelength values greater than the wavelengths that corresponds to optical band gap [13, 14].

Absorbance coefficient α associated the strong absorption region of the film and it was calculated from the absorbance (A) and the film thickness (t) using the relation [15, 16].

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

However, the absorption coefficient α was analyzed using the following expression for optical absorption of semiconductors [16]

$$(\alpha h\upsilon) = K\ (h\upsilon - Eg)\ n/2 \qquad (3)$$

Where k is the Boltzmann's constant, Eg is separation between valence and conduction bands and n is a constant equal to 1 for direct band gap semiconductor

The optical band gap *Eg* can be estimated from the Tauc plot [17]. Figure 4 shows the optical band gap of the deposited ZnS thin film. For crystalline semiconductors, n can take values l/2, 3/2, 2 or 3 depending on whether the transitions are direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively [18]. The exact values of band gap was determined by extrapolating the straight line portion of the$(\alpha h\nu)1/2$ versus hv graphs to the hv axis, where *a* is the optical absorption coefficient, hv is the incident photon energy and n depends on the kind of optical transition.

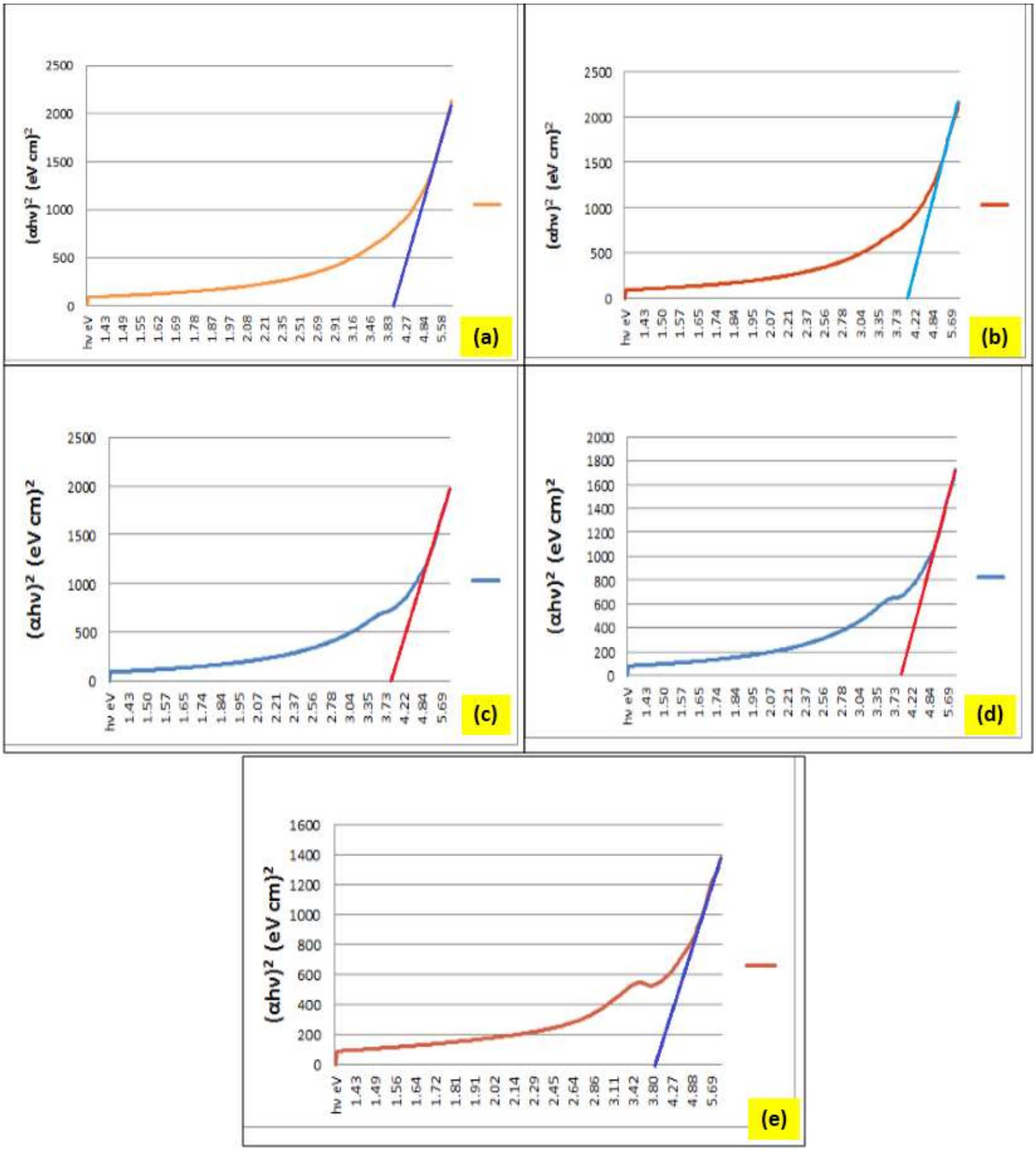

Fig 4. Optical property of ZnS thin film

3.4. ELECTRICAL PROPERTIES

The electrical resistivity of ZnS thin film was measured using four probe method as shown in figure 5 with the variation of log of resistivity (log ρ) with 1/T x 10^{-3} K for thin film. The resistivity follows the relation as below:

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

Where ρ is resistivity at temperature T, ρ_0 is a constant, k is Boltzmann constant, E_a is the activation energy for conduction. From the activation plot, it was noticed that the resistivity of ZnS sample decreases with temperature indicating the semiconducting nature of thin film.

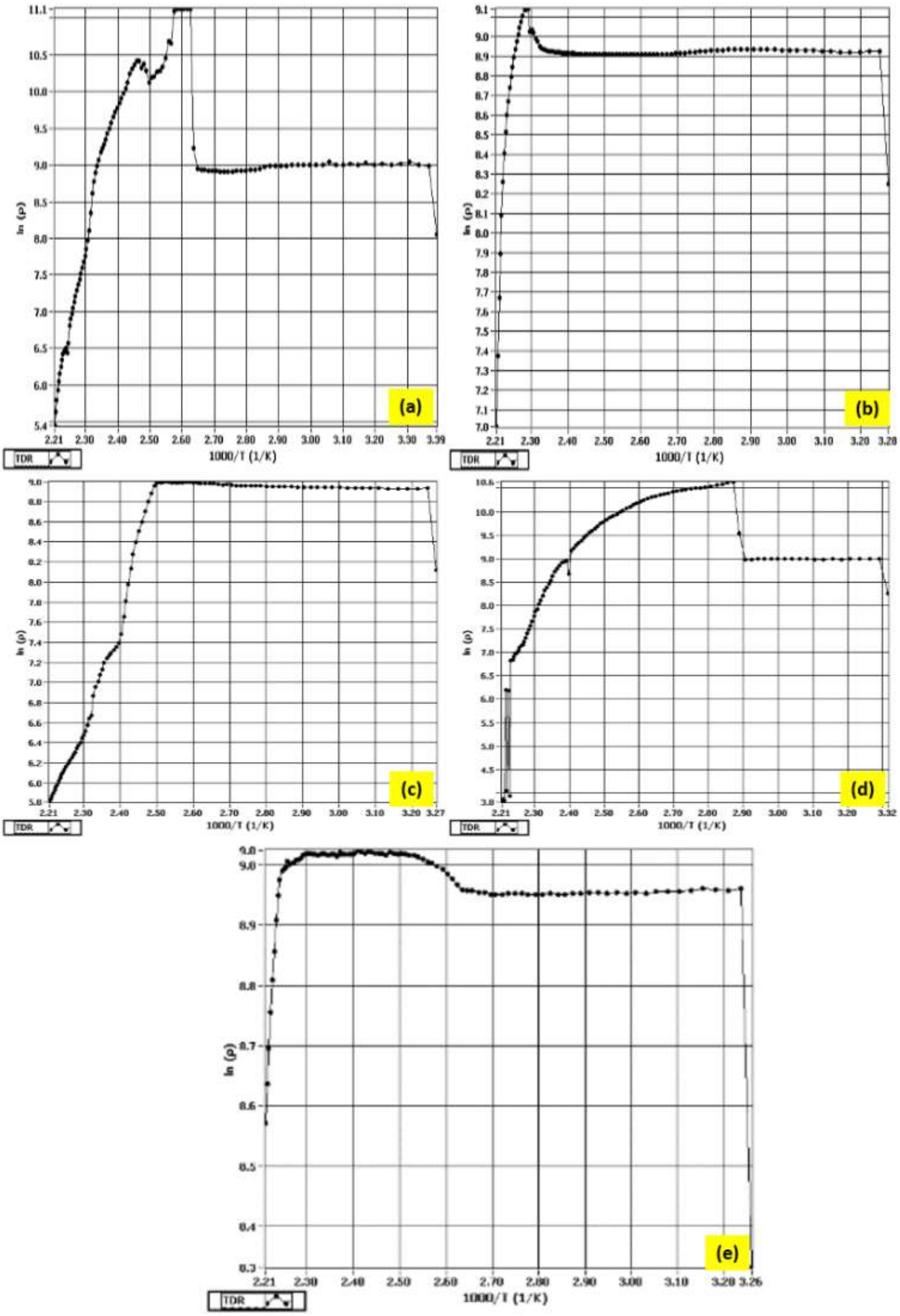

Fig 5. Thermal plot of ZnS thin film

From the above plot, the thermal activation energy was calculated using relation (4) [19,20]. Moreover, the resistivity of the film sample was measured at 500˚K and is found to be 0.36 x 10^5 Ω-cm with an activation energy of 0.82 e v.

4. CONCLUSIONS

The ZnS thin films are synthesized using nebulized spray pyrolysis technique at different temperatures ranging from 250ºC to 450ºC. The crystal structure and grain size of the particles were determined using XRD analysis and ensured that the sprayed thin films of ZnS showed the presence of hexagonal structures. However, the surface morphology of the film was studied by SEM and AFM, which explained that the grain sizes are influenced by the substrate temperatures. Moreover, the optical band gap was found to be 3.45 e v and the electrical resistivity of ZnS thin film was noted as 0.36x10^5 Ω-cm with an activation energy of 0.82 ev.

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