

1-1-2010

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M. RUHUL AMIN BHUIYAN

M. MONJARUL ALAM

M. ABDUL MOMIN

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BHUIYAN, M. RUHUL AMIN; ALAM, M. MONJARUL; and MOMIN, M. ABDUL (2010) "Effect of substrate temperature on the optical properties of thermally evaporated ZnS thin films," *Turkish Journal of Physics*: Vol. 34: No. 1, Article 5. <https://doi.org/10.3906/fiz-0902-9>
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Effect of substrate temperature on the optical properties of thermally evaporated ZnS thin films

M. Ruhul Amin BHUIYAN, M. Monjarul ALAM, M. Abdul MOMIN

*Department of Applied Physics, Electronics and Communication Engineering, Islamic University,
Kushtia-7003, BANGLADESH
E-mail: mrab_iu@yahoo.com*

Received 09.02.2009

Abstract

Zinc Sulfide (ZnS) thin films were formed onto cleaned glass substrates using the thermal evaporation method in vacuum. The substrate temperature was varied between as-deposited and 150 °C, keeping the film thickness and the rate of evaporation fixed at 200 nm and $0.3 \text{ nm} \cdot \text{s}^{-1}$, respectively. The film thickness was measured in situ by a quartz crystal thickness monitor. The structure of the films was ascertained by x-ray diffraction (XRD) method. The XRD spectra show that the films are polycrystalline in nature, which possess hexagonal structure. The optical properties of the films were ascertained by UV-VIS-NIR spectrophotometer (photon wavelength ranging between 300 and 2500 nm). The optical transmittance and reflectance were utilized to compute the absorption coefficient, band gap energy and refractive index of the films. Nature of the optical transition of the films has been observed in direct allowed with band gap energies between 3.37 and 3.46 eV depending on substrate temperatures. The refractive index was found to vary inversely with incident photon energy.

Key Words: ZnS thin films, substrate temperature, band gap energy, refractive index.

1. Introduction

Oil and gas, which at present are the main sources of energy, will eventually exhaust after sometime, necessitating the search for newer energy resources. Nuclear energy is one option, but it induces acute radioactive pollution and has technical problems. The Sun is a huge source of energy that can be converted into electrical energy, for example, via solar cells and is the best alternative option. Zinc Sulfide (ZnS) is a wide band gap and direct transition semiconductor [1]. Consequently, it is a potentially important material to be used as an antireflection coating for heterojunction solar cells [2] and important device material for the detection, emission and modulation of visible and near ultra violet light [3, 4]. In particular, ZnS is believed to be one of the most

promising materials for blue light emitting laser diodes [5] and thin film electro luminescent displays [6]. In the present paper, effects of substrate temperature on the optical properties of ZnS thin films have been studied.

2. Experiment

2.1. Growth of the films

Films of ZnS were thermally evaporated onto chemically and ultrasonically cleaned glass substrates using oil diffusion pump (E306A, Edwards, UK) in vacuum ($\approx 10^{-7}$ mbar). The source material (elemental ZnS) was evaporated from a tungsten boat and the substrate was placed at a distance of 20 cm from the source. The films were deposited at various substrate temperatures. The thickness and the rate of evaporation of the films were measured in situ by using the quartz crystal thickness monitor (FTM5, Edwards, UK). The obtained thickness of the films was 200 ± 10 nm.

2.2. Structural measurements

The x-ray diffraction (XRD) was used to investigate the structure of ZnS thin films. The diffraction patterns were recorded by using a Philips X'Pert PRO model PW3040 XRD system with Cu-K α radiation, operated at 40 kV and 30 mA, with angular range $10^\circ \leq 2\theta \leq 100^\circ$.

2.3. Optical measurements

2.3.1. Transmittance, reflectance and thickness

The variations of transmittance and specular absolute reflectance of the films with wavelength of light incident on them were measured by using a dual-beam UV-VIS-NIR recording spectrophotometer (Shimadzu UV-3100, Japan) in the photon wavelength range from 300 to 2500 nm. An integrating sphere detected light signals coming from the samples. The thickness of the films was rechecked using an infrared interference method [7], which depends on the reflectance characteristics of the films. In this method the thickness of a film is given by

$$d = \frac{\Delta m}{2\sqrt{n^2 - \sin^2 \theta}} \frac{1}{(1/\lambda_1) - (1/\lambda_2)}, \quad (1)$$

where n is the refractive index of the film, θ the incident angle of light to the sample, λ_1 and λ_2 are the peak or valley wavelengths in the reflectance spectrum and Δm denotes the number of peaks or valleys between λ_1 and λ_2 , where, $\lambda_2 > \lambda_1$.

2.3.2. Absorption coefficient and band gap energy

For transmittance T at normal incidence and reflectance R at near-normal incidence of light on the films, expression for the multiple reflected systems has been given by Heavens [8]. Tomlin [9] simplified those expressions for absorbing films on non-absorbing substrates and are expressed as

$$\frac{1 - R}{T} = \frac{1}{2n_1(n^2 + k^2)} \left[\begin{array}{l} n\{(n^2 + n_1^2 + k^2) \sinh 2\alpha_1 + 2nn_1 \cosh 2\alpha_1\} \\ + k\{(n^2 - n_1^2 + k^2) \sin 2\gamma_1 + 2n_1k \cos 2\gamma_1\} \end{array} \right], \quad (2)$$

$$\frac{1+R}{T} = \frac{1}{4n_1(n^2+k^2)} \left[\begin{array}{l} (n^2+k^2)\{(n^2+n_1^2+k^2)\cosh 2\alpha_1 + 2(nn_1+k)\sinh 2\alpha_1\} \\ +(-n^2-k^2)\{(n^2-n_1^2+k^2)\cos 2\gamma_1 + 2(n-n_1k)\sin 2\gamma_1\} \end{array} \right], \quad (3)$$

where, n and n_1 are the refractive indices of the film and substrate, respectively; k is the extinction-coefficient of the film; $n_1 = 1.45$, $\alpha_1 = 2\pi k d/\lambda$ and $\gamma_1 = 2\pi n d/\lambda$, where λ is the wavelength of light and d the thickness of the film. Equations (2) and (3) were solved for k and n utilizing computerized iteration process. The absorption coefficient α was then calculated using $\alpha = 4\pi k/\lambda$. Dependence of absorption coefficient, α on photon energy has been analyzed with the existing models to find the nature and extent of the band gap energy.

3. Results and discussion

Figure 1 shows the x-ray diffraction (XRD) spectra for three different substrate temperatures, 50, 100 and 150 °C for ZnS thin films. These spectrums were obtained by scanning 2θ in the range from 10 to 100° and reveal the polycrystalline nature of the films. Comparison of d -values with ASTM data for ZnS shows that the material is ZnS. These spectrums matched well with the standard spectrums of ZnS that possess hexagonal structure with average lattice parameter $a \approx 0.3778$ nm. Lattice parameter c could not be found. A qualitative estimate of the grain size of the films deposited at different substrate temperature was calculated by using the well-known Scherrer's formula [10], simplified by Bragg,

$$B_{\text{crystallite}} = \frac{0.94 \lambda}{L \cos \theta}, \quad (4)$$

where λ is the wavelength of $\text{CuK}\alpha$ radiation, and L is full-width half-maximum (FWHM) width. The unit of L should be converted into radian. Therefore the above equation takes the form

$$B_{\text{crystallite}} = \frac{50.97 \lambda}{L \cos \theta}. \quad (5)$$

The grain size was changed from 12.7 to 18.4 nm as substrate temperature was changed from 50 to 150 °C for (210) peak.

Figure 2 shows the optical transmittance spectra having different substrate temperature between as-deposited and 150 °C for ZnS thin films. All the films demonstrate more than 70% transmittance at wavelengths longer than 400 nm, which is comparable with the values for ZnS thin films identified by other workers [11]. Below 400 nm the films exhibit a sharp fall in transmittance (hence a strong increase in absorption). Above 400 nm the transmittance is variatively (or quasi-) stable across the temperatures. Experimental results from other workers [12–14] on ZnS thin films report similar behavior. These spectra ascertain interference of the light transmitted through the films and the substrate.

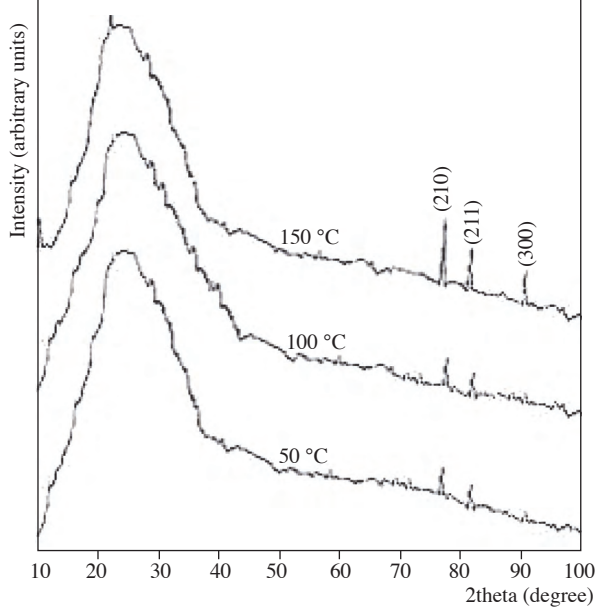


Figure 1. XRD spectra of ZnS thin films having different substrate temperature of deposition.

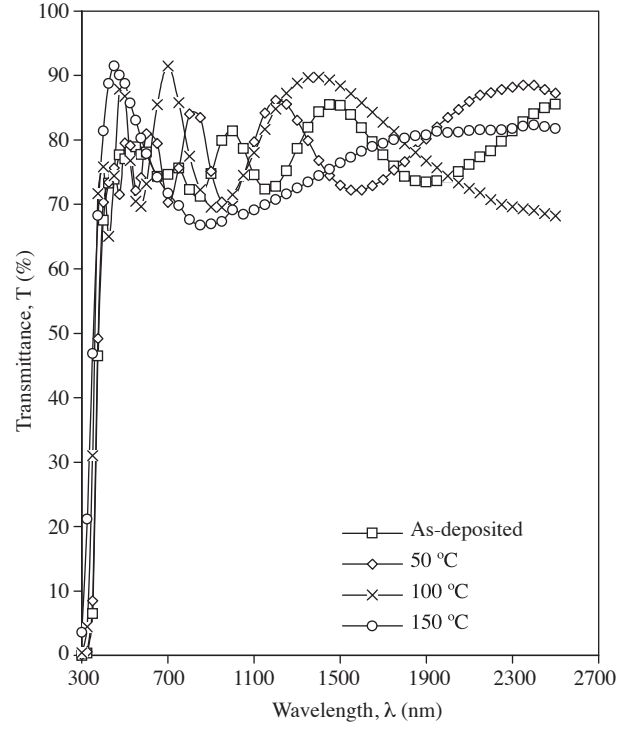


Figure 2. Dependence of optical transmittance on wavelength for ZnS thin films having different substrate deposition temperatures.

Figure 3 depicts the optical absorption spectra for ZnS thin films deposited at different substrate temperatures. Study of materials by means of optical absorption provides a simple method for explaining some features concerning the band structure of materials. In the present investigation, optical absorption in ZnS thin films with different substrate temperature was studied. The nature of transition (direct or indirect) is determined by using the relation [15]

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu}, \quad (6)$$

where $h\nu$ is the photon energy, E_g the band gap energy, and A and n are constants. For direct transition, $n = 1/2$ and indirect transition, $n = 2$.

Analysis of the absorption coefficient α above the fundamental edge shows that the rise of α in the photon energy range $3.30 \leq h\nu \leq 4.13$ eV follows a relation for direct transition. The band gap energy E_g was determined via a plot of $(\alpha h\nu)^2$ as a function of $h\nu$ (as shown in Figure 4) in the photon energy range $3.30 \leq h\nu \leq 4.13$ eV. The band gap energy increases from 3.37 to 3.46 eV, as the substrate temperature increases from as-deposited to 150 °C having thickness fixed at 200 nm. In our sample, the band gap energy varies directly with the substrate temperature, which reasonably conforms to the other workers [16–18]. The calculated optical parameters are summarized in Table 1.

Figure 5 shows the variation of refractive index with photon energy for various substrate temperatures. The refractive index is found to decrease with increase in photon energy. The refractive indices of the films

were found to be in the range of 1.75 to 2.79, depending on photon energy between 0.605 and 1.127 eV. Such a difference is mainly due to the larger grain size and lower strain in the films deposited at higher temperatures.

Table 1. Optical parameters of ZnS thin films.

Substrate Temperature (°C)	Energy gap, E_g (eV)	A ($\text{cm}^{-1}\text{eV}^{1/2}$)
As-deposited	3.37	7.724×10^5
50	3.38	6.77×10^5
100	3.43	4.40×10^5
150	3.46	2.35×10^5

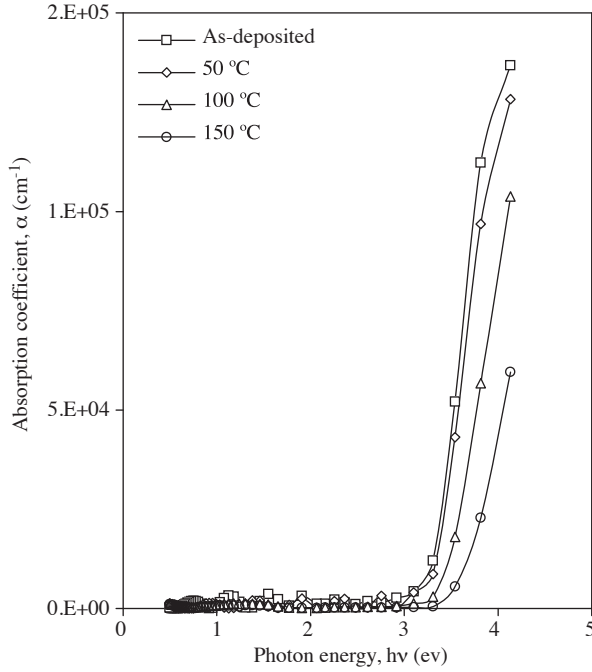


Figure 3. Dependence of absorption coefficient on photon energy for ZnS thin films having different substrate deposition temperatures.

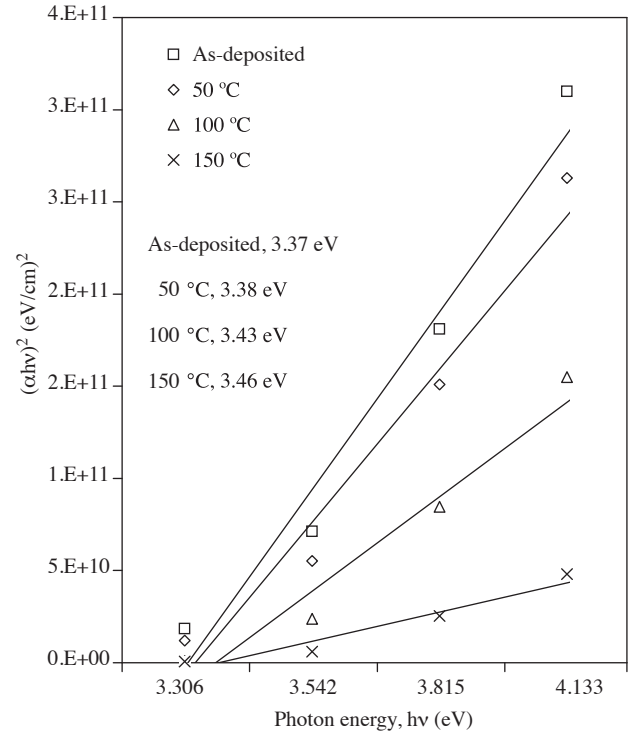


Figure 4. Dependence of $(\alpha h\nu)^2$ on photon energy for ZnS thin films having different substrate deposition temperatures.

The refractive index dispersion data was evaluated according to the single effective oscillator model proposed by Wemple and Di Domenico [19, 20]. It is well known from dispersion theory that, in the region of low absorption, the index of refraction n is given in a single oscillator model by the expression

$$n^2(h\nu) = 1 + \frac{E_d E_0}{E_0^2 - (h\nu)^2}, \quad (7)$$

where $h\nu$ is the photon energy, E_0 is the single oscillator energy and E_d is the dispersion energy. Parameter E_d , which is a measure of the intensity of the interband optical transitions, does not depend significantly on the

band gap or the density of the valence electrons. The oscillator strength is derived from the slope of the straight line portion of the curve $1/(n^2-1)$ versus $(h\nu)^2$. Figure 6 shows the dependence of $1/(n^2-1)$ on $(h\nu)^2$ for ZnS films having different substrate temperatures. It was observed that the strength of the oscillator increases with increase in substrate temperature.

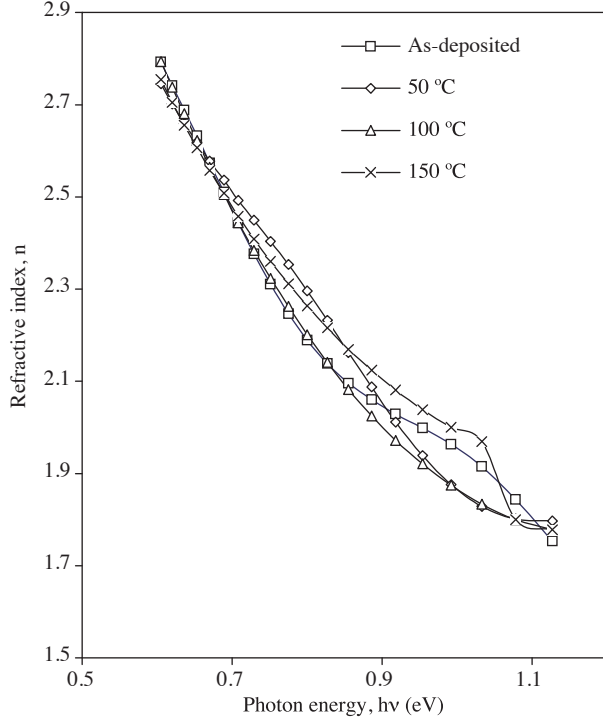


Figure 5. Dependence of refractive index on photon energy for ZnS thin films having different substrate deposition temperatures.

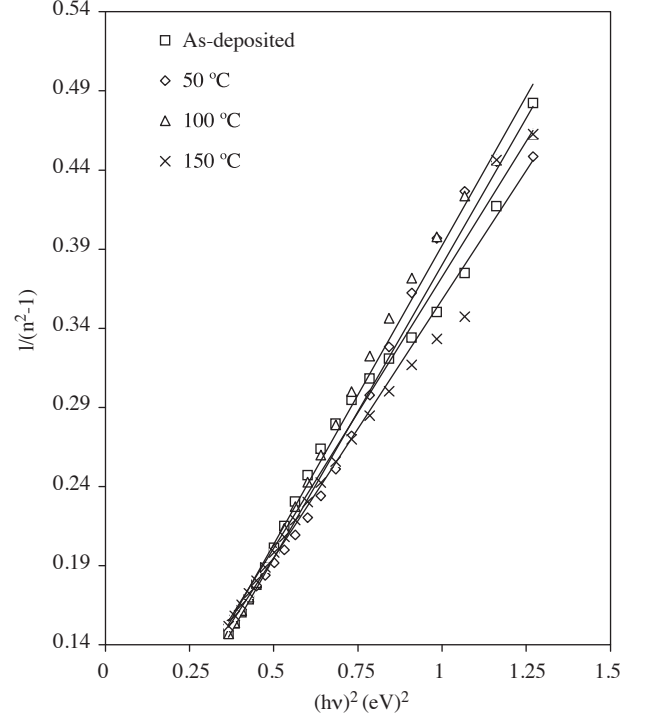


Figure 6. Dependence of $1/(n^2-1)$ on $(h\nu)^2$ for ZnS thin films having different substrate deposition temperatures.

The oscillator energy can be considered as an average energy gap and almost verifies the relation $E_0 \cong 2.0E_g^{\text{opt}}$. It was found that E_d varies between 8.84 and 22.57 eV for as-deposited films and E_0 varies from 6.74 to 6.90 eV for the different substrate temperatures. Similar to the description of Swanepoel [21], the bonds in our samples are supposed to be strongly covalent, and the increase in E_d has to be attributed to higher number of the nearest neighbors in the alloy with respect to pure compounds.

4. Conclusions

The ZnS thin films, grown by thermally vacuum evaporation method in the present investigation, have been structurally and optically characterized to assess the good quality films for photovoltaic application. The films were polycrystalline and it exhibits hexagonal structure in nature. The nature of the variation of optical properties seems to be reasonable to conclude that the substrate temperature has an influence to change the optical band gap energy. The dispersion of the refractive index follows a single oscillator model. The films have optimum properties for their application in fabricating as window material for heterojunction solar cells.

Acknowledgements

We are thankful to Mr. Syed Ayubur Rahman and Mrs. Jahanara Parvin of the Atomic Energy Centre, Dhaka for their assistance in preparing the samples.

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