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Abstract

Thin films of zinc sulphide were prepared using a flash evaporation technique. The obtained thin films were subjected to heat treatment to investigate the effect of annealing on the transmittance spectrum and the electronic transitions. It has been found that annealing affected the transmission spectrum and caused an increase in the direct optical band gap. The optical parameters, oscillator energy E_0 and dispersion energy E_d were determined using the Wemple DiDomenico single oscillator model. The optical energy gap obtained from the Wemple and DiDomenico model was in good agreement with the optical energy gap proposed by the Tauc theory.

Introduction

Zinc sulphide (ZnS) has attracted much attention from the viewpoint of fabrication of many devices. ZnS is highly suitable as a window layer in heterojunction photovoltaic solar cells because the wide band gap decreases the window absorption losses and improves the short-circuit current of the cell (Fathy et al. 2004). Thin films of ZnS doped with transition metal elements or rare earth elements have also been used as effective phosphor materials (Takata et al. 1990). In the area of optics, ZnS can be used as a reflector because of its high refractive index (Antony et al. 2005 and Ruffiner et al. 1989), as a dielectric filter because of high transmittance in the visible region (Roy et al. 2006), and as a light emitting diode in the blue to ultraviolet spectral region due to its wide band gap (Lopez et al. 2005).

Thin films of ZnS are produced by different techniques such as chemical vapor deposition (Tran et al. 1999), atomic layer epitaxy (Oikkonen et al. 1988), direct current (DC) electrodeposition (Lokhande et al. 1988), radio-frequency (RF) reactive sputtering (Shaoi et al. 2003), chemical bath deposition (Ben et al. 2008), and spray pyrolysis (Oztas and Yazici 2004).

In the present work, we report the effect of annealing on the optical transition of ZnS using a flash evaporation technique.

Methods

Thin films of ZnS were deposited on glass substrate utilizing a flash evaporation technique. High-purity ZnS powder (99.99%) from Aldrich company was ground. This powder was evaporated using a molybdenum boat filament in a high-vacuum chamber $> 10^{-5}$ torr.

The optimum conditions for obtaining uniform films were at a substrate temperature of 100 ^{o}C, and deposition rate 0.8 nm/s. The distance between filament and substrate was kept at 10 cm. The thickness of the as-deposited films was about 0.5 μm determined by optical interferometer method.

Optical and transition spectra were recorded in the wavelength range 300 - 900 nm using a double beam UV/Vis Shimadzu Corporation (Japan).

A computer program was used to calculate the absorption coefficients and the electronic transitions.

Results and Discussion

Typical transmission spectra for ZnS samples as a function of annealing temperature (200 ^{o}C for 2 hours) are presented in Fig. 1. The transmission peaks are shifted toward lower wavelengths after

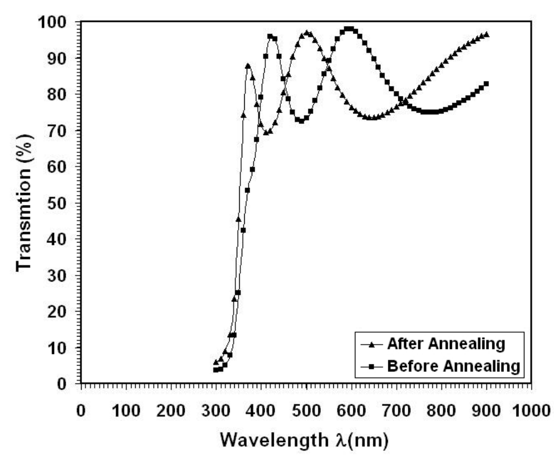

Fig. 1 Transmission of ZnS thin film versus wavelength before and after annealing.

annealing compared to the transmission peaks of deposited films. The average transmission in the visible spectrum was 72-97%. The absorption coefficient (α) was calculated with the help of the following relation (Shamala et al. 2004):

$$T = (1-R)\, e^{-\alpha d} \ldots (1)$$

where (d) is the thickness of the film. (T) and (R) are the transmittance and reflectance, respectively. Fig. 2 shows the calculated absorption coefficient $\alpha(h\upsilon)$, as a function of photon energy. It is clearly seen that α is greater than 10^4 cm^{-1} when ($h\upsilon$) is greater than 3.2 eV before annealing and 3.45 eV after annealing.

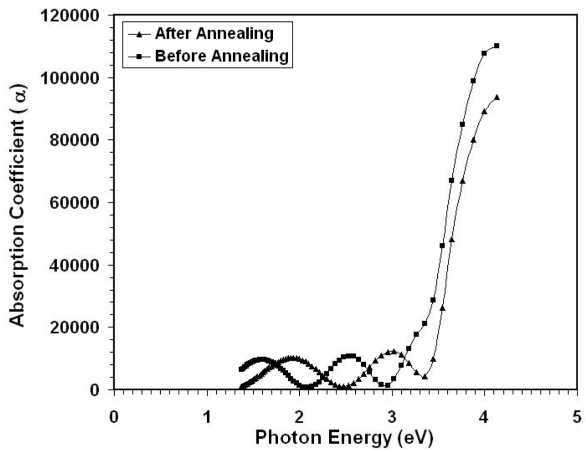

Fig. 2. Absorption of ZnS thin film versus photon energy

The band gap energies of these films were calculated with the help of an absorption spectrum. In general, the absorption coefficient and photon energy ($h\upsilon$) are related by the Tauc plot (Tauc and Meneth 1972):

$$\alpha = \frac{A}{h\nu}\,(h\nu - E_g)^{\,n} \ldots (2)$$

where (A) is a constant and (n) assumes values of (1/2, 2, 3/2 and 3), for allowed direct, allowed indirect and forbidden direct and indirect transitions, respectively. Fig. 3 and Fig. 4 show the curves of $(\alpha h\upsilon)^2$ versus photon energy before and after annealing.

The curve has a good straight-line fit over the higher-energy range above the absorption edge indicative of a direct optical transition near the absorption edge. Based on Fig. 3 and Fig. 4 the direct energy gap was calculated to be 3.6 eV and increases to 3.65 eV after annealing. These values are in good agreement with the reported data obtained using other techniques (Sehhar et al. 1999, Thangaraju and Kalionnan 2000, and Tanusevski and Poelman 2003). This increment could be attributed to the increase in

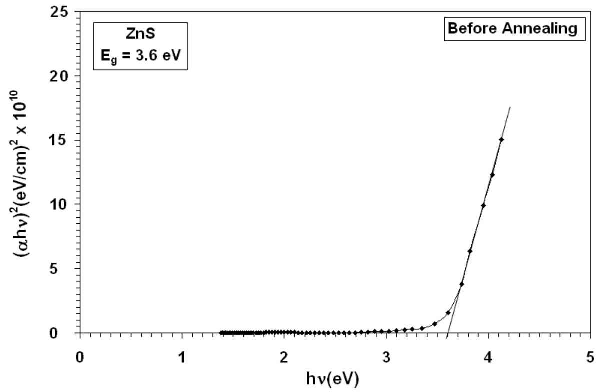

Fig. 3. $(\alpha h\upsilon)^2$ for ZnS thin film versus photon energy before annealing.

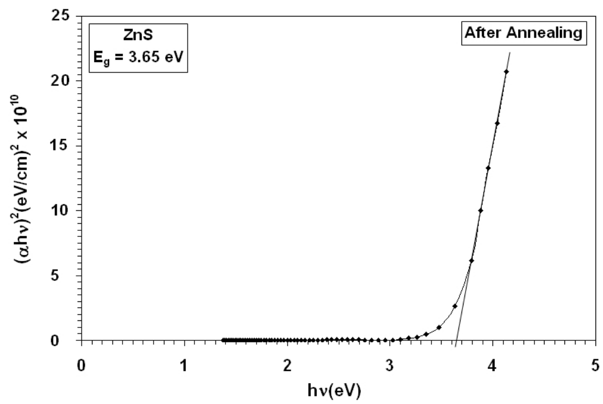

Fig. 4. $(\alpha h\upsilon)^2$ for ZnS thin film versus photon energy after annealing

crystallite size, which induced a decrease in dislocation density. We used a linear curve fitting to obtain the Urbach tail, which is defined as the width of the localized states available in the optical band gap that affects the optical band gap structure and optical transitions. The Urbach tail is determined by the following relation (Urbach 1953):

$$\alpha = \alpha_o \exp\left(\frac{E}{E_o}\right) \ldots (3)$$

where E is the photon energy, (α_o) is constant and E_v is the Urbach energy, which refers to the width of the exponential absorption edge.

Fig. 5 shows the variation of ln(α) versus photon energy, for ZnS thin films before and after annealing. The value of E_o were calculated from the slope, and the obtained values are given in Table 1, which indicates that Urbach energy values of ZnS film decrease after annealing . It can be clearly seen that the width of the band tail, i.e. the Urbach energy, decreases slightly with increasing annealing temperature, indicating an improvement of the quality of the film due to the

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Table 1 Optical parameters of Zn thin films

Sample	E_g^{opt} (eV) by Tauc	E_d (eV)	E_o (eV)	E_g (eV) by W. D.	E_U (eV)
Before annealing	3.6	2.84	7.28	3.64	1.38
After annealing	3.65	3.70	7.42	3.71	1.10

annealing process. The $E_{U,}$ values change inversely with optical band gaps of the films. This decrease leads to a redistribution of states from band to tail, thus allowing for a greater number of possible band to tail and tail transitions (Oleary et al. 1997).

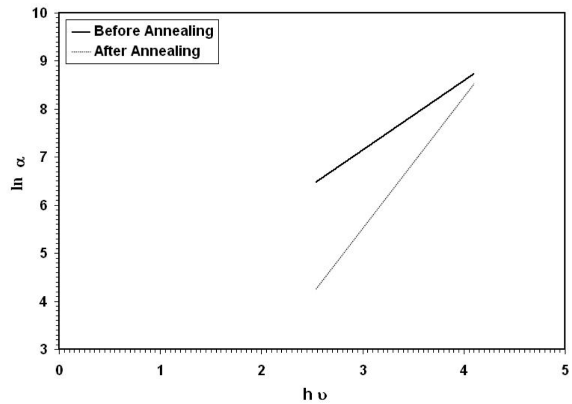

Fig. 5. ln α as a function of hυ.

The dispersion in refractive index can be determined by the single-oscillator model proposed by Wemple and Didomenico. The spectral dependence of the refractive index (n) according to this model is then defined by the equation (Wemple and DiDomenico 1971):

$$n^2 - 1 = \frac{E_o E_d}{E_o^2 - h\upsilon^2} \dots (4)$$

where E_o is the single-oscillator energy parameter and E_d is the dispersion energy, which is a measure of the strength of the interband transitions.

A plot of $(n^2\text{-}1)^{-1}$ versus E^2 would be linearly fitted and would give the values of E_o and E_d from the slope ($1/E_oE_d$) and the intercept of the y-axis (E_o/E_d). Typical curves for ZnS before and after annealing are plotted in Fig. 6. The oscillator energy E_o is an average energy gap and could be related to the optical band gap, E_g by the approximation $E_o \approx 2E_g$ (Tigau 2005). The obtained values of E_o, E_d, E_g, are listed on Table 1.

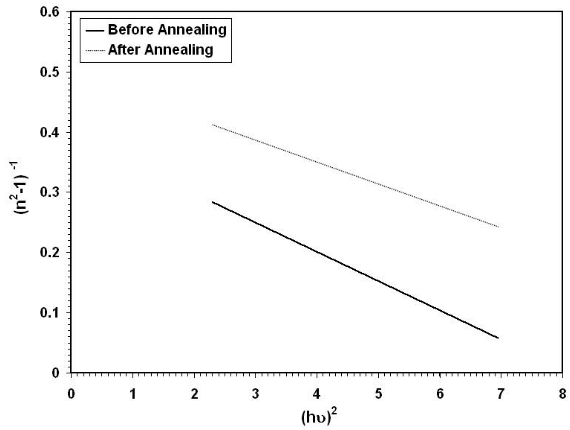

Fig. 6. $(n^2 \text{-}1)^{-1}$ as a function of (h

Conclusions

From these results, we conclude that annealing of zinc sulphide films grown by flash evaporation reduces lattice strain, producing a more perfect crystallite and decreasing the number of micro voids. The values of the optical energy gap proposed by the Wemple-DiDominco model were in good agreement with a Tauc plot.

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