Effects of substrate temperature and annealing on the structure and optical properties of ZnS film

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ABSTRACT

Effects of substrate and annealing temperature on the microstructure, morphology, and optical properties of ZnS films were investigated. ZnS films were deposited on glass substrates by an electron beam evaporation system at different substrate temperatures and annealed at different temperatures in air. The structure and morphology of the film were studied by X-ray diffraction and atomic force microscopy. Transmittances of film were measured by spectrophotometer. Refractive indices and extinction coefficients were calculated from all transmittance data. Experimental results show that the as-deposited ZnS film exhibiting cubic structure, and the crystallinity is apparently improved with the increase of substrate temperature or annealing temperature. It is also found that film surface changes to ZnO after the film is annealed at 500 ^{o}C. The average surface grain size and root mean square surface roughness increase with the increase of annealing and substrate temperatures. Additionally, the increase of substrate temperature or annealing temperature will increase the pores in films, which results in the decrease of refractive indices and increase of extinction coefficients of the film.

Keywords: ZnS; Optical film; Optical constants; Substrate temperature; Annealing

1. INTRODUCTION

Zinc sulfide (ZnS) film has unique physical properties, such as high refractive index, low optical absorption in the visible and infrared light range, and wide optical gap, such film is widely used in many optical and electronic areas. In the area of optics, ZnS can be used as reflectors and dielectric filters because of its high refractive index and high transmittance in visible range. ZnS can be used for fabrication of optoelectronic devices such as blue light-emitting diodes, electroluminescent devices, electrooptic modulator, optical coating, heterojunction solar cells, and photoconductor. Many growth techniques have been reported to prepare ZnS thin films, such as sputtering [1], pulsed-laser deposition [2], metalorganic chemical vapor deposition [3-6], electron beam evaporation [7], photochemical deposition [8] and chemical bath deposition [9]. Among these methods, electron beam evaporation is the most interesting because the advantages of electron beam evaporation are stability, reproducibility, high deposition rate and the compositions of the films are controllable.

The structure and properties of ZnS films are different with different deposited technique. For example, Zhang et al. [4] fabricated single cubic phase ZnS films by plasma-assisted metalorganic chemical vapor deposition. Subbaiah et al. [10] investigated the structural, electrical and optical properties of ZnS films deposited at different temperatures using close-spaced evaporation for photovoltaic applications. In the previous reports, it has been confirmed that the substrate temperature and annealing will strongly affect the structure and optical properties of the sputtered Nb_2O_5 films [11]. Roy et al. [9] had reported the effect of annealing on structure and optical properties of ZnS films fabricated by chemical bath deposition technique. The substrate temperature and annealing will also affect the structure and optical properties of ZnS film deposited by electron beam evaporation. Therefore, the effects of substrate temperature and annealing on the properties ZnS films should be well understood from a fundamental as well as from an applied point view. In this paper, the effects of substrate and annealing temperature on the structure and optical properties of ZnS films deposited by electron beam evaporation were investigated.

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2. EXPERIMENT

ZnS films were deposited by electron beam evaporation by a DMDE-450 vacuum deposition system. The BK7 glass substrates (Ø=25mm) were cleaned in acetone and ethanol before deposition. The base vacuum level was 3.0×10^{-3} Pa, and the deposition pressure was about 5.0×10^{-3} Pa. The average deposition electric current was about 25 mA. The nominal film thickness was controlled by a MKY optical thickness monitor. Five samples with different substrate temperatures of 20, 50, 100, 150, and 200 °C were fabricated. Moreover, four films deposited at 200 °C substrate temperature were annealed at temperatures of 200, 300, 400, 500 °C for 1 h in air.

The crystal structure of the films was examined by X-ray diffraction (XRD). XRD study was carried out on an X-ray diffractometer (RIGAKU D/MAX2500) with high-intensity Cu K_α radiation (λ=1.5418 Å). The morphology of films was observed by an atomic force microscopy (AFM) (CSPM 400) under ambient conditions. Scans were taken under the contact mode and over areas of 2 × 2 um^2 for root mean square (RMS) surface roughness calculation. The normal incidence transmittances of the films were recorded by a Perkin Elmer Lambda 950 UV/VIS/NIR spectrophotometer in the wavelength range 300–1500 nm. Refractive index (*n*), extinction coefficient (*k*) and film thickness (*d*) of the films were determined from all the normal incidence transmittance data [12].

3. RESULTS AND DISCUSSION

3.1 Crystal structure

Fig. 1 shows the XRD patterns of ZnS films deposited at different substrate temperatures (T_s). As can be seen in Fig. 1, all the films grown at different substrate temperatures have only one peak at 2θ=28.6° with (111) plane, which indicates that the films are distinctly single crystalline with a preferential orientation, and the planes are parallel to the substrate surface [13]. Moreover, as the substrate temperature increases from 20 to 200 °C, the intensity of the diffraction peak increases monotonously. This is the result of the improvement of the crystallinity. Fig. 2 represents the XRD patterns of ZnS films annealed at different temperatures (T_a) which were deposited at 200 °C substrate temperature. Comparing Fig. 1 with Fig. 2, it is found that the position and the intensity of diffraction peak of the film annealed at 200 °C are similar to those of the as-deposited film with 200 °C substrate temperature. As shown in Fig. 2(a), the intensity of diffraction peak of the film annealed at 300 °C is clearly stronger than that of the film annealed at 200 °C. The intensity of diffraction peak of the film, however, reduces slightly as the annealing temperature is more than 300 °C. Increasing the annealing temperatures further to 500 °C, a new peak appears at 2θ=34.5° as shown in Fig. 2(b). The new peak is due to (002) plane of ZnO according to the standard XRD-card. The main reason is that the surface of ZnS film was oxidized when it was annealed at 500 °C in air. This behavior is similar to that ZnS film changes to ZnO film when ZnS film was annealed at 900 °C in an oxygen ambient, which is reported by Zhang et al. [6].

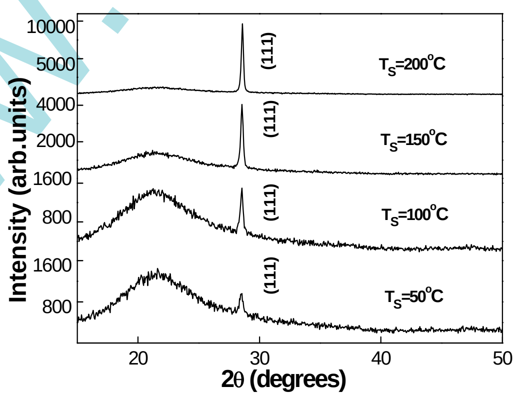

Fig.1: X-ray diffraction patterns for ZnS films deposited at different substrate temperatures

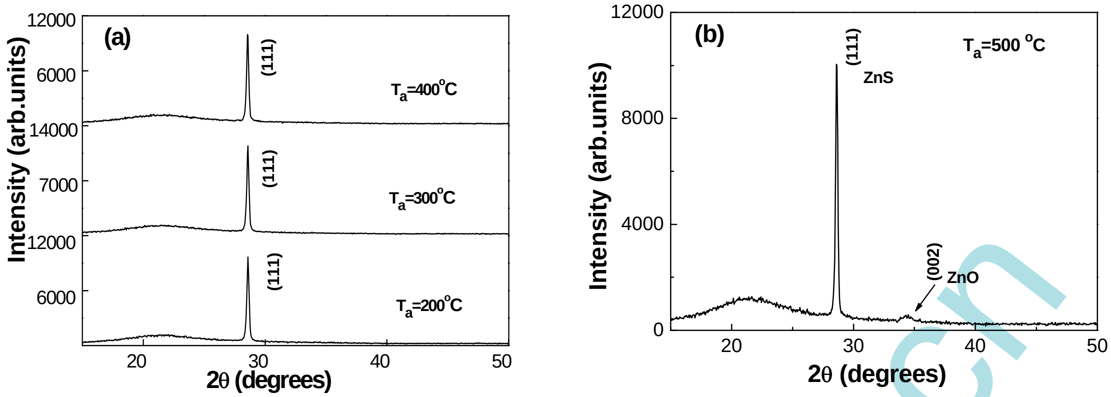

Fig.2: X-ray diffraction patterns for ZnS films annealed (a) at 200, 300 and 400 ^{o}C, (b) at 500 ^{o}C, which were deposited at 200 ^{o}C

3.2 Surface morphology

The evolution of surface morphology of ZnS films annealed at temperatures between 200 and 500 ^{o}C, via AFM measurements, are presented in Fig. 3, and these films were deposited at 200 ^{o}C substrate temperature. As indicated in Fig. 3, the average surface grain size increases from 24 nm to 30 nm as the annealing temperature increases from 200 to 500 ^{o}C. Accordingly, RMS surface roughness increases slowly from 2.8 to 3.3 nm when the annealing temperature increases from 200 to 500 ^{o}C. Obviously, the average surface grain size and RMS surface roughness of the films increases with increasing annealing temperature, which is result of the movement of the atoms or molecules on film surface as the films annealed at high temperature.

Additionally, the variation of surface morphology of the films deposited at different substrate temperatures (between 20 and 200 ^{o}C) has also been investigated by AFM measurements. It is found that the average surface grains size and RMS surface roughness increase with the increase of the substrate temperatures.

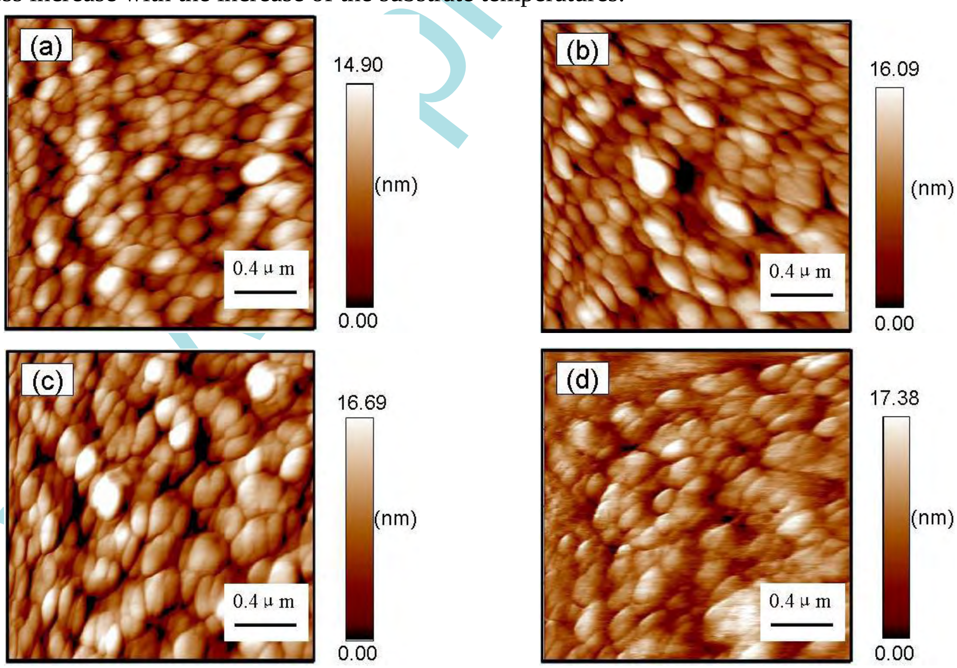

Fig. 3: Surface morphology of the ZnS film annealed at 200,300,400,500 ^{o}C respectively

3.3 Optical properties

Fig. 4 shows the normal incidence transmittances of ZnS films annealed at temperatures between 200 and 500 ^oC with wavelength from 300 to 1500 nm. As shown in Fig. 4, the interference peaks shift to shorter wavelengths and amplitude of the spectra decreases with increasing annealing temperature, which is due to the variations of the structure, morphology and composition of the films after the films were annealed at high temperature.

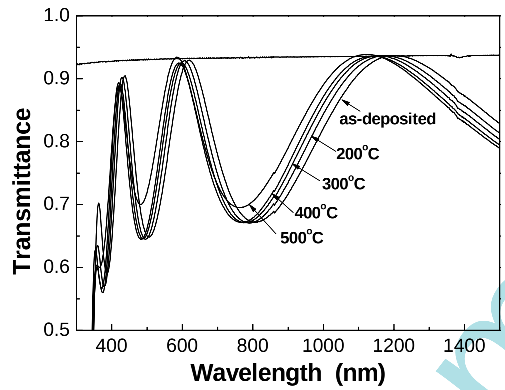

Fig.4: Transmittances of the ZnS films annealed at different temperatures at the wavelength from 300 to 1500 nm

Refractive indices, extinction coefficients and thicknesses of the films were determined from all the normal incidence transmittance data [12]. Refractive indices and extinction coefficients as a function of wavelength of the films annealed at temperatures between 200 and 500 ^oC are shown in Fig. 5 and 6, respectively. Table 1 lists the optical constants at 550 nm wavelength and thicknesses of the films annealed at different temperature. Film thickness decreases with increasing annealing temperature as shown in Table 1. As can be seen in Fig. 5 and Table 1, refractive indices of the films decrease slowly as the annealing temperature increases from 200 to 400 ^oC. Accordingly, extinction coefficients increase slowly with increasing annealing temperature. Refractive indices decrease and extinction coefficient increase as the increase of the annealing temperature are due to the increase of pores and surface roughness (as discussed in surface morphology) when films were annealed at high temperature. However, there is a sharp decrease in refractive index when the annealing temperature increases to 500 ^oC as indicated in Fig. 5. This sharp decrease in refractive index is attributed to the surface of ZnS film begins to be oxidized when film is annealed at 500 ^oC in air. Generally, refractive index of ZnS film [14] and ZnO film [15] is about 2.3 and 2.0 at 550 nm wavelength respectively. Therefore, the surface of the film annealed at 500 ^oC is ZnO, as can be seen in XRD result, which decreases the refractive index when film is annealed at 500 ^oC.

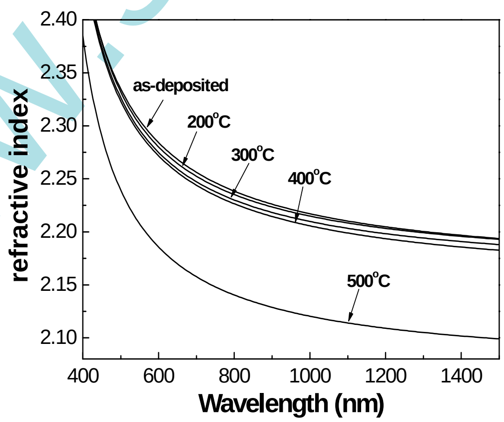

Fig.5: Refractive indices as a function of wavelength of ZnS films annealed at different temperatures

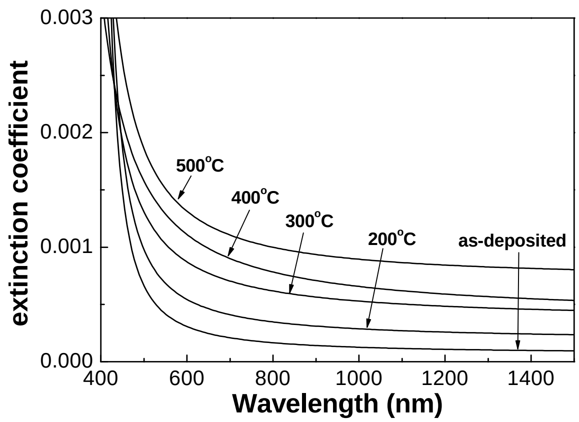

Fig.6: Extinction coefficients as a function of wavelength of ZnS films annealed at different temperatures

Table 1:Optical constants at 550 nm wavelength and thicknesses of ZnS films deposited at 200 °C substrate temperature and annealed at different temperatures

Temperature (°C)	as-deposited	annealed at 200 °C	annealed at 300 °C	annealed at 400 °C	annealed at 500 °C
n	2.306	2.300	2.296	2.292	2.206
k	4.11×10^{-4}	6.84×10^{-4}	1.028×10^{-3}	1.291×10^{-3}	15.13×10^{-3}
d (nm)	273	266	263	259	257

Optical constants of ZnS films deposited at substrate temperature between 20 and 200 °C were also calculated from all of their normal incidence transmittance data. Optical constants at 550 nm wavelength are presented in Table 2. Refractive indices decrease and extinction coefficients increase with the increase of substrate temperature as shown in Table 2, which is because of the increase of the surface roughness and pores in the films as measurement by AFM.

Table 2:Optical constants at 550 nm wavelength of ZnS films deposited at different substrate temperatures

Temperature	20 °C	50 °C	100 °C	150 °C	200 °C
n	2.330	2.317	2.312	2.308	2.306
k	9.5×10^{-5}	1.37×10^{-4}	3.56×10^{-4}	3.92×10^{-4}	4.11×10^{-4}

4. CONCLUSION

Single crystalline ZnS films were deposited on glass substrates by an electron beam evaporation system. The structure and optical properties of the films deposited at different substrate and annealing temperatures were investigated. From the experimental results, it is found that the crystallinity is apparently improved as the increase of the substrate temperatures or annealing temperatures. The films grown at these temperatures exhibited cubic structure. The average surface grains size and root mean square surface roughness increase with increasing annealing temperatures. Refractive indices decrease slowly with increasing annealing temperature from 200 to 400 °C. Refractive index has a sharp decrease after the film was annealed at 500 °C, which is due to the film surface begins to be oxidized at this temperature. Additionally, the increase of the substrate temperatures or annealing temperatures increase the pores in the films, which result in the decrease of refractive index and increase of extinction coefficient of the films.

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