ZnO Nanorods Grown Electrochemically on Different Metal Oxide Underlays

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Abstract. In this study we present results on electrochemically grown ZnO nanorods on different metal oxide underlays, such as ZnO seed layers with different morphologies, ZnS and TiO$_2$ compact thin films produced by spray pyrolysis on transparent conductive oxide (TCO) substrates. Also in this work we present results on ZnO nanorods directly deposited on some chosen TCO substrates. The relationship between nanorod formation and substrate properties were studied. All ZnO nanorod layers were grown electrochemically using ZnCl$_2$ aqueous solutions (c=0.2 mmol/L) at the bath temperature of 80 °C during one hour. The structural properties and morphology of metal oxide underlays and ZnO nanorods grown on them were studied by scanning electron microscopy (SEM), x-ray diffraction spectroscopy (XRD). Depending on the substrate morphology, ZnO rods with different dimension, orientation, shape and density were obtained. For instance, larger rods (d~200 nm, l~700 nm) were obtained on substrates, such as ITO/glass, FTO/glass and ZnO:In/ITO/glass. Smaller rods (d~60 nm, l~350 nm) were obtained on smooth, uniform and fine-grained underlays, such as ZnS and TiO$_2$.

1. Introduction

Zinc oxide (ZnO) is an n-type II-VI semiconductor with a direct band gap (3.37 eV) and large exciton binding energy of 60 meV [1-2]. ZnO has attracted research interest in recent years due to its potential applications in various nanodevices such as lasers and light emitting diodes [3], gas sensors [1, 4], field emission devices [1, 4] and solar cells [4, 5]. For hybrid organic/inorganic solar cells with “absorber layer/ZnO nanorod/blocking layer/TCO (transparent conductive oxide)” structure, it is highly important to synthesize ZnO nanorod/blocking layer/TCO structures. In order to increase the solar cell performance, it is desired to obtain high aspect ratio (l/d, where l – length and d – diameter) conductive ZnO nanorods. Among various deposition techniques, electrodeposition is a promising approach for growing ZnO nanorods, because it is simple, low-cost, low temperature and easily scalable to large-area deposition [6-7].

Morphology of the substrate has a particular significance in nanorods growth. A seed layer (usually ZnO thin film) is required prior to the electrodeposition of the ZnO nanorods to contribute the rods growth or improve their vertical alignment [1, 8, 9]. For some applications (emitting diodes, solar cells), it is required to grow ZnO nanorod directly on a transparent conductive oxide [10-11]. In this paper, we present a study on the growth of ZnO nanorods by electrodeposition on various substrates: 1) commercially available indium tin oxide (ITO) and fluorine doped tin oxide (FTO) coated glass substrates, 2) set of ZnO seed layers with various morphologies prepared by spray pyrolysis onto ITO/glass substrates and 3) ZnS and TiO$_2$ thin films deposited by spray pyrolysis on ITO/glass
substrates. Herein we study relationship between the initial morphology of the substrate and final morphology of the ZnO nanorod layer. The morphology and structural properties of the substrates and ZnO nanorods deposited on them, respectively, are studied by means of high resolution scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques.

2. Experimental

2.1. Synthesis details
Prior the deposition, ITO and FTO covered glass substrates were washed thoroughly with soap, ethanol and sulphuric acid. The samples were rinsed with deionised water after each cleaning step. On some chosen ITO/glass and FTO/glass substrates, the ZnO nanorods were deposited directly onto the substrate. Commercially available ITO/glass substrates have been chosen for the deposition of metal oxide underlays such as ZnO seed layers, ZnS and TiO$_2$ thin films prepared by using spray pyrolysis method as described in details earlier [12-13]. Electrodeposition of ZnO nanorods was carried out potentiostatically in a three-electrode glass cell, where the TCO/glass was used as a working electrode, while a silver/silver chloride/3M KCl (Ag/AgCl/KCl) and a platinum (Pt) wire were used as reference and counter electrodes, respectively.

Solution of 0.2 mmol ZnCl$_2$ (Sigma-Aldrich), and 0.1 M KCl in amount of 50 ml was utilized as a supporting electrolyte. The growth temperature was kept at 80 $^\circ$C using a temperature controlled circulating bath. Deposition time was fixed to 1 hour. Electrochemical deposition was done under -1.0 V potential, vs the reference electrode using the Radiometer Analytical potentiostat PGP201.

2.2. Characterization
The morphology of the substrates was studied by the high resolution scanning electron microscope Zeiss EVO-MA15 at the operating voltage of 10 kV. The crystal structure of the nanorods was characterized by using X-ray diffraction on a Rigaku Ultima IV diffractometer using CuK$\alpha$ radiation ($\lambda=1.5406\text{Å}$, 40 kV at 40 mA). Crystals density was evaluated from the SEM surface images, from area of 6.2 $\mu$m$\times$4.7 $\mu$m.

3. Results and Discussion

3.1. Deposition of ZnO rods on TCO electrodes
In this study two different types of conducting electrodes were used: commercially available ITO and FTO coated glass substrates. The SEM images of TCO electrodes are shown in figure 1a (from ITO/glass) and in figure 1c (from FTO/glass). Corresponding morphologies of the electrodeposited ZnO layers directly grown on ITO and FTO electrodes are presented in figures 1b and 1d, respectively. As can be seen from the figures, the final shape of the ZnO nanorods differs depending on the substrate morphology. In case of ITO/glass, the rods are thinner (d~170 nm, l~700 nm) and show higher density ($\sim7.4\times10^8$ cryst/cm$^2$) than those grown on FTO/glass (d~300 nm, l~600 nm, density $\sim6.5\times10^8$ cryst/cm$^2$). Such difference can be explained by the difference in the morphology of the substrate. Higher density of the grains on the FTO electrode (Figure 1c) provoke large amount of nuclei that can further coalescence and promote the lateral growth of the crystal. Similar behaviour has

Figure 1. SEM images of: a) ITO/glass substrate; b) ZnO nanorods grown onto ITO/glass, c) FTO/glass substrate, d) ZnO nanorods grown onto FTO/glass.
already been reported for spray pyrolysis deposited ZnO nanorods on ITO/glass and FTO/glass substrates [14-15]. The resistivity of the substrates might be also a reason of such difference in final shape of the ZnO crystals. In our case, the ITO has lower resistivity ($\rho \sim 15-20 \ \Omega \cdot \text{cm}$) than resistivity of the FTO substrate ($\rho \sim 150 \ \Omega \cdot \text{cm}$). It was reported earlier by Kim et al., that conductive substrates greatly affect on the structural and optical properties of ZnO nanorods [16].

3.2. Deposition of ZnO nanorods on ZnO seed layers obtained by spray pyrolysis

In previous studies on ZnO thin films by spray pyrolysis [17-19], it was shown that temperature, concentration of the precursor solution (zinc acetate), dopant type and amount are the most important technological parameters that influence the morphology of the film. Here we prepared ZnO seed layers by spray pyrolysis on ITO/glass substrates using different technological parameters mentioned above. The morphology of ZnO seed layers are shown in figures 2a, 2c, 2e and 2g. The SEM images of ZnO nanostructures grown on those seed layers are presented in figures 2b, 2d, 2f and 2h, respectively.

Seed layer SL-1 is compact and flat, composed of densely packed fine grains. As a result, ZnO nanorods grown on SL-1 have a diameter of 80 nm and length of ca. 270 nm, and show uniform dense coverage (figure 2b). SL-2 seed layer from solution with higher concentration at the same temperature have highly structured surface composed of the flake-like grains with different sizes (figure 2c). Because of such nonuniformity in the dimensions of the grains on this substrate, the sizes of the ZnO rods vary greatly. ZnO nanorod layers compose of smaller crystals ($d \sim 80 \ \text{nm}$) as well as of much larger crystals ($d \sim 350 \ \text{nm}$) with length of ca. 300 nm (figure 2d). Seed layer SL-3 is also composed of grains with different shapes including platelets and nanoneedles (figure 2e). The ZnO nanostructures grown on this seed layer are mixture of fat and thin compactly standing ZnO crystals ($d \sim 150-300 \ \text{nm}$, $l \sim 150 \ \text{nm}$) (figure 2f). The ZnO nanorods have been deposited also onto ZnO:In seed layer. SEM image for SL-4 seed layer is presented in figure 2g and for the resultant ZnO nanorod crystals in figure 2h. Rods have uniform dimensions ($d \sim 200 \ \text{nm}$, $l \sim 700 \ \text{nm}$) comparable to those grown on bare ITO/glass layer. Rods grown on ZnO:In are markedly larger than those grown on undoped ZnO layers, that might be explained with difference in conductivity of ZnO:In and ZnO films [20-21].

XRD patterns of ZnO seed layers and of samples with ZnO nanorod grown on those seed layers are presented in figure 3. All the samples show the reflections at $2 \theta$ of 31.73°, 34.36° 36.21° and 62.75° corresponding to the (100), (002), (101) and (103) planes of ZnO (PDF 01-080-0074) [20].
For the SL-1 seed layer, the $I_{(002)}/I_{(100)} \approx 1$ and $I_{(002)}/I_{(101)} \approx 4$ (figure 3a). As in ZnO powder reference [20] the $I_{(002)}/I_{(100)} \approx 0.7$ and $I_{(002)}/I_{(101)} \approx 0.4$, thus the crystallites in SL-1 film are orientated along the (002) plane parallel to the substrate. The $I_{(100)}/I_{(002)} \approx 1.9$ is characteristic of the SL-2 ZnO seed layer, in ZnO powder $I_{(100)}/I_{(002)} \approx 1.4$, thus the orientation is along the (100) plane (figure 3b). For the SL-3 ZnO seed layer the $I_{(103)}/I_{(002)} \approx 2$, in ZnO powder $I_{(103)}/I_{(002)} \approx 0.7$, thus the crystallites are orientated along the (103) plane (figure 3c). According to XRD pattern of ZnO:In film (figure 3d), the intensity of the (002) reflection is negligible and the intensity of the (101) is the strongest, the crystallites do not have preferred orientation. Observed result is in a good correspondence with the results of earlier studies [21]. Therefore, according to the XRD patterns presented in figure 3, all the ZnO underlays show different crystallographic orientations. Herein are presented intensities ratios of resultant ZnO nanostructured layers: $I_{(002)}/I_{(101)} \approx 1.6$, $I_{(100)}/I_{(101)} \approx 1.2$, $I_{(103)}/I_{(002)} \approx 2.2$, $I_{(002)}/I_{(101)} \approx 1$ (figures 3a, b, c, d, respectively). Comparing them with the ZnO powder references [20] where the $I_{(002)}/I_{(101)} \approx 0.4$, $I_{(100)}/I_{(101)} \approx 0.56$, $I_{(103)}/I_{(002)} \approx 0.7$, $I_{(002)}/I_{(101)} \approx 0.4$ it seems that for all resultant ZnO nanostructured layers intensities ratios changed. Orientation along the (002) plane is characteristic of all electrodeposited ZnO layers except of ZnO rods on seed layer SL-2 (figure 3b). It could be that differences in seed layer thicknesses (SL-2 is deposited from more concentrated solution than SL-1 and thus SL-2 layer is probably thicker [15, 22]) or surface morphologies (compare figures 2a and 2c) are responsible for such kind behavior. XRD study shows that the ZnO rods grow preferably along the (002) plane parallel to the substrate independent of the orientation of corresponding ZnO seed layer.

3.3. Deposition of ZnO nanorods on ZnS and TiO$_2$ underlays grown by spray on ITO/glass substrates

For some purposes (dye-synthesized solar cell etc.) it is important to have a less conductive thin barrier layer between TCO and ZnO nanorods, therefore it is important to find out technological parameters in order to grow nanorods on such types of the substrate. Here we prepared ZnS and TiO$_2$ thin films by spray pyrolysis using knowledge of the earlier studies on ZnS [23] and TiO$_2$ films deposition by spray [24]. Both ZnS and TiO$_2$ films have smooth morphologies according to SEM images (figures 4a and 4c). Both substrates resulted in very uniform and dense coverage of well-shaped hexagonal ZnO nanorods. The dimension of the rods grown onto ZnS are slightly larger (d~150 nm, l~450 nm), than those grown on TiO$_2$, (d~60 nm and l~370 nm). The difference in rods dimensions could be explained by different surface roughness on ZnS and TiO$_2$ underlays.

![Figure 3. XRD patterns of the nanorods grown on different ZnO seed layers: a) SL-1; b) SL-2; c) SL-3; d) SL-4; x – reflections from ITO/glass substrate.](image)

![Figure 4. SEM images of the a) ZnS underlay; b) ZnO nanorods deposited on underlay (a); c) TiO$_2$ underlay; d) ZnO nanorods deposited on underlay (c).](image)

4. Conclusions
Herein we presented a study on the growth of ZnO nanorods by electrodeposition on various substrates: commercially available ITO, FTO substrates on glass, metal oxide underlays such as ZnO seed layers, ZnS and TiO$_2$ thin films prepared by using spray pyrolysis. The underlays with highly structured surface composed of grains with different sizes provoke the growth of ZnO crystals with different sizes and shape. ZnO rods were grown on smooth, flat, uniform and fine-grained substrates, such as ITO, FTO, ZnS and TiO$_2$ thin films, ZnO seed layer obtained at 320 °C and c=0.05 mol/L and indium-doped ZnO seed layer. The conductivity of the substrates might also affect the shape of resultant ZnO crystals. Electrically more conductive substrates- such as ITO, FTO and indium-doped ZnO seed layer provoke the growth of ZnO rods with larger dimensions. Thus, dimensions, shape and density of the rods depends strongly on the properties of the substrate or seed layer used, the orientation of the seed layer has minor effect.

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