

Original Research paper

Chemical bath deposition of ZnSe thin films: Investigations of the growth conditions

ABSTRACT

The main objective of this work was to deposit zinc selenide thin films onto glass substrate by using chemical bath deposition technique. ZnSe films could be used in solar cell applications. The chemical bath deposition method was chosen due to have many advantages if compared to other deposition techniques. Zinc acetate and sodium selenosulphate were used to provide the zinc and selenide ions, respectively. X-ray diffractometer, energy dispersive X-ray analysis (EDAX) and UV-Visible spectrophotometer technique were applied in order to study the properties of obtained ZnSe films which prepared under various pH values ranged from 10.2 to 11.2. The zinc rich content could be observed at these pH values as indicated in EDAX results. The band gap was determined by using absorption spectra. The band gap was increased from 2.7 to 2.85 eV as the pH was increased from 10.2 to 11.2.

Keywords: Thin Films, zinc selenide, chemical bath deposition, band gap

1. INTRODUCTION

The preparation and deposition of chalcogenide thin films are considered as interesting research activities in material chemistry since few decades ago. Because of they have a wide range of applications for solar cells, optoelectronic devices, electronic devices, thin films transistors, and laser devices. Zinc selenide is an example of II-VI compound semiconductor with a direct band gap material. Literature reviews indicated that several methods have been used to prepare zinc selenide thin films such as thermal evaporation [1], atomic layer deposition [2], electrodeposition [3], electron beam evaporation [4], reactive evaporation method [5], pulsed laser deposition [6], successive ionic layer adsorption and reaction [7] and chemical bath deposition [8-12].

In this work, the chemical bath deposition of ZnSe films from an alkaline bath was reported and discussed. This method is chosen because of many advantages such as simple, cheaper and can produce large area of deposition if compared with other deposition techniques. Therefore, many researchers have prepared various types of chalcogenide metal thin films using this method [13-30]. Here, chemical bath deposition method is used to deposit materials onto substrate. During the deposition process, selenide ions will combine to zinc ions to form zinc selenide films. In other words, the formation of a solid phase from a solution could be observed. It is spontaneous reaction. Generally, researcher can describe this method involves two major steps, namely nucleation and growth process. Eventually, the chemical bath deposition method uses a controlled chemical reaction to achieve desired binary, ternary or quaternary compound.

The influence of pH which ranged from 10.2 to 11.2 was studied. To our knowledge, there is no report on the investigation of composition of ZnSe films by using EDX technique in the presence of zinc acetate and sodium selenosulphate solutions.

2. MATERIALS AND METHODS

All chemicals such as zinc acetate, hydrazine hydrate, ammonia and hydrochloric acid were of analytical grade and were applied in this experiment without further purification. Microscope glass slide was used as substrates. These substrates were rinsed with ethanol, distilled water and dried in oven as described previously [31] before use. Zinc selenide thin films were prepared from a bath containing 20 mL of zinc acetate (0.1M) and 2 mL of hydrazine hydrate (55%). The pH of the solution was adjusted to pH 10.2, 10.5, 10.8 & 11.2 by addition of ammonia using the pH meter in order to establish the influence of the pH on the properties of the deposits. Following that, 0.01M of sodium selenosulphate (20 mL) was added before the substrate was immersed in bath. The deposition was conducted at 70 °C for 100 min. After completion of deposition process, the deposited films were removed from beaker, washed with distilled water and dried in air.

Energy Dispersive X-ray analysis was used to analyze the elemental composition of the films under scanning electron microscope (JEOL, JSM-6400). Perkin Elmer UV/Vis Lambda 20 Spectrophotometer was used to study the optical absorption in ZnSe thin films. In this experiment, the film-coated microscope glass slide was placed across the sample radiation pathway while the uncoated microscope glass slide was put across the reference path.

3. RESULTS AND DISCUSSION

The obtained chemical bath deposited ZnSe films were analyzed in the range from 300-800 nm using UV-Visible spectrophotometer. The absorption spectra indicate that all the films could be used in solar cell applications because of gradually increasing of absorbance value as shown in Figure 1. In other words, these results point out that the growth of ZnSe films could be carried out in basic media. However, the highest absorption behavior could be seen in the films prepared in pH 10.2. These data supported the literature review which reported by Ezema et al [32].

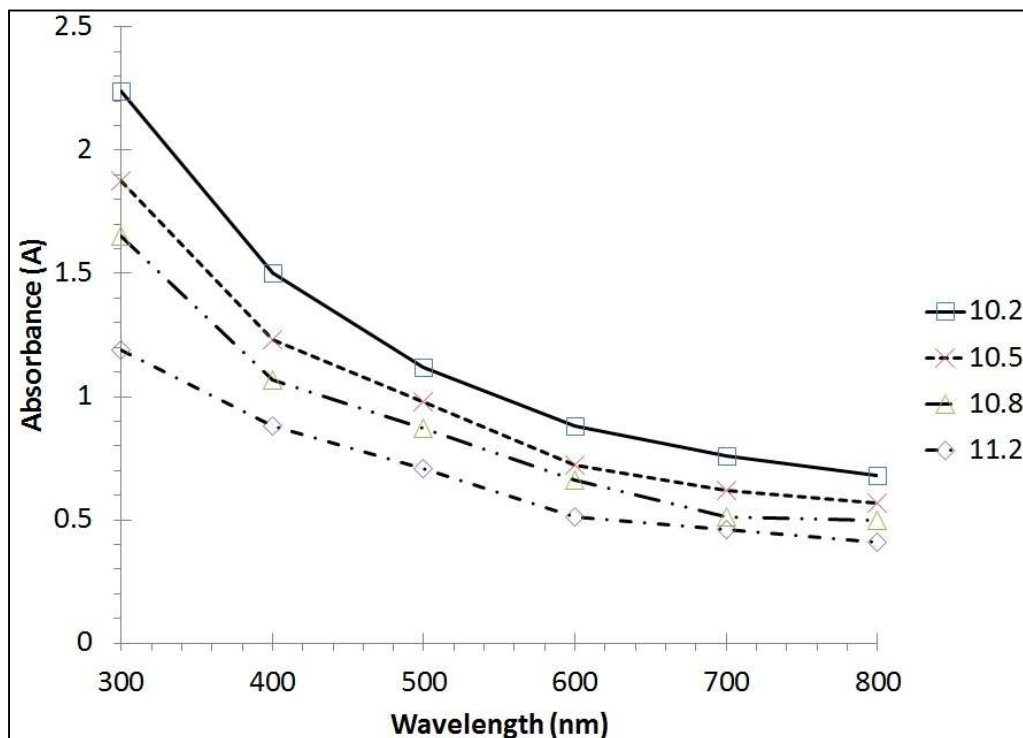


Figure 1. Optical absorbance versus wavelength of ZnSe films obtained at various pH values

On the other hand, band gap could be calculated by using the Tauc equation as described in equation 1.

$$A = \frac{[k(h\nu - E_g)^2]^n}{h\nu} \quad [E1]$$

The symbols such as ν , h , E_g and k could be defined as frequency, Planck's constant value, band gap value and constant value, respectively. The band gap energy could be determined by using absorption data. The band gap such as 2.7, 2.75, 2.85 and 2.8, could be obtained for the films prepared at pH 10.2, 10.5, 10.8 and 11.2, respectively (Table 1). The obtained band gap values match with other researchers which the ZnSe thin films prepared using various deposition methods such as thermal evaporation, spray pyrolysis, vacuum evaporation, electro deposition and chemical bath deposition (Table 2).

Table 1. Band gap of ZnSe films prepared at various pH values

pH	Band gap (eV)
10.2	2.7
10.5	2.75
10.8	2.85
11.2	2.8

Table 2. Band gap of ZnSe films reported in the literature which prepared using different deposition methods

Deposition method	Band gap (eV)
Thermal evaporation	2.76 [1]
Chemical bath deposition	2.6-2.69 [9]
Spray pyrolysis	2.65-2.7 [33]
Electro deposition	2.66 [34]
Vacuum evaporation	2.63 [35]
Thermal evaporation	2.14-2.58 [36]
Chemical bath deposition	1.6-1.75 [37]
Chemical bath deposition	2.9 [38]
Chemical bath deposition	2.85 [39]
Successive ionic layer adsorption and reaction	2.8 [40]
Electrodeposition	2.6-2.7 [41]
Thermal evaporation	2.799-2.803 [42]

The compositional of zinc selenide thin films was studied using energy dispersive X-ray analysis (EDX). These samples were confirmed contain zinc and selenium ions based on the EDX data as presented in Table 3. However, the content of zinc and selenium depends on the pH values. The EDX results indicate that the zinc content increases from 50.11% to 50.77 % as the pH was increased from 10.2 to 11.2. Among these samples, the films prepared at pH 10.2 are nearer to stoichiometry.

Table 3. Atomic composition obtained by EDX of ZnSe films deposited at various pH values

pH	Zinc content (%)	Selenium content (%)
10.2	50.11	49.89
10.5	50.34	49.66
10.8	50.66	49.34
11.2	50.77	49.23

4. CONCLUSIONS

ZnSe thin films have been successfully deposited onto glass substrate using chemical bath deposition technique. The band gap was measured from the absorption spectra and its value was keep increasing with the pH value. The ZnSe films prepared at the pH 10.2 show the highest absorption characteristics if compared to the pH values.

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