EFFECT OF CURRENT DENSITY ON STRUCTURAL AND OPTICAL PROPERTIES OF In DOPED ZnO THIN FILMS GROWN ON COPPER SUBSTRATE BY ELECTRODEPOSITION METHOD

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In doped ZnO thin films have been grown on copper substrates from acidic zinc oxide solution by Potentiostat-Galvanostat electrolysis process. The crystal structure and surface morphology of the as-grown films have been investigated by X-ray powder diffraction (XRD), Fourier transform infrared spectra (FTIR), UV–Vis absorbance spectra and Scanning electron microscopy (SEM). The results of XRD and FTIR analyses have confirmed the formation of hexagonal wurtzite structure of In doped ZnO. Particle size is found to increase from 20nm to 33nm with current densities. The SEM results have indicated the porous surface characteristic of the films. The optical band gap value is found to vary from 3.40 eV to 3.60 eV with current density which results increase in particle size.

1. Introduction

ZnO is a wide band-gap semiconductor (3.37 eV) with high exciton binding energy (60 meV). It finds potential applications in many fields such as light emitting diodes, laser diodes [1, 2], piezoelectric transducers [3], varistors [4], and transparent conducting film destined for solar-cell devices [5]. For many of these applications, it is very important to control the ZnO physical properties by doping. Usually, n-type conductivity is obtained by doping Al, Ga or In. On the other hand, reports on p-type ZnO are scarce it is difficult to grow ZnO with p-type conductivity [6]. Synthesis of ZnO thin film can be achieved using a lot of different techniques. Among them the most commonly used are physical vapour deposition [7, 8], chemical vapour deposition [9], metal organic chemical vapour deposition [10, 11], spray pyrolysis [12, 13], and sol gel method [14]. The electrodeposition method has many advantages such as low process temperature and cost effective compared to other techniques mentioned above. Hence electrodeposition has been used to grow ZnO thin films in the present work. It is noteworthy to point out that ZnO thin films deposited using physical techniques offer the best performance (good quality films with high electrical conductance and transparency). However, one should bear in mind that films deposited using low-cost chemical techniques also exhibit low resistivity values and high optical transmittances as compared to those produced using physical methods. Electrodeposited ZnO thin films have been studied widely for solar cell applications [15]. The growth conditions of ZnO thin films deposited by electrodeposition technique have been optimized with the help of data available in the literature.

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2. Sample preparation

Zinc oxide thin films were grown on copper substrates by electrodeposition technique. The copper substrates were purchased from the local market and are act as working electrodes. Zinc nitrate thin films were grown on these substrates. The electroplating system used in the present work was constructed based on a classical two-electrode device plate. Before electrolysis, the electrochemical cell was immersed into de-ionized water and it was stirred for about 15 min. The galvanostatic was used for obtaining zinc nitrate thin film. The counter electrode was zinc. A rigorous substrate preparation of metallic substrates was necessary in order to obtain a reproducible deposition quality. The metallic substrates of coating area is (3x2 cm^2), and then it is cleaned with dilute sulphuric acid and distilled water by using ultrasound. The electrolytic bath for the electrodeposition process was composed of 2M of zinc nitrate as supporting electrolyte. The pH is same for all samples (pH=3). ZnO thin films were electrodeposited by potentiostat. Galvanostat was used to perform the electrodeposition process at constant cathodic potential during one hour. Samples were deposited for different current densities at 12, 18, and 24 mA/cm^2 and the temperature is maintained at 50^{0}C.

3. Characterization techniques

The crystal structure of ZnO thin films were examined by XRD. XRD measurements were carried out using a Bruker AXS D8 Advance X-ray powder diffractometer and were performed in glancing angle X-ray diffraction (GXRD) mode. The crystallite size of the deposited films can be calculated from the Scherrer's formula [16],

$$D= 0.94\lambda/\beta COS\theta \qquad (1)$$

where λ is the X-ray wavelength (1.54056 X 10^{-10} m), θ is the Bragg diffraction angle of the XRD peak in degree, and β is the full width at half maximum. The morphology of the prepared films was analyzed using a Jeol Model JSM - 6390LV scanning electron microscope (SEM).

The optical properties (reflectance) were measured at room temperature in the wavelength range 175 – 3300 nm using a Varian, Cary 5000 spectrophotometer fitted with an integrating sphere. FTIR measurements were made to identify the presence of certain functional groups in a molecule. The FTIR measurements were performed using Thermo Nicolet, Avatar 370 in the spectral range 400-4000 cm^{-1}. They vibrate about some mean position. IR spectrum of a compound is the superposition of absorption bands of specific functional groups. The test device used is composed of a Galvonastat potential, the large zinc counter electrode and the working electrode prepared for the sample to be studied. The deposited materials have been studied by diverse techniques of characterization such as X-Ray diffraction, scanning electron microscopy to study the morphology, FTIR to identify the presence of certain functional groups in a molecule. In addition, different measures to characterize the optical properties have been obtained using the reflectance spectra.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of In doped ZnO thin films grown on copper substrates are shown in Fig. 1. Detailed analysis of XRD patterns have showed that In doped ZnO films have crystallized in hexagonal Wurtzite structure. The well defined peaks which correspond to In doped ZnO indicate the crystalline quality of the films. The peaks observed were labelled suitably with help of data available in literature [18] as shown in fig. 1. Moreover, the sharpness of the peaks increases gradually with current density as shown in the figs. 1a to 1c. This indicates that more amount of In

doped ZnO segregates on the surface of the film with current density. Diffraction peaks due to the copper substrates are also found to appear in the diffraction patterns and in fact, these peaks dominate the peaks of In doped ZnO in terms of intensity [17].
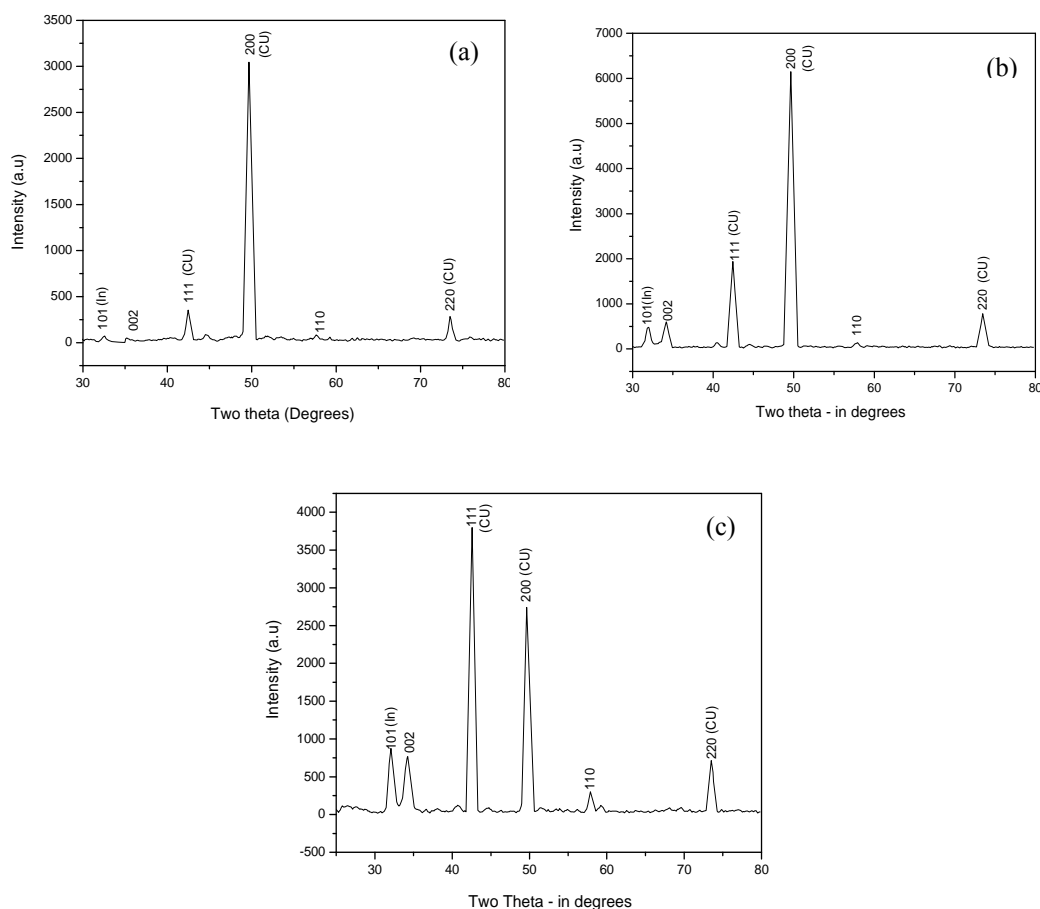

Fig.1 XRD pattern of ZnO films electrodeposited at different current densities and temperatures. (a) current density 12 mA cm-2 and temperature 50 °C, (b) current density 18 mA cm-2 and temperature 50°C, and (c) current density 24 mA cm-2 and temperature 50°C.

From the patterns, it is observed that the 200 reflection from Cu substrate is found to have highest intensity. Using the peak positions of In doped ZnO peaks, the unit cell parameters were calculated as $a =0.349$ nm and $c =0.5205$ nm, which are in good agreement with the JCPDS data (card number 008). In the XRD patterns, the intensity of 200 reflection of Cu decreases whereas the intensity of 200 increases with increase in current density. This indicates that Cu diffuses more to the surface of the film and get oriented more in the [111] direction.

3.2 Scanning Electron Microscopy

The surface morphology of the three films which were grown on copper substrates using different current density was studied using SEM. The SEM image of In doped ZnO thin films grown on copper substrate are shown in Fig. 2 (a, b, and c). Figure 2a shows flakes like structure of In doped ZnO and Cu which is expected to segregate on the surface of the In doped ZnO film. Figure 2b shows that the flake like structure of In doped ZnO have become sphere shaped particles and the concentration of In doped ZnO particles is increased appreciably. Figure 2c shows that Cu particle adopted thin sheet like structure and on which In doped ZnO clusters are sticking.
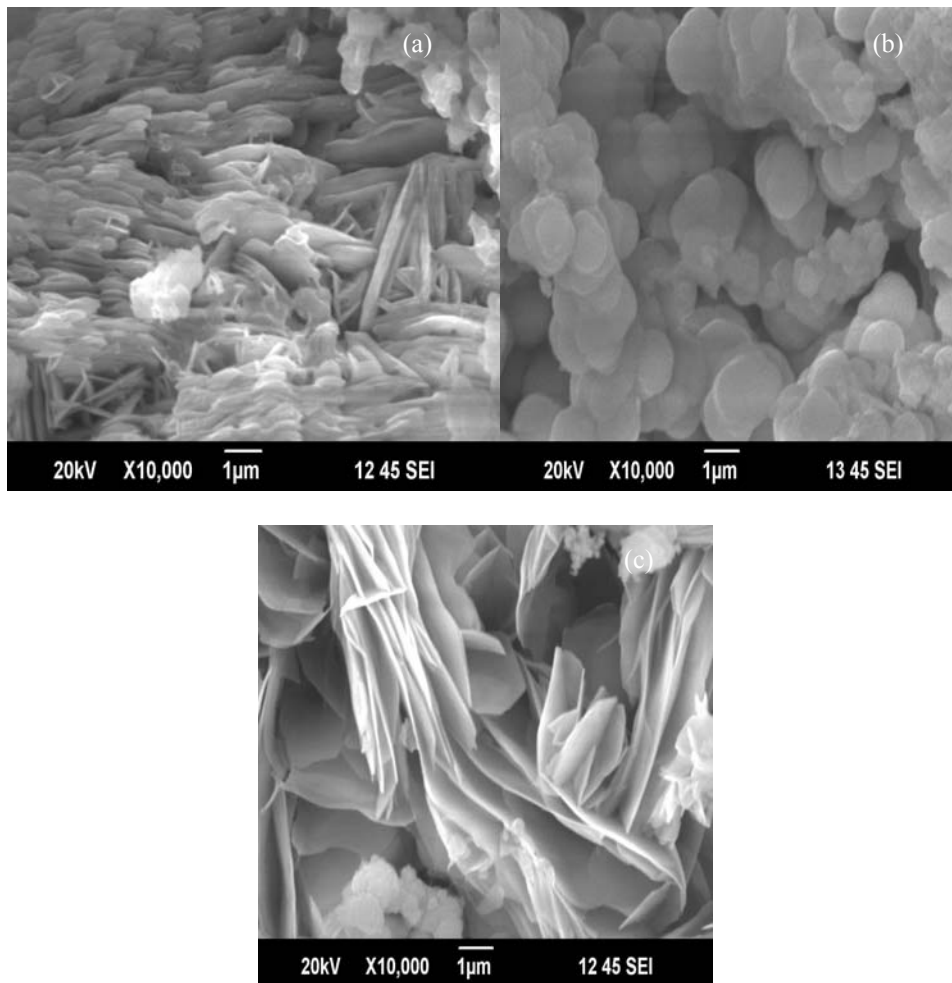
Fig. 2 Electron micrographs of ZnO films electrodeposited at different current densities and temperatures. (a) current density 12 mA cm-2 and temperature 50 ℃, (b) current density 18 mA cm-2 and temperature 50℃, and (c) current density 24 mA cm - 2 and temperature 50℃.

3.3 Optical properties of the In-doped ZnO films

Fig. 3 (a, b, and c) shows the reflectance spectra of the In-doped ZnO films. From these spectra, the average values of the optical transmission in the visible range (200–2000 nm) were estimated. It is seen that the reflectance is limited only by the surface reflectance of about 30% in the visible region. The fundamental absorption edge of the films corresponds to electron transitions from valence band to conduction band and this edge can be used to calculate the optical band gap of the films. In the direct transition, the absorption coefficient can be expressed by [19, 22].

$$(Ah\chi) = A (h\chi - Eg) \tag{1}$$

Where A is a constant, hv is the photon energy and Eg is the optical band gap. Figure 3 (a, b, and c) shows optical reflectance spectra of the ZnO thin films prepared using different current densities are (12, 18 and 24 mA/cm^2) and bath temperature is at 50^{0}C. The band gap value of the ZnO thin films prepared are 3.60eV, 3.54eVand 3.40eV respectively.
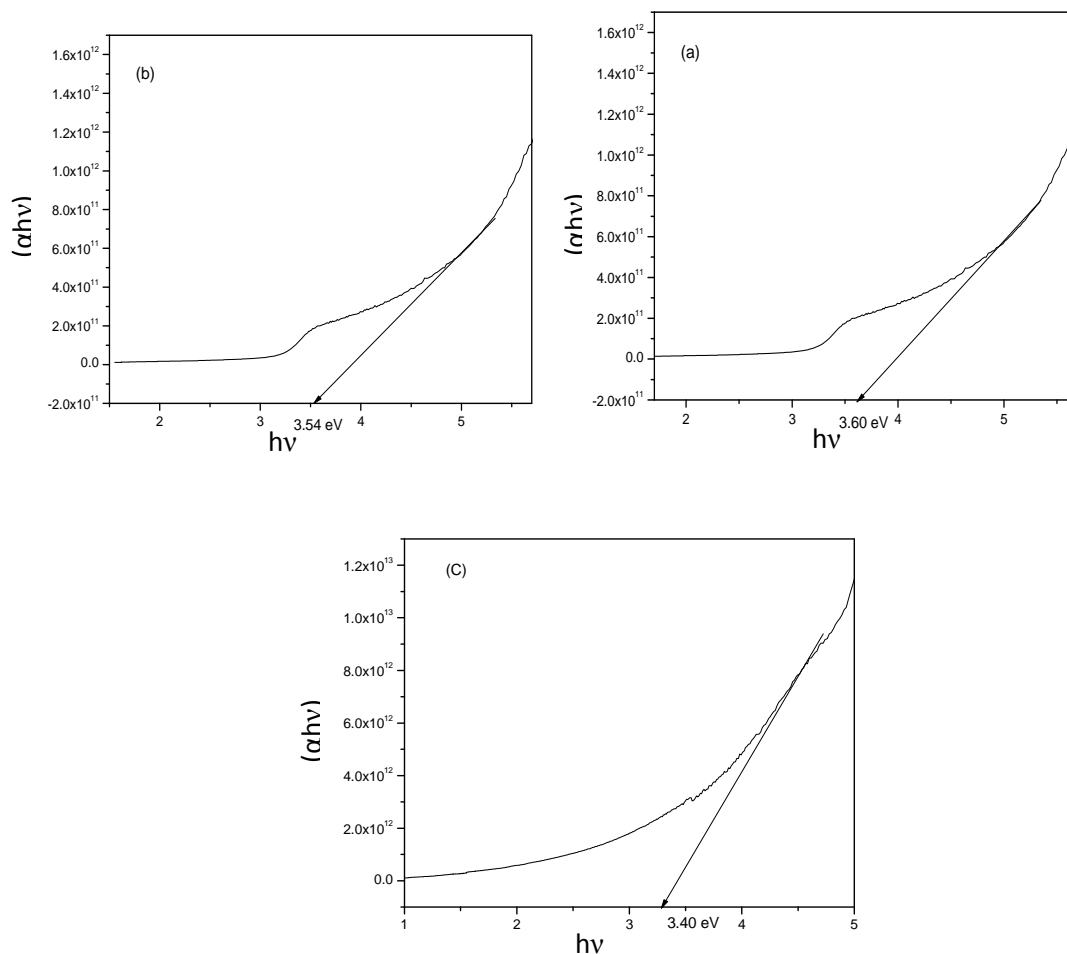
Fig. 3 Optical reflectance spectra ZnO films electrodeposited at different current densities and temperatures. (a) current density 12 mA cm-2 and temperature 50 ℃, (b) current density 18 mA cm-2 and temperature 50℃, and (c) current density 24 mA cm-2 and temperature 50℃.

This shows that when the current density increases as the band gap decreases, it may be due to increase in particle size, called quantum size effect. Fig. 5 shows plots of $(\alpha h\nu)^2$ vs. hv.

3.4 EDAX analysis

Figure 4 shows the EDAX spectra of In ZnO on Cu substrate. Analysis of EDAX spectra shows that the concentration of Zn and O are closed to each other. This indicates that the formation of ZnO. In addition, small amount of In and other elements are found to present in the spectra. Apart from this, the presence of Cu also noted form the EDAX. This is due to Cu substrate.
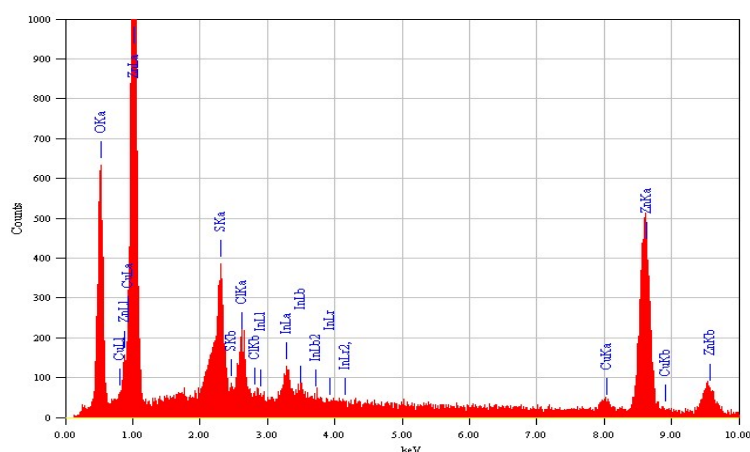
Fig. 4 EDAX spectra of In doped ZnO grown on Cu substrate.

3.4 FTIR Spectra

Fig. 4 shows the FTIR spectrum of the In doped ZnO films grown on Cu substrates which was acquired in the range of 503–4000 cm^{-1}. The purity and molecular structure of films were analyzed by Fourier transform infrared spectroscopy (FTIR). ZnO powder shows a broad band below 550 cm^{-1}. The FTIR spectrum of commercial zinc oxide powder showed a broad band above 559cm^{-1} related to the characteristic adsorptions of zinc oxide [20]. The broad peak at 3440cm^{-1} can be attributed to the vibration of OH groups of adsorbed water molecules, other small peaks at 1639, 1384 and 1142 cm^{-1} are related to adsorbed carbonate moieties [20]. The FTIR spectrum of pure CH deposits showed a broad peak around 3442cm^{-1} related to hydroxyl stretching, a peak at 1638cm^{-1} attributed to C- O (amide I) stretching mode, a peak at 1384cm^{-1} assigned to –C–O stretching mode of –CH2–OH groups [21]. The FTIR spectra of the composite deposits showed that the peaks observed in the spectrum of pure CH at 1639 and 1090cm^{-1}, shifted to 1639 and 1142cm^{-1}, respectively. The peaks at 3373 and 1639cm^{-1} are attributed to O–H stretching vibration and H–O–H bending vibration respectively, assigned to small amount of H_2O existing in the nanocrystalline ZnO. Other small peaks at 1639 cm^{-1} and 1384 cm^{-1} may be due to small amount of impurities present in the film. The band at 3373 cm^{-1} corresponds to hydroxyl groups on the ZnO surfaces and of adsorbed water molecules within the molecule. The peak at 1142 cm^{-1} may be due to the –CH$_3$ group [22].
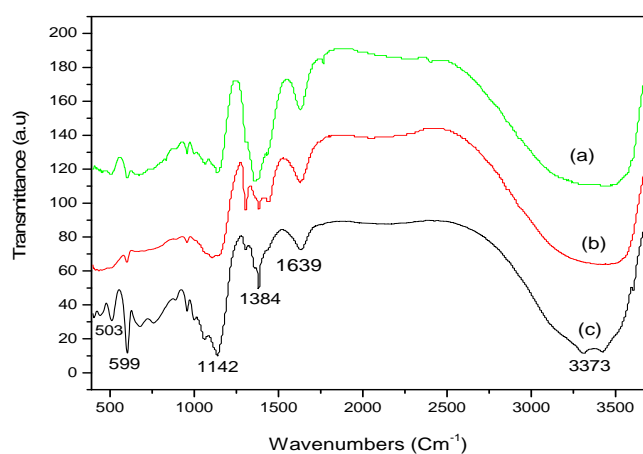

Fig. 5. FTIR spectra of ZnO films electrodeposited at different current densities and temperatures. (a) current density 12 mA cm-2 and temperature 50 ℃, (b) current density 18 mA cm-2 and temperature 50℃, and (c) current density 24 mA cm-2 and temperature 50℃.

4. Conclusions

ZnO thin films have been deposited on Copper substrates by an electrochemical method. The results of XRD analyses have confirmed the formation of In doped ZnO with hexagonal wurtzite structure. The cell parameters of the unit cell are determined as a=0.325 nm and c=0.523 nm. The crystallite size is calculated to be about 33 nm. The SEM micro structural studies revealed a good homogeneity across the entire surface of each film, and. The In doped ZnO films grown at different current densities show quite different morphologies. Electrodeposited ZnO thin films show a very high crystallite orientation along the c-axis. The optical band gap value is found to be in the range from 3.60 to 3.40 eV.

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