The influence of substrate temperature on the structural and optical properties of ZnS thin films

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Thin films of ZnS were deposited on soda lime glass substrates by a modified close-space sublimation technique. The change in optical and structural properties of the films deposited at various substrate temperatures (150−450°C) was investigated. *X*-ray diffraction spectra showed that films were polycrystalline in nature having cubic structure oriented only along (111) plan. The crystallinity of films increased with the substrate temperature up to 250°C. However, crystallinity decreased with further increase of substrate temperature and films became amorphous at 450°C. The atomic force microscopy data revealed that the films become more uniform and dense with the increase of substrate temperature. Optical properties of the films were determined from the transmittance data using Swanepoel model. It was observed that the energy band gap is increased from 3.52 to 3.65 eV and refractive index of the films are decreased with the increase of substrate temperature. Moreover, considerable improvement in blue response of the films was noticed with increasing substrate temperature.

1. Introduction

In addition to several other factors, energy conversion efficiency of a solar cell depends on the material of the buffer layer. Up till now highest energy conversion efficiency of a solar cell has been reported with the CdS buffer layer [1]. Despite the fact that CdS is a toxic material and about 20% of incident photons are absorbed in buffer layer due to its narrow bandgap (~ 2.42 eV) [2]. In comparison with CdS, ZnS is environmental friendly and a wide bandgap material (~ 3.6 eV). Therefore ZnS is a prospective contender for the buffer layer of the upcoming family of solar cells. ZnS films have also several other applications in the area of light emitting diodes [3], electroluminescent devices [4], antireflection coatings and optical filters [5,6]. Previously, ZnS thin film have been deposited by thermal evaporation [7], electron beam evaporation [8], chemical vapor deposition [9], chemical bath deposition [10], pulsed laser deposition [11], molecular beam epitaxy [12] and close-space sublimation [13]. In the present study we have prepared ZnS thin films by a modified closed space sublimation apparatus. In particular, the influence of substrate temperature on the structural and optical properties has been systematically investigated.

2. Experimental

High purity (99.9%) ZnS powder was used as a source for deposition of ZnS films on soda lime glass substrates. The glass substrate were first treated with detergent and washed in running water. The substrates were then dried with a fine tissue paper and cleaned with isopropyl alcohol (IPA) in an ultrasonic cleaner. All the films were deposited by CSS technique, using a high vacuum coating unit. But our experimental set up was slightly different from the conventional CSS device. In conventional CSS device, the source to substrate distance is usually few millimetres, but we kept source to substrate distance equal to 50 mm. Within this distance we installed film thickness and deposition rate measurement device. Thickness of various films was in range of 315 to 400 nm. The molybdenum boat was used as source for ZnS powder. A vacuum of $\leq 10^{-5}$ mbar was maintained in the chamber during deposition. The substrate temperature during deposition was varied from room temperature to 450°C. The adhesion of the films deposited at the room temperature was not good, but the films deposited at substrate temperature ≥ 150°C were strongly adherent to the substrate. Film thickness and deposition rate (1.20−1.40 nm/s) were monitor by the Edwards film thickness monitor FTM5. Structure of the films was determined by *X*-ray diffraction (XRD) at room temperature by Bruker D8 diffractometer using Cu K_α radiation in the scanning mode. The surface morphology of the films was investigated by atomic force microscope (AFM). Transmission of the films was measured in the range of 300−2000 nm using Perkin Elmer Lambda 19 UV/VIS/NIR spectrophotometer and UV Win Lab software. Thickness and refractive indices of these films were determined by fitting the transmittance data.

3. Results and discussion

The ZnS films prepared by CSS at various substrate temperatures were uniform, pinhole free and strongly adherent to the substrate. The XRD profiles of ZnS films deposited at the substrate temperatures of 150, 250, 350 and 450°C are shown in Fig. 1. All the films showed a single peak at $2\theta \approx 28.50°$ that is due to the (111) reflection of ZnS. The reflections due to other planes of ZnS were not detected, which suggest that films have cubic structure. These results are in good quantitative agreement with the

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recent work of Subbaiah et al. [13] for ZnS films deposited by CSS technique. The structure of ZnS film is known to depend on the deposition technique. For instance, thermally evaporated ZnS films are generally cubic [14,15], ZnS films grown by sulfurizing of RF sputtered ZnO was hexagonal in nature [16] and films grown by spray pyrolysis had mixed cubic and hexagonal phases [17]. The XRD spectra also show that the (111) peak intensity and sharpness increases with substrate temperature up to 250°C, then decreases and films become amorphous at 450°C. The decrease of crystallinity with increasing substrate temperature might be due to re-evaporation of sulfur from the surface of the film because of its high vapor pressure [13]. Fig. 2 shows the AFM images of ZnS films deposited at 150, 250 and at 350°C substrate temperatures. Films were uniform and densely packed with average RMS roughens in the range of 8–12 nm. AFM images also revealed that films become more uniform and dense with the increase of substrate temperature.

Next, the effect of substrate temperature on the optical properties of ZnS films was investigated using the Swanepoel method [18]. The refractive index and thickness of films were calculated by fitting the transmission data to the following equation:

$$T = \frac{Ax}{B - Cx\cos\phi + Dx^2}, \qquad (1)$$

where T is the normal transmittance for the system consisting of thin film on a transparent substrate surrounded by air, and taking into account all multiple reflections at the interface for the case of $k^2 \ll n^2$, where k is the extinction coefficient of the film, which is true for this kind

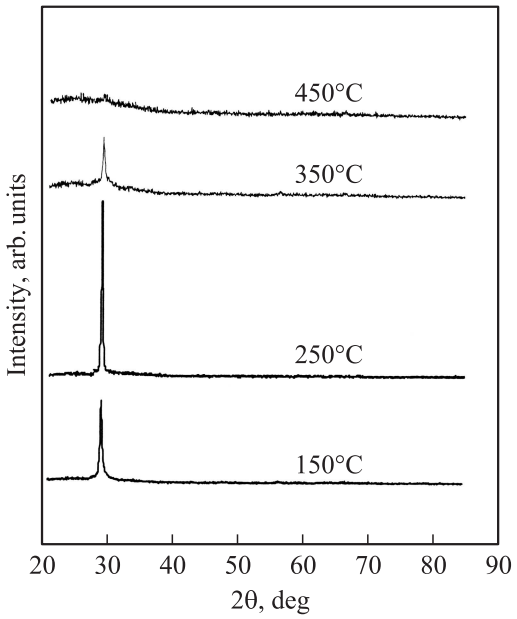

Fig. 1. XRD pattern of ZnS films deposited at various substrate temperatures.

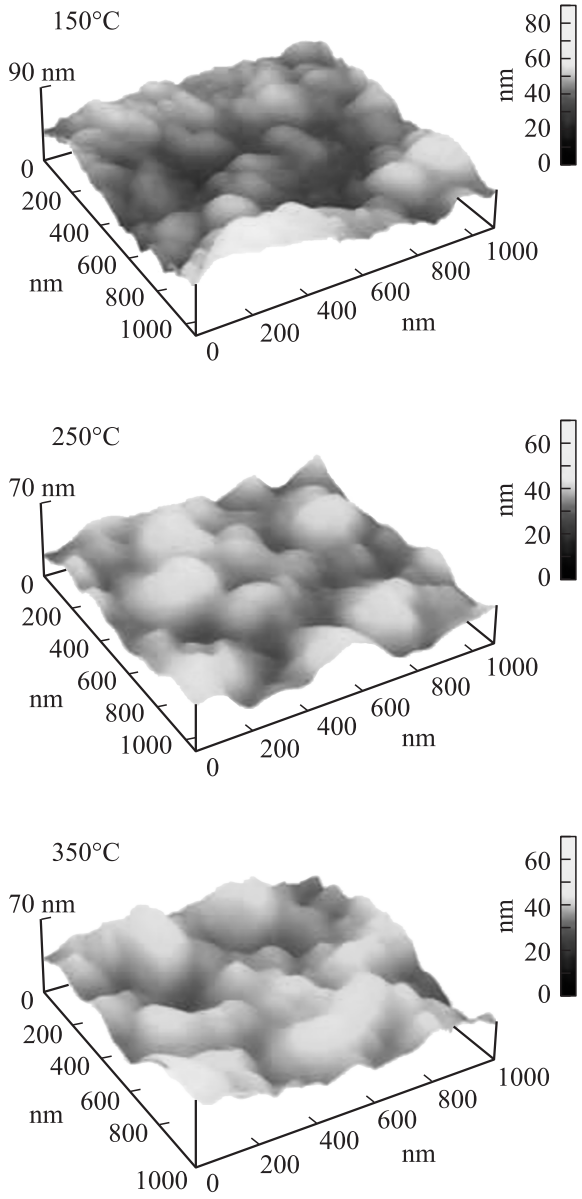

Fig. 2. AFM images of ZnS films deposited at the substrate temperatures of 150, 250 and 350°C.

of semiconductor thin films [19]. The other variables are defined as

$$A = 16n^2 s, \quad B = (n+1)^3(n+s^2),$$

$$C = 2(n^2-1)(n^2-s^2), \quad D = (n-1)^3(n-s^2),$$

$$\phi = 4\pi nd/\lambda, \quad x = \exp(-\alpha d), \quad k = \alpha\lambda/4\pi.$$

Here n and s are the refractive index of the film and the glass substrate respectively, d is the thickness of the film and α is the absorption coefficient of the film. An empirical formula for dependence of n on λ is given as [18],

$$n = a + \frac{b}{\lambda^2}, \qquad (2)$$

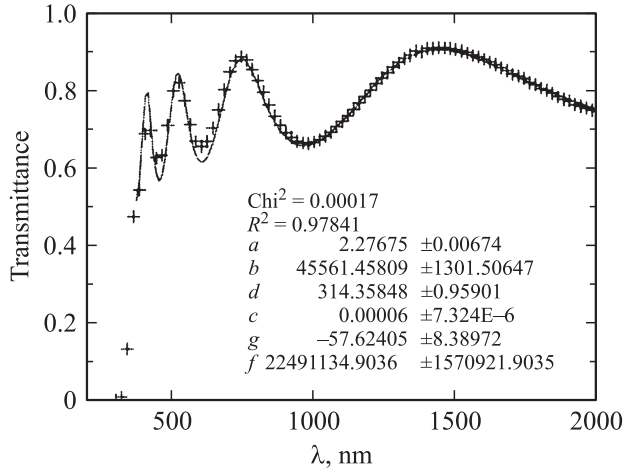

Fig. 3. Transmittance data of a ZnS film deposited at the substrate temperature 350°C along with the fitted curve (solid line).

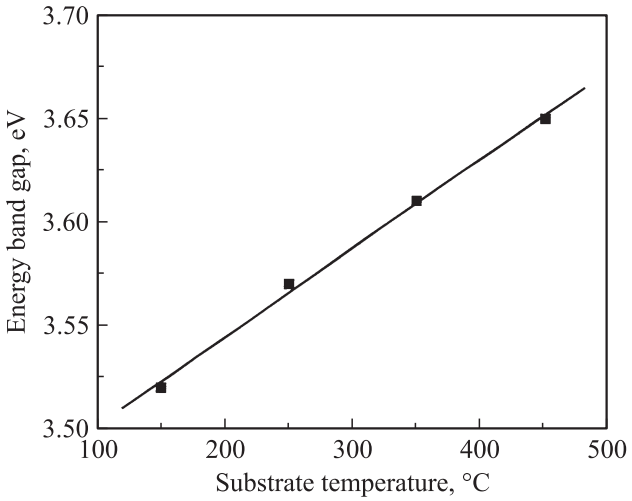

Fig. 4. Variation of energy bandgap of ZnS films deposited at various substrate temperatures. Solid line is linear fit to the data points.

where a, b are constants. The α dependence of λ can be approximated [18,19] as

$$\alpha = c + \frac{f}{\lambda} + \frac{g}{\lambda^2}, \qquad (3)$$

where c, f and g are constants. Fig. 3 shows the resulting fit of Eq. (1) to the experimental data. It is clear that it provides a good fit in transparent as well as in medium absorption region. By using the values of n and d, which were determined from the fitted curve, α was calculated in the high absorption region. In this case the exact solution of Eq. (1) for x is

$$x = \frac{[C\cos\phi + A/T] - [(C\cos\phi + A/T)^2 - 4BD]^{1/2}}{2D}, \qquad (4)$$

where all the parameters are already defined. The energy bandgap of the films were calculated using the Tauc relation [20] in which a graph between $(\alpha h\nu)^2 vs.\ (h\nu)$ is plotted, where $h\nu$ is the photon energy. The absorption coefficient α was determined from the transmittance T as $T = e^{-\alpha x}$, where x is thickness of the film. The energy bandgap E_g was determined by extrapolation of the linear portion of $(\alpha h\nu)^2 vs.\ (h\nu)$ curves to $(\alpha h\nu)^2 = 0$. The variation of E_g as a function of the substrate temperature of the film is plotted in Fig. 4. The measured energy bandgap linearly rises with substrate temperature. The straight line $E_g = 3.46 + 4.30 \cdot 10^{-4} T_s$ provides best fit to the experimental data. Where T_s is the substrate temperature. The band gap of the films deposited at the substrate temperature of 450°C is in good agreement with the results of Chu et al. [21]. The band gap of the film deposited at the substrate temperature of 250°C, however, is slightly higher than the recently reported results of Subbaiah et al. [13]. The plots of refractive index versus wavelength for the ZnS films deposited at 150, 250 and 450°C substrate temperatures are shown in Fig. 5. Following trends can be deduced from these plots: (i) The refractive index of ZnS film decreases on increasing the substrate temperature throughout the investigated wavelength range. (ii) The refractive indices of all the films are higher at shorter wavelengths, and (iii) decreases with increase of the wavelength towards infrared region. The optical measurements of Fig. 6 show how the transmittance of ZnS films changes with the substrate temperature. One can notice slight improvement in the optical transmission, in the visible and near infrared region, with the increase of substrate temperature. The observed increase of transmittance with increasing substrate temperature may be due to decrease in the crystallization of a film at higher substrate temperatures (see Fig. 1). The shift of absorption edge towards the UV region (see inset of Fig. 6) with increasing substrate temperature may be due to the degradation in crystallization of the films above 250°C. The improvement of the blue response of the film is beneficial in several

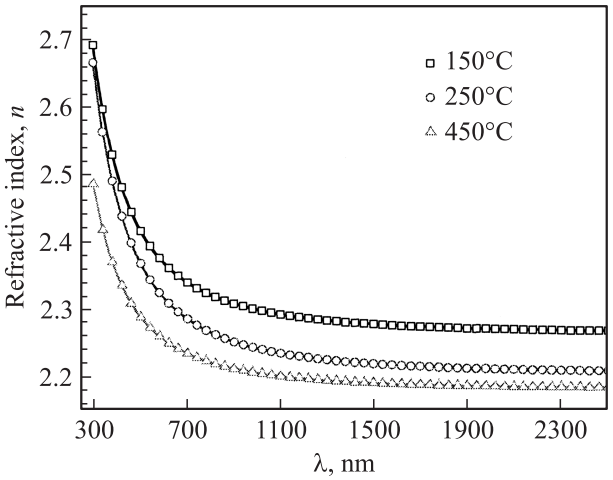

Fig. 5. Refractive indices of ZnS films deposited at various substrate temperature.

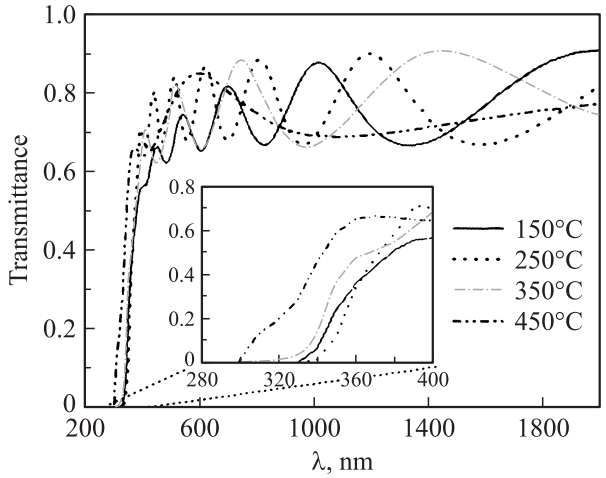

Fig. 6. Transmittance of ZnS films deposited at various substrate temperature. Inset shows the effect of substrate temperature on the absorption edge.

optical applications like the photovoltaic devices, blue light emitting diodes and laser diodes.

In conclusion, we have investigated the effect of substrate temperature on the structural and optical properties of ZnS films deposited by the close-space sublimation. It was found that structural and optical properties of ZnS films are sensitive to the substrate temperature. The crystallinity of films increased with the substrate temperature up to 250°C. The films became more uniform and dense with the increase of substrate temperature. The optical energy bandgap increased linearly with substrate temperature T_s and this linearity is found as $E_g = 3.46 + 4.30 \cdot 10^{-4} T_s$. The refractive index of the films decreased with the increasing substrate temperature. Moreover, considerable improvement in blue response of the films was noticed with increasing substrate temperature.

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