Chapter 4

Electrochemical synthesis of ZnO nanowires films and their field emission studies
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4.1. Introduction:

This chapter describes the systematic studies on the influence of the process variables such as deposition time and concentration of the electrolyte on the structural and morphological features of the ZnO thin films. The effect of annealing process on the as-synthesized films in air at 400 °C for 4 hours has been investigated. The synthesized nanostructure thin films were characterized by various techniques. Finally, a possible mechanism describing the evolution of different morphologies and growth of the ZnO nanostructures is also discussed.

4.2. Experimental details:

Electrochemical synthesis of ZnO thin films was carried out in a conventional three electrode electrochemical cell in aqueous solution containing a mixture of ZnCl₂ and H₂O₂ (analytical grade) as a supporting electrolyte. The use of H₂O₂ is convenient since it is highly soluble in the aqueous medium and does not produce undesirable byproducts upon reduction. All deposition experiments were carried out at 82 °C, in which a polycrystalline Zn foil (purity ~ 99.99%, Alfa Aesar), platinum sheet and a saturated calomel electrode (SCE, E₀ = 0.244 V) were used as the working, counter and reference electrodes, respectively. In order to reveal the influence of the process variables, depositions were made using electrolytes of different molar concentrations, 0.002 M (ZnCl₂ = 0.002 M and 0.01 M H₂O₂), 0.004 M (ZnCl₂ = 0.004 M and 0.02 M H₂O₂), 0.016 M (ZnCl₂ = 0.016 M and 0.04 M H₂O₂) and deposition intervals of 10, 20, 30 and 40 minutes durations. A computer controlled electrochemical analyzer (Model-1100A Series, CH Instrument, USA) was used to maintain the cathodic polarization condition at -1.4 V with respect to the SCE. The electrolyte was constantly stirred during the deposition. Prior to each electrodeposition experiment,
the substrate and the platinum electrode were ultrasonically cleaned in acetone and methanol, for 10 minutes in each solvent, respectively. The working electrode (Zn foil), after the fixed deposition time, was removed from the electrolyte and dried in air. For each case, the 'as-synthesized' thin film was annealed in air at ~ 400 °C for 4 hours. The heating rate was 3 °C/min.

The cathodic electrodeposition of ZnO from aqueous solution of zinc salt occurs as per the following reactions [1]:

\[
\begin{align*}
  \text{H}_2\text{O}_2 + 2 \text{e}^- & \rightarrow 2\text{OH}^- \\
  \text{Zn}^{2+} + 2\text{OH}^- & \rightarrow \text{Zn(OH)}_2 \\
  \text{Zn(OH)}_2 & \rightarrow \text{ZnO} + \text{H}_2\text{O}
\end{align*}
\]

(4.1)  (4.2)  (4.3)

In the first step, hydroxide ions are generated at the surface of the cathode (working electrode) by the reduction of an oxygen precursor (equation-1) which react chemically with Zn\textsuperscript{2+} ions in the solution to form Zn(OH\textsubscript{2}) at the cathode (equation-2). Subsequently, Zn(OH\textsubscript{2}) is spontaneously dehydrated into ZnO particles on the working electrode (equation-3).

In order to study, the synthesis parameters of the various specimens are listed in Table (4.1).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Electrolyte</th>
<th>Time deposition (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ZnCl\textsubscript{2} + H\textsubscript{2}O\textsubscript{2} + 2x10\textsuperscript{-3} M + 1x10\textsuperscript{-3} M</td>
<td>40</td>
</tr>
<tr>
<td>B</td>
<td>ZnCl\textsubscript{2} + H\textsubscript{2}O\textsubscript{2} + 4x10\textsuperscript{-3} M + 2x10\textsuperscript{-3} M</td>
<td>40</td>
</tr>
<tr>
<td>C</td>
<td>ZnCl\textsubscript{2} + H\textsubscript{2}O\textsubscript{2} + 16x10\textsuperscript{-3} M + 4x10\textsuperscript{-3} M</td>
<td>40</td>
</tr>
</tbody>
</table>

Table (4.1): The experimental parameters of the specimens.
4.3. Results and discussions:

4.3.1. Deposition time and electrolyte concentration studies:

In order to study the influence of deposition time and concentration of the electrolyte, initially the deposition time was optimized and then the synthesis was carried out at different electrolyte concentrations for the optimized deposition interval. Figure (4.1) depicts the SEM images of the ‘as-synthesized’ ZnO thin films deposited for 10, 20, 30 and 40 minute durations, using a fixed electrolyte concentration of ~0.002 M. The micrographs clearly show that the growth rate is proportional to the deposition time. The ZnO thin film, deposited for 10 minute duration, shows uniform ‘granular’ morphology on the entire substrate surface. With the increase in the deposition time, the grains were observed to agglomerate to form ‘platelet’ structures (as seen in Figure 4.1(c)). For the deposition interval of 40 minute, the ZnO thin film exhibited two distinct morphologies, the ‘2-dimensional’ (2-D) sheets randomly oriented on the area near the electrolyte-air interface and the ‘granular’ structures below the interface region (Figure 4.1(d) and its inset). The formation of randomly oriented 2-D sheets on the area near the interface region may be attributed to the specific growth mechanism. It may be speculated that, the OH\(^-\) generation rate is more in the vicinity of the electrolyte-air interface region than elsewhere, as the interface region gets a continuous supply of oxygen from the ambient due to continuous stirring. The more is OH\(^-\) generation rate, more is the rate of formation of ZnO particles. These ZnO particles do not find new nucleation sites and get attached to the ‘platelet’ structures.

Upon annealing in air at ~400 °C for 4 hours, interestingly, all the films exhibited formation of ZnO wires on the entire substrate surface, irrespective of the initial morphology. The typical ‘post-annealed’ SEM images corresponding to 10 and 40 minutes deposition duration are shown in Figure (4.2). The density of ZnO wires is seen to be higher in the 40 minutes case as compared to the 10 minutes case, which is attributed to the higher growth rate and growth time. Zhang et al. have reported formation of nanowires upon annealing the electrochemically synthesized ZnO thin film on conducting glass substrate [2]. Although the authors claim formation of
nanowires, a careful observation of the SEM images reveals the presence of '2-D nanosheets' along with a few nanowires. Also the aspect ratio of these nanowires is less than that obtained in the present case. Evolution of various morphologies of electrodeposited zinc metal films on indium-tin oxide coated glass substrates, subjected to annealing in air at different temperatures, has been recently reported by Zou et al. [3]. It is interesting to note that the authors have not observed formation of nanowires upon annealing. The formation ZnO wires with high density and higher aspect ratio, in the present case, is noticeable.

Figure (4.1): SEM images of the as-synthesized ZnO thin films deposited using electrolyte concentration of 0.002 M for (a) 10, (b) 20, (c) 30 and (d) 40 minute durations. The inset in figure (d) depicts the SEM image of the area below the electrolyte-air interface region.

Figure (4.1): SEM images of the as-synthesized ZnO thin films deposited using electrolyte concentration of 0.002 M for (a) 10, (b) 20, (c) 30 and (d) 40 minute durations. The inset in figure (d) depicts the SEM image of the area below the electrolyte-air interface region.
4.3.2. XRD studies:

The XRD patterns of the specimens A, B and C (annealed in air at $\sim 400 \, ^{\circ}\text{C}$ for 4 hours) depicted in Figure (4.3), exhibit a set of well defined diffraction peaks indicating polycrystalline nature of the thin films. The diffractions peaks are indexed to the wurtzite hexagonal phase of ZnO, by comparing the observed d-values with the standard JCPDS data [4]. The XRD patterns of the as-synthesized specimens (before annealing) were found to be identical to those depicted in Figure (4.3), except that the intensities of the diffraction peaks are less than those of the post-annealed case. We have not observed any diffraction peaks corresponding to Zn (OH)$_2$ phase, indicating the formation of exclusively the ZnO phase under the experimental conditions.
4.3.3. SEM studies:

The SEM images of as-synthesized and post-annealed thin films of specimens A, B and C are as seen in Figures (4.4), (4.5) and (4.6), respectively. In case of the as-synthesized films, the surface exhibits two distinct morphologies, viz. 2-D sheets on the region in the vicinity of the electrolyte-air interface and granular structures on the area below this interface (deep inside the electrolyte). The 2-D sheets are seen to be randomly oriented but most of them are perpendicular to the substrate surface. The thickness of these sheets ranges from 30 to 100 nm. The granular structures have diameters ranging from 200 nm to 500 nm and are densely packed.

Figure (4.3): XRD patterns of ZnO thin films (specimens A, B and C) post-annealed in air at 400 °C for 4 hours.
Figure 4.4: SEM images of the as-synthesized ZnO thin film specimen A corresponding to (a) electrolyte-air interface region (b) the area below this region, respectively; (c) and (d) are the SEM images of Specimen A post-annealed in air at 400 °C for 4 hours, recorded at different magnifications.

A careful observation of the SEM images shows that as the concentration of the electrolyte is increased, (i) density of the 2-D sheets increases, (ii) more and more 2-D sheets get vertically aligned, (iii) at higher concentration, the 2-D sheets are characterized by well defined sharp edges depicting hexagonal shape and (iv) the "granular structures (formed on the area below the interface) show more surface roughness. The observed variation in the surface morphology can be attributed to
higher growth rate due to availability of large number of precursors with the increased concentration of the electrolyte.

Figure (4.5): SEM images of the as-synthesized ZnO thin film specimen B corresponding to (a) electrolyte-air interface region (b) the area below this region, respectively; (c) and (d) are the SEM images of Specimen B post-annealed in air at 400 °C for 4 hours, recorded at different magnifications.

It is interesting to note that the surface morphology of the annealed films is characterized by the presence of the ZnO wires on the entire substrate surface, irrespective of the initial morphology, in each case. As seen from the Figures (4.4), (4.5) and (4.6), the ZnO wires have average diameters of ~150 nm, 120 nm, 100 nm
and length of several μm, ranging from 2 to 20 μm. The ZnO wires are randomly oriented and a few of them are seen to be protruding outside the substrate surface. A careful observation of the micrographs shows that with the increase in the concentration of the electrolyte, the wires become thinner, longer and exhibit higher density.

Figure (4.6): SEM images of the as-synthesized ZnO thin film specimen C corresponding to (a) electrolyte-air interface region (b) the area below this region, respectively; (c) and (d) are the SEM images of Specimen C post-annealed in air at 400 °C for 4 hours, recorded at different magnifications.
4.3.4. EDS studies:

A typical EDS spectrum of specimens C shown (Figure (4.7)) the presence of Zn and O only, indicating the chemical composition of ZnO.

![Figure (4.7): A typical EDS spectrum of the post-annealed specimen C.](image)

4.3.5. TEM studies:

In order to investigate whether the ZnO wires are ‘nanocrystalline’ or not, the specimens were characterized using transmission electron microscope (TEM). A typical TEM image of specimen C, shown in Figure (4.8(a)), indicates that the wires have diameters in the range of 30 - 40 nm. Figure (4.8(b)) shows a magnified TEM image of one of such ZnO nanowire. A careful observation of the images reveals that the nanowires are tapered at the end, with apex diameter < 10 nm. A high resolution
transmission electron microscope (HRTEM) image, shown in Figure (4.8(c)) clearly indicates crystalline nature of the ZnO nanowires. The selected area electron diffraction (SAED) pattern shown in Figure (4.8(d)) also confirms the polycrystalline nature of the ZnO nanowires. Thus the TEM results clearly indicate formation of nanocrystalline ZnO wires.

Figure(4.8): TEM images of the post-annealed ZnO thin film specimen C (a) showing a number of ZnO nanowires, (b) an individual ZnO nanowire, (c) HRTEM image and (d) selected area electron diffraction (SAED) pattern.
4.3.6. PL studies:

A study of the photoluminescence (PL) spectrum is an effective technique to evaluate both ZnO defects in the ZnO lattice and its optical property. A typical PL spectrum of ZnO exhibits emission peaks UV (~ 380 nm), blue (~ 460 nm), green (~ 510 nm) and red/orange (600 - 650 nm) [5, 6]. The PL spectra of the post-annealed specimens A, B and C are shown in Figure (4.9). For all the specimens, the ultraviolet (UV) emission band, centered at ~ 385 nm is observed. The UV emission is known to be due to the direct recombination of free excitons [7]. The relatively weak UV emission observed in specimens B and C can be attributed to the presence of the defect states that may trap the photo-generated holes and/or electrons. Other peaks at ~ 411 nm (for specimen B and C only), ~ 470 nm (blue emission) and ~ 519 nm (green emission) may be due to the defect state luminescence. The visible luminescence mainly originates from defect states such as Zn interstitials and oxygen vacancies [8, 9]. Specimen C shows a number of peaks in the visible emission region suggesting that the defect level and surface recombination rate is higher in thinner nanowires [10].

![Figure (4.9): Photoluminescence spectra of specimen A, B and C (post-annealed in air at 400 °C for 4 hours.)](image)
4.3.7. Growth models:

Vapor-Liquid-Solid (VLS) and Vapor-Solid (VS) mechanisms have been proposed to explain the self-catalysis growth of the 1-Dimensional nanostructures. The VLS process consists primarily of three steps, (1) formation of the liquid alloy droplet, (2) formation of the crystal nucleus upon gas adsorption and supersaturation and (3) axial growth of the crystalline seeds to form nanowires. The diameter of nanowires grown via the VLS process is determined by the size of liquid alloy droplet. The main characteristic of the VLS process is the existence of a nano-sized alloy droplet which acts as a nucleation site or seed for the growth of the nanostructures and the alloy droplet is mostly seen at the apex of the nanostructures [11, 12]. As we have not observed the presence of such droplets at the tip of the nanowires, the growth of nanowires, in the present case, is suggested to be different form the VLS mechanism. The VS mechanism involves condensation (at low temperature region) directly from the vapor phase (high temperature region). This mechanism results in a very typical morphology wherein the diameter of the micro- and/or nanostructure decreases gradually to form a sharp tip [13, 14]. In the present studies, although the TEM results reveal tapering of the ZnO nanowires at the apex, the formation of ZnO nanowires can not be attributed to the VS growth process. This is because in the present experiment it is difficult to identify the high and low temperature regions. Hence it can be proposed that the growth of the ZnO nanowires occurs via the gas-solid-tip growth process [15, 16]. During annealing in air at ~ 400 °C, the Zn atoms undergo solid-phase diffusion through the surface of Zn foil and oxygen from the atmosphere may react with the previously formed Zn/ZnO grains and sheets (nucleation sites) leading to the growth of ZnO nanowires on the substrate surface. The growth direction is likely to be determined by the balance between the growth rate and the diffusion rate of Zn atoms along a given direction and this makes the [101] axis a preferential growth direction of the ZnO nanowires. The TEM observations reveal gradual narrowing of the wires towards the end/apex. This shows that the Zn atom diffusion appears to be the limiting factor, and the growing tip results into tapering due to restricted supply of Zn.
4.3.8. FEM studies:

The field emission current density versus applied field (J-E) curves of the specimens A, B and C (post-annealed in air at 400 °C for 4 hours) recorded at the base pressure of 1 x 10⁻⁸ mbar is depicted in Figure (4.10). A semi-transparent phosphor screen, used as an anode, was held parallel to the cathode at a distance of ~ 1 mm. A pre-conditioning treatment, in terms of removal of the surface asperities and/or contaminants present on the emitter surface via ion bombardment was performed. For this purpose, the emitter was held at -2 kV with respect to the anode for 5 minutes. The values of the turn-on field, required to draw an emission current density of 0.1 μA/cm², are observed to be ~ 1.24 V/μm, 1.2 V/μm and 1.32 V/μm for specimens A, B and C, respectively. These values of the turn-on field were found to be reproducible and are lower than these reported for various ZnO nanostructures such as nanowalls (3.6 V/μm) [17], nanoneedles (2.4 V/μm) [18], nanopins (1.92 V/μm) [19] and nanowires (1.91 V/μm) [20]. As the applied voltage was increased, the emission current was observed to increase very rapidly and the current density of ~ 10 μA/cm² was drawn from the specimens A, B and C at an applied field of ~ 1.9 V/μm, 1.64 V/μm, and 1.96 V/μm, respectively. In the present studies, the turn-on field value is found to be influenced by the electrolyte concentration and the lowest value has been observed for specimen B as compared to the specimens A and C. The variation in the turn-on field can be attributed to the morphological features of the ZnO nanowires. As seen from the SEM results, although the ZnO nanowires in specimen C have smaller average diameter, their areal density is more. The higher areal density of the nanowires may result in the enhancement of the threshold field due screening effect. As the ZnO nanowires in the specimen B are sharper than those in the specimen A, it is expected that they will exhibit lower value of the turn-on field. In the present studies, the current density J is defined as J = I / A, where I is the measured emission current and A is the total area of the emitter. The dimensions of specimen A, B and C are 1cm x 1cm respectively, possessing total area ~ 1cm². Similarly, the applied field (E) is defined as E = V/d, where V is the applied potential and d is the separation between the anode and the cathode. This field is also referred to as an average field.
Figure (4.10): Field emission current density versus applied field (J-E) curves of (a) specimen A (b) specimen B and (c) specimen C. The insets depict the corresponding Fowler-Nordheim (F-N) plots.

The emission current density–applied field characteristics were analyzed by the Fowler–Nordheim (F–N) equation [21].

\[
J = A \left( \frac{\beta^2 E^2}{\phi} \right) \exp \left[ - \frac{B \phi^{3/2}}{\beta E} \right]
\]  

(4.4)

where, \(J\) is the emission current density, \(A\) (1.54 x 10^{-6} \text{ Ampere eV V}^{-2}) and \(B\) (6.8 x 10^{3} \text{ V eV}^{-3/2} \text{ µm}^{-1}) are constants, \(\phi\) is the work function and \(\beta\) is field enhancement factor.
R. Forbes has calculated the values of these constants using generalized correction factors that are functions of applied electric field and work function of the emitter [22]. The F-N theory is known to be valid for metallic emitters only. Analysis of the field emission data from a semiconducting emitter is not straightforward and various effects due to band bending, field penetration, variation in the barrier height, effective electron mass, and so on, need to be taken into account in order to explain the field emission characteristics [23-28]. The absence of a simple model, which takes into account the effect of all the above parameters related to the semiconducting emitter, has constrained the researchers to use the existing F-N theory for the analysis of the field emission data from such emitters.

The insets in Figure (4.10) depict the corresponding In (J/E^2) versus (1/E) curves, known as F-N plots, derived from the observed J-E characteristics. It is interesting to note that, all the plots exhibit non-linear nature over the entire range of the applied field. Similar non-linear F-N plots for various ZnO nanostructures and other semiconducting emitters [29-31]. The observed non-linearity has been attributed to the semiconducting nature of the emitter. For semiconducting emitters, the observed non-linearity can be understood on the basis of the emission mechanism. It is believed that, initially when the applied field is low, the emission current originate mainly from the conduction band and as the applied field is increased further, the valence band electron also tunnel out and contribute to the emission current [29].

For field emission based electron sources, along with the emission competence, the emission current stability is also a decisive parameter. The field emission current stability of the ZnO nanowires thin films has been investigated at the base pressure of \( \sim 1 \times 10^{-8} \) mbar. The I-t plots recorded over the duration of more than 6 hours are seen in Figure (4.11). The specimen A exhibits a good emission current stability and the current fluctuations are observed to be within ±10% of the average value. Excellent emission current stability is observed for specimen B, characterized by fluctuations within ±5% of the average value. In case of the specimen C, the emission current exhibits excursions to higher and lower values, with some ‘spike’ type fluctuations superimposed on it. The ‘spikes’ in the emission current are due to adsorption, desorption and/or migration of the residual gas molecules on the emitter surface. The excursions may be attributed to the variation in the number of emission sites. As the
morphology of the specimen C is characterized by ZnO nanowires possessing high aspect ratio, the mechanical stress induced by the applied electric field may cause change in the orientation of the wires. The field emission images recorded at the onset of the current stability measurement are shown as insets in the I-t plots.
Figure (4.11): Field emission current stability (I-t) plots of (a) specimen A, (b) specimen B, (c) specimen C. The inset shows a typical field emission image.

All the emission images exhibit a large number of bright spots, each corresponding to an emission site. The emission images are consistent with the emitter surface morphology. We have also studied the post field emission surface morphology of the emitters. The SEM images (not shown here) showed no severe deterioration of the emitter morphology indicating the robust nature of the ZnO nanowires.

4.3.9. Conclusions:

Nanocrystalline ZnO thin films have been synthesized by cathodic electrodeposition from aqueous solution on Zinc substrate. The XRD patterns show that the ‘as-synthesized’ and ‘post-annealed’ ZnO films posses a hexagonal wurtzite structure. The surface morphology of the as-synthesized ZnO thin film is found to be
influenced by the electrolyte concentration and deposition duration. The ‘as-synthesized’ ZnO thin films, prepared under the optimized conditions, show two distinct type of morphology, characterized by ‘2-D nanosheets’ and ‘granular nanostructures’ in the regions near the electrolyte-air interface and below it, respectively. Annealing of the thin films in air results in the formation of ZnO nanowires of high density and high aspect ratio. The SEM and TEM analysis reveal that the ZnO wires are nanocrystalline in nature having average length ranging from 2 to 20 μm and diameter in the range of 30 - 40 nm. The turn-on field, required to draw an emission current density of 0.1 μA/cm², was found to be ~ 1.24 V/μm, 1.2 V/μm and 1.32 V/μm for specimens synthesized using different concentrations of the electrolyte, which are lower than those reported for various ZnO nanostructures. The F-N plots show non-linear behaviour in the entire range of the applied field indicating semiconducting nature of the emitter. The ZnO nanowires show excellent emission current stability at the present value of ~ 10 μA over duration of more than six hours.
References:


