Effects of Annealing and Thickness on the Structural and Optical Properties of Crystalline ZnS Thin Films Prepared by PVD Method

H. Amrollahi Bioki and M. Borhani Zarandi

Department of Physics, University of Yazd, Yazd, Iran

***Corresponding author:** hojjat2222@yahoo.com

Abstract— Zinc Sulfide (ZnS) thin films were deposited on glass substrates at the pressure of 10^{-6} mbar by thermal resistor evaporation technique. The effects of annealing on the structural, optical properties of ZnS films were studied. Crystalline ZnS films have been analyzed by X-ray diffraction. Only cubic phase with the preferred (111) plane was found in ZnS films. Optical characteristics were studied as a function of annealing temperature and thickness in air. The results show that the energy band gap was found to be about 3.5 eV. It was observed that the energy gap decreases with the increase in the film thickness and increases with the increase in the annealing temperature.

KEYWORDS: Thin films, ZnS, Optical Properties, Vacuum Evaporation, Annealing, XRD, Crystallinity.

I. INTRODUCTION

Zinc sulfide (ZnS) is a wide gap and direct transition semiconductor [1] and belonging to the II-VI group is one of the promising materials for electronic devices. Consequently, it is a potentially important material to be used as an anti reflective coating layer for hetero-junction solar cells [2]. It is an important device material for light emitting diode [3] and other optoelectronic devices such as blue light emitting diode [4], electro luminescence devices and photovoltaic cells which enable wide application in the field of displays [5], sensors and lasers [6]. It can crystallize in two allotropic forms: a cubic form (c-ZnS) with sphalerite structure and a hexagonal form (h-ZnS) with wurtzite structure. In recent years nanocrystalline ZnS attracted much attention because the properties in nano form differ significantly from those of their bulk counter parts. Therefore much effort has been made to control the size, morphology and crystallinity of ZnS thin film. There has been growing interest in developing techniques for preparing semiconductor nano particles and films.

In recent years, there has been a great deal of interest in the fabrication of thin films of zinc sulphide by techniques like chemical bath deposition [7-8], RF sputtering [9], plasma assisted MOCVD [10], SILAR method [11]. Moreover, the technique is quite attractive when the product demands high physical and chemical perfection with near net shaping capability.

In our work, ZnS films were deposited with vacuum evaporation technique at room temperature. Then these ZnS films were submitted to thermal annealing at different temperatures in order to improve their properties. In this paper we report the microstructure and optical properties of ZnS thin films that prepared vacuum evaporation.

II. EXPERIMENTS DETAILS

ZnS films with thickness varying from 75 to 225 nm were deposited on glass substrates using VAS BUC coating unit (Model 78535-

France). The substrates with dimensions of 76mm×25mm were cleaned in acetone and methanol using ultrasonic bath and then dried by nitrogen. Further, the substrates were subjected to glow discharge cleaning before deposition. ZnS granule with 99.99٪ purity supplied by Jiangyan ATS Optical Material Co., Ltd. deposited on glass substrate by a tungsten boat was used as a support to evaporate. A quartz crystal monitor mounted near the substrate was used for in situ measurement of the thickness of the thin films as well as the evaporation rate, which was kept around 0.3 nm/s by using thickness monitor (Model FTM6). The pressure of chamber was about 1.5×10^{-5} mbar. ZnS thin films with a thickness of 100 nm on cleaned glass substrates samples were annealed in air for an hour at temperatures 100, 200, 300 and 400 °C. The structural characterization of the film was carried out using Xray diffractometer [XRD] (D8 Advance system from Bruker company) with Cu kα radiation (λ=1.542 Å) in 2θ range from 15-60°. The composition of the films on glass substrates was investigated by energy dispersive analysis of X-ray [EDAX] (Oxford 7538 EDX analyzer). The optical absorbance as well as transmittance spectra of ZnS thin films was obtained in UV-Vis spectrophotometer (Cintra101) in the wavelength range of 350-800 nm.

III. Results and Discussion

A. *XRD measurements*

Figure 1(a) depicts the X-ray diffraction patterns of ZnS films without heat treatment and annealed in the air at 100, 200, 300 and 400 °C. Diffraction angles and Miller indices of the peaks are shown in figure. The strong XRD peaks at $2\theta \approx 28.6°$ correspond to both diffraction angles of the (111) plane of cubic ZnS. Therefore, the ZnS films deposited on a glass substrate by vacuum deposition where the cubic structure and the c-axis of crystallites were mostly oriented perpendicular to the substrate. The grain size of the crystallite (diameter D_{hkl}) was determined from the full width at half maximum ($\Delta\omega_{2\Theta}$) of the (111) peaks by using the Scherer formula [12]:

$$D_{hkl} = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

where K is a constant, λ is the X-ray wavelength (0.1542 nm), β is the full width at half maximum (FWHM) of the film diffraction peak at 2θ, where θ is the Bragg diffraction angle. Here K=0.89 for spherical shape (evidence from TEM) [13]. Annealing caused by the rearrangement of ions Zn and S inside the ZnS lattice and to the diffusion of atoms or ions into its volume. The values of D_{hkl} were determined according to Fig. 1, and introduced in Table 1 for ZnS thin films without heat treatment and for annealed samples at 100, 200, 300 and 400 °C in air. The largest value of the full width at half maximum at 100 °C showed that the size of the crystallites and unit cell volume were minimum at this temperature. The variation of Zn and S chemical compositions in ZnS films under different annealing temperatures analyzed by EDAX, using an acceleration voltage of 15 kV. All samples prepared at various annealing temperatures were non-stoichiometric, and Zn had more content than S. The Zn/S ratio decreased slowly as the annealing temperatures were elevated. When the temperature reached to 300 °C, the ZnS film showed nearly equal counts for Zn and S. However, as the annealing temperature increased to 400 °C, the Zn/S ratio of the films also increased to 1.08. This increase can be attributed to the re-evaporation of sulfide from the film surface.

Figure 1(b) gives a comparison among the XRD patterns of 75, 150 and 225 nm thickness as-deposited ZnS films. All samples have cubic structure with a (111) preferred orientation at 2θ = 28.3º which showed improvement upon film thickness increment. Increasing film thickness not only intensified the characteristics peak of ZnS, but also led to appearance of two other peaks in the XRD pattern due to improvement of its crystallinity. This matter may be attributed to the

temperature increment of the substrate due to higher thickness and deposition time [14].

Table 1 Structural properties and crystallite sizes of ZnS films as-deposited and annealed at different temperatures

Annealing Temperature (°C)	2θ (degrees)	β (degrees)	Grain size D (nm)	Zn/ S ratio
As deposited	28.597	0.338	24	1.23
100	28.634	0.386	21	1.21
200	28.623	0.324	25	1.18
300	28.628	0.288	28	1.02
400	28.691	0.314	26	1.08

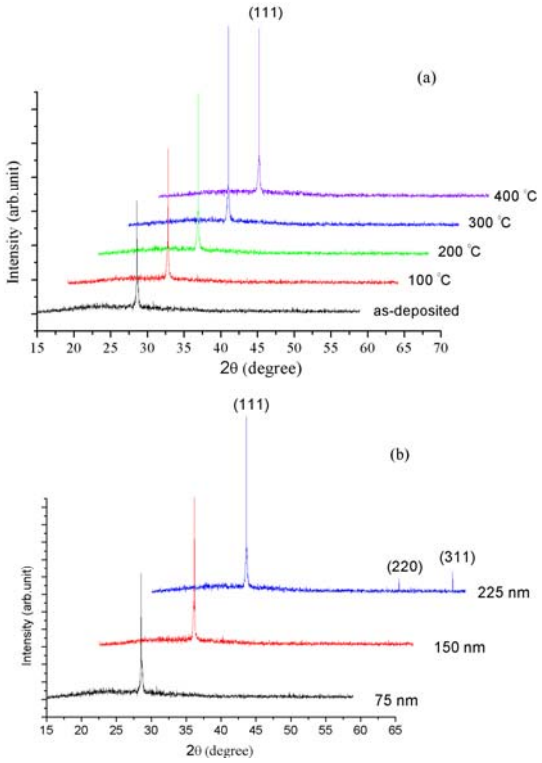

Fig. 1 X–ray diffraction patterns of ZnS films (a) at various annealed temperatures in the air, (b) as-deposited with different thickness.

B. *Optical measurements*

Optical properties of ZnS thin films were performed by measuring transmittance and absorbance of ZnS films on glass substrates in the range of wavelength 350–800 nm by subtracting the glass substrate as a reference. The transmittance values of as-deposited and annealed films by using double beam automated spectrophotometers (Cintera 101) and given in Fig. 2. The optical transmission of the films varied from 60% to 95% in the region of visible wavelengths. The absorption coefficient (α) was analyzed using the following expression for near edge optical absorption of semiconductors:

$$\alpha h\upsilon = k\left(h\upsilon - E_g\right)^{m/2} \tag{2}$$

where k is constant, E_g is the energy gap between the valance and conduction bands and m is a constant that is equal to 1 for direct band gap semiconductors. Using the fundamental relations of photon transmission and absorbance,

$$I = I_0 \exp\left(-\alpha t\right) \tag{3}$$

where t is the thickness and

$$A = \log\left(I_0 / I\right) \tag{4}$$

We have $\alpha = 2.303\, A/t$.

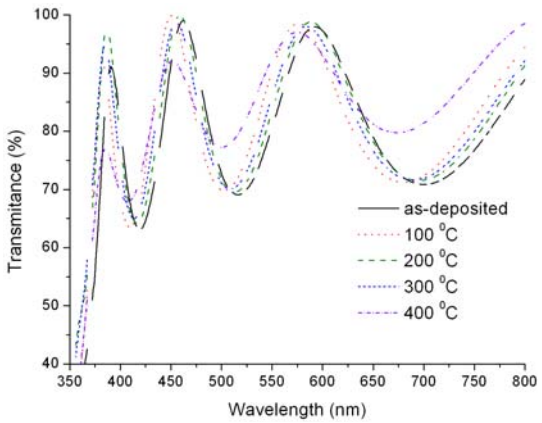

Fig. 2 Transmittance spectra of ZnS films as-deposited and annealed in the air.

The band gap values were determined from the intercept of the straight line portion of the $(\alpha h\upsilon)^2$ versus the hυ graph on the hυ-axis using computer fitting program. The linear part shows that the mode of transition in these films is of direct nature. Figure 3 depicts the plot of $(\alpha h\upsilon)^2$ versus photon energy, hυ, for ZnS films as-deposited and annealed films. The optical band gap value for as-deposited films was 3.25 eV, but the value increased after annealing to 3.32 eV except for 400 °C where it decreased to 3.28 eV. The band-gap values

are lower than bulk value of hexagonal ZnS because of quantum confinement of ZnS nanocrystals. It is consistent with the literature [15].

As the annealing temperature increases, transmission spectra of the annealed films exhibit a decrease in the optical transmittance with its absorption edge shifts gradually towards lower wavelength and shrinks the band gap (see Figs. 2 and 3).

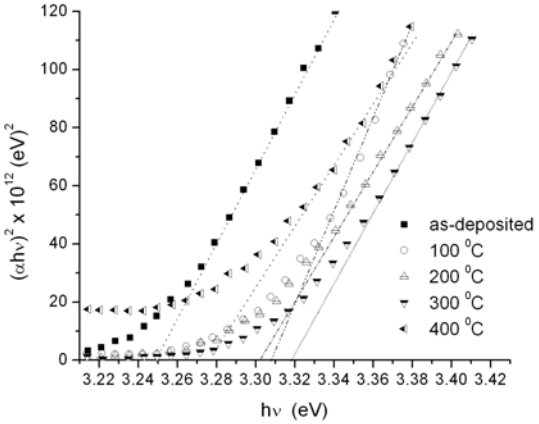

Fig. 3 Plot of (αhυ)2 versus photon energy for ZnS films as-deposited and annealed at different temperatures.

Figure 4, shows the transmission spectra of ZnS thin films as-deposited at room temperature in varying thickness from 75 to 225 nm. The absorbance spectra of thin films, with different thickness, are shown in Fig. 5. These spectra reveal that films, grown under the same parametric conditions have low absorbance in the visible and near infrared regions. However, absorbance in the ultraviolet region is high. The enhanced absorption is observed in the neighborhood of λ = 360 nm. As the thickness increases, the maximum absorption peak shifts towards lower wavelength and shrinks the band-gap. Also with increasing thickness, the overall absorbance increases. This is because of the reason that in case of thicker films more atoms are present in the film so more states will be available for the photons to be absorbed.

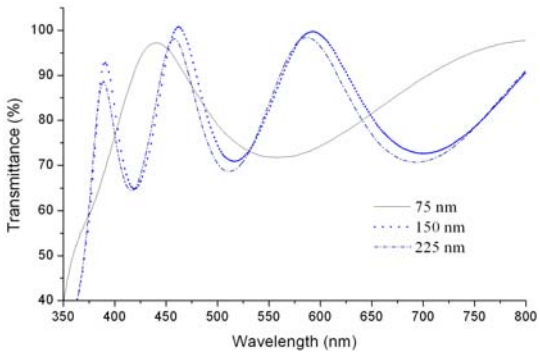

Fig. 4 Transmittance spectra for as-deposited ZnS films at room temperature.

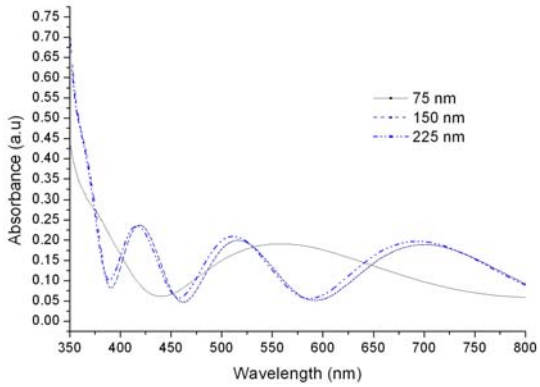

Fig. 5 Transmittance spectra for as-deposited ZnS films at room temperature.

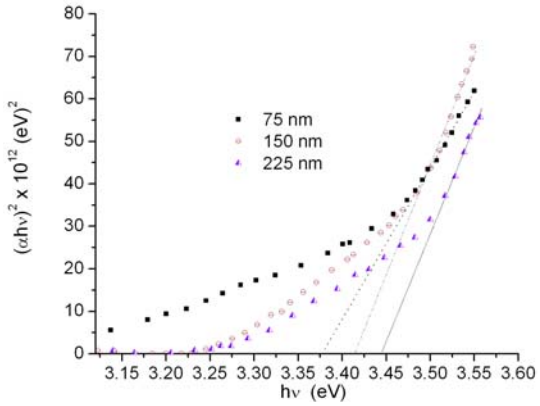

Fig. 6 Variations of (αhυ)2 versus hυ for as-deposited ZnS films at room temperature

Figure 6 gives the plot of $(\alpha h\nu)^2$ in terms of band gap for as-deposited ZnS films at room temperature. As specified in the figure, band gap of the as-deposited ZnS films of 75 nm, 150 nm and 225 nm thick are 3.38 eV, 3.42 eV and 3.45 eV respectively. The band gap of 225

nm sample is closer to bulk cubic phase (~3.5eV) and single crystal ZnS (~3.6 eV) values than that of other samples.

Figure 7 illustrates the optical reflectance spectra for ZnS thin flms. The reflectance has been found by using the relationship:

$$R(\lambda)+A(\lambda)+T(\lambda)=1 \quad (5)$$

The reflectance of ZnS thin films is small in the near infrared and visible region. The overall reflectance of the film increases with the film thickness.

For normal reflectance [16], we have,

$$R=(n-1)^2 / (n+1)^2 \quad (6)$$

where R is the normal reflectance; using the above relation the refractive index, n was determined.

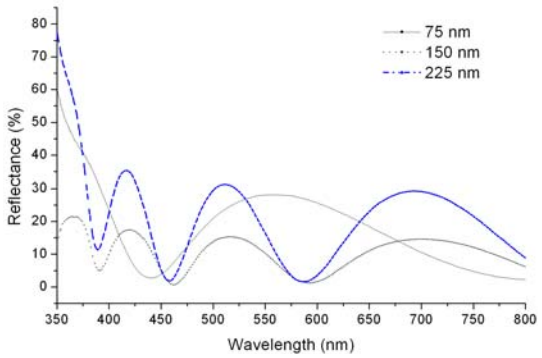

Fig. 7 Reflectance spectra for as-deposited ZnS films at room temperature.

Figure 8 demonstrates the variations in the refractive index with the incident photon wavelength. The increase in the film thickness results in the over all increase in the refractive index. This increase is due to the over all increase in the reflectance with the film thickness which is consistent with the well-established result that the crystallinity of the films improves on increasing thickness. Better crystallinity of the films i.e. larger grain size leads to the higher value of n [17], which in turn increases the optical reflectance. Thus on increasing of thickness, decrease in the optical transmittance may be attributed to the larger grain size of the films.

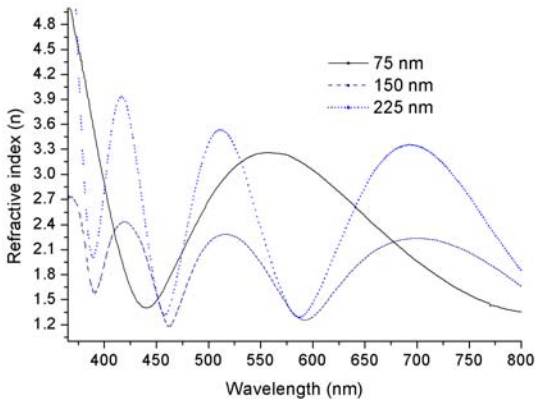

Fig. 8 Refractive index of as-deposited ZnS films versus incident photon energy at room temperature.

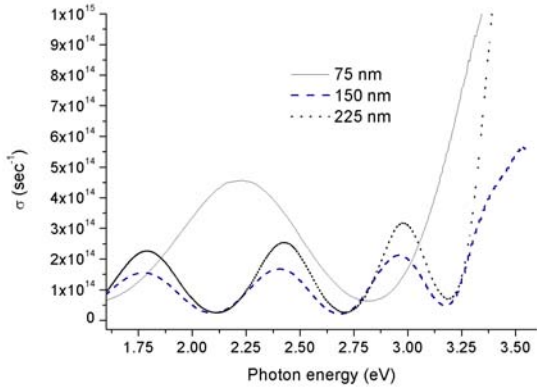

Fig. 9 Optical conductivity for as-deposited ZnS films versus incident photon energy at room temperature.

The peak value of the refractive index for the ZnS thin films of various thickness vary in the range of 1.52 to 3.84, which is in good agreement with the value 2.62 reported in [18], [19].

Figure 9 shows the variation of optical conductivity with the incident photon energy. The optical conductivity was determined using the relation [18]:

$$\sigma=\alpha nc/4\pi \quad (7)$$

where c is the free space velocity of light.

The enhanced optical conductivity at the lower wavelengths is due to the high absorbance of the films in that region.

IV. CONCLUSION

ZnS thin films prepared by thermal evaporation technique have been characterized using optical measurements and deductions to obtain such optical and structural properties as the XRD and T-R-A spectra, optical band gap energy, refractive index, optical conductivity etc. The variations of these with incident photon energy have been studied. ZnS films at various annealing temperatures have a cubic structure with a preferred orientation of (111). All the films exhibit high transmittance (~ 60 - 95 %) and low absorbance. The value of optical conductivity is in the range of $(0.2\text{-}9)\times10^{14}$ sec^{-1} at room temperature. Over the annealing temperature of 100 $^{\circ}$C, annealing caused by the high rearrangement of ions Zn and S inside the ZnS lattice and includes crystalline evolution. The increase in film thickness was found to improve the film crystallinity. The film thickness increment enhanced the band gap energy to a value near to that of the ZnS single crystal.

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Mr. Hojjat Amrollahi Bioki was born in 1980; he received his B.Sc. and M.Sc. degrees in physics from Yazd University, Yazd, Iran. He was selected as the best researcher certification in December 2009 in Yazd University. After his graduation he is working in coating laboratory as an instructor with graduate students at the department of physics of Yazd University.

Dr. Mahmood Borhani Zarandi was born in 1958. He received his B.Sc. and M.Sc. degrees in physics from Shahid Beheshti University, Tehran, Iran. He received his PhD in 2007 from Shahid Bahonar, Kerman, Iran. Today he is an Associate Professor at Faculty of Physics of Yazd University.

His research focuses on high energy electron beams on mechanical and electrical properties of polymers and semiconductors.

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