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Influence of deposition temperature on structural, morphological and optical properties of ZnS thin films

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Abstract

ZnS thin films were deposited onto glass substrates by chemical bath deposition (CBD) technique at different deposition temperatures (75°C, 80°C, 85°C, 90°C) with non-toxic complexing agent tri-sodium citrate. Effects of deposition temperature on structural, morphological and optical properties of thin films were investigated by using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and UV-Visible Spectroscopy respectively. The XRD results show that all produced ZnS thin films have cubic structure. The calculated grain size values are between 13-26 nm. It was observed that the grain size values increase and crystallization of films improve as the deposition temperature increases. The FESEM images reveal that film surfaces are formed by almost homogeneously dispersed nanostructured particles. Optical characterization results show that ZnS thin films have high transmittance of about 80% in the range of 400–800 nm with band gap energy values between 3,52 - 3,65 eV. As the deposition temperature increases the band gap energy values increase. According to these results, it was observed that the structural, morphological and optical properties of ZnS films vary depending on the deposition temperature.

Key words: ZnS thin films, chemical bath deposition, structural properties, morphological properties, optical properties

Introduction

ZnS is an important II–VI compound semiconductor, due to its higher transmission, high refractive index [1] and wide band gap [2]. It has a wide range of applications in optoelectronic devices such as solar cells, visual displays, transparent conductors, photodetectors, etc [3]. Also, ZnS is non-toxic, abundant and environmentally safe [4]. It has great importance in light emitting diodes, cathode-ray tubes, thin film electroluminescence and window layers in photovoltaic cells due to its wide band gap [5].

There are many deposition methods of ZnS thin films such as thermal evaporation method [6], ion assisted thermal evaporation [7], RF sputtering [8], spray pyrolysis [9], atomic layer deposition [10], electrochemical deposition [11], electron beam evaporation [12], SILAR [13], sol-gel [14], chemical bath deposition [15]. In this study, chemical bath deposition technique which is simple, safe and economic technique to deposit thin films has been used. In ZnS thin film studies with chemical bath deposition technique, generally toxic hydrazine hydrate (N_2H_4) is used as complexing agent [16, 17]. In this work non-toxic tri-sodium citrate

($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) has been used as complexing agent instead of toxic hydrazine hydrate. For this reason, this work is an environmentalist work.

ZnS thin films have been deposited onto glass substrates by chemical bath deposition (CBD) technique at different deposition temperatures (75°C, 80°C, 85°C, 90°C). Effects of deposition temperature on structural, morphological and optical properties of thin films have been investigated by using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and UV-Visible Spectroscopy.

Experimental Details

The Chemical bath deposition (CBD) technique is one of the simplest technique to deposit thin films. This technique is performed in a batch reactor, requiring only a substrate to be immersed in a solution of aqueous precursors. Highlights of this technique include low cost, operation at atmospheric pressure, and scalability to large area substrates.

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), non-toxic tri-sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) and Tiourea (N_2SCH_4) from Sigma Aldrich were used for the preparation of ZnS films by chemical bath deposition technique. Firstly, 0.15 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 0.5 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 1 M N_2SCH_4 solvates were prepared separately and then mixed together. To make the pH value of the final solution at 10, 28% aqueous ammonia solution was added. 10 mm x 10 mm glass microscope slides were used as substrate for thin films. Glass substrates were cleaned with acetone, methanol and distilled water. The two pre-cleaned glass substrates were immersed in the bath and heated by temperature-controlled magnetic stirrer. The bath temperature was set to 75°C, 80°C, 85°C and 90°C in 90 minutes named as A1, A2, A3 and A4 respectively. The coated films were washed with distilled water and dried at room temperature. Nomenclature of ZnS thin films has been given in Table 1.

Table 1 Nomenclature of ZnS thin films

Deposition temperature	Serial name
75°C	A1
80°C	A2
85°C	A3
90°C	A4

Results and Discussion

The crystalline structure of the ZnS thin films was investigated by X-ray Diffraction (XRD) measurements. XRD measurements were performed by Panalytical Empyrean X-ray diffractometer using CuK_α ($\lambda=1.5405 \text{ \AA}$) radiation in the 2θ range 20° - 60° with a scanning speed of $2^\circ/\text{min}$ at the room temperature. X-ray tube operated at 45 kV and 40 mA. In Fig. 1, XRD patterns of A1, A2, A3 and A4 series have been presented comparatively.

Figure 1 XRD patterns of ZnS thin films

XRD diffraction patterns of obtained ZnS thin films have matched with the cubic structured ZnS [ICDD data: 98-016-2754]. As shown in Fig. 1, the crystallinity of the ZnS structure is poor. Also Agawane et al. and Wei et al. reported that ZnS structure was poor crystal in the literature [1, 16]. In A1 series, no peak formation has been observed in films prepared at 75 °C deposition temperature. (111) peak of cubic ZnS structure has been formed in A2, A3 and A4 series. As seen from the XRD patterns, the peak intensity of A4 is greater than the peak intensity of the other series. Peak intensities increase as the deposition temperature increased. A4 series have a preferential orientation towards (111) peak formed at $2\theta \approx 29.41^\circ$.

The full width at half maximum (FWHM) values, the grain size (D) of crystallites and the dislocation density (δ) values were determined by XRD results. The grain size of crystallites was calculated by using Scherrer's equation [18];

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where λ ; the wavelength of X-rays, β ; the full width at half maximum value and θ is the angle of diffraction. The dislocation density, defined as the length of dislocation lines per unit volume of the crystal was calculated by following equation [19];

$$\delta = \frac{1}{D^2} \quad (2)$$

The FWHM values, the grain sizes and dislocation densities of the ZnS thin films were given in Table 2.

Table 2 The FWHM values, the grain sizes and dislocation densities of the ZnS thin films

Serial name	FWHM	D (nm)	$\delta \text{ (nm)}^{-2}$
A1	-	-	-
A2	0,6182	13	5,66
A3	0,4613	17	3,15
A4	0,3154	26	1,47

The grain size and dislocation density values of the A1 series could not be calculated because no peak formation was observed in the A1 series and no FWHM value was found. It is seen that the grain size value in A4 series is greater than the others. Grain size values increase as the deposition temperature increased. Also, A4 series has the smallest dislocation density value. Dislocation density values decrease as the deposition temperature increased. The greater grain size and smaller dislocation density values indicate better crystallization of the sample [19]. The crystallization of the A4 series is better than the other series because of their smaller dislocation density and greater grain size values. It was observed that crystallization of films improve as the deposition temperature increases.

Figure 2 FESEM images of ZnS thin films

The surface morphology of the films was studied by FESEM (Zeiss Supra 40VP) at 30.000 magnifications. In Fig. 2, FESEM images of ZnS thin films have been presented. As it is seen

in the images, the film surfaces are formed by almost homogeneously dispersed nanostructured particles. It is also seen that there are no accumulations in the form of agglomerations and there are no gaps on the surface, so that the grains are held together better. When the images of ZnS thin films are examined, it is seen that the grain size values increase as the deposition temperature increased. This result confirms the XRD results. The average grain size calculated from FESEM images for the A4 series is 30-35 nm. These results are in good agreement with XRD measurements.

The chemical compositions and elemental mapping of ZnS thin films were also obtained using the Energy Dispersive X-Ray Spectrometer (EDX) detector (BRUKER). In Table 3, EDX results show that the thin films contain Zn and S.

Table 3 EDX results of the ZnS thin films

Serial name	Zn (%)	S (%)
A1	59,89	40,11
A2	62,07	37,93
A3	61,29	38,71
A4	58,98	41,02

Fig. 3 shows an elemental mapping image taken from A4 series. The green dots in the image represent the sulfur (S) atoms, and the red dots represent the zinc (Zn) atoms. The red and green dots are evenly dispersed over the structure. This result shows that the structure is zinc sulfide (ZnS).

Figure 3 Elemental mapping images of A4 series

Absorption studies were carried out by Perkin Elmer Lambda 25 UV-Vis Spectrometer between 300-1100 nm wavelengths to determine the band gap of the films. The band gap values of the obtained films were determined according to the Tauc Method [20]. Fig. 4 shows plots of $(\alpha h\nu)^2$ vs. $h\nu$. The band gap values of the ZnS thin films were calculated from theses plots. The point at which the linear part of the graph cuts the $h\nu$ axis gives the band gap value of the material. The band gap values of the ZnS thin films are given in Table 4. The

band gap energy is widened as the deposition temperature increases. The band gap value of the A4 series (3,65 eV), which is close to the band gap of ZnS semiconductors, is consistent with the literature [1, 15, 16].

Figure 4 The plots of $(\alpha h\nu)^2$ vs. $h\nu$ of ZnS thin films

Table 4 The band gap values of the ZnS thin films

Serial name	Band gap value (eV)
A1	3,52
A2	3,55
A3	3,61
A4	3,65

The optical transmittance spectra of the obtained thin films were taken at a wavelength range of 300-1100 nm. In Fig. 5, optical transmittance spectra of all series have been presented comparatively. A decrease in the optical transmittance spectra has been observed with increasing deposition temperature. This decrease in the optical transmittance value is due to the increase in the thickness of the films with the deposition temperature.

Figure 5 The optical transmittance spectra of ZnS thin films

Conclusion

ZnS thin films were deposited onto glass substrates by chemical bath deposition technique at different deposition temperatures with non-toxic complexing agent tri-sodium citrate instead of toxic hydrazine hydrate. For this reason, this work is an environmentalist work. Effects of deposition temperature on structural, morphological and optical properties of thin films were investigated. In A1 series at 75° deposition time, no peak formation has been observed in XRD patterns. (111) peak of cubic ZnS structure in the XRD pattern has started to be observed at 80° deposition temperature. (111) peak of cubic ZnS structure has been formed in A2, A3 and A4 series. A4 series have greater peak intensity, larger grain size and smaller dislocation density values than the other series. According to these results, A4 series is the best crystalline sample in this study. It was observed that crystallization of films improve as the deposition temperature increases. When the FESEM images of ZnS thin films have been examined, it has seen that the film surfaces are formed by almost homogeneously dispersed nanostructured particles. It has also seen that the grain size values increase as the deposition temperature increased. This result confirms the XRD results. The band gap energy has been widened as the deposition temperature increases. A4 series band gap value (3.65 eV) is close to the band gap of ZnS semiconductors. Also, a decrease in the optical transmittance spectra has been observed with increasing deposition temperature. As a result of these investigations:

- ZnS semiconductor thin films can be easily deposited by Chemical Bath Deposition technique, an easy to apply and economical technique.
- ZnS structure can be formed with non-toxic complexing agent tri-sodium citrate instead of toxic hydrazine hydrate.
- The structural, morphological and optical properties of obtained ZnS thin films are significantly affected by the deposition temperature.
- The crystallization, grain size value and band gap energy of thin films improve as the deposition temperature increases.

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