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Characterization of nanostructured ZnO grown by linear sweep voltammetry

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ABSTRACT

Highly transparent and well aligned ZnO nanorods (NRs) have been synthesized by linear sweep voltammetry (LSV) on fluorine doped tin oxide (FTO) glass substrates. The effect of electrodeposition parameters such as sweep rate and number of cycles was investigated by scanning electron microscopy (SEM), X-ray diffraction, photoluminescence (PL) and UV–visible spectroscopy. The deposited ZnO NRs show hexagonal zincite structure and a high transmittance up to 95% in the near infrared and part of the visible region. The density, the orientation and the optical properties of ZnO NRs were strongly affected by the type of the sweep rate, and this was related to the nucleation mode involved in each case.

1. Introduction

Zinc oxide is a well-known n-type semiconductor, with a large band gap (3.36 eV) and large exciton binding energy (60 meV) at room temperature [1]. Because of these characteristics, ZnO has attracted global interest for potential applications, for instance LED applications [2,3], sensors [4] and photovoltaic [5]. In solar cells, ZnO is widely used in different solar cells structure such as Cu_2ZnSnS_4 [6], CuInGaSe [7], perovskite solar cells [8] and polymeric solar cells [9].

Different morphologies of ZnO nanostructures like nanorods, nanotubes, and nanoparticles have been deposited by various processes [10–13]. A large variety of these techniques require sophisticated instruments with high temperature and high vacuum and thus high cost. Thereby, there is a growing interest in cost effective wet chemical techniques like sol–gel [14], chemical bath deposition (CBD) [15], successive ionic layer adsorption and reaction (SILAR) [16], spray pyrolysis [17] and electrodeposition [18–22]. Considering the current interest in the nanostructured oxides, electrodeposition is an excellent method to deposit nanostructured zinc oxide. In addition, it has several obvious advantages, such as simple, a low cost process and a good quality of deposited films [19]. Furthermore, this technique allows the use of different shapes and kinds of substrates and leads to different sizes and shapes of zinc oxide [20].

In this study we report on the growth of ZnO NRs by a linear sweep voltammetry technique in aqueous zinc nitrate solution. The effect of electrodeposition parameters was investigated by studying the morphological, structural and optical properties of deposited zinc oxide.

2. Experimental procedure

The electrochemical growth of ZnO NRs was carried out in a classical three electrodes system, where a platinum metal sheet (2 cm²) as counterelectrode and saturated calomel electrode (SCE = +0.24 vs. SHE) as a reference electrode. FTO substrates were used as a working electrode. The choice of FTO is justified by its low resistivity (6–8 Ωm) and transparency (70–81% in the range of 400–800 nm). Prior to electrodeposition, the substrates (1 cm^2) were cleaned ultrasonically in HCl aqueous solution for 10 min, acetone for 10 min and bidistilled water. Finally they were dried in ambient air. The aqueous solution used to deposit ZnO NRs consisted of 1 mM $Zn(NO_3)_2 \cdot 6H_2O$ and 0.1 M KCl. The pH value of the solution was 5.4. The distance between the FTO substrate and the counterelectrode was maintained at 3 cm. Bidistilled water was

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used for the preparation of our solutions. Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%) and potassium chloride (KCl, 99.5%) were purchased from Aldrich chemical company. All the samples were deposited at 65 °C without magnetic agitation. After the electrodeposition, all the samples were annealed for 1 h at 350 °C in air.

The electrochemical studies were carried out using a VoltaLab PGZ 301 equipped with Volta Master 4 software. X-ray diffraction was performed using a Bruker with K-Alpha 1 ($\lambda = 1.54060$ Å). The surface morphology of deposited zinc oxide was observed by an environmental scanning electron microscope ESEM (Quanta 200-FEI). The optical properties were evaluated by an ultraviolet–visible (UV–vis) spectrometer (Shimadzu UV-3101PC spectrophotometer) at room temperature.

3. Results and discussion

3.1. Growth mechanism

The growth mechanism of ZnO is known and well described in many works [21,22]. Under appropriate potential, the reduction of nitrate ions is taking place near the cathode leading to the formation of OH^- ions and automatically an increase in the local pH. The generated hydroxide reacts with Zn^{2+} to form $Zn(OH)_2$ at the cathode. $Zn(OH)_2$ is spontaneously dehydrated into ZnO. This process can be summarized by the following equations [23]:

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

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

$$Zn(OH)_2 \rightarrow ZnO + H_2 \quad (3)$$

Corresponding to the overall reaction:

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

In order to highlight the ZnO deposition mechanism, voltammetry experiments were performed on FTO substrate in an aqueous solution containing 1 mM of $Zn(NO_3)_2 \cdot 6\ H_2O$ and 0.1 M KCl at 65 °C (Fig. 1). The potential scan was initiated in the negative direction from the open circuit potential at scan rate of 10 mV/s. The voltammogram recorded shows an increase of the cathodic current with negative scan of the electrode potential from −0.5 V which might be related to the reduction of nitrate ions. Consequently, no electrochemical reaction is taken place under −0.5 V as reported by different studies [18,23]. During the reverse anodic scan, no anodic peak was observed which indicates that no zinc metal was previously deposited. These results are in good agreement with other studies [24,25].

Based on voltammetry cyclic results, ZnO NRs were electrochemically synthesized using a linear sweep voltammetry technique, which is based on linear variation of applied potential between two values. In this work, the potential was varied between −0.4 and −1.1 V (vs. SCE). Two different samples were deposited using LSV technique under different conditions. While sample A was prepared under a varied potential starting from −0.4 to −1.1 V with a sweep rate Sr = −1 mV/s (reverse sweep), sample B was prepared under a varied potential starting from a higher negative value −1.1 V and decreasing to −0.4 V with a sweep rate Sr = +1 mV/s (direct sweep). In order to increase the thickness of deposited NRs, the scan was repeated three times for both samples. The deposition time was around 35 min.

3.2. Structure analysis

Fig. 2 shows X-ray diffractogram of samples A and B grown using different sweeps rate: Sr = +1 mV/s and Sr = −1 mV/s. In addition to FTO peaks (denoted as *), the X-ray diffractogram shows three peaks at $2\theta = 31.78°$ ($d_{100} = 2.816$ Å), $2\theta = 34.64°$ ($d_{002} = 2.601$ Å) and $2\theta = 36.29°$ ($d_{101} = 2.475$ Å). Those peaks are due to the diffraction of (100), (002) and (101) planes. All the diffraction peaks can be indexed to the hexagonal phase of ZnO (Zincite, space group P63mc, JCPDS Card no. 36-1451). The peak (002) is the strongest in sample B, which means that the nanorods were grown with a *c*-axis preferential orientation, while in the other sample, the (002) peak intensity decreases. The grain size of the samples was evaluated from the XRD line broadening using the Scherrer method:

$$D = k\lambda/\beta \cos\theta \quad (5)$$

where *D* is the crystallite size, λ (0.154060 nm) is the wavelength, *k* a constant equal to 0.9, β is the peak width at halfmaximum and θ is the peak position. The average crystallite size was found to be 42 nm for both ZnO samples.

3.3. Surface morphology of ZnO

Fig. 3 displays a typical plan view micrographs of deposited samples using LSV technique. All the samples are composed of nanorods with well-defined hexagonal facet. As shown in Fig. 3 (a) and (b), sample A is composed of nanorods with an average diameter size of about 200 nm and a very low density of nuclei

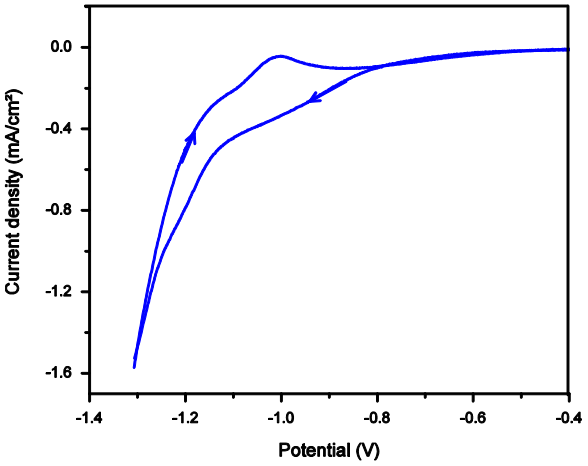

Fig. 1. Cyclic-Voltammetry *J–V* characteristic of FTO/glass substrate electrode for the solution containing 0.1 M KCl + 1 mM $Zn(NO_3)_2$ at pH = 5.4. The scan rate was 10 mV/s and the temperature was maintained at $T = 65$ °C.

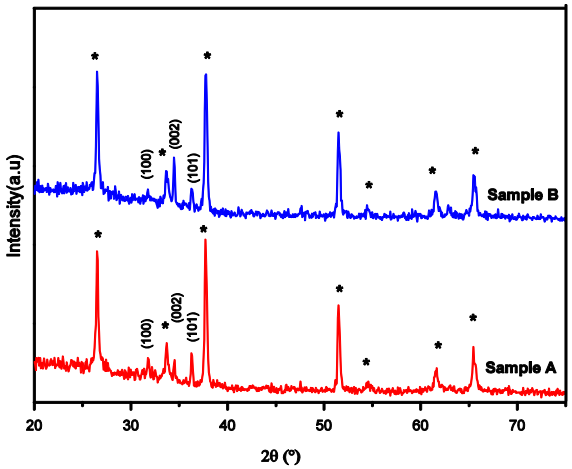

Fig. 2. XRD patterns of ZnO NRs grown using LSV technique, sample A: reverse sweep with Sr = −1 mV/s and sample B: direct sweep with Sr = +1 mV/s.