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Deposition and Characterization of ZnSe Nanocrystalline Thin Films

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Abstract. ZnSe nanocrystalline thin films were deposited at different deposition times by using the Chemical Bath Deposition (CBD) technique. Effects of deposition time on structural, morphological and optical properties of the obtained thin films were characterized. X-ray diffraction (XRD) analysis was used to study the structural properties of ZnSe nanocrystalline thin films. It was found that ZnSe thin films have a cubic structure with a preferential orientation of (111). The calculated average grain size value was about 28-30 nm. The surface morphology of these films was studied by the Field Emission Scanning Electron Microscope (FESEM). The surfaces of the thin films were occurred from small stacks and nano-sized particles. The band gap values of the ZnSe nanocrystalline thin films were determined by UV-Visible absorption spectrum and the band gap values were found to be between 2.65-2.86 eV.

INTRODUCTION

II-VI group compounds semiconductor is very important for applications in the fields of optical devices and in solar cells [1]. ZnSe is a major member of the II-VI semiconductors and has a wide direct band gap of 2.7 eV [2] and a high refractive index [3]. It has a low optical absorption [4] and high transparency in the visible spectrum [5]. Due to its unique physical properties, it has a large potential use in thin film transistors, photovoltaics, laser screens and light emitting diodes [6]. In thin film solar cells, ZnSe is preferred as buffer layer because of its non-toxicity and wider band gap [7].

ZnSe thin films can be produced by several methods such as electron beam evaporation technique [8], electrochemical deposition [9], RF sputtering [10], thermal evaporation [11], metal organic chemical vapor deposition [12], vacuum evaporation [13] and chemical bath deposition [14]. Among these various techniques of thin film deposition, chemical bath deposition technique is vacuum-free, safe, economic and simple technique. In this work, ZnSe nanocrystalline thin films were deposited onto glass substrates by using the chemical bath deposition technique at different deposition times and effects of deposition time on structural, morphological and optical properties of the obtained thin films were characterized. In literature, ZnSe thin film deposition takes several hours by chemical bath deposition technique [15-17]. In this study, ZnSe structure was formed in as short as 40 minutes.

EXPERIMENTAL DETAILS

The Chemical bath deposition method is one of the easiest techniques to deposit thin films. This method is carried out in a batch reactor, requiring only a substrate to be submerged in a solution of aqueous precursors such as complexing agents, metal salts, and pH buffers. Highlights of chemical bath deposition involve low cost, operating at atmospheric pressure, and suitable to large area substrates.

ZnSe thin films were synthesized by chemical bath deposition technique. Zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and selenourea ($\text{SeC}(\text{NH}_2)_2$) from Sigma Aldrich were used to produce ZnSe thin films, as well as hydrazine hydrate ($\text{N}_2\text{H}_5\text{OH}$) from Merck as a stabilizer and 28% aqueous ammonia (NH_4OH) was used to pH fixed to 10. Firstly 0.5 M $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.4 M $\text{SeC}(\text{NH}_2)_2$ and 0.5 M $\text{N}_2\text{H}_5\text{OH}$ were prepared in equal volumes and then mixed together. After the bath was prepared, the two pre-cleaned glass substrates were submerged in the bath and heated at 80°C by temperature-controlled magnetic stirrer. The films were deposited for 20, 40, 60 and 80 minutes and named as Z1, Z2, Z3 and Z4 respectively. Nomenclature of ZnSe thin films has been given in Table 1. The produced thin films were washed with distilled water and dried at room temperature.

TABLE 1. Nomenclature of ZnSe thin films.

Deposition time (min)	Serial name
20	Z1
40	Z2
60	Z3
80	Z4

Deposition time impact on structural, morphological and optical properties of the obtained ZnSe thin films were specified using X-Ray Diffraction (XRD) Technique, Field Emission Scanning Electron Microscope (FESEM) and UV-Visible Spectrophotometer respectively.

RESULTS AND DISCUSSION

The crystalline structure of the ZnSe thin films was characterized by X-ray Diffraction (XRD) measurements. XRD measurements were carried out 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. XRD diffraction patterns of obtained ZnSe thin films have matched with the cubic structured ZnSe [ICDD data: 98-004-1983]. XRD patterns of ZnSe thin films were given in Fig. 1, comparatively.

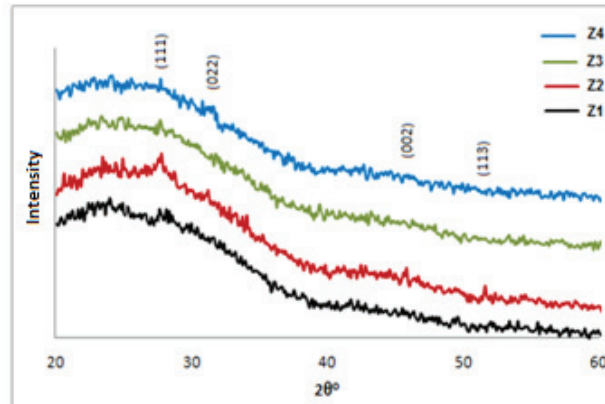


FIGURE 1. XRD patterns of ZnSe thin films.

In Z1 series, (111) peaks of cubic ZnSe structure in lower intensity in the XRD pattern have been investigated at 20 min deposition time. In Z2 series, (111), (022), (002) and (113) peaks of cubic ZnSe structure have been constituted with the deposition time of 40 min. In Z3 and Z4 series, (111) and (022) peaks have been constituted with the deposition time of 60 min and 80 min. Obtained thin films have (111) as the preferred orientation. According to the XRD spectra, the peak intensities of Z2 are higher than the peak intensities of Z1, Z3 and Z4 series. Higher peak intensities indicate that the crystallinity of the thin film is better [18]. The calculated average grain size value from XRD data is 11 nm for Z1, 28 nm for Z2, 18 nm for Z3 and 14 nm for Z4 series. The greater grain size values specify better crystallization of the thin film [19]. Z2 series deposited at 40 min deposition time has better crystallinity than the other series due to their greater peak intensities and greater grain size values.

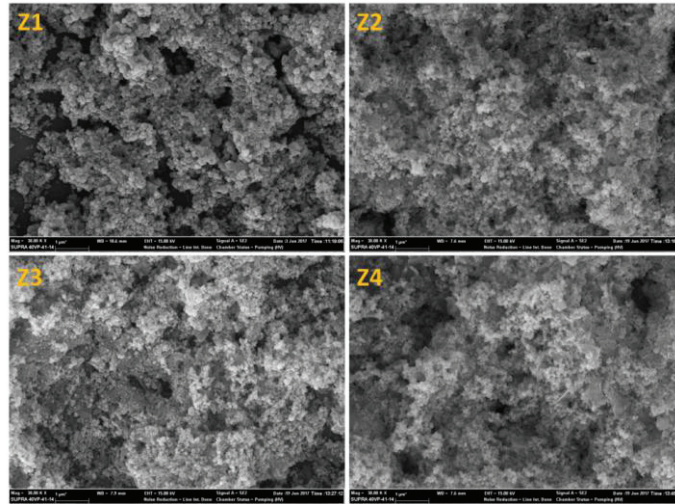


FIGURE 2. FESEM images of ZnSe thin films.

The surface morphology of the nanocrystalline thin films was specified by FESEM (Zeiss Supra 40VP) at 30.000 magnifications. FESEM images of ZnSe thin films have been presented in Fig. 2.. When these images are investigated, it is seen that the surfaces of the films are occurred from small stacks and nano-sized particles in places. The calculated average grain size value from FESEM images is 25-30 nm for Z2 series and this value is in concordance with value calculated from XRD measurements.

Absorption studies were applied 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]. Plots of $(\alpha h\nu)^2$ vs. $h\nu$ and band gap values of ZnSe thin films have been shown in Fig. 3.. The band gap values of the ZnSe thin films were calculated from these 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 value of the Z2 series was determined as 2.72 eV, which is very close to that of bulk ZnSe (2.70 eV) [3].

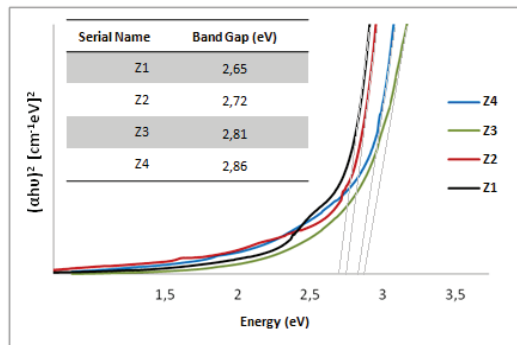


FIGURE 3. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ and band gap values of ZnSe thin films.

CONCLUSION

ZnSe nanocrystalline thin films have been deposited onto glass substrates by chemical bath deposition technique at different deposition times and effects of deposition time on structural, morphological and optical properties of thin films have been investigated. All the obtained thin films have a cubic structure with a preferential orientation of (111). It was found that the crystallization of the Z2 series deposited at 40 min deposition time is better than the other series because of their greater peak intensities and greater grain size values. The calculated average grain size value from XRD data is 28 nm for Z2. When the FESEM images of ZnSe thin films have been examined, it has been seen that the surfaces of the films are occurred from small stacks and nano-sized particles in places. The calculated average grain size value from FESEM images is 25-30 nm for Z2 series and this value is in good agreement with value calculated from XRD measurements. The band gap value of the Z2 series was found to be 2.72 eV, which is very close to that of bulk ZnSe. These results indicate that Z2 series deposited at 40 min deposition time has been showed best structural, morphological and optical properties. In literature, ZnSe thin film deposition takes several hours with chemical bath deposition technique, it has been determined that ZnSe nanocrystalline thin film deposition lasted only 40 minutes with the chemical bath conditions used in this study.

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