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EFFECT OF ANNEALING TEMPERATURE ON STRUCTURAL, MORPHOLOGY AND OPTICAL PROPERTIES ON ZnS THIN FILMS BY SOL-GEL METHOD

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ABSTRACT

Zinc sulphide (ZnS) thin films were prepared by the sol-gel technique. This study focused on nanocrystalline structure and optical properties in four different temperature which are at 250 °C, 300 °C, 350 °C and 400 °C on quartz slide. The obtained reaction product was a transparent and colloidal solution. SEM, EDX, XRD, UV-Vis and PL were used to characterize the sample. SEM shows the film are thicker and have bigger grains size at 400 °C compared to the film at 250 °C with the grain size between 39.0 - 63.3 nm and 22.3 - 29.0 nm respectively. EDX analysis confirmed the thin film consisted of zinc and sulphur. XRD shows development of well-crystallized film with pure wurtzite structure after annealing. XRD spectrum indicates that the films are amorphous and have cubic zinc blend structure. The films also shows good optical properties with high transmittance of range 85 % - 95 % in the visible region and the band gap value are around 3.8 eV. Photoluminescence have been studied and the film annealed at 250 °C was existed in blue transmission spectrum in visible region at wavelength about 490 nm. While for the annealed temperature at 300 °C, 350 °C and 400 °C are exist at green transmission spectrum in visible range having wavelength in between of 495 nm to 497 nm.

INTRODUCTION

Zinc sulphide belongs to the II–VI family of semiconducting material and receiving ever-increasing attention due to its wide and variety of applications. Owing to the wide band gap value of 3.7 eV, it can be used for fabrication of optoelectronic devices such as blue light-emitting diodes, electroluminescent devices, n-window layers for thin film hetero junction solar cells, photoconductor and especially photovoltaic device [1]. It is also being used as buffer layers in CuInSe- and CuGaSe2- based solar cells [6]. Thin films of ZnS doped with transition-metal element or rare-earth element has also been used as effective phosphor material [4]. In the area of optics, ZnS can be used as reflectors [5] and dielectric filters (A.M. Ledger, 1979) because of its high refractive index and its high transmittance in visible range. In this paper, we focus on the preparation of nanocrystalline zinc sulphide by a simple sol-gel technique. The annealing temperature was set for 250 ^{o}C, 300 ^{o}C, 350 ^{o}C, and 400 ^{o}C. The effects of annealing on the structural, surface morphological and optical properties are systematically examined.

EXPERIMENTAL METHOD

ZnS nanostructures were prepared by the sol-gel method. A total of 0.96 mmol of zinc acetate, and 6 mmol of thiourea were dissolved in l000 ml of water in a beaker with continuous stirring for 1 hour. The pH of the resulting aqueous mixed solution was adjusted to 3.5 with nitric acid with continuous stirring for another 1 hour, and then the mixed solution was kept in an ice-cold water bath for 30 minutes. Meanwhile, 0.8 mmol of sodium sulphide was dissolved in 800 ml of water with stirring in a beaker that was kept in an ice-cold water bath for 30 minutes. The NaS solution was then slowly added to the above solution mixture followed by continuous stirring for 30 minutes till a transparent and stable colloidal solution was obtained. Quartz substrates were used in this study. The substrates were cleaned using isopropyl alcohol and acetone, ultrasonically clean for 10 minutes, and then dried in air. The ZnS solutions were dropped onto quartz substrates and then the deposition process was done using spin coating. Finally, the samples were annealed with different temperature, which were 250 ^{o}C, 300 ^{o}C, 350 ^{o}C and 400 ^{o}C.

RESULTS AND DISCUSSION

Zinc sulphide exists in sphalerite, cubic (zinc blend) and hexagonal forms. The cubic form is stable at room temperature, while the less dense hexagonal form (wurtzite) is stable above 1020^{o}C at atmospheric pressure (B.Gilbert et al, 2002). The structure properties of this film were characterized by X-Ray Diffraction. From Figure 1, ZnS appears almost in amorphous form. The difference annealing temperature does not affect any obvious different in XRD pattern as there was only one peak that occurred in XRD pattern. As the annealing temperatures increases, the diffraction peaks of samples become sharper due to the coarsening of grains.

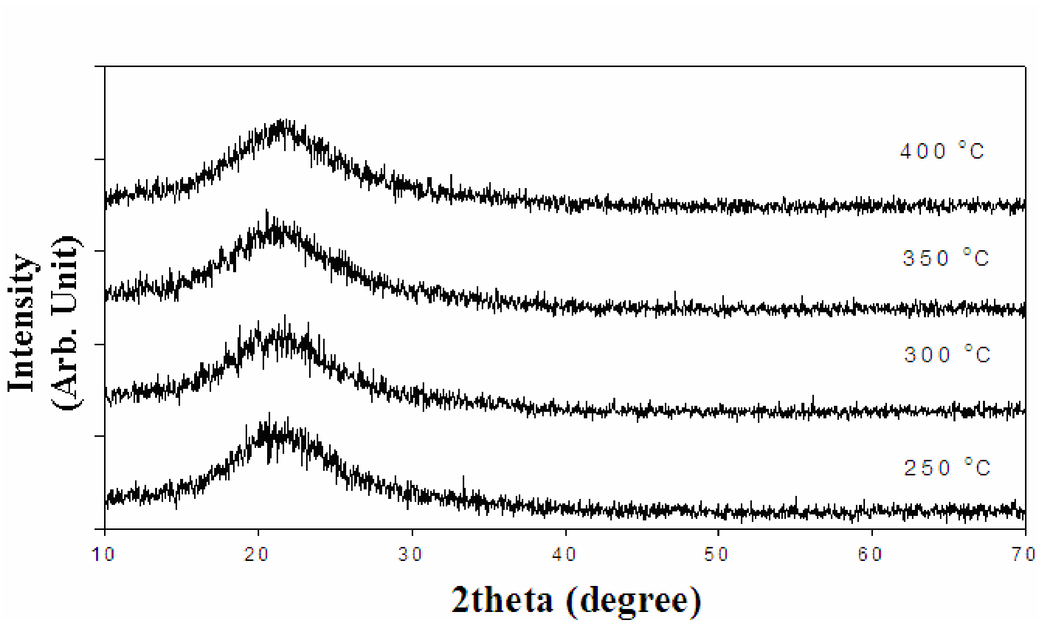
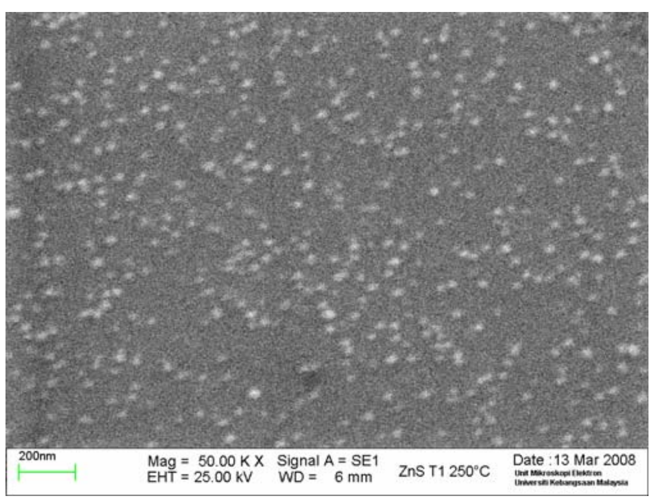
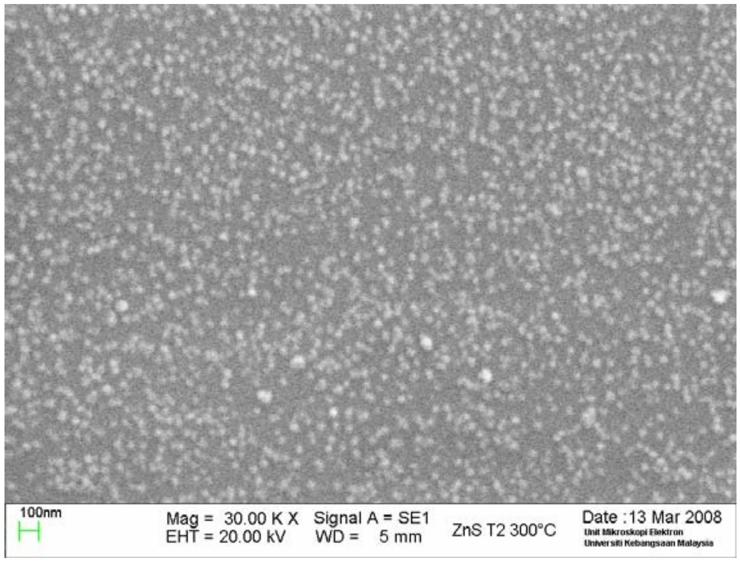


Figure 1: X-ray diffraction pattern of ZnS produced by annealing at 250^{o}C, 300^{o}C, 350^{o}C and 400^{o}C

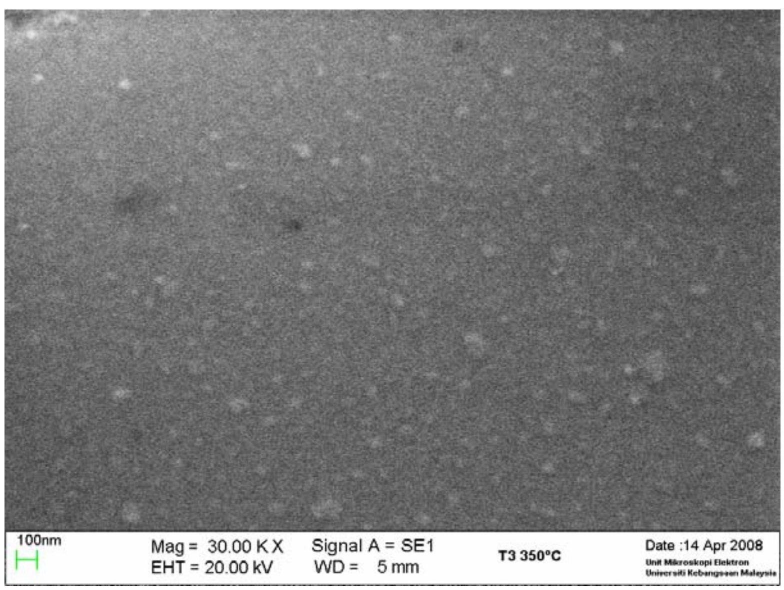
SEM brings microscopic information of the surface structure and roughness. In this work, it appears to be a helpful technique to specify the growth mode via the study of a surface roughness, and to determine the effect of the different annealing temperature on the film morphology. Figures 2, 3, and 4 shows the surface of ZnS layers obtained at four different annealing temperatures. A slight increase of the grain size follows the increase of the annealing temperature but does not improve the surface roughness. Concerning the nucleation stage film growth proceeds by nucleation of crystallites then formed grains which coalesce to cover the entire substrate surface and to show a dense structure. These results are consistent with previous reports (M. Forment et al, 1993).



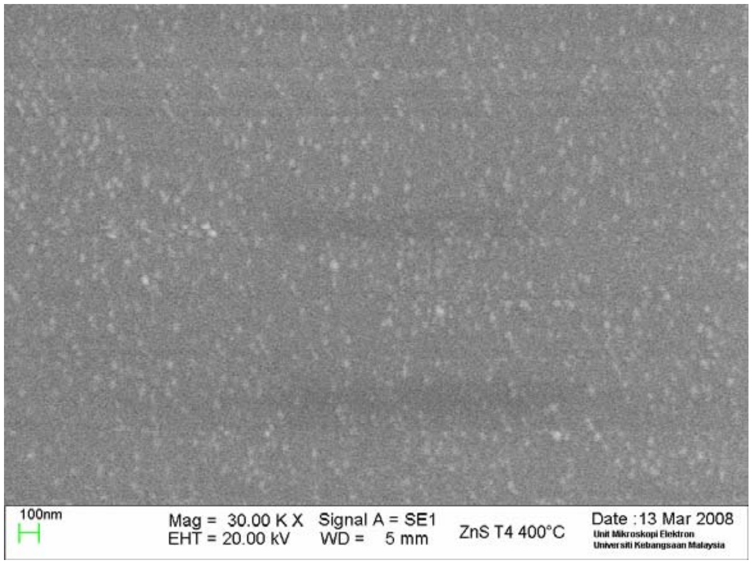
(a)


100nm
Mag = 30.00 K X
EHT = 20.00 kV
Signal A = SE1
WD = 5 mm
ZnS T2 300°C
Date :13 Mar 2008
Unit Mikroskopi Elektron
Universiti Kebangsaan Malaysia

(b)


100nm
Mag = 30.00 K X
EHT = 20.00 kV
Signal A = SE1
WD = 5 mm
T3 350°C
Date :14 Apr 2008
Unit Mikroskopi Elektron
Universiti Kebangsaan Malaysia

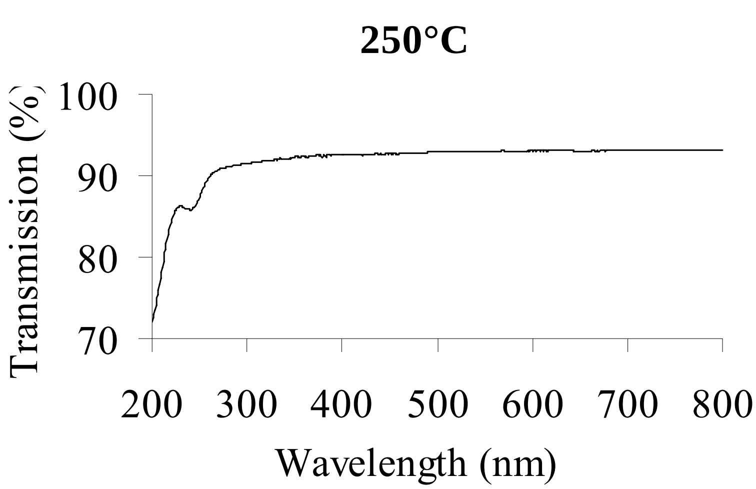
(c)



(d)

Figure 2: SEM image of ZnS thin film grown at 250 ^{o}C, 300 ^{o}C, 350 ^{o}C and 400 ^{o}C

The optical properties of the films deposited on quartz substrates were determined from the transmission and reflection measurements in the range 200 – 800 nm. Figure 3 shows the transmission spectra of annealed ZnS films, with different temperature. The thickness of the film was about 93.79 nm, 107.2 nm, 119.1 nm, 127.3 nm for each annealing temperature. The results show that the optical transmission is more than 92 % in the visible range for annealed films. The increase of the annealing temperature follows the increase of the optical transmission. To summarize, films grown at low growth rate (250 ^{o}C) are thinner and have lower absorption, whereas, films grown at higher growth rate (400 ^{o}C) are thicker and have higher absorption.



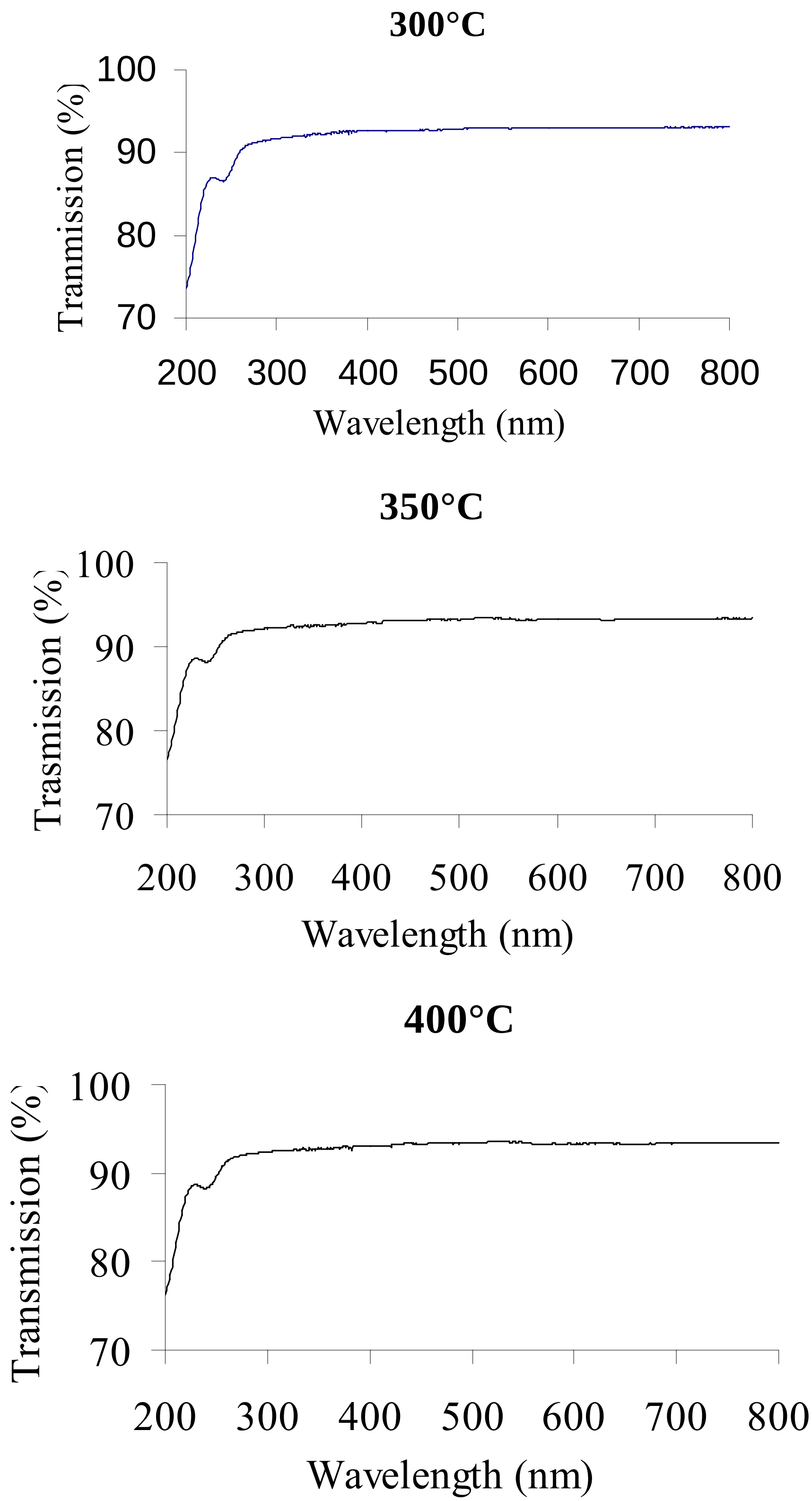
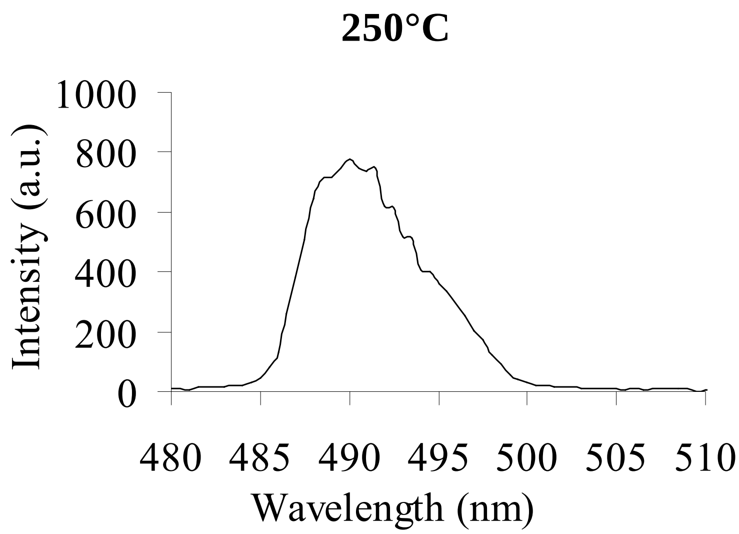
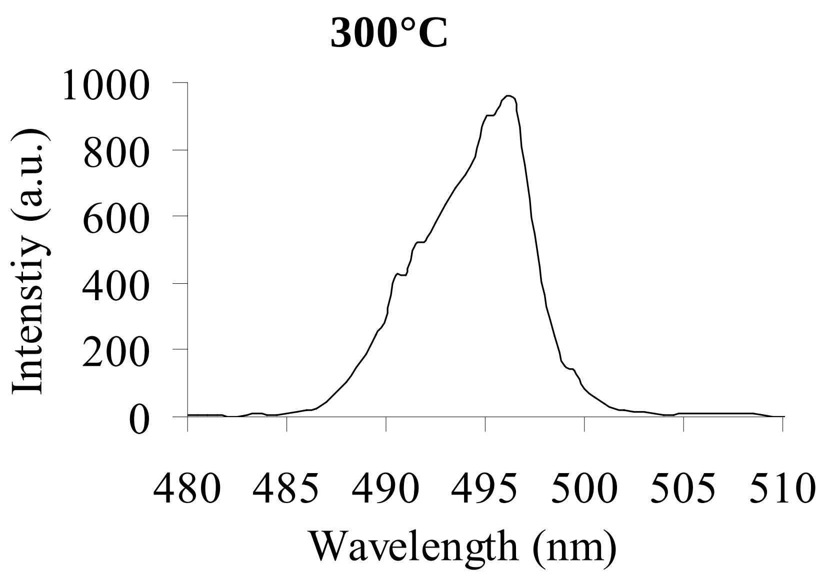


Figure 3: Optical transmission spectra of annealed ZnS films on quartz substrates.

Photoluminescence (PL) is an easy-to-use and sensitive probe of defect levels inside the forbidden band. Based on Figure 4, we could see that the highest intensity was about 1000 a.u occurred when the annealing temperature was set at 400 °C





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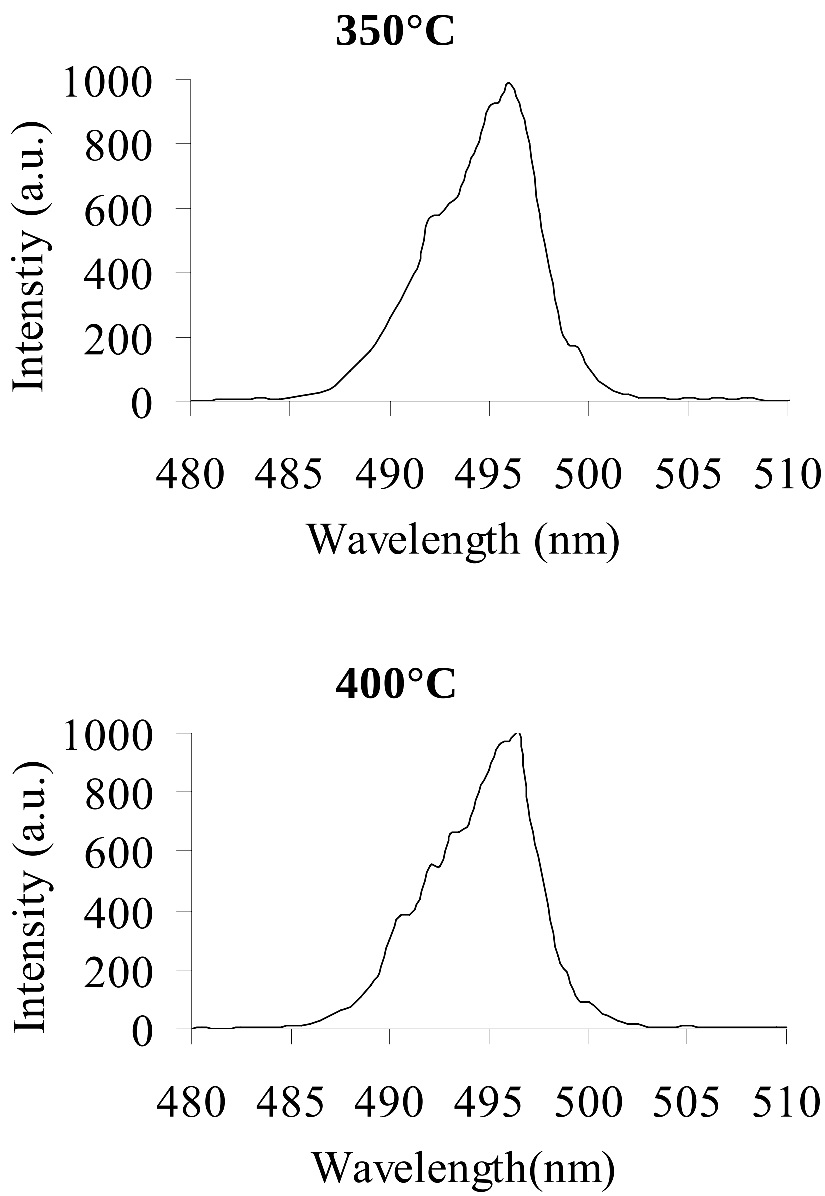

Figure 4: PL spectra of ZnS thin film for different annealing temperature

The transmission data have been applied for evaluating the band gap energy of the films. In order to calculate the optical band gap energy (E_{opt}) of the thin films, we assume the absorption coefficient is

$$\alpha = 1/d \ln 1/T \quad (1)$$

where T is transmittance and *d* is the film thickness. Structure of ZnS has a direct band gape and the absorption edge for the direct interband transition is given by:

$$(\alpha h\upsilon)^2 = C(h\upsilon - E_{opt}) \qquad (2)$$

Where C is a constant for direct transition, *h* is the Planck`s constant and υ is the frequency of the incident photon. Figure 5 shows relation between annealing temperature and band gap energy for ZnS thin films with various annealing temperatures. The optical band gap energies determined from obtained spectra are 3.1, 3.3. 3.6 and 3.8 eV for ZnS thin films with annealing temperature of 250 ^{o}C, 300 ^{o}C, 350 ^{o}C and 400 ^{o}C respectively.

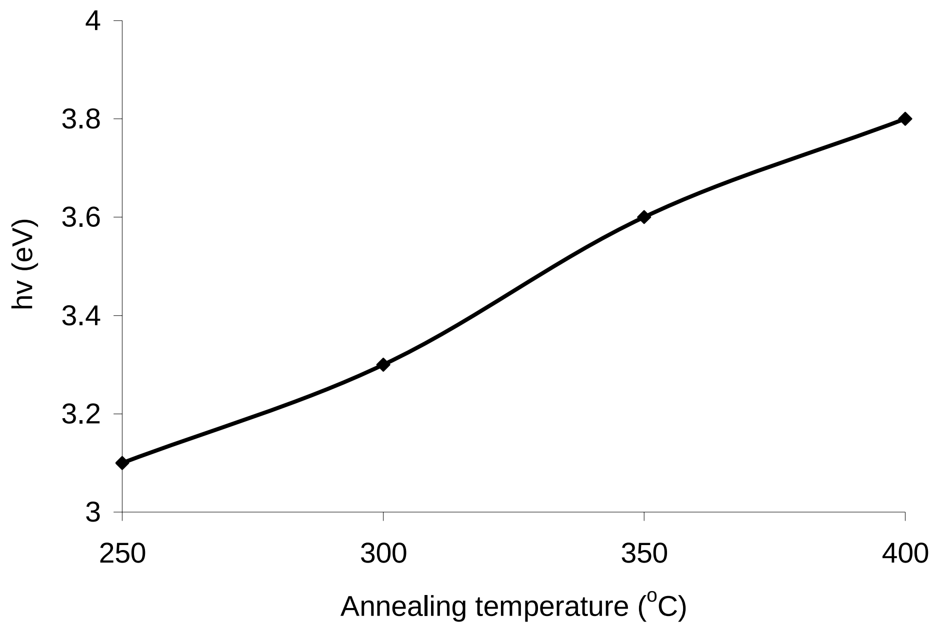

Figure 5: Relation between annealing temperature and band gap energy.

CONCLUSION

Zinc sulphide thin films were prepared on quartz substrates by the sol gel method. The films are in good quality, adherent and uniform. There is a good agreement between XRD, SEM, and optical results. These studies show that the annealing temperature contributes noticeably to the growth and to the structure of deposited films. It is particularly observed that the best crystallinity of the ZnS thin films is obtained at 400 ^{o}C. ZnS film prepared with 400 ^{o}C shows a high transmission coefficient (92%). The grain sizes are estimated to be in the range of 22 - 62 nm.

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