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Optical and structural study of electrodeposited zinc selenide thin films

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Abstract

Electrochemical deposition and characterization of zinc selenide (ZnSe) thin films deposited onto tin oxide (SnO_2) coated conducting glass plates from an aqueous bath containing $ZnSO_4$ and SeO_2 is discussed in this paper. The effect of electrolyte composition, deposition potential, pH and temperature on the properties of ZnSe films has been studied. The deposited ZnSe films have been characterized by X-ray diffraction (XRD), energy dispersive X-ray (EDX), scanning electron microscope (SEM) and optical absorption studies for their structural, compositional and optical properties. Raman spectroscopic and photoluminescence studies were also carried out and the results are discussed. The electrolyte composition plays a major role in the production of stoichiometric ZnSe films. Inclusion of excess elemental selenium in the film is unavoidable, however annealing improves the stoichiometry of the film.

Keywords: Semiconductor; Thin films; Zinc selenide; Electrodeposition; II–VI Compounds

1. Introduction

Wide band gap semiconductor thin film heterostructures are extensively studied for optoelectronic applications, such as, light emitting and laser diodes. Particularly, ZnSe is an interesting II–VI compound semiconducting material, widely used in optoelectronic devices, because its band gap (2.7 eV) belongs to the visible region [1]. Therefore, there is currently a major interest in ZnSe based materials suitable for the fabrication of light-emitting devices operating in the blue-green region [2] and in the manufacture of optical components, mirrors, lenses etc. for IR lasers [3,4]. A number of methodologies are employed in the formation of high quality ZnSe thin films, including chemical vapor deposition [5], molecular beam epitaxy [6,7], atomic layer epitaxy [8], pulsed laser, metalorganic chemical vapor deposition [9], sputtering [10], and other advanced techniques [11–13]. However, there is an interest to investigate other approaches too, which could open new or supplementary possibilities in terms of device properties, structure or engineering.

Electrodeposition and chemical bath depositions [14,15] are the alternative methods that are particularly adapted for the deposition of chalcogenide materials. Chemical bath depositions of sulfides and selenides are already used for producing interfacial buffer layers in high efficiency thin film solar cells based in copper indium gallium diselenide. Among the direct wide-band semiconducting materials, the zinc chalcogenide compounds have been the objects of numerous studies concerning thin film electrodeposition from aqueous solutions. Recently, electrodeposition has emerged as a simple, economical, low temperature and viable technique, which could produce films of good quality for device applications [16]. The attractive features of this method are the convenience for producing large area devices and possibility to control the film thickness, morphology and stoichiometry of the films by readily adjusting the electrical parameters, as well as the composition of the electrolyte solution. The works available concerning the optical study of electrodeposited ZnSe films are less in number. Therefore we decided to deposit ZnSe thin films by electrodeposition and to study their properties. In this study, we have prepared a series of ZnSe thin films by electrodeposition from an aqueous bath containing $ZnSO_4$ and SeO_2. The influence of growth conditions such as deposition potential, temperature and concentration of the constituents of the bath on crystallinity and composition of the film was studied. In order to characterize the ZnSe thin films for their structural and optical properties, scanning electron microscopy (SEM), X-ray diffraction (XRD, energy dispersive X-ray (EDX), photoluminescence (PL), Raman spectroscopy and optical absorption techniques were employed. Both absorp-

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tion and photoluminescence techniques were used to find out the optical band gap energy of the ZnSe films.

2. Experimental details

A series of ZnSe films was prepared electrochemically by co-deposition of zinc and selenium using aqueous solutions of $ZnSO_4$ and SeO_2. Fluorine doped tin oxide (SnO_2) covered conducting glass plates of resistance 15 $\Omega\,cm^{-1}$ where used as substrate in this deposition. These conducting glasses of approximately 1 cm^2 area were cleaned with detergent, dried and degreased with acetone and distilled water. The electrolyte bath contained aqueous solutions of 50–300 mM of $ZnSO_4$ and 0.2–2 mM of SeO_2. The chemicals used in this deposition were of Analar® grade and they were used without further purification. Deposition of the films was carried out cathodically using a potentiostat (EG & G Princeton Applied Research, Model 362) with standard three-electrode system. ZnSe films were deposited at different potentials using graphite as counter electrode and saturated calomel electrode (SCE) as reference electrode. The deposition potential was varied in the range between −0.6 and −1.2 V versus SCE with different bath temperatures and pH between 2 and 3. Thickness of the film was measured using weight gain and ellipsometric methods. Structure of the films was analyzed using X-ray diffraction (XRD) by Bruker Discover D8 diffractometer using Cu kα radiation (λ = 0.15418 nm) and Philips scanning electron microscope (SEM) attached with energy dispersive X-ray (EDX). Optical absorption, photoluminescence, Raman spectra and compositional analysis were also carried out for the films grown at optimized condition. Optical absorption study was performed with a UV–vis–NIR Spectrophotometer (Hitachi) and room temperature Raman spectra were obtained by using He–Ne laser as an excitation source with a maximum power of 25 mW. Photoluminescence measurements were carried out in a closed cycle refrigeration system (Janis) using He–Cd laser as an excitation source. The luminescent radiation was collected and directed into a spectrometer and recorded by a photon counting system.

3. Result and discussion

3.1. Growth kinetics

The films deposited with the concentrations around 300 mM $ZnSO_4$ and 1 mM SeO_2 at the potential around −0.8 V versus SCE, current density 1 mA cm^{-2} and temperature 70 °C resulted in uniform and good quality films. The pH of the electrolyte solution played a major role in the deposition of the film and it was found that the pH value around 3 was suitable for the electrodeposition of ZnSe thin films. In the case of electrodeposition of ZnSe, the use of low concentration of selenous acid and high concentration of zinc salt is the usual approach [17], because the zinc is a less noble constituent of the compound. In this way, the rate of the following reaction can be lowered, which is one of the paths for the incorporation of excess elemental selenium in the film:

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \quad (1)$$

The influence of bath concentration of $ZnSO_4$ and SeO_2 on the film thickness is shown in Figs. 1 and 2, respectively. The film thickness linearly increases with concentration of both precursors and deposition time. However the increase is restricted to a very low concentration range and it gets saturated at higher concentrations of both precursors. We observed less adherent, uncontrolled and non-reproducible growth rate for the concentrations of $ZnSO_4$ and SeO_2 above 400 and 2 mM, respectively. EDX measurements showed that the excess inclusion of elemental selenium in the deposited film is unavoidable. This is because,

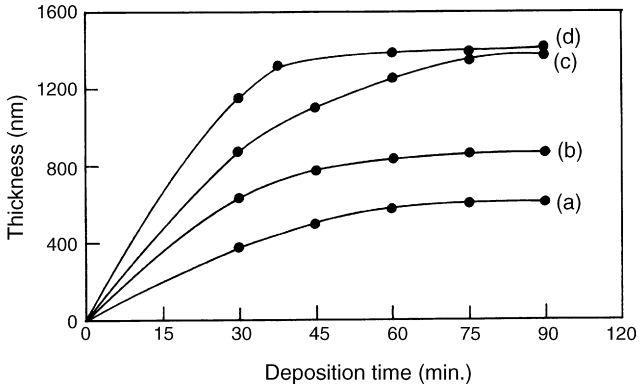

Fig. 1. Variation of film thickness with concentration of $ZnSO_4$, (a) 0.1 M, (b) 0.2 M, (c) 0.3 M and (d) 0.4 M. Bath, 1 mM SeO_2; potential, −0.8 V; pH, 2.5; temperature, 70 °C.

the adsorption of Zn^{2+} ion is playing vital role in obtaining stoichiometric films. If the adsorption sites were occupied by other species (i.e. H_2SeO_3 or any) the rate of Zn^{2+} reduction was reduced compared to SeO_2 reduction, thus Se clusters could be formed. If once the Se clusters have reached a certain size they react slowly to give ZnSe. Low concentration of selenous acid was found to give stoichiometric and good ZnSe films. However, too low concentration of the selenous acid (<0.5 mM) gives low deposition rate and poor quality of the film.

3.2. Structural studies

X-ray diffraction studies were done in order to identify crystallinity and phases of the grown films. From the XRD profile, the inter planer spacing d_{hkl} was calculated for the (1 1 1) plane using the Bragg's relation:

$$d_{hkl} = \frac{n\lambda}{2\sin\theta} \quad (2)$$

where λ is the wavelength of the X-ray used, d the lattice spacing, n the order number and θ is the Bragg's angle. The factor d is related to $(h\,k\,l)$ indices of the plane and the dimension of the unit cells. The crystallite size (D) of the films were calculated from Scherrer's formula from the full width at half maximum

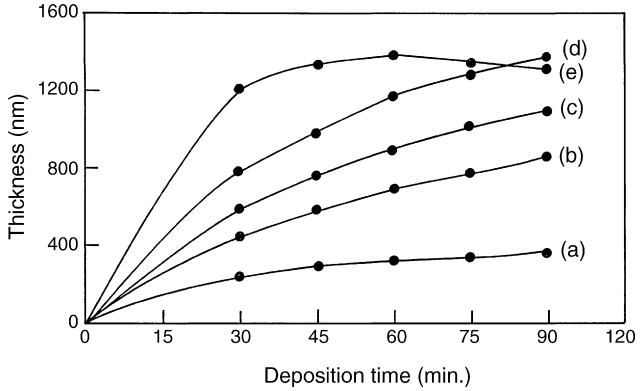

Fig. 2. Variation of film thickness with concentration of SeO_2, (a) 0.5 mM, (b) 1.0 mM, (c) 1.5 mM, (d) 2.0 mM and (e) 2.5 mM. Bath; 0.3 M $ZnSO_4$; potential, −0.8 V; pH, 2.5; temperature, 70 °C.