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Properties of ZnSe films brush plated on high temperature substrates

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Abstract

ZnSe thin films were brush plated on substrates maintained at temperatures in the range 30 – 90 °C from the precursors. The films exhibited cubic structure. Optical band gap of 2.70 eV was obtained. XPS measurements indicated the formation of ZnSe. AFM studies indicated the formation of fine grains of the order of 50 nm, for the films deposited on room temperature substrates. Luminescence emission was observed at 675 nm for an excitation of 450 nm.

Keywords: ZnSe; Semiconductor; Thin film; Electrodeposition; Brush plating

1. Introduction

Zinc selenide is one of the most interesting binary wideband gap II–VI semiconductors, which has potential applications in the fabrication of blue light emitting diodes, blue lasers and as window material in the field of photovoltaics [1]. Several techniques like vacuum evaporation [2], chemical bath deposition [3], spray pyrolysis [4], pulse electrodeposition [5], electrodeposition [1,6] and pulsed laser deposition [7] have been employed for the depostion of ZnSe films. All the reports have presented results on electrical, optical and photo activity. In this work, results on structural, optical, and luminescent properties of brush plated ZnSe films are presented. To our knowledge this is the first report on brush plated ZnSe films.

The brush plating technique, also known as selective plating, differs from traditional tank or bath plating in that the work piece is not immersed in a plating solution (electrolyte), instead, the electrolyte is brought into contact with the part and applied by a hand-held anode or stylus, which incorporates an absorbent wrapping for applying the solution in the work piece (cathode). A direct current power pack drives the electrochemical reaction, depositing the desired metal on the surface of the substrate. In practice, movement between the anode and cathode is required for optimum results when plating, stripping, activating and so on. Currently, a broad range of metals can be plated by brush plating. The key advantage of brush plating is portability. Many systems can be moved to various locations in a production facility or be transported to the job site. Selective plating is also versatile: it permits most electroplate types to be deposited onto any conductive substrate that can be touched with an electrode. Cast iron, copper, stainless steel and aluminium can be plated by this method and exhibit good adhesion. Limited adhesion can be obtained with other materials such as titanium, tungsten and tantalum.

Brush plating allows higher current densities than tank plating, which translates into higher deposition rates, up to 0.0100 mm/min. In addition, inherently precise thickness control permits plate buildup or repair without the need for subsequent machining. The brush plating technique though widely used for depositing metals has

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been earlier employed for the deposition of CdSe films [8,9]. To our knowledge this is the first report on ZnSe films grown by the brush plating technique. In this work, results on ZnSe films brush plated on titanium and conducting glass substrates maintained at high temperatures are reported.

2. Experimental

Zinc selenide thin films were deposited on titanium and conducting glass substrates by the brush plating technique at different substrate temperature in the range of 30–90 °C using 3 ml of 0.25 M zinc sulphate and 3 ml of 0.01 M selenium dioxide at a current density of 100 mAc m^{-2} The duration of deposition was 10 min. The thickness of the films was estimated by gravimetry and it was found to vary between 1.2 and 2.5 μm according to the temperature of deposition. Structural characterization was carried out by X-ray diffraction (XRD) studies using CuK_α radiation. Employing a 35CF JEOL scanning electron microscope, morphological studies were carried out. Optical studies were made on the films deposited on conducting glass substrates with a Hitachi UV–VIS–NIR spectrophotometer. XPS studies were made using ESCALAB. Luminescence emission spectra of the samples were recorded at room temperature using a mercury lamp source. The excitation wavelength was 450 nm and the emission was recorded in the wavelength range 550–720 nm.

3. Results and discussion

XRD patterns of the films heat treated at different substrate temperatures in the range 30–90 °C are presented in Fig. 1. It is observed that the films exhibit cubic structure with peaks corresponding to (111), (220) and (311) orientations. For the films deposited at room temperature, two peaks corresponding to the substrate Ti are observed, as the deposition temperature increases, the intensity of the peak corresponding to (111) orientation also increased, indicating the preferential orientation of the films in this direction, the peaks corresponding to titanium are also absent. Composition of the films before and after heat treatment were estimated by EDAX measurements and it was found to be 49.4% Zn and 50.6% Se for the as-deposited films.

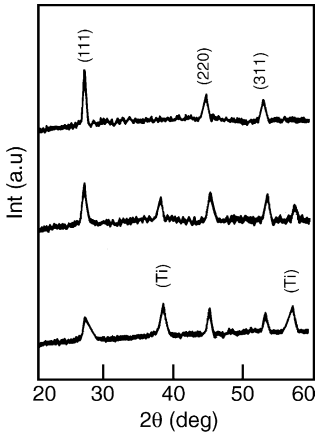

Fig. 1. X-ray diffraction pattern of ZnSe films deposited at different substrate temperatures: (a) 30 °C, (b) 50 °C, (c) 90 °C.

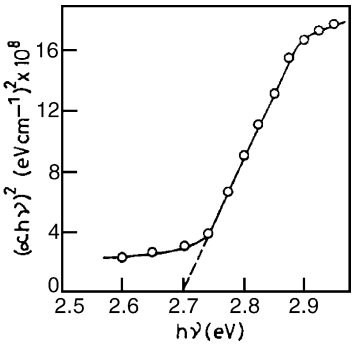

Fig. 2. $(\alpha h\nu)^2$ vs $h\nu$ plot for ZnSe film.

Optical absorption studies were made on the films deposited on conducting glass substrates in the wavelength range 300–900 nm at room temperature to ascertain the nature of the band gap. For allowed direct transitions, the absorption coefficient 'α', near the absorption edge is given by [10]

$$\alpha = (A/h\nu)\left(h\nu - E_g\right)^{1/2} \quad (1)$$

Where h is the Planck's constant, ν is the frequency of the incident light and A is related to the effective mass of holes and electrons. A plot of $(\alpha h\nu)^2$ vs $h\nu$ (Fig. 2) for the films deposited on substrates at 90 °C was linear, indicating the direct band nature of the films. Band gap obtained by extrapolating the linear portion was 2.7 eV. Atomic force microscope studies indicated smaller grains and some large clusters that accumulated small particles were obtained on the surface of the ZnSe film grown at 30 °C (Fig. 3a). On the other hand, larger grains were observed on the surface of the films deposited at higher temperatures (Fig. 3b–d). Uniform, continuous distribution and particles with average sizes of 80 nm were obtained at higher temperatures.

To examine the chemical composition of the films, the XPS spectra of the ZnSe films grown at different substrate temperatures were measured and as a representative case results are reported for the film deposited at 90 °C (Fig. 4). The XPS spectra of the films exhibit the binding energies of the $Zn(2p_{3/2})$ and $Se(3d_{5/2}$ and $3d_{3/2})$ level. As shown in the Fig. 4a, the peak energy levels associated with $Zn(2p_{3/2})$ appeared at about 1022 eV, which is in good agreement with the literature [11]. These findings are characteristic of the Zn in ZnSe and are in good agreement with the literature [11]. Fig. 4b shows the binding energies of the $Se(3d_{5/2}$ and $3d_{3/2})$ levels at 53.9 and 59.2 eV respectively. In order to make a compositional analysis in the whole thickness of the film, XPS measurements were performed on films submitted to sputtering at different times. The study indicates an increasing Zn/Se atomic ratio with depth, varying from 0.97 at the surface to 1.5 close to the film

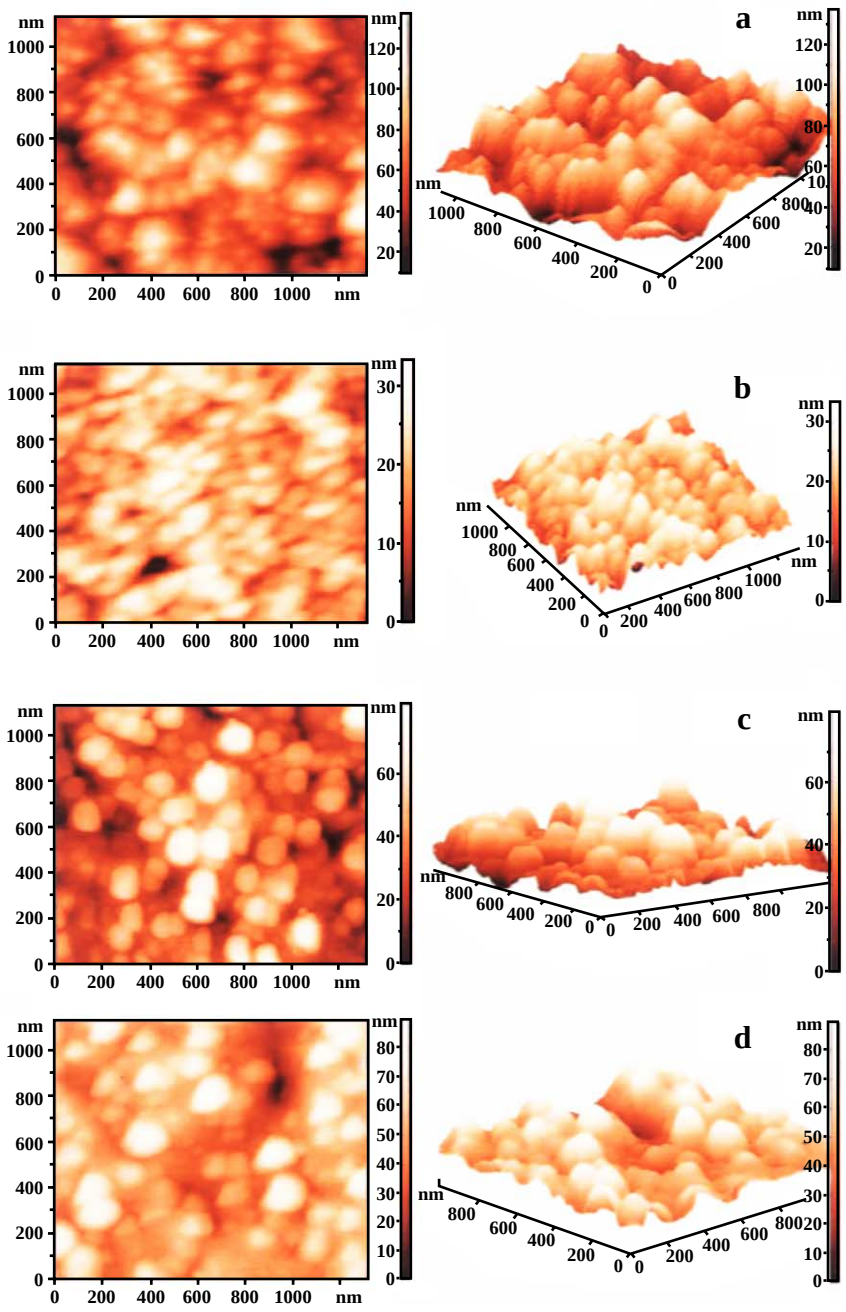

Fig. 3. Atomic Force Micrograph of ZnSe film deposited at (a) 30 °C, (b) 50 °C, (c) 70 °C, and (d) 90 °C.

substrate interface. Similar type of increase in Zn/Se ratio with depth was observed for chemical bath deposited ZnSe films [11].

Photoluminescence (PL) spectra were recorded at room temperature using an excitation wavelength of 450 nm. The spectra peaks at 675 nm (Fig. 5) and the PL intensity was found to increase with annealing temperature. The PL emission from the undoped ZnSe has been attributed to the presence of native defects like zinc and selenium vacancies or interstitials, which are likely to be introduced during the growth process [12]. Self activated centers arising from complexes of zinc vacancies and shallow donors (selenium interstitials) would occur around 2.0 eV [13]. The emission band observed in the present case at 675 nm may be attributed to the above complex, since EDAX studies have indicated a slight excess of selenium.

4. Conclusions

The results of this investigation indicates that the simple and economical brush plating technique can be employed for the preparation of luminescent ZnSe films. Further work is on to scale up the process for large area film deposition.

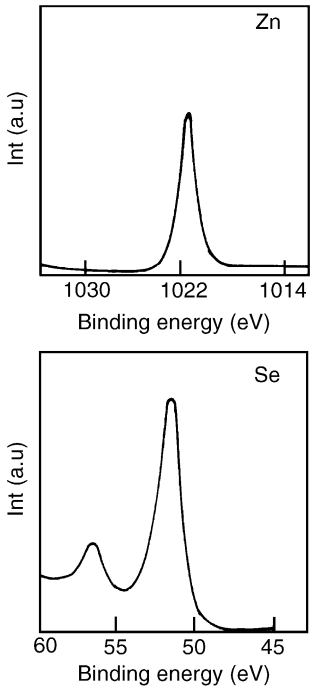

Fig. 4. XPS spectra of ZnSe film deposited on substrates at 90 °C.

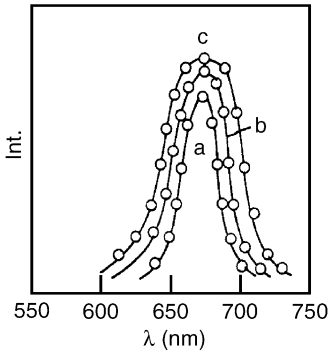

Fig. 5. Photoluminescence spectra of ZnSe films deposited at different temperatures: (a) 30 °C, (b) 50 °C, (c) 90 °C.

This can be employed for the commercial production of large area films. Further improvement in the performance can be made by heat treatment steps as well as by in situ doping with copper or manganese.

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