Spectroscopic Ellipsometry Studies on ZnS Thin Films Deposited by Sol - Gel Method Whit Un-Annealed and Annealing Temperature

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Abstract

In the present work, zinc sulfide thin films were deposited on glass substrates by sol-gel process with coating speed of 3600 rpm. Zinc acetate (Zn $(CH_3COO)_2.2H_2O$) and thiourea (CH_4N_2S) were used as precursors. Two-methoxyethanol and monoethanolamin were used as solvent and stabilizer respectively. The optical properties of ZnS thin films such as refractive index, extinction coefficient, dielectric function and optical band gap energy of the films were obtained by spectroscopic ellipsometry analysis method in the wavelength range of 300 - 800nm. The incidence angle of the layers kept 70º. The measured spectroscopic ellipsometry parameters Ψ_{exp} and Δ_{exp} are fitted against the designed model by minimizing the square error (MSE). Considering the data obtained, it can be deduced that the optical properties of ZnS films is highly influenced by annealing temperature. The extinction coefficients of the films were decrease with change in annealing temperature of the films. From these results it is found that the energy gap of the ZnS films decreases whit annealing temperature of the films in the range of 3.20-3.12eV.

Keywords: Spectroscopic ellipsometry; Annealing temperature; Thin film; Zinc sulfide; Optical properties.

Introduction

ZnS has attracted considerable research interest due to its variety of applications, such as optoelectronic devices [1], photoluminescence [2], photoconductors [3], optical sensors [4], and etc.
ZnS is an important direct gap semiconductor with band gap of ≈3.58eV [7].
ZnS films have been deposited by a number of methods including chemical bath deposition [8], electro chemical deposition [11], chemical vapor deposition [12] and sol-gel method [13]. Among these, sol-gel spin coating deposition method is a nonexpensive and simple method of producing zinc sulfide films which covers large areas.
Spectroscopic ellipsometry (SE) is an optical measurement technique that characterizes light reflection (or transmission) from samples [14]. This method measures the two values (Ψ, Δ) which represent the amplitude ratio and phase difference between light waves known as p- and s-polarized light waves respectively. In spectroscopic ellipsometry, (Ψ, Δ) spectra are measured by changing the wavelength of light. Using SE method one can evaluate the optical constants and thicknesses of the layers.
In this work the optical properties of ZnS thin films with un–annealed and annealing temperature were examined using spectroscopic ellipsometry measurement. The optical characteristics of the films produced by this method are described and it is shown that they are similar to zinc sulfide films produced by other methods.

Materials and method

ZnS thin films were synthesized via simple sol–gel spin coating method. The sol was prepared with Zn $(CH_3COO)_2.2H_2O$ and CH_4N_2S as starting precursors and 2-methoxyethanol and monoethanolamine as solvent and stabilizer respectively. The molar ratio of monoethanolamine to zinc acetate was maintained at 1.0. The S/Zn molar ratio was 1 in the mixture. To obtain a homogeneous solution, it was stirred at 80°C for 120 min. The solution was aged for 24 h at room temperature. Before the deposition, the substrates were cleaned thoroughly using acetone and de–ionized water. The films were deposited on glass substrates with spin coating speeds of 3600 rpm. After deposition, the films were preheated at 200ºC for 10 min and then one of them were annealed at 300ºC for 1 hour.

Results and Discussion

The optical properties of ZnS thin films grown on glass substrates were investigated by using spectroscopic ellipsometric measurements. The experimental data was taken at an incident angle of 70º and then fitted theoretically using Lorentz model. The measured spectroscopic ellipsometry parameters Ψ_{exp} and Δ_{exp} fitted against the designed model in the spectral range from 300 to 800 nm by minimizing the square error (MSE), is shown in figures 1 and 2 respectively.

The (Ψ, Δ) measured from ellipsometry are defined from the ratio of the amplitude reflection coefficients for p- and s-polarizations:

$$\rho \equiv tan\psi \exp(i\Delta) \equiv \frac{r_p}{r_s} \qquad (1)$$

The mean square error is calculated by following equation.

$$(MSE)_{\chi^2} = \frac{1}{N}\sum_{i=1}^{N}\frac{(Mes_i - Th_i)^2}{\sigma_i^2} \qquad (2)$$

Where σ_i is standard deviation of the i-th data point, N is number of data point, Mes_i is i-th experimental data point and Th_i is i-th calculated data point from assumed theoretical model. The best match between the experimental and fitted data obtains when the MSE exhibits a minimum value.
The model used to analyze the ellipsometry data consists of a glass substrate, ZnS thin film, surface roughness layer and air. Surface roughness layer was modelled by effective medium approximation (EMA). The model used to analysis is shown in Fig.3.

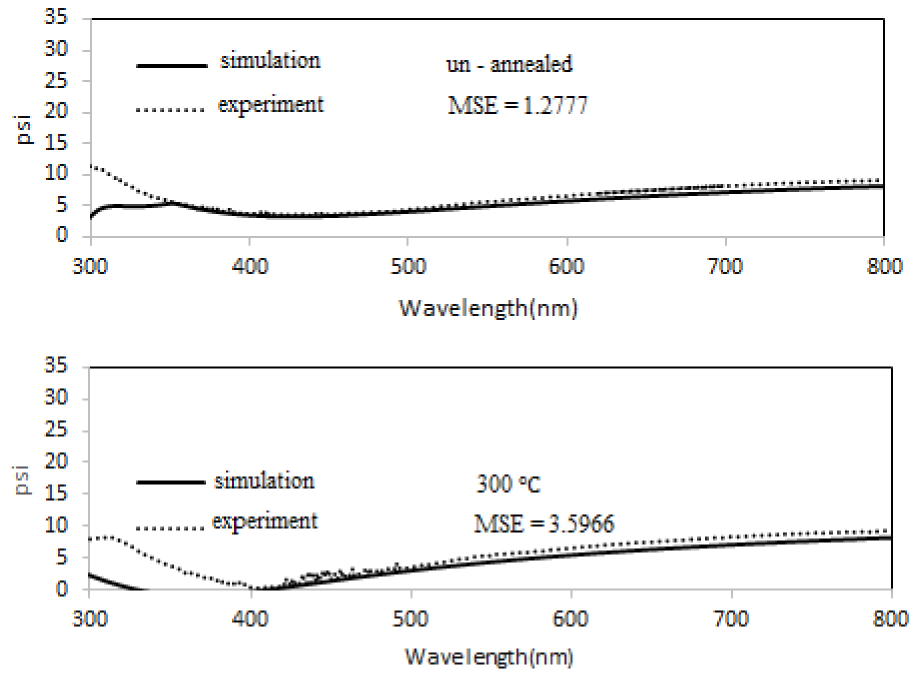

Fig. 1. Spectra of ‘Ψ’ as a function of wavelength for ZnS thin films.

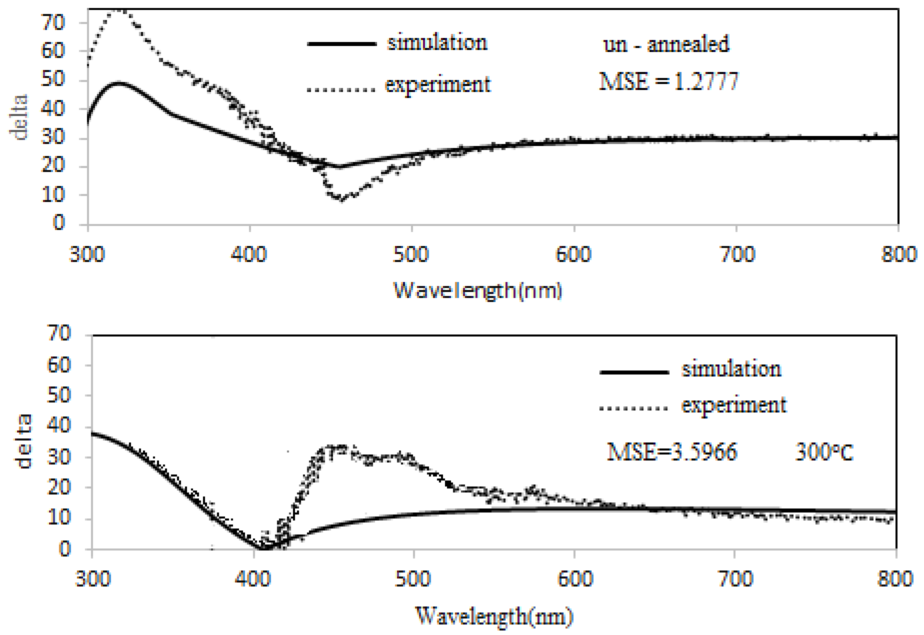

Fig. 2. Spectra of ‘Δ’ as a function of wavelength for ZnS thin films.

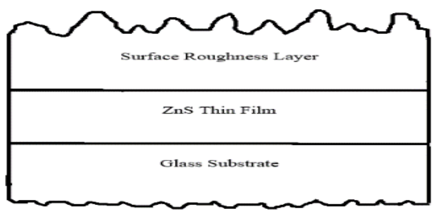

Fig. 3. The model used for analysis the ellipsometry data.

The calculated refractive index (n) of the ZnS thin films using spectroscopic ellipsometry method is shown in Fig.4. By increasing wavelength, the refractive index in all samples shifted to a constant value.

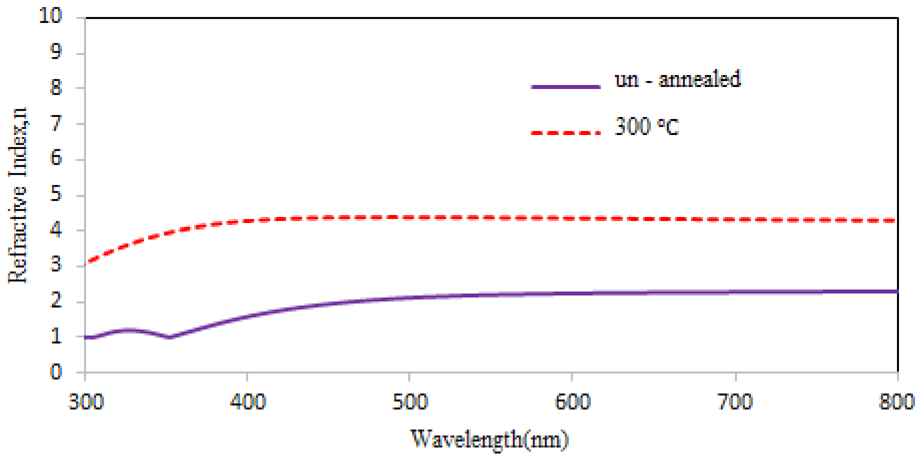

Fig.4. Variation of n as a function of wavelength for ZnS thin films.

The extinction coefficient (k) as a function of wavelength for ZnS thin films were calculated using spectroscopic ellipsometry method (Fig.5). It can be deduced from Fig.5 that by increasing wavelength, the extinction coefficient (k) of all layers decreases at about 325 nm. This means that in the visible wavelength region the samples get more transparent.

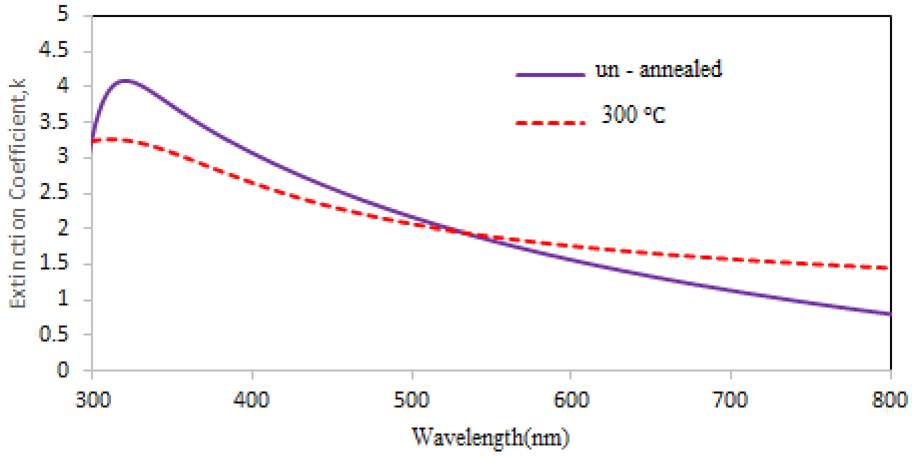

Fig. 5. Variation of k as a function of wavelength for ZnS thin films.

The real and imaginary part of dielectric function obtained by spectroscopic ellipsometry measurement method is shown in Fig. 6. By changing in annealing temperature leads to change in real part of dielectric function values as a function of wavelength, which is shown in Fig.6a. Fig. 6b shows that by, changing in annealing temperature the imaginary part of dielectric function increases and a peak can be seen.

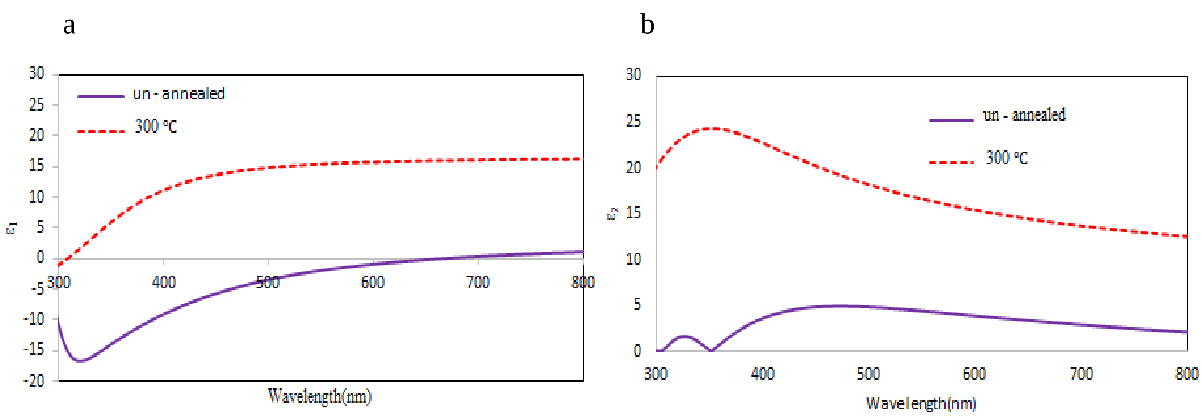

Fig.6. Variation of ε_1 (a) and ε_2 (b) as a function of wavelength for ZnS thin films.

We have calculated the absorption coefficient as a function of wavelength in ZnS thin films. The optical absorption coefficient is determined using the following equation [16].

$$\alpha = \frac{4\pi k}{\lambda} \qquad (3)$$

Where (k) is the extinction coefficient and λ is the wavelength. As is shown in Fig.8, by changing in annealing temperature the absorption coefficient decreases slightly. Also for all films it can be deduced from Fig.8 that increasing wavelength leads to decreasing of absorption coefficient to a constant value in visible range.

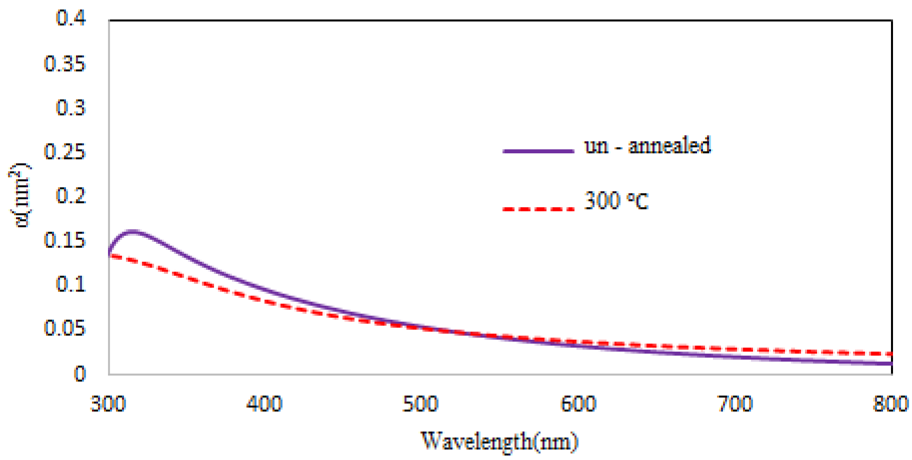

Fig.8. Variation of absorption coefficient (α) for ZnS thin films.

The optical band gap (Eg) of ZnS thin films was calculated using the absorption coefficient (α) for allowed direct transitions and is given by Eq.4 [17].

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \qquad (4)$$

Where A is an energy dependent constant, Eg is the band gap of the material , hυ is photon energy, and n is an index that theoretically equal 1/2 for ZnS whit direct band gap energy .

The optical band gap was calculated by extrapolating the linear portion of the $(\alpha h\upsilon)^2$. As shown in Fig.9 the direct band gap energy decreases from about 3.20 to 3.12 with changing in annealing temperature. The decrease of optical band gap could be attributed to the structural and morphological change in the films [18, 19]. Other possibilities to explain this change in optical band gap could be related to high temperature annealing leads to transition from cubic to hexagonal phase [20].

It may be deduced that by increasing annealing temperature, S atoms evaporates from the films and replaces by O atoms so the films change to ZnO and as a result the optical band gap reduced [21].

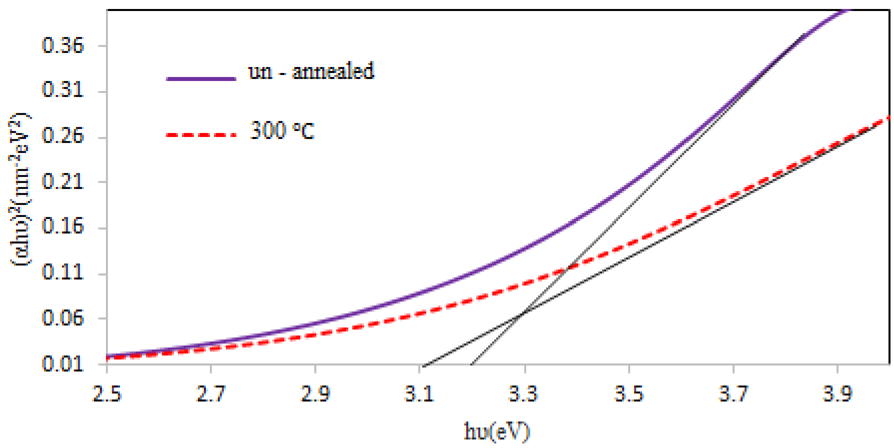

Fig.9. Variation of band gap for ZnS thin films.

Conclusions

ZnS thin films have been prepared by sol–gel spin coating method on glass substrates. Optical constant (n and k) of the films were determined using spectroscopic ellipsometry method also the optical band gap energy of the samples evaluated using tauc relation. The band gap energy of the ZnS thin films is found to be dependent on the annealing temperature. It was found that the energy gap of the ZnS films were decrease with increasing annealing temperature in the range of 3.20-3.12eV.

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