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STRUCTURAL AND OPTICAL PROPERTIES OF ZnO NANO PARTICLES GROWN ON COPPER SUBSTRATE BY ELECTRODEPOSITION METHOD

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ZnO thin films which consist of nano particles have been deposited on copper substrates by the galvanostatic electrodeposition process using Zinc Nitrate as precursor. The effect of current density on structural, morphological and optical properties of ZnO films nano particles has been studied. Based on the results obtained from these studies, the optimum deposition conditions have outlined. The rate of deposition of ZnO thin film is found to be larger in an acidic solution than in a basic solution. Structural, morphological and optical properties of electrodeposited ZnO were investigated using X-ray diffraction, scanning electron microscopy (SEM) and optical absorbance. Analysis of diffractograms has revealed that electrodeposited films have crystallized in hexagonal structure with the reflection from (002) plane as strongest one. From the SEM micrographs, the grain size is observed to be in the range 1.0 μm. Optical studies have showed that the band gap of the electrodeposited films varies from 3.59 to 3.72 eV depending on the current density.

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1. Introduction

ZnO, a wide band gap semiconductor, has received considerable attention recently for various potential applications in low-voltage and short-wavelength opto-electronic devices such as light emitting diodes and laser diodes [1, 2]. ZnO films have been prepared by many different techniques, such as plasma-assisted molecular beam epitaxy [3], chemical vapour deposition [4], and pulsed laser deposition [5], Chemical vapor deposition [8], metal organic chemical vapor deposition [9, 10], sol–gel processing [11] and spray pyrolysis [12–14]. Electrodeposition, another similar approach, has several advantages over above techniques such as low temperature processing and low cost [6, 7]. ZnO thin film is an important oxidic semiconducting material, which is characterized by a high transmission in the visible spectral range and is electrically conductive. Consequently, this oxide semiconductor offers important applications in solar cells, transparent electrodes, and flat-panel displays, thin film field-effect transistors, sensors, etc. [15-18].

2. Experimental details

2.1. Thin film deposition

Zinc oxide thin films were grown by electrodeposition technique on conducting substrates (copper). Copper sheets were previously polished with emery paper and rinsed first with acetone

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and then immersed into de-ionized water and stirred for about 15 min. The electroplating system works based on a classical two-electrode device. In this, copper was used as working electrode wheras zinc was used as counter electrode. The cleaned metallic substrates of coating area 3x2 cm^2 were used for deposition. Zinc nitrate was commercially purchased (company name: Nice) with 4N purity. During electrolytic bath for the electrodeposition process, 2M of Zinc Nitrate was used as supporting electrolyte. The pH of the electrolyte was kept at 3 for all samples. Galvanostat was used to perform the electrodeposition process at constant cathodic potential. Duration of deposition was one hour for all samples. Current densities of values 12, 18, 24 and 30 mA/cm^2 were used for growing different samples. The bath temperature was maintained at 323 K.

2.2. 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 [19],

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

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.

3. Results and discussion

3.1 X-ray Diffraction analysis

Fig. 1 shows typical XRD patterns of ZnO thin films deposited on copper substrates using different current densities such as 12, 18, 24 and 30 mA/cm^2 with bath temperature 323 K. The peaks corresponding to the hexagonal (wurtzite) ZnO are found in the XRD pattern. In addition, the reflections which belong to copper substrate are also observed in the XRD pattern. The observed peaks are labeled suitably in Fig 1. [20].

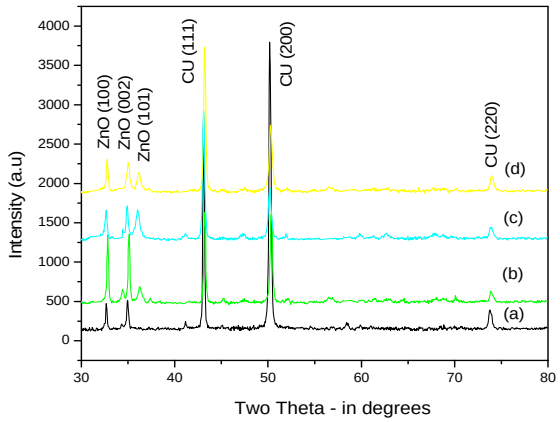

Fig. 1 XRD pattern of ZnO films electrodeposited at 323 K for different current densities. (a) Current density- 12 mA cm^{-2} (b) Current density- 18 mA cm^{-2} (c) Current density - 24 mA cm^{-2} and (d) Current density - 30 mA cm^{-2}

The peaks correspond to the reflections from (1 0 0), (0 0 2),(1 0 1), (1 1 1), (2 0 0) and (2 2 0) planes are observed at 2θ values around 31.8, 34.5, 36.2, 43.2, 50.35, and 74.1°, respectively. Two intense peaks originated from the copper substrate were also identified [21]. The sharpness of the peak related to the ZnO structure indicates a good polycrystalline nature of the deposited film. It is to be noted here that the (002) peak is more intense and all four films show a privileged

growth direction along the c-axis. The unit cell parameters determined from peaks present in the XRD pattern as a = 0.325 nm and c =0.5206 nm using equation 2, which are in good agreement with the reported values, JCPDS data number 008 [22].

$$d = \frac{1}{\sqrt{\frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}}}$$

All the peaks identified are from either ZnO or Cu, and there are no additional lines corresponding to Zn and other oxides phases. This shows that preferred orientation of ZnO films is along [0 0 2] direction. The size of the particle is determined to be in the range 400 to 700 nm. This shows the formation ZnO nano particles in grown thin films. The particle size is found to increase with increase of current density.

3.2 Scanning Electron Microscopy

The surface morphology of the four films grown on copper substrates was studied using SEM image. The SEM image of a ZnO thin film grown on copper substrate shows a good homogeneity over the whole surface and are shown in Fig. 2 (a, b, c and d). Analysis of SEM images revealed that ZnO films grown on similar substrates with different current densities at same bath temperature have different morphologies. The SEM image of the film grown with current density 12 mA/cm^2 shows seeds of paddy like structure and the film grown with 18 mA/cm^2 shows jasmine like structure. Similarly, mixed flowers structure and cauliflower like shaped structure are observed fro the films grown with 24 and 30 mA/cm^2, respectively. Particle sizes were found to vary from 0.5 to 1 μm. This can be correlated with the full-width at half-maximum (FWHM) of the (0 0 2) peak in the XRD patterns. This observation corroborated the XRD results regarding particle size.

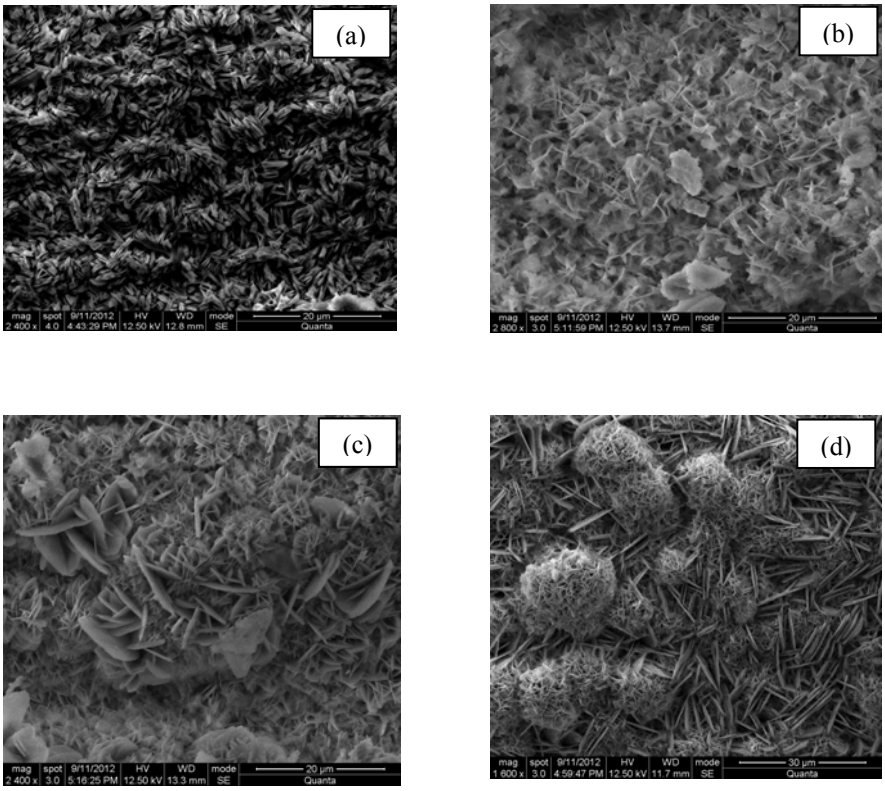

Fig.2 SEM pattern of ZnO films electrodeposited at 50^{0}C
(a) current density; 12 mA cm^{-2} (b) current density; 18 mA cm^{-2}
(b) current density; 24 mA cm^{-2} (d) current density; 30 mA cm^{-2}

3.3 UV reflectance spectra

Figure 3 (a,b,c and d) shows optical reflectance spectra of the ZnO thin films prepared using different current densities (12, 18, 24 and 30 mA/cm^2) at a bath temperatures of 50°C. The band gap value of the ZnO thin films prepared using different current densities (12, 18, 24 and 30 mA/cm^2) at a bath temperature of 50^{0}C are 3.51 eV. 3.59 eV, 3.64 eV and 3.72 eV, respectively. This shows that the band gap increases with increase of current density, it may due to the formation of larger ZnO particles in the film [23]. The result is in good agreement with the SEM results. The most convenient method for determining the bandgap energy is from transmittance spectroscopy; but it is not possible to measure the transmitted spectra for thin films grown on top of opaque substrates. Hence, for studying the bandgap, optical reflectances have been used [24].

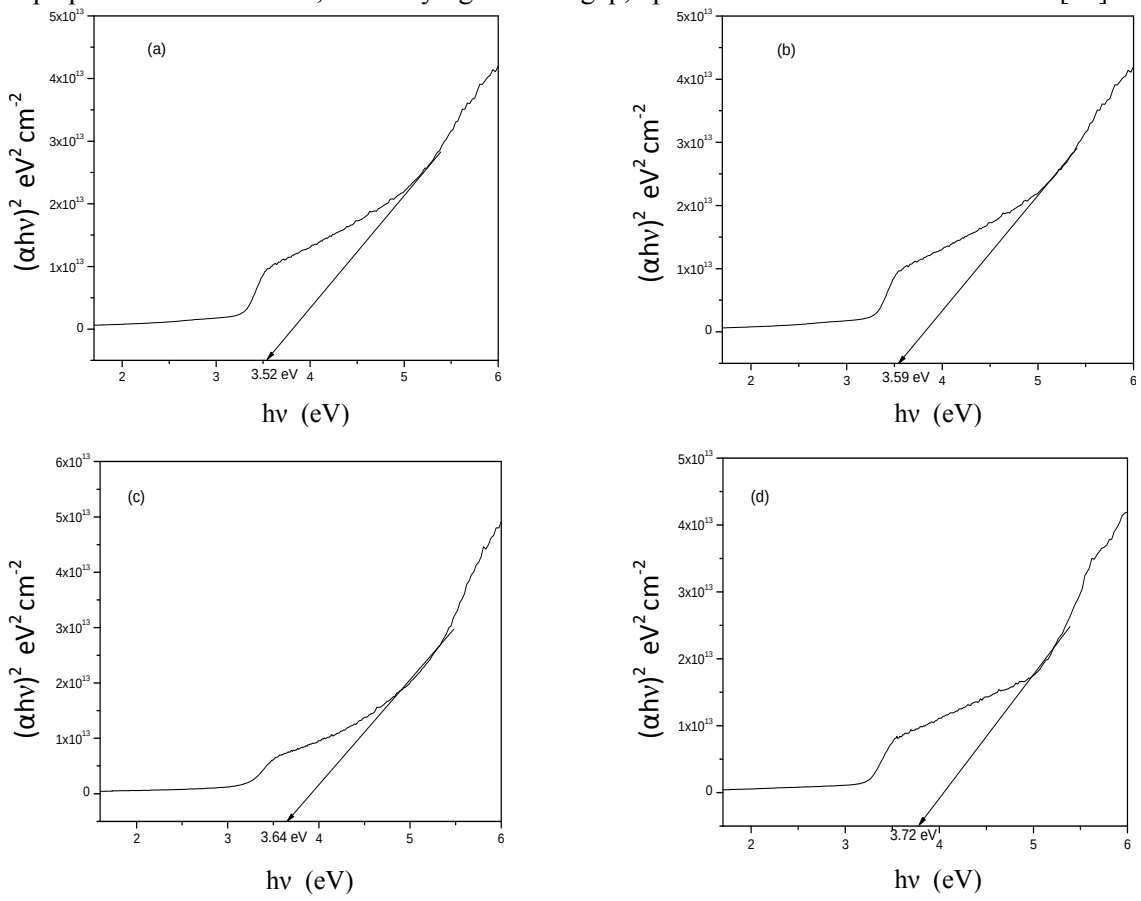

Fig. 3 UV reflectance spectra at 50^{0}C
(a) Current density; 12 mA cm^{-2} (b) Current density; 18 mA cm^{-2}
(c) Current density; 24 mA cm^{-2} (d) Current density; 30 mA cm^{-2}

4. Conclusion

ZnO thin films which consist of nano particles have been deposited on copper substrates by an electrodeposition method with different current densities at a bath temperature 323 K. These films deposited on Cu substrates show quite different morphologies. XRD experiments show that our films are crystallized in the hexagonal Wurtzite structure with cell parameters a=0.325 nm and c=0.523 nm. Electrodeposited ZnO thin films show very high crystallite orientation along the c-axis. Preferential orientation of grains depends on the nature of substrate and bath temperature. Preferential orientation along the (0 0 2) axis, which is perpendicular to the substrate surface, was observed for all films deposited on copper substrate. The particle size (400-700 nm) is found to

increase with increase of current density. It has been observed that the direct band gap energy was increased from 3.51 to 3.72 eV due to variation in particle size. We proposed that this increase in band gap energy may be due to the low oxygen content of the sample surface after current treatment.

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