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Influence of annealing temperature on the structural, optical and electrical properties of amorphous Zinc Sulfide thin films

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Abstract. Zinc sulfide films have been deposited on glass substrates at room temperature by the chemical bath deposition technique. The growth mechanism is studied using X-ray diffraction, scanning electron microscopy, optical absorption spectra and electrical measurements. The as-deposited film was given thermal annealing treatment in air atmosphere at various temperatures (100, 200, 300 400 and 500 ºC) for 1 h. The annealed film was also characterized by structural, optical and electrical studies. The structural analyses revealed that the as-deposited film was amorphous, but after being annealed at 500 ºC, it changed to polycrystalline. The optical band gap is direct with a value of 4.01 eV, but this value decreased to 3.74 eV with annealing temperature, except for the 500 ºC anneal where it only decreased to 3.82 eV. The refractive index (n), extinction coefficient (k), and real (ε_1) and imaginary (ε_2) parts of the dielectric constant are evaluated. Raman peaks appearing at ~478 cm^{-1}, ~546 cm^{-1}, ~778 cm^{-1} and ~1082 cm^{-1} for the annealed film (500 ºC) were attributed to $[TO_1+LA]_\Sigma$, $2TO_\Gamma$, $2LO$, $3LO$ phonons of ZnS. The electrical conductivities of both as-deposited and annealed films have been calculated to be of the order of ~10^{-10} $(\Omega\ cm)^{-1}$.

1. Introduction

Zinc sulphide (ZnS) is an important optoelectronic material for use in the violet and blue spectral regions because of its wide band gap. This II–VI compound semiconductor material has been studied extensively for a variety of applications, for example, in optical coatings, solid state solar window layers, electro-optic modulators, photo conductors, field effect transistors, optical sensors, photo catalysts, electroluminescent materials [1], phosphors and other light emitting materials [2, 3]. ZnS is characterized by an n-type direct wide band gap in the range of 3.79–3.93 eV [4] for the wurtzite phase and 3.6 eV for the cubic phase. Besides, it has become very attractive due to its low toxicity compared to other semiconductors. A wide variety of synthesis methods have been used to prepare ZnS nanocrystals, such as solvothermal [5], hydrothermal and thermal evaporation methods [6], RF sputtering [7], molecular beam epitaxy (MBE) [8] and chemical bath deposition (CBD) [9]. Among these, chemical bath deposition is the least costly low-temperature technique to deposit large-area thin films of semiconductors.

In this work, the structural, optical and electrical properties of an as-deposited ZnS film grown by the CBD technique and the crystallographic, optical and electrical properties of the annealed ZnS film have been studied. The refractive index, extinction coefficient and dielectric constants as a function of wavelength for both as-deposited and annealed ZnS films were investigated from the absorption, transmittance and reflection data, and the results are discussed. Moreover, the *I-V* measurements were taken to calculate electrical conductivities.

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2. Experimental procedure

Thin films of ZnS were prepared by the CBD method, using the deposition solution reported previously [10]. Such films were deposited from the deposition solution that was prepared as follows: 1.25 ml of 1 M $ZnSO_4 \cdot 7H_2O$, 1.5 ml of 3.75 M triethanolamine $[(HOCH_2CH_2)_3N]$, 1 ml of ammonia/ammonium chloride (NH_3/NH_4Cl, pH = 10.55) buffer solution, 0.05 ml of 0.66 M tri-sodium citrate ($C_6H_5Na_3O_7$), 0.5 ml of 1 M thioacetamide (CH_3CSNH_2) were mixed; then enough deionized water was added to get a total solution volume of 25.05 ml. The deposition was made on a glass substrate at room temperature. ZnS nucleated onto the submerged surfaces including the beaker walls over about 24 h for a single deposition run. For two deposition runs, the thin film obtained from the first run was submerged into freshly prepared solution for another 24 hours. In order to see how annealing will affect the structural, optical and electrical properties of the film, the obtained film was heated to 100, 200, 300, 400, and 500 °C for 1 h in air atmosphere.

The X-ray diffraction (XRD) spectra for as-deposited and annealed film were obtained using an X-ray diffractometer (Rigaku Rint 2000) with Cu-$K\alpha_1$ monochromatic radiation at 40 kV and 30 mA. Surface morphology of both as-deposited and annealed films was performed by scanning electron microscopy (SEM) in a JEOL JSM-5500LV. The Raman spectroscopy was performed at room temperature using a Raman spectrometer (Bruker Senterra) with a 532 nm (20 mW) Ne laser line as an excitation source. Optical transmission data were obtained by a UV-visible spectrophotometer (Shimadzu UV-2101PC).

3. Results and discussion

No peaks corresponding to the hexagonal phase were observed for the as-deposited film, which confirmed the amorphous nature of the as-deposited ZnS thin film. Figure 1 (a) and (b) show the SEM micrographs of the as-deposited and the annealed ZnS film deposited at 30 ºC for 96 h. It is clearly seen that the film after annealing looks somewhat different from the as-deposited one. The as-deposited ZnS thin film shows uniform, continuous and dense microstructures. However, annealed film has some cracks originated from tensile strain. The tensile strain developed in the annealed film may be due to the differences in thermal expansion coefficients of the substrate and deposited material and/or the crystallization process during annealing which may cause vacancies to diffuse to the surface of the film [11].

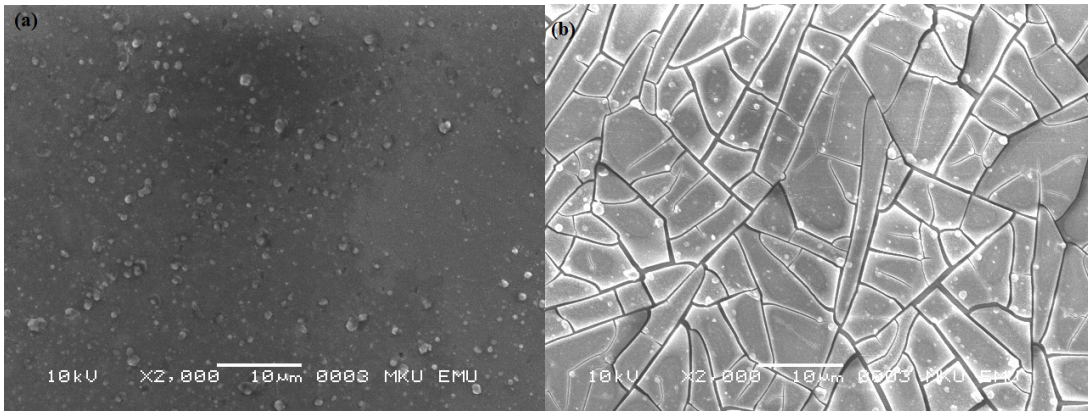

Figure 1. (a) SEM micrographs for ZnS films (a) as-deposited at 30 °C; (b) annealed in air atmosphere at 500 °C for 1 h.

Figure 2 shows the XRD pattern of the ZnS thin film annealed at 500 °C for 1 h in air atmosphere. As seen from this figure, the deposited film has become polycrystalline after being annealed at 500 ºC. The annealed film exhibits only one weak diffraction peak corresponding to the (008) plane of the hexagonal ZnS based on PDF card no: 39-1363. The structural data are also in agreement with our previous work [12] and that reported by Cheng *et al* [13]. It can be concluded that post-deposition annealing slightly improves the crystallinity.

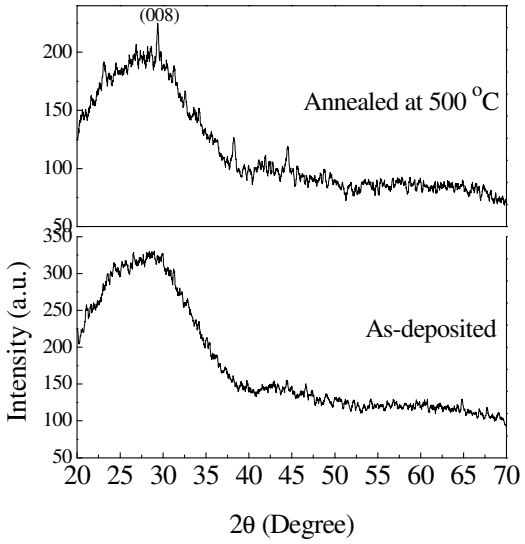

Figure 2. X-ray diffraction pattern of ZnS thin films a) as-deposited b) annealed at 500 °C.

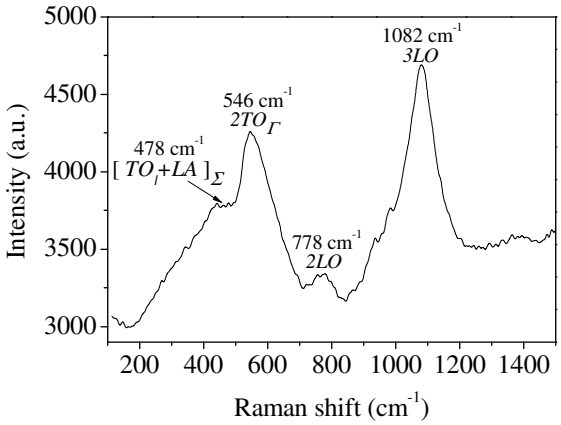

Figure 3. Raman spectra from 100 to 1500 cm^{-1} of the ZnS film annealed at 500 °C

The Raman spectrum of the annealed ZnS film is shown in figure 3. The first order Raman phonon observed at ~478 cm^{-1} corresponds to the $[TO_I + LA]_\Sigma$. The second order Raman phonons observed at ~546 cm^{-1} and ~778 cm^{-1} might originate from the $2TO_\Gamma$ and *2LO* respectively. The third order Raman phonons observed at ~1082 cm^{-1} can be assigned as the 3*LO* mode. The Raman phonon modes reported here are in good agreement with our previous work [10, 14] and data reported by Serrano *et al* [15] and Zhang *et al* [16]. From figure 4, the transmittance in the visible region of the as-deposited ZnS film was ~58 % and when annealed in air for 1 h at different annealing temperatures from 100 to 500 °C, it decreased to ~40 %.

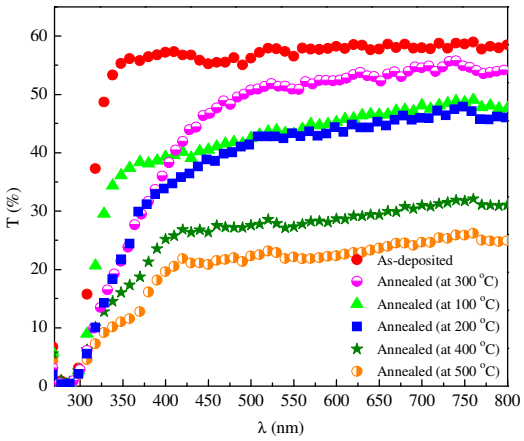

Figure 4. Transmission spectra from 270 to 800 nm of as-deposited and annealed ZnS thin films.

The absorption coefficients (α) for as-deposited and annealed ZnS films were calculated by the following relation [10]: $\alpha = 1/t \ln[(1-R)/T]$. The absorption coefficient for the amorphous film was ~10^5 cm^{-1}, it increased to ~10^6 cm^{-1} for the crystalline film. Figure 5 shows the variation of $(\alpha h\nu)^2$ vs. $h\nu$ of the as-deposited and annealed ZnS thin films at annealing temperatures ranging from 100 to 500 °C. The band gap energy was derived by extrapolating the straight-line portion of the $(\alpha h\nu)^2$ vs.

$h\nu$ plot to zero absorption. The optical band gap of the as-deposited ZnS thin film was 4.01 eV. From figure 6, it can be seen there is a decrease (to ~3.8 eV) of the band gap for all temperatures.

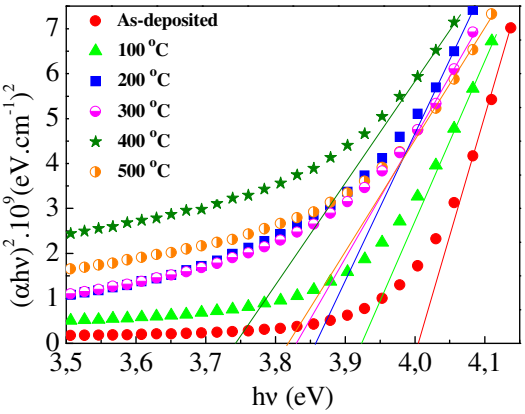

Figure 5. The plots of $(\alpha h\nu)^2$ versus $h\nu$ for as-deposited and annealed ZnS thin films.

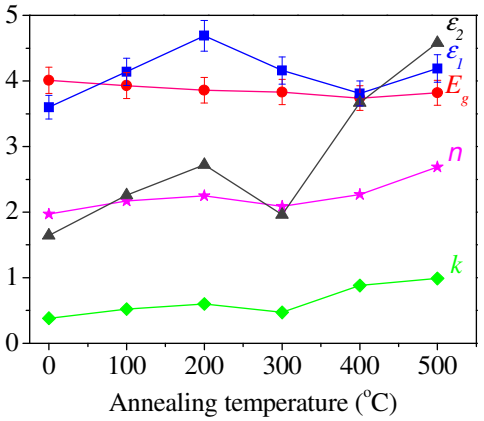

Figure 6. E_g, n, k, ε_1 and ε_2 for as-deposited and annealed ZnS films versus anneal temp.

Figure 6 also shows the variation of the band gap (E_g), refractive index (n), extinction coefficient (k), and real (ε_1) and imaginary (ε_2) parts of the dielectric constant as a function of the annealing temperature. The detailed calculations of these parameters also are given in previous studies [10, 17]. Moreover, the electrical conductivities of as-deposited and annealed films with Au contacts have been measured to be of the order of ~10^{-10} $(\Omega\ \mathrm{cm})^{-1}$. The detailed information about calculating electrical conductivity of both as-deposited and annealed ZnS films are given in [4, 10]. The calculated electrical conductivity values are in agreement with other work [18].

4. Conclusion

In summary, X-ray diffraction analysis indicated that as-deposited ZnS films were amorphous, and heat treatments improved the structure. The Raman spectra of annealed ZnS samples showed first, second and third order Raman phonons. The optical band gap of optical transition has been determined to be 4.01 eV for direct transition, and it decreased from this value to ~3.8 eV with an increase in annealing temperature. The electrical conductivities for as-deposited and annealed ZnS films with Au contacts were found to be of the order of 10^{-10} $(\Omega\ \mathrm{cm})^{-1}$.

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