CHAPTER IV
Effect of Bath Temperature on the Electrodeposition of Zinc Oxide thin films
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CHAPTER-IV
Effect of Bath Temperature on the Electrodeposition of Zinc Oxide thin films

4.1. Outline

In this chapter the temperature dependent nucleation and growth mechanism of the electrodeposited zinc oxide (ZnO) thin films on fluorine doped tin oxide (FTO) coated (10-20 Ω/cm²) glass substrates from acetate solution were examined by using chronoamperometry technique. The morphological, compositional and structural properties were studied by scanning electron microscopy, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction techniques. The current transients were analyzed by fitting chronoamperometric data into the Scharifker-Hills nucleation model.
4.2. Introduction

Zinc oxide (ZnO), II–VI compound semiconductor with direct band gap energy of 3.37 eV and a relatively high exciton binding energy (60 meV) at room temperature, is an excellent material for UV lasers [1]. It offers many complementary and competitive advantages to GaN, which has a similar band gap and lattice constant. It has been used for applications such as transparent conducting films, solar cell windows, photonic devices in ultra violet range, light emitting diodes and laser diodes over GaN [2]. The development of simple, low-cost, and solution deposition methods to grow zinc oxide has attracted much attention in recent years. The special interest is the preparation of highly porous, high surface area ZnO films due to their importance in the fields of high efficiency dye-sensitized solar cells, gas sensors etc. [3]. It is well-known that pure zinc oxide exhibits a luminescence in near-UV (3.2–3.3) eV by the recombination of bound excitons, [4] and a very broad green luminescence band [5].

Some groups reported molecular oxygen or nitrate ions [6,] as precursors for ZnO electrodeposition. The reaction mechanism in presence of molecular oxygen was discussed by D. Lincot et al. and stated that in the formation of ZnO the alternative reaction of hydroxide formation may take place [7]. R.E. Marotti et al. have systematically studied the dependence of band gap energy on the deposition temperatures [8]. A template-free electrodeposition (ED) method for preparing highly ordered ZnO nanoneedle arrays on oriented gold film coated silicon (Au/Si) substrate at a lower temperature (70°C) and at atmospheric pressure was used by Weiping Cai [9]. Films of high structural quality have been produced at a temperature around 70°C [4] by D. Lincot et al. in 2005. Organic molecules [10] or metal-organic complexes [11] in the inorganic oxide matrix during the deposition can significantly enhance the kinetics of oxygen reduction reaction and allow the preparation of films at lower over voltages.

In this chapter, we report on the preparation and characterization of ZnO thin film deposited at various temperatures by a simple electrochemical technique. The electrochemical properties such as nucleation density, saturated nuclei density, nucleation rate constant, nucleation growth mechanism and chemical state of ZnO thin films were studied.
4.3. Experimental procedure

Zinc oxide thin films were deposited from an aqueous zinc acetate (HIMEDIA AR grade, 99.5%) bath containing 50 mM zinc acetate solution and 0.1M KCl. The bath solution was complexed at pH 10.5 by adding NaOH solution to the zinc acetate solution. This solution is denoted as precursor solution. Electrolytic baths maintained at different temperatures were utilized for the deposition on ultrasonically cleaned F-doped SnO₂ (FTO) conducting glass substrates of 3 cm² area (10-15 Ω/cm).

Electrochemical measurements were performed by using potentiostat EG & G make Versastat-II (PAR 362) model controlled by personal computer (PC) in three electrode cell configuration with electrochemistry software M270. The electrochemical quartz crystal (EQCM) measurements were taken using electrochemical analyzer (model-CHI-400A) made by CH instrument, USA. EQCM measurements were performed onto platinum electrode of 1 cm² area in specially designed electrochemical cell. The EQCM measurements were performed with electrolytic baths, containing oxygen and Zn⁺², only oxygen and zinc alone. The scan rate, 10mV/s was kept constant for all the experiments. The thin films of zinc oxide were obtained by potentiostatic electrodeposition at -0.750 mV (vs SCE) for 60 minutes with FTO coated conducting glass substrate as a working electrode, a platinum wire as a counter electrode and saturated calomel electrode (SCE) as a reference electrode (SCE, \( E_0 = 244 \text{ mV Vs SHE, the standard hydrogen electrode} \)). The working and counter electrodes were placed parallel to each other separated by a distance of 1 cm. Oxygen gas was bubbled through the bath during the electrodeposition. Zinc acetate can react with water in presence of dissolved oxygen to form ZnO at this potential as follows.

The mechanism for the formation of OH⁻ from dissolved \( \text{O}_2 \) is as follows

\[
2\text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 4\text{OH}^- \quad (4.1)
\]

In presence of zinc acetate following reaction takes place

\[
\text{Zn(CH}_3\text{COO)}_2 + 2\text{H}_2\text{O} \rightarrow \text{Zn}^{+2} + 2\text{CH}_3\text{COOH} + 2\text{OH}^- \quad (4.2)
\]

The overall reaction for the formation of ZnO is

\[
\text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (4.3)
\]
The bath temperature was maintained at 35°C, 55°C and 75°C, and accordingly samples are denoted as S₁, S₂, S₃, respectively and those produced at room temperature are denoted as S₀. The surface morphology of the samples was observed using a JEOL-JSM-6360 scanning electron microscope (SEM). X-ray diffraction (XRD) spectra of the films were recorded on an X-ray diffractometer (Philips PW-1710) with Cu-Kα radiation of 1.5418 Å wavelength. The film thickness was measured using the AMBIOS make XP-1 surface profiler. The chemical state of the species in the thin film were analyzed by using X-ray photoelectron spectroscopy model PHOIBOS HSA3500 100 R4 [HWT type] with Mg analyzer of energy 1253.6 eV. The three dimensional morphology of the growth was examined by using atomic force microscopy (AFM), Nanoscope instruments USA, in contact mode, with V shape silicon nitride cantilever of length 100 μm and spring constant 0.58 N/m.

4.4. Results and Discussion

4.4.1 Cyclic Voltammetry and EQCM Study

The room temperature cyclic voltammetric study was carried out in the potential range +0.2 to -0.8 V vs SCE from 50 mM zinc acetate solution at 10 mV/s. Figure 4.1 (a-b) is associated with the reduction-oxidation behavior of the electrolyte on Pt electrode (area 1 cm²) accompanied by a concurrent shift in the frequency of the quartz crystal electrode with applied voltage. The arrows show the scan direction. The scans were initiated at +0.2 V vs SCE, reversed at -0.8 V (vs SCE) and terminated at +0.2 V (vs SCE). During the cathodic scan a peak at -0.4 V (vs SCE) due to oxygen reduction [3,6-7] is observed and the onset of Zn⁺² reduction is observed at -0.7 V (vs SCE), which can be seen in figure 4.1a as rise in current density and in figure 4.1b as increase in mass deposited onto the Pt electrode. According to EQCM theory [12,13], such a shift is proportional to an increase of mass on the electrode surface according to equation 4.

\[ \Delta f = \frac{-2f_0^2 \Delta m}{A/N_{q}^{1/2}} \quad (4.4) \]
where $f_0$ is resonant frequency (Hz), $\Delta f$ is frequency change (Hz), $\Delta m$ is mass change (g), $\rho_q$ is the density of quartz ($\rho_q = 2.648 \text{ g/cm}^3$), and $\mu_q$ is shear modulus of quartz ($\mu_q = 2.947 \times 10^{11} \text{ g/cm.s}^2$). The above relationship shows that, an increase in mass leads to a decrease in frequency, and that the magnitude of the change in frequency is directly proportional to the mass change. This is the basis for quantitative measurements of mass changes using the EQCM.

During the cathodic scan a peak at -0.4 V (vs SCE) is due to reduction of oxygen in the solution (figure 4.1a). This causes local pH to increase and a deep at -0.6 V on I-V curve. Further rise in the cathodic current beyond -0.6 V (vs SCE) reveals reduction of Zn$^{+2}$ on the electrode. Subsequently ZnO growth takes place via intermediate steps of hydroxide formation [12]. The onset of deposited is at -0.6 V (SCE) followed by rapid rise due to growth of ZnO (figure 4.1b). Upon reversal of plot scan the mass deposited on to the electrode continues to increase up to -0.55 V (vs SCE) and it is leveled off at -0.3 V (SCE). Here oxidation does not lead to decrease in mass indicating the presence of zinc oxide on the surface of electrode. This is in contradiction to the case of the bath with presence of zinc species alone in the solution, where increase in mass with cathodic current and decrease in mass with anodic current is observed (figure 4.2a). In this case there is no zinc oxide species deposited onto the surface of the working electrode, mass becomes almost zero during reverse scan as seen from figure 4.2 b. Similarly bath in presence oxygen species alone in the solution, diffusion controlled reaction takes place without increase in mass (figure 4.2c).

4.4.2. Nucleation and Growth modeling

Scharifker and Hills [14] model is further used to describe the nucleation process during initial few seconds using chronoamperometric techniques. Progressive nucleation corresponds to slow growth of nuclei on a less number of active sites, all activated at same time. Instantaneous nucleation corresponds to fast growth of nuclei on many active sites, all activated during the course of electro-reduction [15, 16]. Hence the transients have been further analyzed in reduced form in terms of the maximum current $i_{\text{max}}$ and the time at which the maximum current is observed, $t_{\text{max}}$ [14]. This
method of obtaining information about kinetics of the nucleation process has been used extensively for wide variety of systems [17, 18].

The fitting of the experimental curves with theoretical curves for the cells at different bath temperature are shown in Figure 4.3(a-d). At the room temperature the experimental curve resembles progressive nucleation process [15, 16]. At 35°C the data neither follows progressive nor instantaneous growth mechanism. Hence it follows an intermediate nucleation mechanism. Upon further increase in bath temperature (55°C and 75°C) instantaneous nucleation growth mechanisms prevail.

Figure 4.1 (a-b). The reduction-oxidation behavior of the electrolyte on Pt electrode (area 1 cm²) accompanied by a concurrent shift in the delta mass of the quartz crystal electrode with applied voltage
Figure 4.2 (a-b). Cyclic voltammetry and EQCM behavior in presence of only Zn species into the electrolyte.

Figure 4.2 (c). Cyclic voltammogram in presence of only oxygen species into the electrolyte.
Figure 4.3 (a-d) The non-dimensional \((i/i_{\text{max}})^2\) Vs \(t/t_{\text{max}}\) plots for Zinc oxide electrodeposition onto FTO coated conducting glass substrates for the samples a) \(S_0\) 25°C (room temp.), b) \(S_1\) 35°C, c) \(S_2\) 55°C and d) \(S_3\) 75°C.
4.4.3. X-ray diffraction (XRD) study

The structural changes and identification of phases were studied with the help of XRD technique. The diffraction angle 2θ was varied between 10 and 100°. Figure 4.4 shows the X-ray diffraction spectra of the films deposited at different bath temperatures. All the samples show polycrystalline nature. The peaks can be assigned to the (002), (200), (202), (203), (110), (103), and (104) planes of hexagonal wurtzite structure of ZnO (JCPDS data file number 75-1533, for ZnO). The (002), (103), (200), (104) crystal planes, becomes more prominent with increase in deposition bath temperature. The diffraction peaks related to FTO coated conducting glass substrates are indicated by *. The increase in deposition temperature leads to the increment in the crystallinity of the films is clearly observed in the XRD patterns. Figure 4.5 shows the average crystallite size along (002) peak estimated from the full width half maximum (FWHM) values of diffraction peaks using the Scherrer Formula [19].

\[
D = \frac{0.9\lambda}{\beta \cos \theta} \quad (4.5)
\]

where D is the crystallite size, β is the broadening of diffraction line measured at half of the its maximum intensity in radiance (FWHM), λ is the X-ray wavelength (1.5406 Å) used and θ is the diffraction angle. From this figure it is observed that the average crystallite size increases with bath temperature.

4.4.4. X-ray Spectroscopic Study

XPS analysis of ZnO films was performed to determine the chemical state of constituent element. Detailed analysis of as-prepared zinc oxide thin film was carried out by investigating Zn2P3/2, O1s and C1s core level spectra. The binding energies are calculated by taking carbon C1s peak (284.6) as reference. Figure 4.6 shows the typical wide XPS spectra of ZnO thin film deposited at 75°C. The Zn2P3/2, O1s and C1s spectra were observed at 1021.4 eV, 530.6 eV and 283.8 eV respectively. Figure 4.7 (a-b) shows core level XPS spectra of O1s, and Zn2P3/2 respectively. The peaks with low binding energy (530.6 eV) correspond to O^2- on normal wurtzite structure of
ZnO single crystal [20]. The binding energy of Zn2P3/2 peak of ZnO thin film is observed at 1021.4 eV as shown in figure 4.7b. This value is close to ZnO in agreement with literature data [20]. Similar XPS results are obtained for other samples.

Figure 4.4 The XRD patterns of the Zinc oxide thin films deposited from 50 mM aqueous zinc acetate solution for the samples S0 (25°C), S1 (35°C), S2 (55°C) and S3 (75°C) (substrate (FTO) peaks are labeled with *).

Figure 4.5. Variation of average grain size calculated from SEM with deposition temperature.
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Figure 4.6. Wide X-ray photoelectron spectra (XPS) for the films deposited at 75°C.

Figure 4.7 (a-b). Core level spectra for (a) oxygen (O1S) and (b) zinc (Zn 2P3/2) for the films deposited at 75°C.
4.4.5. Surface Morphological Study

Zinc oxide electrodeposits were analyzed by SEM to determine the influence of the bath temperature on the morphology. Figure 4.8 (a-d) shows surface morphologies of the films deposited at various deposition temperature viz 35°C to 75°C and 25 °C. Changes in film morphology with the deposition temperature were observed. Well defined grains of about 250 nm are obtained for the films deposited at room temperature (figure 4.8a). The hexagonal grains (shown in inset of figure 4.8 b) of about 400 nm are observed for the films deposited at 35°C. With increase in electrolytic bath temperature above 35°C the film morphologies change substantially and cluster like surface is formed, as shown in figure 4.8 (c and d). The increment in cluster size up to 0.5 μm (figure 4.8 d) is on account of the effect of temperature that causes instantaneous growth of the grains.

4.4.6. Atomic Force Microscopic (AFM) Study

The three dimensional (3D) morphology of the films can be observed by AFM. A quantitative method to examine the surface morphology and structure is obtained by analyzing the surface roughness using AFM. Figure 4.9 (A1, A2, A3 and A4)–(B1, B2, B3 and B4) shows 3D and 2D AFM images recorded for samples S0, S1, S2 and S3, respectively. The most important measurement of surface roughness can be given with a statistical parameter-root mean square (rms or Rq) that is the standard deviation of the height (Z) values within a given area. It has been observed with increase in deposition temperature crystallinity and cluster formation above 35 °C of the ZnO film increases and leads to increase in the surface roughness. Also the roughness of the films were recorded using XP-1 surface profiler and is increased from 27 to 72 nm for the films S0, S1, S2, and S3, respectively.
Figure 4.8(a-d). Scanning electron micrographs recorded for the samples a) S₀ (25°C), b) S₁ (35°C), c) S₂ (55°C) and d) S₃ (75°C).
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Scan size | 5.000 μm
Scan rate | 10.17 Hz
Number of samples | 256

Scan size | 10 μm
Scan rate | 10 Hz
Number of samples | 3
Figure 4.9. (A1, A2, A3 and A4)–(B1, B2, B3 and B4) shows 3D and 2D AFM images recorded for samples S0, S1, S2 and S3, respectively.
4.5. Conclusions

The ZnO thin films were electrodeposited on fluorine doped tin oxide coated conducting glass substrates at various electrolytic bath temperatures from an aqueous zinc acetate solution. The influence of deposition temperature on the nucleation and growth mechanism was studied using cyclic voltammetry and chronoamperometry. EQCM experiments on platinum working electrode revealed onset of mass deposited above -0.7 V (SCE). From the Scharifker-Hills model it is concluded that initially the growth process at room temperature is of progressive nature while for the sample deposited at 35°C electrolytic temperature the experimental curve follows intermediate process. Above 35°C it changes to an instantaneous one. From the X-ray diffraction patterns it is concluded that the films deposited from zinc acetate bath are of pure zinc oxide phase and crystallinity is improved with increase in bath temperature. The morphological changes were observed with deposition temperatures, granular structure changes to cluster like surface. From XPS measurements the chemical state of deposits was confirmed and found to be of pure Zinc oxide.
References
