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The survey of influence of different rotation rates on optical properties of ZnS thin films by spectroscopic ellipsometry method

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Abstract: Zinc sulfide nano layers were deposited on glass substrates by sol-gel process with different coating speeds 3600 rpm, 4800 rpm, 6000 rpm and 7200 rpm. Zinc acetate (Zn(CHC3COO)2.2H2O) and thiourea (CH4N2S) were used as precursors.Two-methoxyethanol and monoethanolamin were used as solvent and stabilizer respectively. The solution was stirred at 80℃ for 120 min. A clear solution was obtained, then that was aged for 24 hour at room temperature. The sample was preheated at 200℃ for 10 min and they were annealed at 500℃ for 1 hour. The optical study of ZnS thin films is carried out by spectroscopic ellipsometry at room temperature. The measured spectroscopic ellipsometry parameters Ψ_{exp} and Δ_{exp} are fitted against the designed model in the spectral range from 300 nm to 800 nm by minimizing the square error (MSE). Different optical constants such as extinction coefficient, band gap and refractive index were investigated by SE800DUV spectroscopic ellipsometry device.

Keywords: spectroscopic ellipsometry, Thin film, Zinc sulfide, Optical properties.

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Introduction

Zinc sulfide (ZnS) is a II – VI semiconductor whith interesting properties for applications in a wide range of areas as optoelectronics or photonics. At room temperature, the most stable phase of ZnS is zinc-blende. A phase transition from cubic to hexagonal phase (wurtzite) occursat 1020°C in bulk ZnS, however in the case of nanostructures the wurtzite phase can be stabilized at room temperature[1]. ZnS has the largest band gap among the II – VI semiconductor, although its value slightly dependson the crystal phas, being 3.72 for zinc-blende and 3.77 eV for wurtzite structure[2].
ZnS films have been deposited by a number of methods including reactive evaporation [3] sputtering [4,5] chemical vapor deposition[6] and atomic layer epitaxy [7]. The characteristic of these methods is that they require expensive deposition equipment particularly where very large areas have to be covered. Various synthetic methods have been employed to synthesize ZnS thin films, such as metal organic chemical vapor deposition (MOCVD) [4], sol–gel deposition [5], radio frequency (RF) magnetron sputtering [6], thermionic vacuum arc [7],and molecular beam epitaxy (MBE) [8].
This paper describes a simple, non – vacuum method of producing undoped zinc sulfide films and it is mainly focused on the synthesize and characterizations of ZnS thin films prepared by the sol – gel spin coating deposition. 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 method.

Materials and method

In this paper zinc sulfide nano layers were deposited on glass substrates by sol– gel process with different coating speeds 3600 rpm, 4800 rpm, 6000 rpm and 7200rpm. They were prepared with Zn (CHC3COO)2.2H2O (Showa Chemical, 99%) and CH4N2S (Showa Chemical, 98%) as starting precursors and 2-methoxyethanol (Echo Chemical , 98%) and monoethanolamine [MEA (TEDIA , 99%) as a solvent and stabilizer in a nitrogen – filled glove box . The molar ratio was 1 in the mixture solution. The solution was stirred at 80°C for 120 min to yield a homogeneous solution. To produce a clear solution, the solution was left for 24 h. The deposition of films on the substrate used a spin – coating technique. The clear solution was dropped on to glass substrate. After deposition by spin coating, the films were dried at 200°C for 10 min on a hot plate in nitrogen – filled glove box. Finally, the films were baked at 500°C for 60 min on a hot plate in nitrogen – filled glove box. The glass substrates were ultrasonically cleaned for 10 min in acetone, then in de–ionized water and dried befor drop coating.

Results and Discussion

The optical propertiesof ZnS thin films was characterized by spectroscopic ellipsometry device and then fitted theoretically by using Lorentz model.

The measured spectroscopic ellipsometry parameter, Ψ_{exp} and Δ_{exp} are fitted against the designed model in the spectral range from 300 nm to 800 nm by minimizing the mean square error (MSE) is shown in figure of 1and 2. Refractive index (n) and extinction coefficient (k) indices for all samples as a function of wavelength at different speed, and they are shown in figure 3 and 4. An evident abnormal dispersion occurs as the photon energy surpasses a threshold value, whereas the extinction coefficient sharply increases above the threshold value. This result indicates the an interband absorption occurs around the threshold value. The optical band gap was calculated by extrapolating the linear portion of the (αhυ) 2 versus hυ curve towards energy axis. The variation of (αhυ) 2 with photon energy hυ is shown in figure 5. The optical energy gaps have linear decreasing trend from 3.43 to 3.25 eV with increase of coating speed 3600 rpm to 7200 rpm.

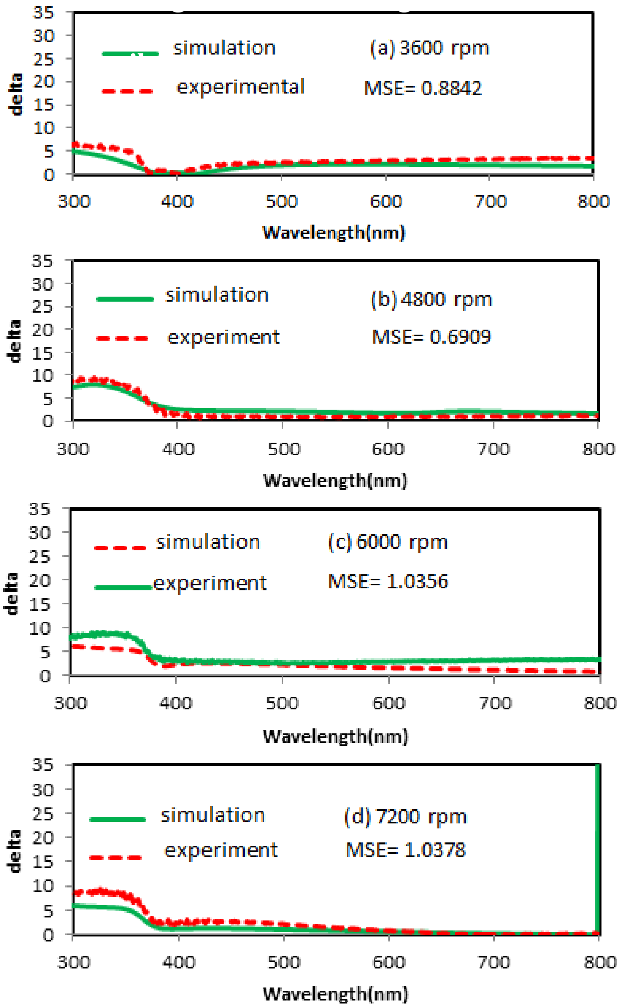

Fig. 1. Spectra of '**Δ**' as a function of wavelength for ZnS thin films with different coating speed.

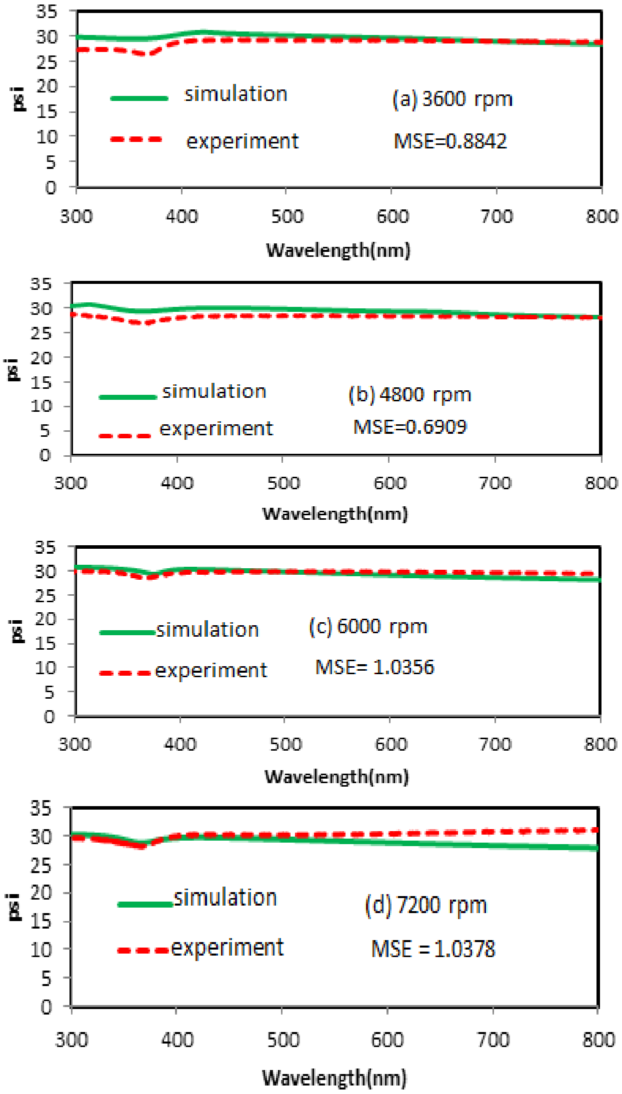

Fig. 2. Spectra of 'Ψ' as a function of wavelength for ZnS thin films with different coating speeds.

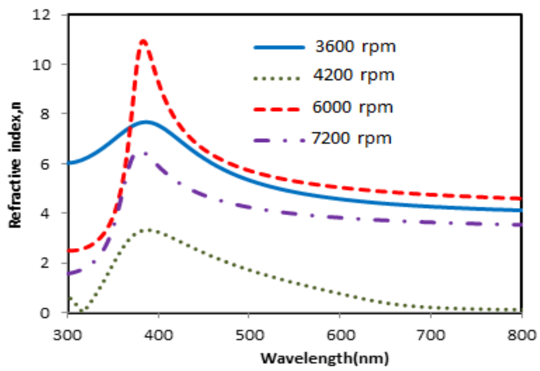

Fig. 3. Variation of 'n' as a function of wavelength for ZnS thin films with different coating speeds.

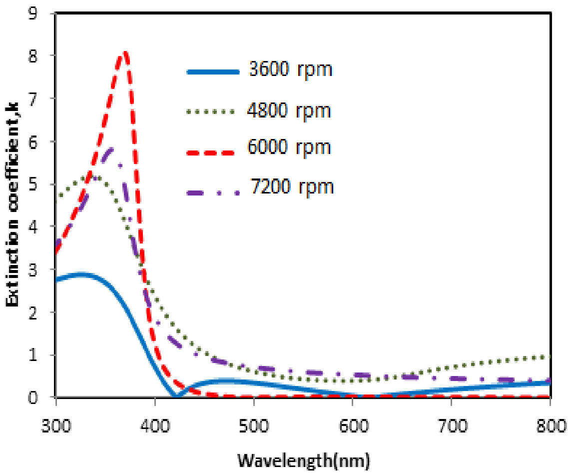

Fig. 4. Variation of 'k' as a function of wavelength for ZnS thin films with different coating speeds.

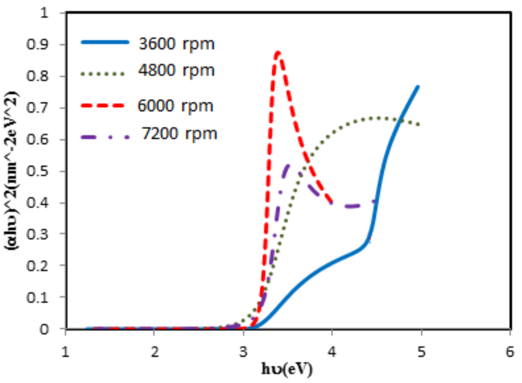

Fig.5. Variation of band gap for ZnZ thin films with different coating speeds.

The band gap of the alloys was determined using tauc plots.

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \quad (1)$$

As shown in fig.5 the direct band gapenergy decreases progressively from about 3.43 eV to 3.25 ev with the decrease in coating speed from 3600 to 7200 rpm. The decrease of optical band gap could be attributed to the structural and morphological chang as well as the stoichiometric deviations in the film which gave rise to the formation of located states in the band gap region. Other possibilities to explain this change in optical band gap could be related to the increase in particle size and this is well known for colloidal semiconductors [8].

Conclusions

In summary, ZnS sulfide nano layers were deposited on glass substrates by sol – gel process with different coating speeds 3600 rpm, 4800 rpm, 6000 rpm and 7200 rpm. Optical constant (n and k) of the films were determined. It may be considered that the deposition of ZnS thin films on glass substrates is coating speed dependent.

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