Electrodeposition of highly oriented ZnO microarrays

ABSTRACT
A highly oriented ZnO microarray was electrodeposited over indium tin oxide (ITO) glass substrate. An aqueous solution of 0.01 M Zn(NO$_3$)$_2$ at a low temperature of 80°C, without any additives was used for the electrodeposition at a predetermined potential (-1.2 V) using cyclic voltammetry (CV). The as deposited ZnO thin film was characterized using XRD and AFM. The XRD pattern reveals the growth of ZnO along a preferred orientation of (002) plane. Particle size from XRD data calculated using Scherrer relation gives 40 nm. AFM image shows that deposited ZnO cluster is highly oriented in one direction. Thus, a simple electrodeposition route could be employed to grow highly oriented ZnO thin film in an efficient way without any additives.
6.1 Introduction

Zinc oxide (ZnO), which is a wide band-gap transparent semiconductor attract a large attention from various researchers during these last few decades [1-9]. ZnO found many applications in the field of optoelectronics, electroluminescent displays (ELDs), field emission displays (FEDs), vacuum fluorescent displays (VFDs), laser diodes and also for the construction of smart devices [10-15]. Many researchers have investigated the control growth of this material. Recent trend shows the production and controlled growth of ZnO nanoparticles in the form of nano-rods [16-24], nanosheets [25-28], nanopillars [29-32], nano-cubes [33-35], nano-wires [36-40], nano-columns [41-44] and column-to-rod bilayers by using various methods, such as physical vapor deposition [45-47], sol-gel process [48-52], chemical vapor deposition (CVD) [53-57], electrochemical deposition [58-62], metalorganic vapor phase epitaxy [63], template assisted growth [64], pulsed laser deposition [65] and soft solution methods [66]. Among these various methods, electrodeposition which is simple and inexpensive is found to be one of the most widely used technique to control the film morphology, thickness, composition and other chemical and physical properties. The various physical and chemical properties of the deposited metal oxide depends on the experimental parameters like electrolyte composition/concentration, bath temperature, solution pH, electrode potential, or current density, deposition time and also on the substrate morphology [16,17,19,20,25,37,41]. In our present study, we have deposited the ZnO nanoparticles on indium doped tin oxide (ITO) (indigenously prepared) conducting glass substrate without using any kind of additives or surfactants. The optimum potential for ZnO deposition was monitored using Cyclic Voltammmeter (CV). Further, the deposited films were characterized using X-ray diffraction (XRD) and Atomic force microscopy (AFM).
6.2 Experimental Details

6.2.1 Preparation of ZnO

All reagents used in this experiment were of analytical grade and used without further purification. Voltammetric studies were carried out using a three-way electrode equipped in electrochemical analyzer (CHInstrument 602C) connected to an IBM computer for data analysis and controlling the instrument. Platinum electrode (99.95% purity supplied by Hindustan Platinum) having a surface area of 4cm² was used as the counter electrode and a saturated calomel electrode (SCE), as the reference electrode for recording all the readings, was connected to the cell through a luggin capillary. The electrodeposition was carried out on steel substrate and ITO conducting glass substrate in a solution of Zn(NO₃)₂ at various concentration range using potentiostatic electrolysis technique. The cyclic voltammogram was recorded from 25 mL of 0.01M Zn(NO₃)₂ solution using ITO glass substrate maintaining the temperature constant at 80°±0.1°C. The scan rate was kept fixed at 10mV/s. After the electrodeposition has been carried out, the deposited films were repeatedly washed with double distilled water and dried in a current of dry nitrogen gas.

6.2.2 Characterization

The prepared samples were characterized by X-Ray diffraction (XRD) using Philips powder diffractometer (model PW 1071) with CuKα (1.5405 Å) radiation and Ni filter. Cyclic voltammeter CHInstrument 602C and SOLVER Atomic Force Microscopy (AFM) model NT-MDT.

6.3 Results and discussion

6.3.1 Cyclic Voltammogram

Fig. 6.1 shows the cyclic voltammograms over steel electrode for various Zn(NO₃)₂ concentrations showing increase in the current density with increase in the concentration. The cyclic voltammogram shows a gradual increase in the cathodic current density with increasing the potential, a small peak at around -1.0V shows the formation of Zn(OH)₂ at the substrate surface which will hydrolysed to
ZnO. As we go on increasing the potential upto -1.5V, it results in bulk deposition of Zn accompanying with hydrogen evolution. So, the potential for ZnO deposition is chosen such that there is optimum deposition of ZnO on the ITO glass substrate.

**Fig. 6.1** Cyclic voltammograms over steel electrode at various Zn(NO$_3$)$_2$ concentrations showing increased in the current as the concentration of Zn(NO$_3$)$_2$ increases

**Fig. 6.2** Cyclic voltammograms over ITO glass electrode at various Zn(NO$_3$)$_2$ concentrations showing increased in the current as the concentration of Zn(NO$_3$)$_2$ increases

The potential at -1.2V with respect to SCE was found to be suitable for ZnO deposition. The electrodeposition of ZnO was carried out for 30 mins on ITO substrate and also on steel substrate for comparing the morphology of ZnO deposits on different substrate. ZnO film deposited on steel substrate was not well adherent to the substrate surface whereas the electrodeposition carried out on ITO conducting glass substrate was found to be highly adherent to the substrate surface.
The open circuit potential for the electrodeposited ZnO electrode is depicted in Fig. 6.3. Similarly, Fig. 6.4 shows the Linear sweep voltammograms for the electrodeposited ZnO over ITO glass electrode from various Zn(NO$_3$)$_2$ concentrations after electrodeposition for 1200 seconds. The deposition of ZnO from different Zn(NO$_3$)$_2$ concentration were made potentiostatically under stationary condition and then immediately oxidized by means of voltammetric scan at 10 mVs$^{-1}$ in the potential range -0.9 to 0.0 V. The stripping potential peak was found to be shifted towards more negative potential for the ZnO deposited from more concentrated bath, which indicates the formation of more stable ZnO deposits at higher concentration (in the above studied concentration range).
6.3.2 X-ray Diffraction

Fig. 6.2 (b) shows the XRD pattern of ZnO deposited over ITO. From the XRD pattern it clearly reveals the deposition of crystalline ZnO. Perusal observation of the XRD pattern (Fig. 6.2 (b)) shows any peaks responsible for ITO (Fig. 6.2 (a)), thus indicating homogeneous deposition of ZnO over ITO. The highest peak intensity for ZnO along (002) plane as compare to the remaining peaks, indicates highly crystalline ZnO with preferred orientation along c-axis perpendicular to substrate. The average crystallite size was calculated using Debye-Scherrer equation from FWHM of highest peak. The crystallite size obtained for the deposited ZnO film is found to be around 40 nm, which is in good agreement with the size calculated from AFM studies.

From Fig. 6.2 (c), it is seen that peaks corresponding to ZnO was also observed which depicts that ZnO can be deposited over steel substrate; however, as compared to the deposits obtained over ITO substrate, the peaks corresponding to ZnO is not well defined. Signal corresponding to steel substrate dominates over the ZnO peaks.

Fig. 6.2 XRD patterns of (a) ITO, (b) ZnO deposited over ITO and (c) ZnO deposited over steel
6.3.3 Atomic Force Microscopy

Fig. 6.3 (a), (b) & (c) shows a typical micrograph of AFM images of the as deposited ZnO over ITO glass substrate. AFM images revealed that the deposited ZnO film has highly directional micron size spindle shaped structure. The spindle shape ZnO microarrays are highly directional and oriented only in one direction, which are closely packed together with each other. Perusal observation shows that the size of each spindle is about 1µm in breath and 2µm in length. Table 1 gives the roughness calculation for the deposited ZnO film. The average roughness value obtained is 55 nm, which is in good agreement with the size calculated from the XRD data. The negative value of Surface skewness (\(S_{sk} = -0.446171\)), indicates the predominance of valleys, and the coefficient of kurtosis, \(S_{ka}\) value less than 3 indicates a bumpy surface. The ten point height, \(S_z\) is used for evaluating the surface texture on limited access surfaces such as small valve seats or the floors and walls of grooves, particularly where the presence of high peaks or deep valleys is of functional significance. The \(S_z\) calculation reduces the effects of odd scratches or irregularities; it gives a value of 267 nm.

![AFM Image](image-url)
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Fig. 6.3 (b) A three dimensional AFM images of as deposited highly oriented spindle shaped ZnO microarrays

Fig. 6.3 (c) Magnified AFM image of the deposited ZnO thin film showing the spindle shaped ZnO microarrays

Fig. 6.4 Particle size distribution of ZnO microarrays deposited at -1.2V vs. SCE for 1800 seconds, over ITO glass substrate, showing 280-380 nm as the average ZnO spindle size
Table 1 Histogram results for ZnO electrodeposited over conducting ITO glass substrate

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
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<tbody>
<tr>
<td>Amount of sampling</td>
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<tr>
<td>Max</td>
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</tr>
<tr>
<td>Min</td>
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<tr>
<td>Peak-to-peak, Sy</td>
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<tr>
<td>Ten point height, Sz</td>
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<td>Average</td>
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<td>Root Mean Square, Sq</td>
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<tr>
<td>Surface skewness, Ssk</td>
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<tr>
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</table>

6.4 Conclusions

In this present work, well aligned spindle shaped ZnO microarrays are successfully electrodeposited in a preferred orientation i.e. (002) plane which is perpendicular to the substrate surface (ITO conducting glass substrate) without the addition of any additives. Comparison of the XRD data for deposits obtained using steel substrate and ITO glass reveals that, well aligned ZnO nanoparticles is electrodeposited preferentially over ITO rather than steel substrate. The crystallite size obtained for the deposited ZnO nanoparticle is found to be around 40 nm, which is in good agreement with the size calculated from AFM studies.
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