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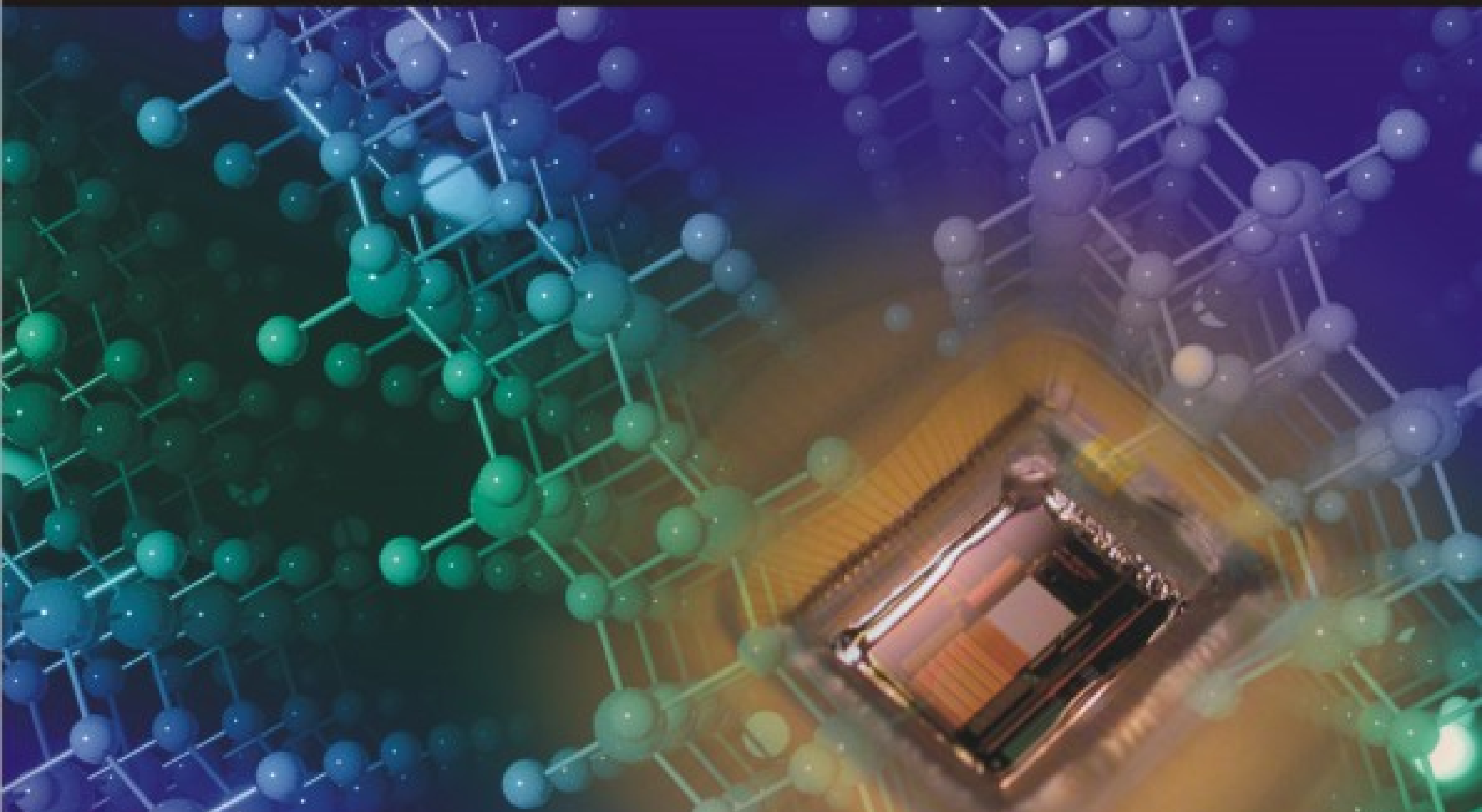

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Synthesis of Nanocrystalline ZnS Thin Films via Spray Pyrolysis for Optoelectronic Devices

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Abstract: ZnS thin films were deposited on the glass substrates at a temperature of 350 °C by a low cost spray pyrolysis technique and annealed at 450 °C and 550 °C in a closed furnace. The as-deposited and annealed films were characterized by Energy Dispersive X-ray, X-ray Diffraction and UV-VIS spectrophotometer and dc conductivity by four probe van der Pauw method. The X-ray diffraction spectra of as-deposited films showed amorphous nature and after annealing at 450 °C and 550 °C the films were found polycrystalline nature with wurtzite hexagonal structure. The optical transmission spectra suggest that the fundamental absorption edge in the films is formed by the direct allowed transition. The optical band gap was decreased from 3.75 to 2.5 eV when the as-deposited films were annealed. The existing results of electrical conductivity and the activation energy reveal the semi-conducting behaviour of the samples. *Copyright © 2013 IFSA.*

Keywords: ZnS, Nano grains, Spray pyrolysis, X-ray diffraction, Band gap.

1. Introduction

Zinc sulphide (ZnS) is an important II-VI semiconducting material with a wide energy band gap of 3.6 eV to 3.7 eV [1-2]. ZnS can have two different crystal structures; zinc blende and wurtzite, both of which have same band gap energy and direct band structure. Due to its high refractive index and high transmittance in the visible range it can be used as reflectors and dielectric filters. It is also used for the fabrication of optoelectronic devices such as blue light-emitting diodes, electroluminescent devices, electro optic modulator, optical coating, hetero junction solar cells, and photoconductor. Generally the functional behaviour of ZnS devices is influenced by the phase composition, thermal stability and morphology of the deposited films which are dependent on the mechanism of the deposition and processing conditions. Several methods have been used to deposit ZnS thin films such as spin coating [3], chemical bath deposition (CBD) [4-5], spray pyrolysis deposition (SPD) [6-7], close spaced vacuum sublimation (CSVS) [8-9], electron beam evaporation [10], and pulsed laser deposition technique (PLD) [11]. The performance and efficiency of thin film-based devices are strongly depends on the structural, electrical and optical properties of the film component. For this reason the study of these properties and the characteristics of the deposited film are very important. It helps to optimize the parameters for better device applications. Moreover the electrical and optical properties of the films are affected by the parameters such as flow rate, substrate temperature, concentration of solution etc, as well as the presence of impurities and defects in the films. Usually post deposition annealing is used to improve the structural, optical and electrical properties of the deposited films. Thus the studies

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concerning the annealing effects on optical and electrical properties are very important, which play a significant role in enhancing the efficiency of the device. In this work the influence of annealing on structural, optical and electrical properties of ZnS films deposited by spray pyrolysis technique is studied.

2. Experimental

2.1. Deposition

Spray pyrolysis is basically a chemical deposition technique in which fine droplets of the desired material solution is sprayed onto a heated substrate. It is a simple and low-cost technique in which the deposition parameters can be easily varied. The experimental setup used for the preparation of pyrolytically spray deposited ZnS films is described here. An aqueous solution of zinc acetate [$Zn(CH_3COO)2.2H_2O$] and thiorea (NH_2CSNH_2) were used to deposit the zinc sulphide thin films on glass substrate. The sprayed solution was made of 0.1 M zinc acetate and 0.1 M thiourea. Deionised water was used as a solvent. Micro glass slides with dimensions of 1 × 25 × 40 mm^3 were used as substrate. The glass slides were first cleaned using soap solution and then boiled in water and then dipped in acetone, and then dry. Compressed air was used as the carrier gas for spraying the solution where the gas pressure was fixed at 0.5 bar. The total volume of the solution sprayed was 100 mL and the flow-rate of spray was kept constant at 4mLmin-1 throughout the whole deposition process. The deposition time was fixed at 10 minutes. An optimized temperature of 350 °C was maintained for the glass substrates. A chromel-alumel thermocouple based digital temperature controller was used to control the temperature. The nozzle to substrate distance was kept fixed at 25 cm. After deposition, films were allowed to cool at an ambient temperature slowly. The as deposited films were then annealed at 450 °C and 550 °C temperature for 1 hr in a closed furnace.

2.2. Characterizations

The composition of the films was studied by EDX analysis. The XRD study was performed for identification of the crystal structure of the as deposited and annealed zinc sulphide thin films. A Philips X'Pert PRO XRD PW 3040 was used to study the materials structure. The monochromatic (using Ni Filter) CuK$_\alpha$ radiation was used whose primary beam power was 60 kV and 55 mA. The value of 2θ was swapped between 20π to 60π. The optical transmission and absorption spectra of the films with respect to glass substrate were taken for wavelength range 300 to 1100 nm using UV-1601 Pc Shimadzu Visible Spectrometer. The film thicknesses of the as deposited and annealed films were measured by the Fizeau fringes method. The d.c electrical conductivity was measured by van-der Pauw four probe method in the temperature range from 27 °C (300 K) to 127 °C (400 K) using a Keithley-616 electrometer.

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) has been used to characterize the surface morphology. The films deposition by the spray pyrolysis is generally polycrystalline or amorphous in nature. Fig. 1 (a-c) show the SEM micrographs of the pure ZnS deposited at 350 °C and annealed at 450 °C and 550 °C respectively. Fig. 1 (a) showed that the film was not uniform, throughout the surface was inhomogeneous but deposition covered the substrate well. The film showed amorphous in nature because grain boundaries could not be defined and the surface was randomly roughness. The surface can be described as a conglomerate random roughness, which is characteristic of an amorphous deposit. The overall morphology of the layers seems to be due to the growth and clustering of initial nuclei. Fig. 1(b) showed annealed samples at 450 °C temperatures. After annealing the surface roughness was increased and the fibrous like structure was observed with nano sized grains of ZnS. It means that sprayed particles (atoms) are adsorbed onto the substrate to form clusters as the primary stage of nucleation. Clusters have a higher energy than the individual atoms, so at higher annealing temperature growing nuclei come into contact to form island stage and appears as fibrous like shape. Fig. 1(c) showed the surface roughness and radius of the clusters also increased. Due to increasing annealing temperatures at 550 °C the cluster migration mechanism also started. Hence the smaller clusters moved randomly and some of them were absorbed by the larger clusters to increase their radius and height.

3.2. Energy Dispersive X-ray

The composition of as deposited and annealed zinc sulphide films was confirmed by energy dispersive X-ray spectroscopy (EDX). Fig. 2 shows the EDX spectra of zinc sulphide thin film of as deposited at 350 °C and annealed at 450 °C and 550 °C. Sulphur deficiency was observed in the as deposited and annealed films. This may be due to the fact that sulphur has great affinity towards oxygen, so it might have converted to SO_2 and then evaporated. There is almost no change in the compositional structure after being annealed at 450 °C temperature. A strong peak is observed which corresponds to Si

(Silicon) and an O (Oxygen) peak is also observed which is due to glass substrate. At high operating voltage the electron beam penetrates the film and reaches the glass surface, which results the Silicon and Oxygen peak. Two different peaks corresponding to Zn (zinc) and S (sulphur) in the spectrum confirms the ZnS thin film. EDX result reveals that the deposited films are very close to the nominal composition, shown in Table 1.

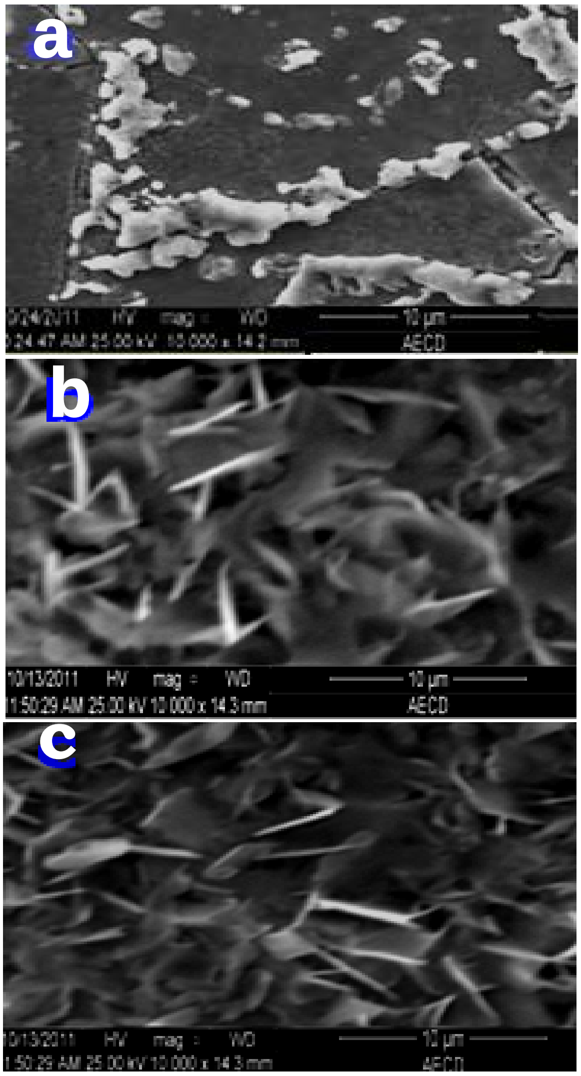

Fig. 1. SEM micrographs of pure ZnS, (a) deposited at 350 °C, (b) annealed at 450 °C, (c) annealed at 550 °C.

Table 1. Atomic % of as deposited and annealed ZnS films.

Sample	Temperature	Zn	S
As deposited	350 °C	53.92	46.08
Annealed	450 °C	56.33	43.67
Annealed	550 °C	57.45	42.55

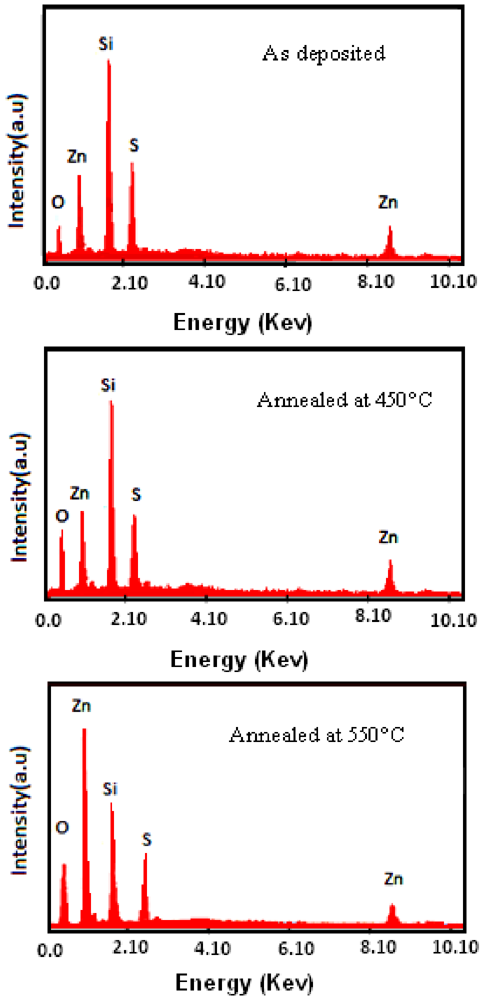

Fig. 2. Energy Dispersive X-ray **(**EDX) spectra of ZnS thin films.

3.3. X-ray Diffraction

Fig. 3 shows the X-ray diffraction pattern of as deposited zinc sulphide thin films at 350 ºC, and annealed at 450 ºC and 550 ºC temperature. The scanning angle range was $20\pi < 2\theta < 70\pi$. The X-ray diffraction pattern of the annealed spray pyrolysed ZnS revealed the crystalline structure. The observed broad hump in all the samples is due to the amorphous glass substrate used. The Lattice parameter of the films has been determined using the formula,

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + kh + k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (1)$$

The crystallite size was calculated by using Scherrer's formula

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

where k is a constant taken to be 0.93, λ is the wavelength used (1.5418 Å), β is the broadening of diffraction line measured at half its maximum intensity in radians and θ is the angle of diffraction. The average grain size of the films was found in the range of 30 to 50 nm, which indicates that the nanometric size of grains has developed in the films.

The diffraction spectra showed that the as deposited film is amorphous. When the samples are heated with 450 °C then several peak of (100), (002), (101), (102), and (103) appeared. But as the annealing temperature increased to 550 °C a new peak of (200) has appeared and (103) vanished. The exhibited peaks are corresponding to hexagonal wurtzite phase of ZnS. The ratio of lattice constants (c/a) for the (101) and (102) planes were estimated to be about 1.606. The results are very similar to the report given by A. U. Ubale [12] and N. Uzar [13] but differ with some other report by D. Nithyaprakash [7], T. Ben Nasrallah [14] A. H. Eid [15], F. Gode [16] and R. K. Murali [17].

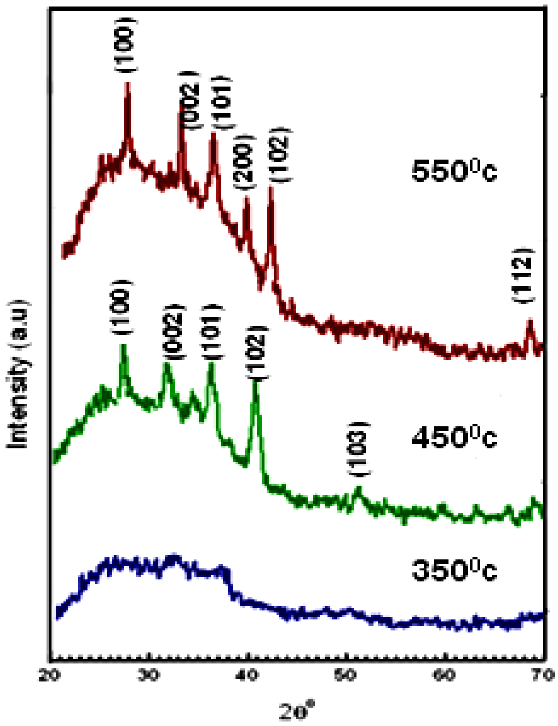

Fig. 3. XRD spectra of as deposited and annealed films.

The spectra indicate that films are prominently single crystalline with a preferential orientation. As the temperature increased the peak intensity increased and no other phases were formed by increasing the annealing temperature.

3.4. Optical Properties

The absorbance and transmittance spectra of ZnS thin films were recorded in the UV-visible near infrared regions (300 nm to 1100 nm.). Optical properties of the as deposited and annealed ZnS thin films such as band gap (E_g), extinction coefficient, refractive index, etc. were calculated from the absorbance and transmittance data. Fig. 4 depicts the variation of absorbance in the UV-visible region for as-deposited ZnS thin films as well as for annealed samples. There is almost no absorption in the visible region for the as deposited films. But when the films were annealed then the absorption peak shifted to longer wavelength region and the absorbance increased sharply at 325 nm wavelength for annealed sample at 450 °C. The transmittance for the as deposited film was 80 % but it decreased to 60 % when it was annealed at 450 °C. The transmittance was almost same for visible range and then decreased sharply. After annealing at 550 °C the transmittance decreased linearly. The decrease in transmittance may be caused by the increase in crystallite size.

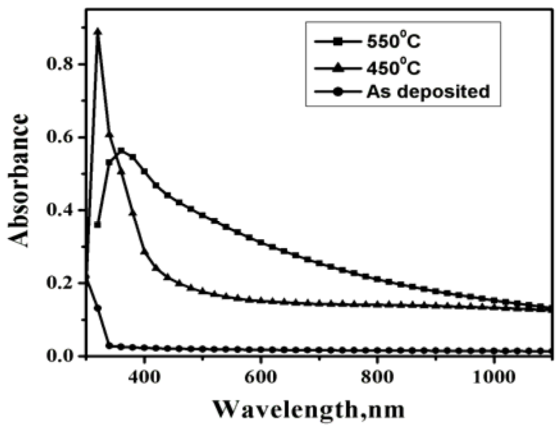

Fig. 4. Absorbance spectra for as deposited and annealed ZnS.

Absorption coefficient α was calculated from

$$\alpha = 2.303\frac{A}{d} \quad (3)$$

where A is the optical absorbance spectra and d is the thickness of the film. The optical band gap of the films was determined from the following relationship

$$\alpha h\nu = C(h\nu - E_g)^{\frac{1}{2}} \quad (4)$$

where C is the constant and E_g is the optical band gap energy. The band gap energy was calculated from the intercept of the extrapolation of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) graph (Fig. 5).

From the extrapolation of the plot, the band gap energy for as deposited films is 3.75 eV. After annealing at 450 °C and 550 °C it has changed to 3.1 eV and 2.5 eV respectively. The refractive index (n) was calculated by using the following equation

$$n=\left(\frac{1+R}{1-R}\right)+\sqrt{\left(\frac{4R}{(1-R)^2}-k^2\right)} \quad (5)$$

where R is the reflectance and k is the extinction coefficient. The reflectance (R) was calculated by using the formula

$$A+R+T=1 \quad (6)$$

and the extinction coefficient (k) was calculated by using

$$k=\frac{\alpha\lambda}{4\pi} \quad (7)$$

The refractive index is found to decrease with increase in wavelength. The values of refractive index for as deposited films at 350 °C are found to be less than those of annealed at 450 °C and 550 °C. Such a difference may be attributed to the increase in crystallite size and lower strain in the annealed films.

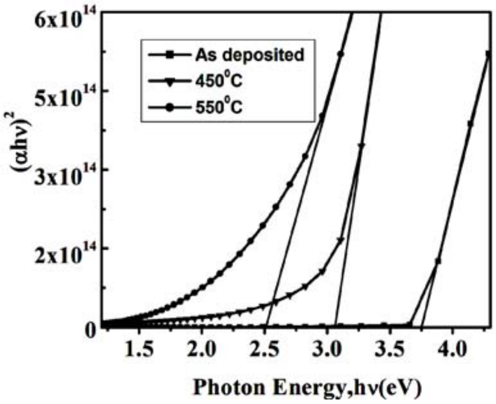

Fig. 5. Variation of $(\alpha h\nu)^2$ with photon energy.

3.5. Electrical Measurements

The electrical measurements were performed on the as-deposited and annealed ZnS films to know the resistivity, activation energy of the charge carriers and other parameters. The electrical characterization of ZnS films was done by means of temperature dependent resistivity and the four probe van der Pauw technique. This study reveals that annealing has a considerable effect on the electrical properties of ZnS thin films.

The electrical conductivity is found to increase after annealing the samples, shown in Fig. 6. The cause of increased electrical conductivity after annealing at 450 °C and 550 °C could be due to the increase in the crystallite size and by the reduction of the width of barrier layers at the grain boundaries. The activation energy was calculated from the slops of log σ vs. 10^3 T^{-1}plots using the relation

$$\sigma=\sigma_0 \exp(\frac{E_a}{KT}), \quad (8)$$

where σ is the conductivity, E_a is the activation energy, K Boltzmann's constant and T is the temperature. The activation energy varied from 0.08 to 0.17 eV. The results are presented in Table 2.

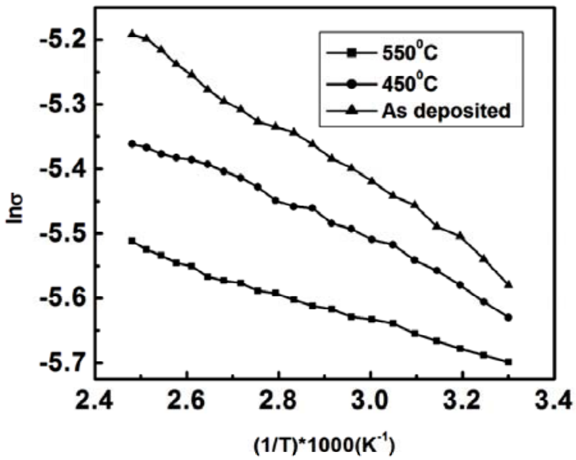

Fig. 6. Plot of log ρ vs. 1/T×1000 for ZnS.

Table 2. Activation energy of ZnS at different annealing temperatures.

Annealing Temperature/°C	Activation Energy/eV
As deposited (350)	0.08
450	0.11
550	0.17

4. Conclusions

ZnS thin films have been deposited on glass substrates by a simple, low cost spray pyrolysis technique at 350 °C. In this study, the annealing effects on the structural, optical and electrical properties have been investigated. EDX spectra showed that the films are in good stoichiometry. But after annealing there is sulphur deficiency observed in the films. X-ray diffraction spectra indicate that the as deposited films are amorphous in nature and the annealed films have a wurtzite hexagonal structure. The direct band gap energy of the films decreased from 3.75 to 2.5 eV. The resistivity and the activation energy were estimated as a function of temperature which exhibits the semiconducting nature. The above results demonstrate that the deposited ZnS films produced by a low cost spray pyrolysis technique could be useful for designing optical devices such as solar cells, optical window layers of photovoltaic cells, photodetectors, photoresistors, etc.

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