A study on Electrodeposited of Zinc Oxide Nanostructures

A.Azizi[1], M. R. Khelladi[1], L. Mentar[1], V. Subramaniam[2]
[1]Laboratoire de Chimie, Ingénierie Moléculaire et Nanostructures, Université Sétif 1, 19000, Algeria
[2] Centro de Investigacion y de Estudios Avanzados del I.P.N (CINVESTAV), Av. Instituto Politecnico Nacional # 2508, Col. San Pedro Zacatenco 07360, Mexico D.F.

e-mail : aziziamor@yahoo.fr

Abstract

Zinc oxide (ZnO) nanostructures prepared by electrodeposition technique from aqueous zinc nitrate solution at 65 °C onto fluorine doped tin oxide (FTO) coated glass substrates were investigated. Characterization of ZnO nanostructures was realized using classical electrochemical techniques, scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. Cyclic voltammetry experiments were performed to determinate the potential for electrodepositio. Since single-step potential experiment in the potential ranges from -1.1 to -1.4 V, the formation of ZnO nuclei in the early deposition stages was proceeded according to the three dimensional (3D) instantaneous nucleation followed by diffusion-limited growth rather than a progressive one. SEM images demonstrated that the morphology of ZnO nanostructures depend greatly on the potential depositions. X-ray diffraction studies revealed that the deposited films were polycrystalline in nature with wurtzite phase.

Keywords: electrodeposition, ZnO, nucleation, morphology, structure

1. Introduction

The synthesis of semiconductor crystals with well-defined shapes, sizes, and structures has attracted extraordinary interest in order to realize their unique properties that not only depend on their chemical composition, but also on their shape, structure, phase, size, and size distribution [1-3]. Zinc oxide is one of the most promising materials for nanotechnology due to its range of potential applications such as sensors, photovoltaic cells, light-emitting diodes and nanogenerators. Among various synthesis methods, electrochemical deposition represents a simple and inexpensive solution based method for synthesis of semiconductor nanostructures. In effect, electrodeposition of Zinc oxide (ZnO) is a versatile growth method and many various nanostructures with a range of morphologies can be easily designed by the technique. Consequently, in recent years, there has been extensive interest in synthesizing various ZnO nanostructures, including nanowires, nanoribbons and nanotubes. The nanostructures growth was controlled by deposition parameters such as electrolyte bath composition, pH, deposition potential or deposition current density and temperature. Consequently, in this work, we carried out an electrochemical study and properties ZnO nanostructures obtained from nitrates solutions at different potentials, in order to comprehend the ZnO electrodeposition process from this system.

2. Materials and Method

ZnO thin films were prepared by electrodeposition from a 0.1 M zinc nitrate aqueous solution with 1 M KNO_3. The pH of solution is fixed at 6. The reaction temperature was kept at 65° C. The deposition process was performed in three-electrode cell with a platinum wire counter

electrode and a saturated calomel reference electrode (SCE, +0.241V vs. SHE). Fluorine doped tin oxide (FTO) coated glass substrate with a resistance of 10 Ω/cm (an area of 1×2 cm^2 exposed to the electrolyte) was used as a working electrode. Before the electrodeposition, the FTO glass was cleaned ultrasonically in acetone, ethanol and then rinsed in distilled water. The ZnO nanostructure was deposited in a potentiostatic mode, using a computer-controlled potentiostat/galvanostat (Voltalab 40) as a potential source.

The surface morphology and microstructure of the ZnO nanostrutures were examined using scanning electron microscope (SEM) Carl Zeiss Model. The structural characterization of the deposits was determined by X-ray diffraction (XRD) analysis, using a Siemens D5000 X-ray diffractometer with CuK_α radiation.

3. Results

In order to investigate the electrochemistry in the deposition process of ZnO, cyclic voltammetry study was performed in the potential range 0 to -1.1 V *vs.* SCE onto FTO-covered glass substrate from zinc nitrate aqueous solution. The potential scan was initiated in the negative direction from the open circuit potential (EOCP) at scan rates of 20 mV s^{-1}. Fig.1 show the cyclic voltammogram of a ZnO film formation onto the FTO electrode surface from the pH 5.5 aqueous solution containing 0.1 M $Zn(NO_3)_2$ and 1 M KNO_3. The decrease in the cathodic voltammetric peak current observed in Fig. 1 was found consistent with the growth of a ZnO film onto the FTO electrode surface.

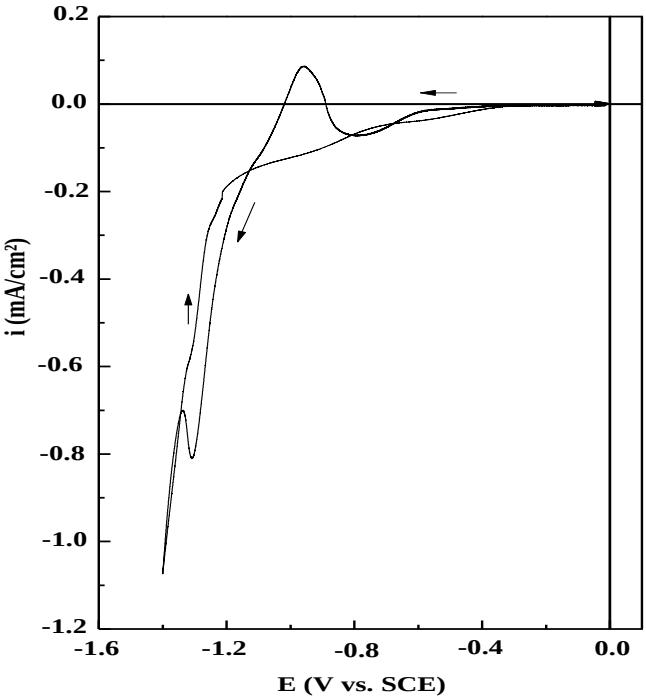

Figure 1. Cyclic voltammogram of FTO substrate recorded in a 0.1 M zinc nitrate aqueous solution with 1 M KNO_3 at 65 °C. Potential scan rate is 20 V/s.

The reduction of nitrate ions generates hydroxide ions at the cathode and hence causes the precipitation of zinc hydroxide onto the cathodic electrode, which is finally dehydrated into ZnO. The electrodeposition process of ZnO nanowires/nanorods mainly includes two parts:

first, an increase of pH, in this case due to the reduction of nitrate ions, and second the precipitation of zinc oxide. On reduction of nitrate in the presence of zinc ions the following two reactions occurs [4, 5]:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (1)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (2)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (3)$$

$$Zn^{2+} + NO_3^- + 2e^- \rightarrow ZnO + NO_2^- \quad (4)$$

The cathodic electrochemical deposition of nanocrystalline zinc oxide at different electrode potentials from was initiated by the reduction of nitrate ions. Nitrate ions at first reduced and form nitrite and hydroxide ions electrochemically. These hydroxide ions react with zinc ions and form zinc hydroxide at the cathode. This zinc hydroxide spontaneously dehydrates and forms zinc oxide.

The nucleation kinetics and growth of ZnO onto FTO surface was studied with the chronoamperometry technique. An example of currents transients obtained at different potentials during ZnO electrodeposition on FTO coated glass substrates are shown in Fig. 2a. In this i–t curves, the current increases rapidly at very short times, and then decays rapidly due to the double layer discharging, and then the current rises due to the birth or nuclei on the surface and growth of the new phase. After the current reaches a maximum value, it decays again, until finally give a common current–time profile at even longer times which is independent of the stepping potential. This behavior is consistent with the development of hemispherical diffusion zones around the growing nuclei which eventually overlap and coalesce corresponding to linear diffusion at a planar electrode. These features are qualitatively consistent with the model of 3D islands growth under the diffusion-limited control. According to this model [6, 7], there are two nucleation modes, instantaneous nucleation and progressive nucleation. If the rate of nucleation is rapid in comparison with the resultant rate of growth, subsequent nuclei are formed at all possible growth sites within very short times and nucleation is considered as instantaneous. However, if the rate of nucleation is slow, nucleation will continue to take place at the surface whilst previous nucleation centers continue to grow, and nucleation is termed progressive. Nucleation and the growth kinetics were investigated by comparing the experimental results to the theoretical model normalized in terms of the maximum current, i_{max}, and the time at with the current density reached its maximum value, t_{max} [6, 7].

Fig. 2b shows the experimental data normalized using $(i/i_{max})^2$ and (t/t_{max}) and the theoretical model curves with respect to two limiting cases of the theoretical three-dimensional nucleation growth models: instantaneous and progressive. It can be seen in the figure that the experimental plots are a good agreement with the instantaneous nucleation mode. In the instantaneous growth mode, the incoming ZnO atoms usually occupy all of the available nucleation sites on the substrates simultaneously at the very early instant of the start of the deposition process. With regard to the initial state of the ZnO film grown onto ITO substrate, Lee et al. [8] demonstrated that the formation of the first layer was in an islands growth mode. It was proved that the initial discrete ZnO islands formed firstly on the substrate, and new nucleation will then cause the increase in the density of the ZnO islands. It is also well understand that the adjacent islands tend to get connected together resulting in the formation of the first layer. In this model, the number of active nucleation sites (N_0) is determined

directly from the current transients using the following equations [6, 7]:

$$N_0 = 0.065(8\pi CM/\rho)^{-1/2}\,(zFC/i_{max}\,t_{max})^2 \quad (5)$$

where C is the bulk concentration, zF the molar charge of electrodepositing species, M and ρ are the molecular weight and the density of deposited material, respectively.

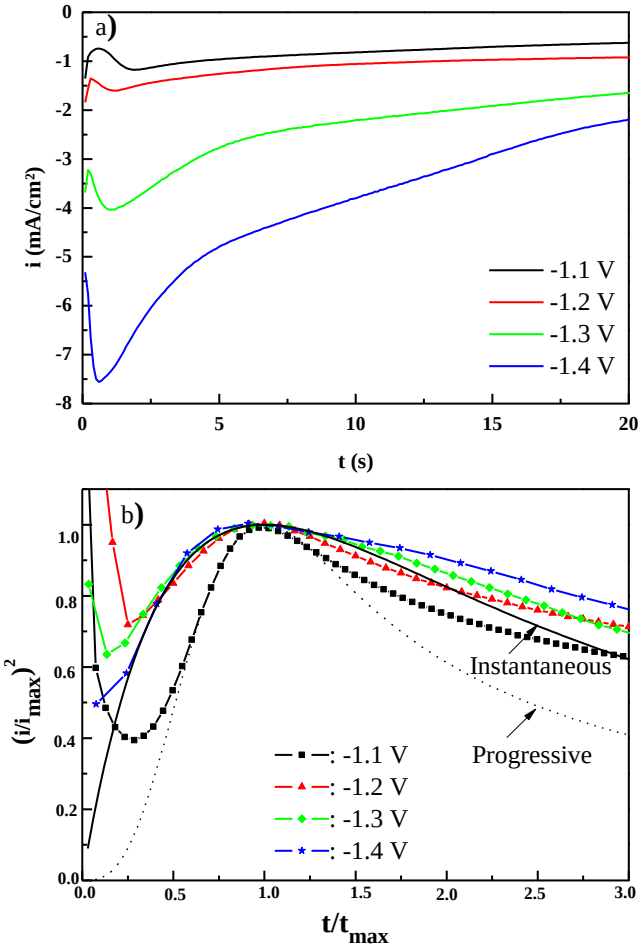

Figure 2. a) Current transients for ZnO deposition on FTO substrates in the potential ranging from -1.1 to -1.4 V. b) Normalized transients $(i/i_{max})^2$ *vs.* t/t_{max} from Fig. 2a. In each plot, the full line corresponds to the calculated curve for instantaneous nucleation and diffusion-limited growth, and the dotted line represents the calculated curve for progressive nucleation and diffusion-limited growth.

Values of i_{max}, t_{max} and N_0 at different potentials are shown in Table 1. From these values, it is evident to see that with the increase in potential, the current maximum t_{max} significantly decreases, and shifts towards shorter times. This characteristic is also typical for 3D electrochemical nucleation and growth of a new phase under the diffusion control.

-E (V)	$-i_{max}$ (mA/cm^2)	t_{max} (s)	10^{-4} N_0 (cm^{-2})
1.10	2.25	3.67	05.87
1.20	2.95	2.14	10.05

1.30	3.48	1.50	14.70
1.40	5.33	0.88	18.22

Table 1: Electrochemical parameters resulting from the current transients for ZnO electrocrystallization onto FTO electrode.

It's well established that the electrodeposition of ZnO is a versatile growth method and many various nanostructures can be easily designed by the technique. Using different potential deposition we obtain different ZnO nanostructures. In order to follow the microstructural evolution of the ZnO film at different potential deposition, scanning electron microscopy (SEM) measurements were performed. Effectively, Fig. 3 shows the SEM images of three different ZnO nanostructures electrochemically grown on FTO-coated glass substrates.

The surface morphology of polycrystalline ZnO films obtained at various potentials is always different. At low magnification (Fig. 3(a)) uniformly distributed crystalline particles are observed for sample deposited at -1.2 V vs. SCE. When viewed at high magnification (Fig 3(a')) it can be seen that the crystal is an agglomerate of triangle-like structures and the neighboring particles merging to form one. With increasing potential, platelets characteristic of the ZnO nanostructure are observed. Effectively, a vertically grown 2-D "nanowall" structure is observed for ZnO deposited on FTO substrate at -1.3 V at different magnification (Fig. 3(b-b')). These nanowalls are found to be well distributed across the substrate, but each wall gets terminated in the lateral growth direction by another intercepting wall. These images were similar to that obtained in the literature [9, 10]. For sample deposited at -1.4 V vs. SCE (Fig 3(c)), a "flakes" like structure of ZnO grown on FTO is presented and are well distributed across the surface of the substrate. Furthermore it can be seen in the high-resolution image (Fig 3(b')) that the structure is filled with pores. The formation of pores can be attributed to the enhanced growth height or roughness of the sample and by the hydrogen evolution that occurred at the cathode surface. However these pores do not alter the structure of the ZnO as it is visible in the image Fig. 3(b'), which shows the patterned grains of the sample that are characteristics of the wurtzite structure [10]. Formation of pores in ZnO structures was reported by many authors.

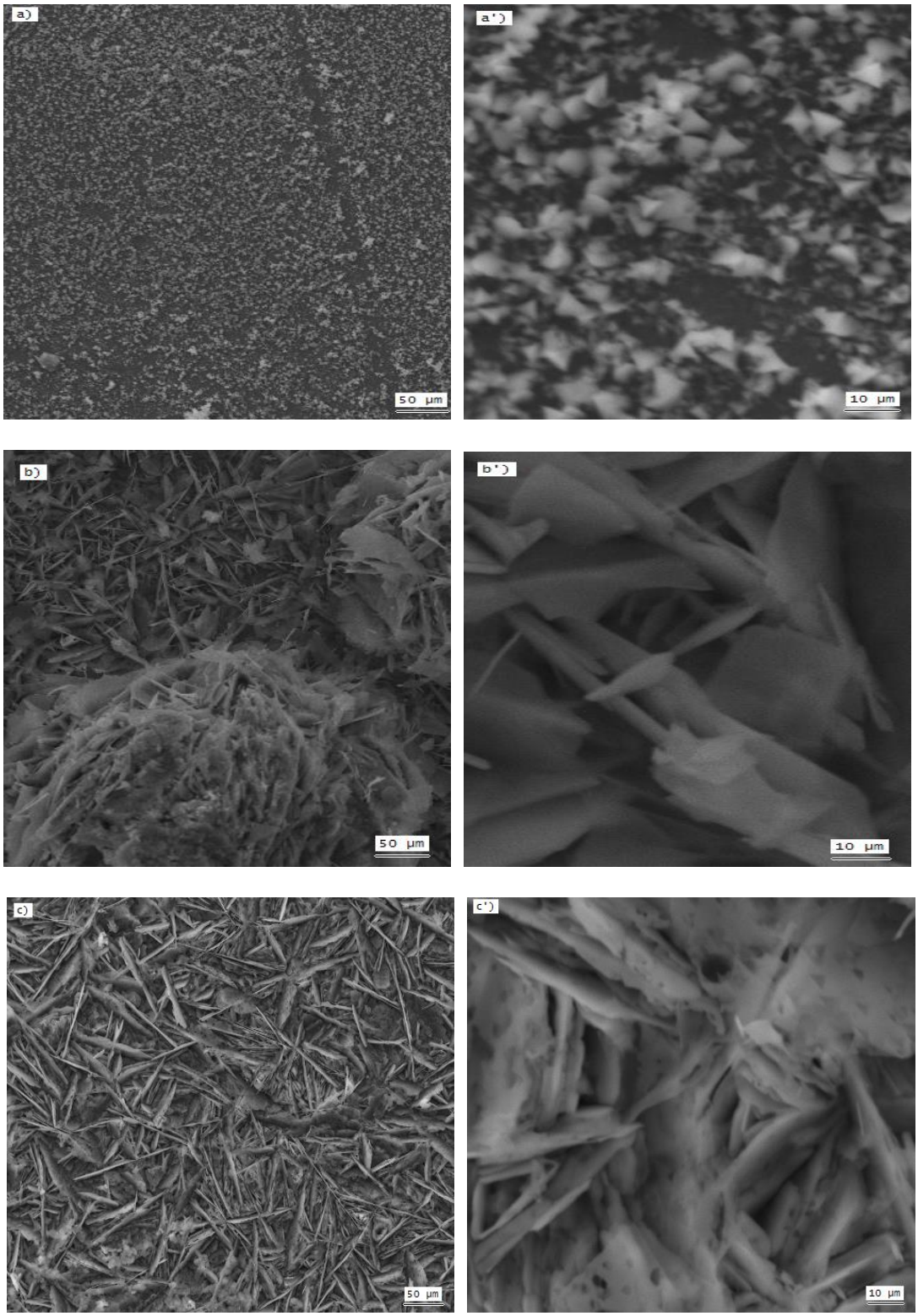

Figure 3. SEM micrographs showing the surface morphology of the ZnO nanostructures deposited at different deposition potential: a) -1.2 V, b) -1.3 V and c) -1.4 V vs. SCE. Fig. 4 a'-c' showing the higher magnification images of the same samples.

These pores are observed with both SEM and AFM techniques that an increase in roughness, due to high ZnO content, leads to formation of large pores without any change in morphology

[11]. The perforated morphology of the as-deposited ZnO nanowalls obtained in the present work could be very promising for applications in dye-sensitized solar cells because of their larger surface area available for adsorbing the dye molecules as sensitizer [12].

The phase and crystallinity of the as-deposited ZnO nanostructures on the FTO glass substrate were investigated using XRD. Fig. 4 shows the X-ray diffraction spectra of ZnO thin films grown at different potentials. The diffraction patterns can be indexed to diffraction peaks from ZnO and substrates. From the XRD spectra, the films are found to be polycrystalline with hexagonal wurtzite structure (JCPDS 01-076-0704) and depend on the deposition potential. In effect, the (002) preferential orientation observed for sample (c) deposited at -1.3 V vs. SCE change to (101) for samples (d) and (e) deposited at -1.4 and -1.5 V vs. SCE, respectively. Moreover, some small peaks are observed for ZnO samples (a) and (b) deposited at high potentials.

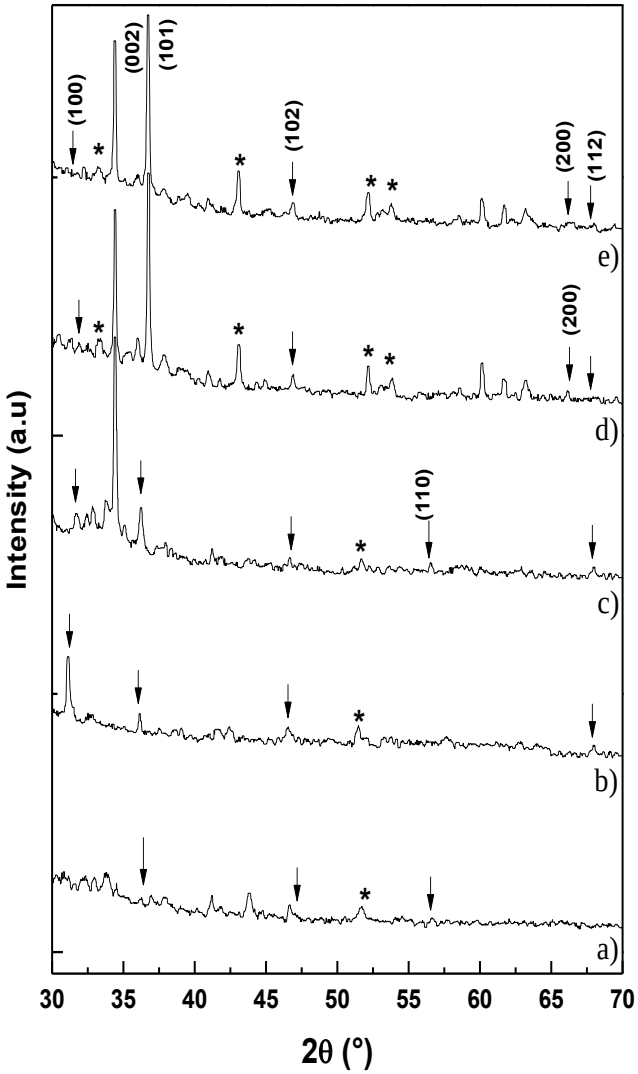

Figure 4. X-ray diffractograms of ZnO nanostructures at various deposition potentials: a) -1.1 V, b) -1.2 V, c) -1.3 V, d) -1.4 V and e) -1.5 V vs. SCE. Composition bath: aqueous solution of 0.1M $Zn(NO_3)_2$ + 1 M KNO_3 and pH 6. * for FTO diffraction peaks.

These specters showed that the structure of the deposited films was sensitive to the electrode potential used for the deposition of ZnO nanostructures. In order to determine the variation of

the average crystallite size (D), the size of the crystallite oriented along the (101) plane is calculated using Scherrer's formula [13]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad [6]$$

where β, θ, and λ are the broadening of the diffraction line measured at half its maximum intensity in radians (FWHM), the diffraction angle and the x-ray wavelength, respectively. The grain size, calculated by the Scherrer equation after correcting for instrumental broadening, from the (101) peak ranges from 50 to 100 nm. From XRD and SEM observation, it is clear that the size, shape of ZnO nanostructures depend on the potential depositions.

Conclusion

In this work, ZnO nanostructures prepared by electrochemical deposition (ECD) method from aqueous zinc nitrate solution at 65 °C onto fluorine doped tin oxide (FTO) coated glass substrates were investigated. Characterization of ZnO nanostructures was realized using conventional electrochemical techniques, scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. Cyclic voltammetry experiments were performed to elucidate the electrodic processes that occurred when potentials were applied and the optimum potential for electrodeposition were determined. From single-step potential experiment in the potential ranges from -1.1 to -1.4 V, the formation of ZnO nuclei in the early deposition stages was proceeded according to the three dimensional (3D) instantaneous nucleation followed by diffusion-limited growth rather than a progressive one. SEM images demonstrated that the morphology of ZnO nanostructures depend greatly on the potential depositions. XRD studies revealed that the deposited films were polycrystalline in nature with wurtzite phase.

References

[1] X. Lan, J. Y. Zhang, H. Gao, T. M. Wang. Morphology-controlled hydrothermal synthesis and growth mechanism of microcrystal Cu_2O. CrystEngComm 2011; 13:63-636.
[2] S. Chatterjee, S. Gohil, B. Chalke, P. Ayyub. Optimization of the morphology of ZnO nanorods grown by an electrochemical process. J. Nanosci. Nanotechnol 2009; 9 (8) 4792-4796.
[3] M. R. Khelladi, L. Mentar, A. Beniaiche, L. Makhloufi, A. Azizi. A study on electrodeposited zinc oxide nanostructures. J Mater Sci: Mater Electron *2013;*24:153-159
[4] T. Pauporte, D. Lincot. Hydrogen Peroxide Oxygen Precursor for Zinc Oxide Electrodeposition I. Deposition in Perchlorate Medium. J. Electrochem. Soc 2001; 148: C310-C314.
[5] M. Izaki, T. Omi. Transparent zinc oxide films prepared by electrochemical reaction. Appl. Phys. Lett 1996; 68 (1996) 2439-2440.

[6] B. Scharifker, G. Hills. Theoretical and experimental studies of multiple nucleation. Electrochim Acta 1983. 28:879- 889.
[7] G. Gunawardena, G. Hills, I. Montenegro, B. Scharifker. Electrochemical nucleation: Part I. General considerations. J. Electroanal. Chem. 1982; 138: 225-239.
[8] J. Lee, S. C. Nam, Y. Tak. On the origin of electrodeposition mechanism of ZnO on ITO substrate. Korean J. Chem. Eng 2005; 22:161-164.
[9] B. A. Taleatu, A. Y. Fasasi, G. Di Santo, S. Bernstorff, A. Goldoni, M. Fanetti, L. Floreano, P. Borghetti, L. Casalis, B. Sanavio, C. Castellarin-Cudia. Electro-chemical deposition of zinc oxide nanostructures by using two electrodes. AIP Adv 2011; 1: 032147.
[10] D. Pradhan, Susanta K. Mohapatra, S. Tymen, M. Misra, K. Tong Leung. Morphology-Controlled ZnO Nanomaterials for Enhanced Photoelectrochemical Performance. Mater. Express 2011; 1: 59-67.
[11] Waldo J. E. Beek, Lenneke H. Slooff, Martijn M.Wienk, JanM. Kroon and Rene' A. J. Janssen. Hybrid Solar Cells Using a Zinc Oxide Precursor and a Conjugated Polymer. Adv. Funct. Mat 2005; 15:1703-1707.
[12] K. Nonomura, D. Komatsu, T. Yoshida, H. Minoura, D. Schlettwein. Dependence of the photoelectrochemical performance of sensitised ZnO on the crystalline orientation in electrodeposited ZnO thin films. Phys. Chem. Chem. Phys 2007; 9:1843- 1849.

[13] B.D. Cullity, Elements of X-ray Diffraction, second ed., Addison-Wesley, Reading, MA, 1978, vol. 91 501.