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Composition, Morphology and Optical Characterization of Chemical Bath Deposited ZnSe Thin Films

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Abstract: ZnSe thin films were deposited on indium tin oxide glass substrates using chemical bath deposition method. The influence of deposition time (30-120 min) on the growth of ZnSe films was reported. The surface morphology and composition were studied using scanning electron microscopy and energy dispersive analyzer X-ray, respectively. The absorption properties, band gap energy and transition type was determined using UV-Visible Spectrophotometer. The films prepared at longer deposition time showed better surface coverage compared with shorter deposition time. The ZnSe films were confirmed by X-ray diffraction pattern and energy dispersive analysis of X-rays analysis. The band gap values calculated from absorption spectra were about 2.55-2.90 eV.

Key words: Chemical bath deposition · Thin films · Semiconductor · Zinc selenide · Deposition time · scanning electron microscopy

INTRODUCTION

Recently, extensive research has been devoted to grow various kinds of nanostructures. Among various semiconductor nanostructures, zinc selenide has been identified as a potential material for device applications such as photovoltaic cells, laser screens, thin films transistors, light-emitting diode and dielectric mirror. Various methods so far adopted for the preparation of ZnSe thin films include chemical bath deposition method [1-3], electrodeposition method [4], pulsed laser deposition [5], electron beam evaporation technique [6], vacuum evaporation [7], successive ionic layer adsorption and reaction [8], molecular beam epitaxy [9] and thermal evaporation [10].

We have selected chemical bath deposition method owing to its many advantages like low cost, large area production, simplicity in instrumental operation and low elaboration temperature. The preparation and studies of metal chalcogenides thin films by chemical bath deposition method can be classified into two categories: namely binary compounds and ternary compounds. Examples of binary compound are CdS [11], In_2S_3 [12], CdSe [13], Sb_2S_3 [14], PbS [15], PbSe [16] and FeS [17]. Meanwhile, $ZnIn_2Se_4$ [18], $Pb_{1-x}Fe_xS$ [19], $CdS_{1-x}Se_x$ [20], $Zn_xCd_{1-x}S$ [21] and CdZnS [22] are examples of ternary metal chalcogenides.

Here, we report the preparation and characterization of ZnSe thin films by chemical bath deposition in the presence of tartaric acid as a complexing agent. The influence of deposition period on the properties of these films is investigated.

MATERIALS AND METHODS

Indium tin oxide (ITO) glass slides were used as the substrate during the deposition process. The substrates were first cleaned in ethanol then ultrasonically washed with distilled water. Finally, substrates were dried in an oven at 90°C. Zinc sulphate, sodium selenite, tartaric acid and hydrochloric acid of analytical reagent grade were used as received. Deionized water (Alpha-Q Millipore)

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with a resistivity of 18.4 MΩcm was used as solvent. Aqueous solutions of zinc sulphate, sodium selenite and tartaric acid were separately prepared before experiment. 25 mL of zinc sulphate (0.15 M) and 25 mL of tartaric acid (0.15 M) were mixed in a beaker. The tartaric acid was served as complexing agent to chelate with Zn^{2+} to obtain Zn-tartaric complex solution. Then, 25 mL of sodium selenite (0.15 M) was added and the pH of the solution was adjusted to 3 by addition of hydrochloric acid using pH meter. Substrates were immersed vertically into beaker. Following that, the deposition was conducted at 80°C. After completion of films deposition (30, 60, 90 and 120 min), the deposited films were washed with distilled water and dried in air for further characterization.

X-ray diffraction analysis was carried out, using a Philips PM 11730 diffractometer for the 2□ ranging from 20° to 60° with CuK_{α} (λ=1.5418 Å) radiation. Surface morphology was studied by JEOL (JSM-6400) scanning electron microscopy operating at an accelerating voltage of 20 kV under 2000X magnification. The elemental composition of the films was investigated by SEM attached with energy dispersive analysis of the X-ray (EDAX) analyzer. Optical absorption study was carried out using the Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The film-coated indium tin oxide glass slide was placed across the sample radiation pathway while the uncoated indium tin oxide glass slide was put across the reference path. The absorption data were used for the determination of the band gap energy.

RESULTS AND DISCUSSION

Figure 1 shows the scanning electron microscopy (SEM) micrographs of the ZnSe thin films deposited at different deposition periods. The SEM micrographs of the films deposited for 90 and 120 min show distribution of grains, which covers the surface of the substrate completely. No pinholes could be detected on the surface of these films. The closely packed grains provide a pinhole free morphology, which could lead to better spatial contact between the grains which is desirable for use in photoelectrochemical cells. These films also show agglomerated structure and exhibit well-defined grain edges compared to the film deposited for 30 and 60 min as well. The films deposited for 30 (2-3 μm) and 60 min (3-4 μm) have smaller grains size. The surface of the substrate can be seen as pinholes due to incomplete coverage over the substrate. The thin films deposition process on a substrate depends chiefly on the formation of nucleation sites and subsequent growth of the films from these centers. The sizes of the grains are noticed to increase as the deposition time is increased to 90 (5-6 μm) and 120 min (5-7 μm). The SEM analysis results proved more favorable for the ZnSe thin films deposited at longer deposition time under these experimental conditions.

The compositional analysis of the thin films was studied using energy dispersive analysis of X-ray (EDAX) method. Table 1 lists the atomic ratio of the zinc selenide thin films prepared under different deposition periods. The ratio of 1:1 of zinc (Zn) and selenium (Se) has been confirmed by EDAX analysis. Figure 2 shows the typical EDAX spectrum for the films deposited for 120 min.

The absorbance spectra for the films deposited under various deposition times were recorded in the wavelength of 300-700 nm (Figure 3). All the films indicate a gradually increasing absorbance throughout the visible region, which makes it possible for this material to be used in a photoelectrochemical cell. Based on the Figure 3, the films prepared for 120 min exhibit higher absorption characteristics as compared to other deposition times, indicating more materials are deposited onto substrate.

Band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with Stern relationship of near-edge absorption:

Table 1: Atomic percentage composition of zinc selenide thin films deposited at various deposition times from EDAX analysis.

	Atomic percentage (%)	
Deposition time (min)	Zn	Se
30	48.13	51.87
60	48.98	51.02
90	49.88	50.12
120	50.11	49.89

Table 2: Band gap values of ZnSe thin films prepared under various deposition times

Deposition time (min)	Band gap (eV)
30	2.90
60	2.80
90	2.60
120	2.55

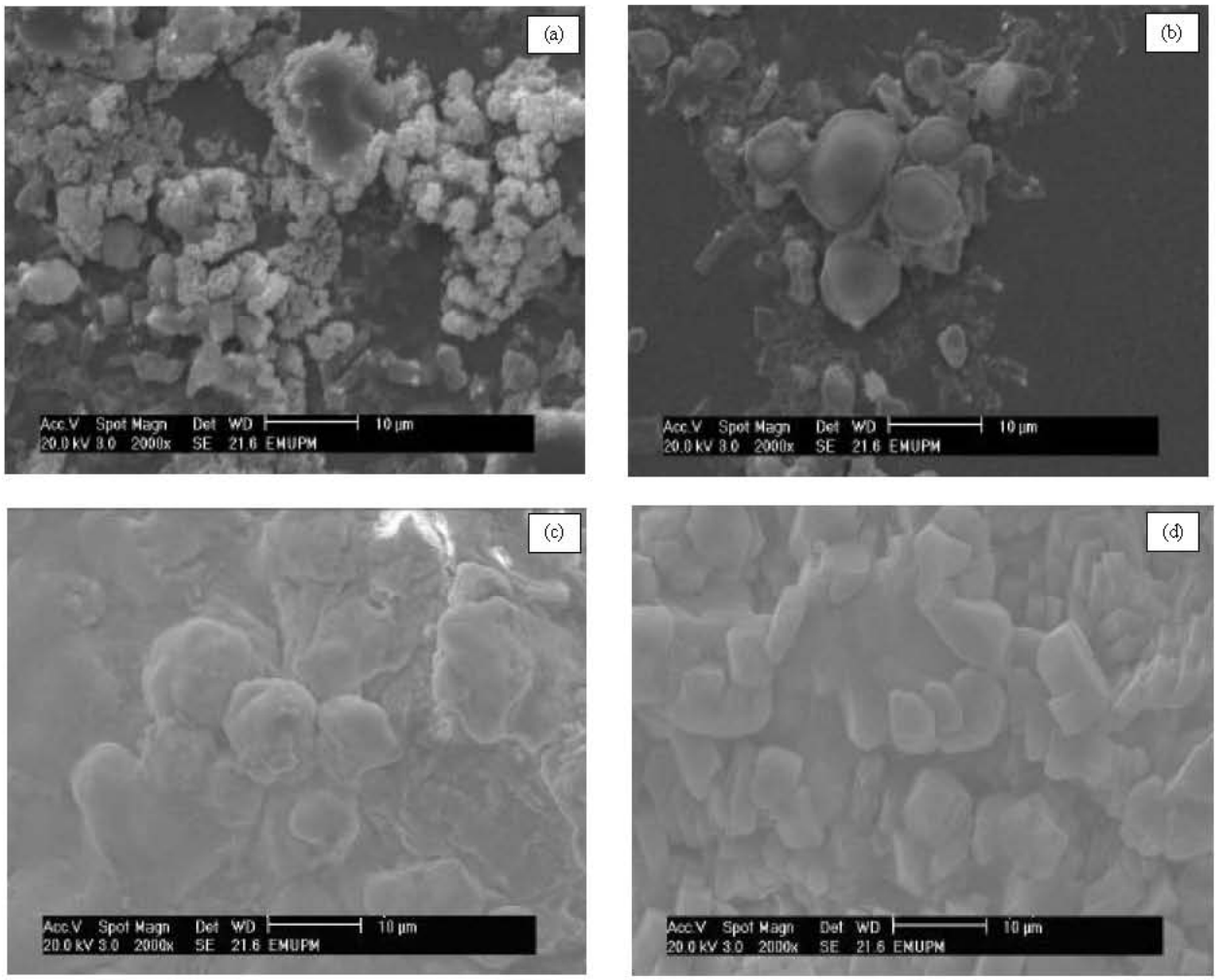

Fig. 1: Scanning electron microscopy (SEM) micrographs of ZnSe thin films deposited at various deposition times. (a) 30 min (b) 60 min (c) 90 min (d) 120 min

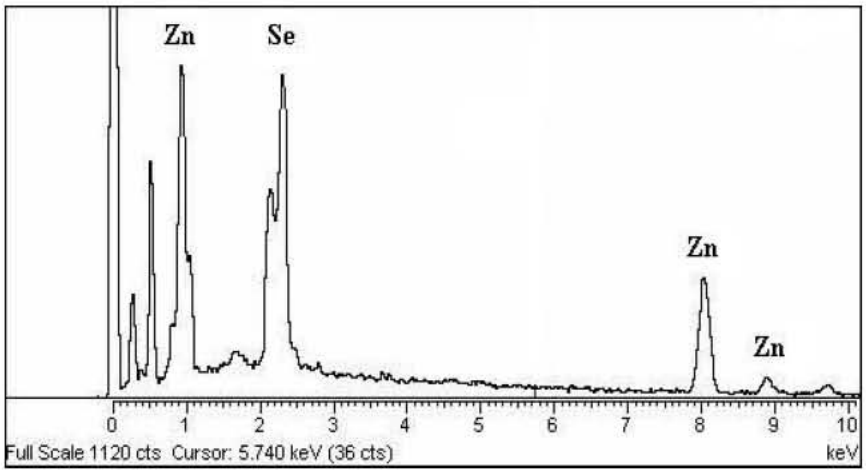

Fig. 2: EDAX spectrum of ZnSe thin films deposited for 120 min

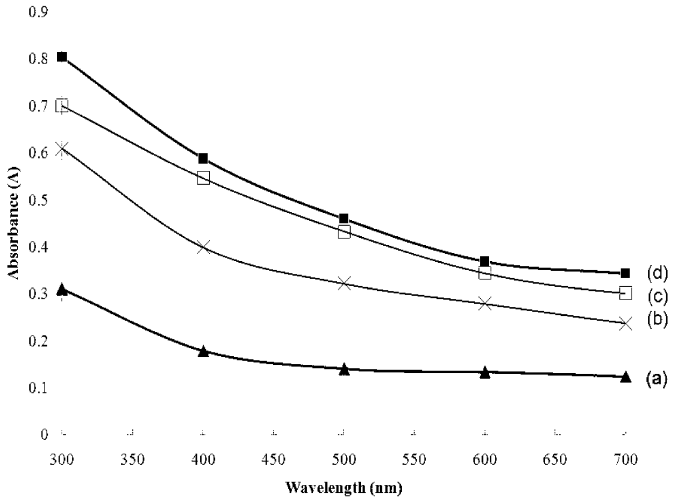

Fig. 3: Optical absorbance versus wavelength of ZnSe thin films deposited at various deposition times. (a) 30 min (b) 60 min (c) 90 min (d) 120 min

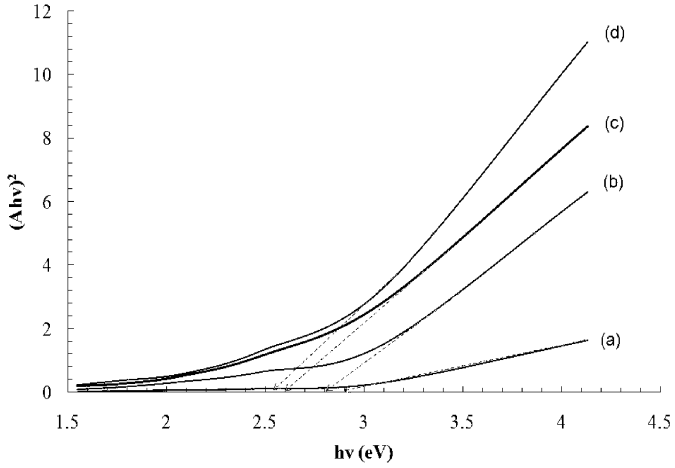

Fig. 4: Plot of $(Ahv)^2$ versus hv of ZnSe thin films deposited at various deposition times. (a) 30 min (b) 60 min (c) 90 min (d) 120 min

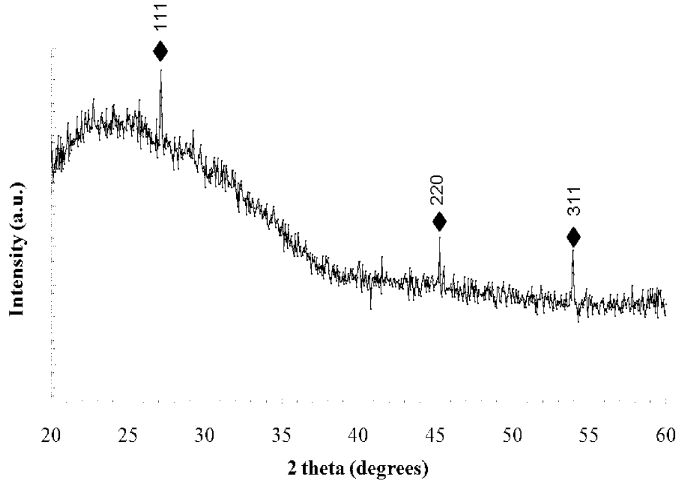

Fig. 5: X-ray diffraction pattern of ZnSe thin films deposited for 120 min

$$A = \frac{[k(hv - E_g)^{n/2}]}{hv} \quad (1)$$

Where v is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4. The value of n is 1 and 4 for the direct transition and indirect transition, respectively. Extrapolating the linear portion of the curve to zero absorption of hv axis gives the band gap value (Figure 4). The band gaps of the films prepared under various deposition times were found between 2.55 and 2.90 eV and these values are given in Table 2. From the results obtained, we can conclude that the band gap values increase as the deposition time is reduced from 120 to 30 min. The obtained band gap values are in good agreement with the value reported earlier [23, 24].

Based on the above observations, we proposed that the films deposited for 120 min show excellent quality of thin films. Therefore, the typical XRD analysis will be carried out for this sample as shown in Figure 5. The observed *d*-spacing values compared with the Joint Committee on Powder Diffraction Standard (JCPDS) *d*-spacing values are in good agreement with standard *d*-spacing values (Reference code: 00-002-0479) [25]. This film shows reflection along (111), (220), and (311) planes corresponding to formation of cubic structure of zinc selenide. This observation is supported by the data obtained from EDAX analysis.

CONCLUSIONS

ZnSe films have been chemically deposited on indium tin oxide substrates from a chemical bath consisted of zinc sulphate, sodium selenite, and tartaric acid solutions. The films prepared at longer deposition time showed better surface coverage compared with shorter deposition time. The ZnSe films were confirmed by X-ray diffraction pattern and energy dispersive analysis of X-rays analysis. The band gap values calculated from absorption spectra were about 2.55-2.90 eV.

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