



Structural evolution of ZnO nanoporous films fabricated using prolonged electrodeposition under pulsed voltages

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ARTICLE INFO

Article history:

Received 5 July 2011

Received in revised form 18 August 2011

Accepted 18 August 2011

Available online 24 August 2011

Communicated by R. Wu

Keywords:

Zinc oxide

Electrochemical growth

Nanostructures

X-ray diffraction

Characterization

ABSTRACT

ZnO nanoporous films consisting nanocrystals on ITO-coated glass substrates were prolongedly electrodeposited under pulse voltages in zinc nitrate solution at room temperature. Their structures were found to be determined by experimental parameters, especially, the voltage and the deposition time. On the basis of the structural characterization, the growth mechanism was proposed as a combined growth process: the competitive growth between lateral overgrowth and nanovoid formation. The structural evolution is believed to be due to the decrease of surface potential with deposition time, leading to the formation of a quasi-two-layer structure. The revealed mechanism here could be helpful to understand the growth and corresponding properties of ZnO films as well as their nanostructures.

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1. Introduction

Zinc oxide (ZnO), which shows a lot of interesting properties such as piezoelectric effect [1], conductive effect [2], acoustic characteristics [3], direct band gap (3.3 eV), and absence of toxicity, have attracted increasing attention because of its application potential in optoelectronic devices [4]. Different methods have been engaged to prepare ZnO films, such as chemical vapor deposition (CVD) [5], thermal oxidation [6], radio frequency magnetron sputtering [7], pulsed laser deposition [8], electron beam evaporation [9], spray pyrolysis [10], and electrodeposition [11]. Among them, electrodeposition from aqueous solutions is widely believed to be a simple, environmentally friendly, and low-cost technique, by which uniform films with good stoichiometry could be produced with flexible controllability in structural properties [12]. Recently, highly oriented ZnO films have been heteroepitaxially electrodeposited onto single-crystal gold and GaN substrates, at 65 °C under direct constant (DC) voltages [13–15].

However, few works focused on the growth mechanism of ZnO film electrodeposited on polycrystalline substrate have been reported to date although ZnO film was electrosynthesized on ITO-coated glass by several researchers [11,12]. Besides, DC voltage was normally adopted during the electrodeposition of ZnO film [11].

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Obviously, if the deposition is conducted under pulsed voltage, the time interval can effectively avoid the accumulation of the Joule heat, making the electrolyte temperature more stable. Besides, the nominal deposition time under pulsed voltage is expanded because the duty ratio is always less than 1 but the valid time is shorter. The expansion in nominal deposition time controlled by duty ratio tuning consequently slows down the deposition process correspondingly especially in the case of rapid growth under high DC voltage and in turn provides a powerful approach to effectively investigate the evolution of morphological and structural properties during the prolonged deposition process, which must be beneficial to understanding of the growth mechanism using electrodeposition and even other methods.

In our previous work we have fabricated ZnO film consisting ZnO nanoparticles on ITO-coated glass by electrodeposition method under pulse voltage at room temperature [16]. The surface morphology of ZnO film synthesized at room temperature is much smoother than that at higher temperature (e.g. 65 °C), which is different from previous results [12]. To go deeper into the formation mechanism, the structures of the ZnO films were analyzed in this work with different experimental parameters, such as the maximal value of voltage and the deposition time. With the help of time expansion by pulsed voltage, the structural evolution on deposition time was investigated in details using scanning electron microscopy (SEM) and low-incident-angle X-ray diffraction (XRD) measurements. The growth mechanism is explored as a combined growth process including lateral overgrowth and nanovoid formation. The evolution of the structural properties

along electrodeposition is considered to be the results of the surface potential decrease with deposition time.

2. Samples and experiments

ZnO nanoporous films were electrodeposited at room temperature (20 °C) on ITO-coated glass substrates in an aqueous solution containing 0.1 M zinc nitrate [Zn(NO₃)₂] with pH of about 5.0. A rectangular pulsed wave (pulsed period: 20 ms; pulsed duration: 1 s) was used in our current study, and therefore the electrodeposition rate is reduced to 1/50. For the sake of simplicity, the maximum value of the pulsed voltage will be used in following description. During electrodeposition process, a simple two-electrode arrangement was used, where ITO-coated glass was served as a cathode, Zn sheet (99.99%) as an anode, and nitrate ions as oxygen precursor. In order to analyze the evolution of the film properties during electrodeposition, several samples with different electrodeposition parameters were synthesized under pulsed voltages. The growth rate was found to be about 300 nm per hour under -1 V in our experiments. XRD analysis was performed with a Siemens D500 diffractometer operating in the normal mode (θ - 2θ) and the detector mode (low-incident-angle) with Cu K α radiation of 1.5406 Å. The surface morphologies were obtained on JSM-6335 SEM equipment of JEOL company.

3. Results and discussions

Morphological characterization demonstrates that all the ZnO films with prolonged electrodeposition exhibit nanoporous structures. The growth rate is disclosed to be ~ 300 nm/h at -1 V and is almost linearly proportional to the applied voltage. Fig. 1 shows the typical surface morphologies obtained by SEM observation of ZnO nanoporous films with different electrodeposition times under -1 V. In sample with deposition time of 180 min, some small crystals are embedded into the matrix of ZnO nanoporous film (Fig. 1(a)). With increasing deposition time to 225 min, the amount of the crystals increases remarkably (Fig. 1(c)). The micro-columns are aggregated to form coarse crystals of thorny shape. If the deposition continued, the fibrous nanosheets were formed after 400 min, as shown in Fig. 1(d). These morphologies of coarse crystals were previously observed in ZnO films electrodeposited under DC voltages [12], which prove the pulsed voltage used in our work can slow down the deposition process with the same final products, making further investigation feasible.

Fig. 2 shows the XRD patterns of ZnO nanoporous films prepared under various pulsed voltages with deposition time of 180 min. All the diffraction peaks obtained were attributed to wurtzite structure of ZnO [12]. The ZnO nanoporous film prepared under -1 V showed preferential orientation of (002) in which the density of surface energy per plane is minimum, while the nanoporous films prepared at high voltages (-2 and -4 V) do not exhibit clear preferential orientation (Fig. 2). In principal, the preferential orientation of ZnO films is governed by an equilibrium process which takes into account surface free energy [17]. A high voltage with a fast growth rate can affect the growth process of ZnO nanoporous film making the growth non-equilibrium. Thus the preferential orientations of the films are disturbed because of the random generation of the ZnO nuclei, which is consistent with the previous results for ZnO films prepared under DC voltages [11]. Fig. 3 shows XRD patterns of ZnO nanoporous films prepared with various deposition times under the pulsed voltage of -1 V. The sample with deposition time of 180 min shows highly (002) orientation, while samples with longer deposition time exhibit a randomly-distributed polycrystal nature. In addition, the existence of ZnO nanoparticles is proved by the slight broadening of the XRD peaks and the ZnO crystal size in nanoporous films

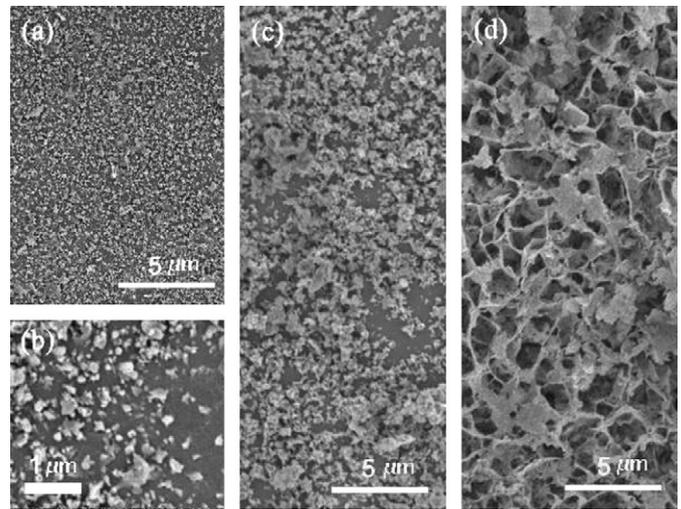


Fig. 1. SEM images of ZnO nanoporous films electrodeposited under pulsed voltage of -1 V with different times: (a) 180 min, (c) 225 min, and (d) 400 min. (b) is a magnified image of (a).

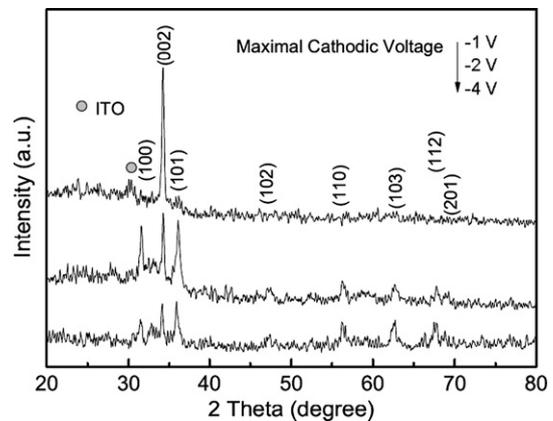


Fig. 2. XRD patterns of ZnO nanoporous films prepared under different pulsed voltages (-1, -2, and -4 V) with the deposition time of 180 min.

can be roughly estimated using Scherrer equation: $D_{hkl} = \frac{K\lambda}{\beta_{hkl} \cos \theta}$, where D_{hkl} is the mean crystallite size for the direction normal to the (hkl) plane, K a constant (the shape factor, and a value of 0.94 is used here), λ the wavelength of x-ray, β_{hkl} the width of the diffraction peak, and θ the half-scattering angle [18–20]. The mean crystal size for all the electrodeposited film calculated using ZnO (002) diffraction peak is ~ 30 nm which is much smaller than the SEM results presented in Fig. 1. The remarkably difference indicates that the ZnO nanoporous film consists the aggregation of the initially formed ZnO nanocrystals [21,22].

In order to further investigate the structural properties of our nanoporous films, sample with deposition time of 225 min under -1 V was selected and measured by low-incident-angle XRD, and the results are shown in Fig. 4. Different incident angles were adopted in the experiment and it is worth noting that at smaller incident-angle information from a thinner layer from the top surface will be collected. At incident-angle of 2°, the XRD pattern shows randomly distributed polycrystalline structure while the intensity of (002) peak increases with the incident-angle. The spectrum measured at an incident-angle of 16° resembles its counterpart obtained using normal θ - 2θ scan. The change of spectral lineshape with incident-angle in Fig. 4 indicates that nanoporous film is inhomogeneous along its growth direction.

On the basis of our XRD results we believe that our ZnO nanoporous film has a quasi-two-layer structure which involves a

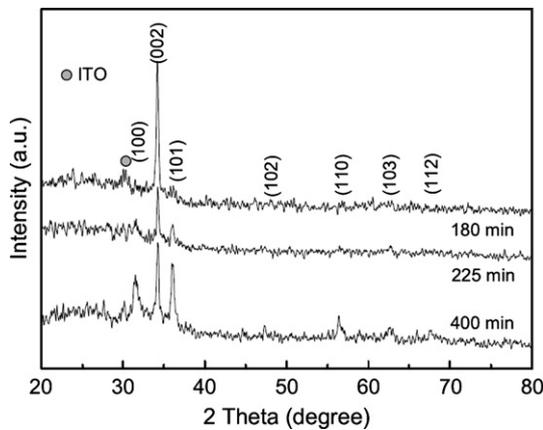


Fig. 3. XRD patterns of ZnO nanoporous films electrodeposited under pulsed voltage of -1 V with different times.

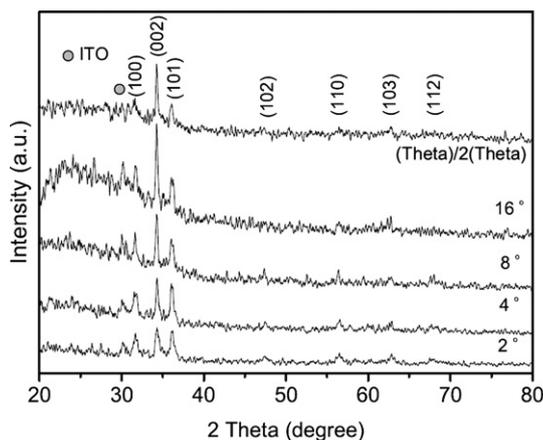


Fig. 4. XRD patterns of ZnO nanoporous film with deposition time of 225 min measured by low-incident-angle mode at different incident-angles.

highly (002) orientated ZnO layer and a randomly oriented polycrystalline structure lied on the former layer. This phenomenon was not observed in previous research work and what mechanism leads to the formation of such unique two-layer structure? Previous researches concerning epitaxial electrodeposition disclose two growth mechanisms: the lateral overgrowth mechanism [23], and a model based on Avrami Theorem and surface defects [14]. The latter model is not suitable for our growth process because of the polycrystalline nature of the ITO substrate, while the lateral overgrowth mechanism should still be applicable. Here, to explain our XRD results, we propose a combined growth mechanism to explain the growth of ZnO nanoporous film on ITO-coated glass: the competitive growth between the lateral overgrowth mechanism [23] and the nanovoid formation during film growth [14]. According the lateral overgrowth mechanism, the deposition proceeds on the epitaxial seeds, with the growth not only perpendicular to the surface but also laterally across the substrate (parallel to the surface) [23]. The nanovoid formation mechanism suggested that the growth of nanoporous films is realized via nanovoid formation (see the diagram in Fig. 5(a)) and can be determined by several experimental parameters such as substrate temperature and deposition kinetic energies [24]. It is well known that the nanovoid volume fraction and mean surface roughness of the deposited film increase with the decrease of deposition kinetic energy [24]. At the initial growth stage of our ZnO nanoporous film, the lateral overgrowth can compensate the formation of nanovoids as shown in Fig. 5(b). The existence of crystals embedded into the whole film as shown in SEM images were an evidence for our consideration. With further

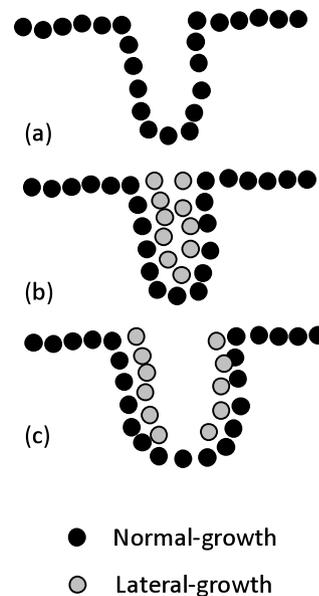


Fig. 5. Schematic diagrams show the formation process of ZnO nanoporous film. (a) Formation of nanovoids at initial stage. (b) Lateral overgrowth compensates the formation of nanovoids. (c) The void volume fraction increases with deposition time and the lateral overgrowth cannot completely compensate it.

increase of deposition time, the current decreases because partial applied voltage is shared by the pre-deposited ZnO film. As a result, the potential on the surface of the film decreases, reducing the deposition kinetic energy. The void volume fraction increases as suggested by molecular dynamic simulation [24] and the lateral overgrowth cannot completely compensate it as shown in Fig. 5(c). Therefore, polycrystal structure with coarse crystals is formed and becomes remarkable with deposition time.

4. Conclusions

ZnO nanoporous films consisting ZnO nanoparticles on ITO-coated glass substrates were prolongedly electrochemical deposited at room temperature using zinc nitrate solution as Zn source under pulsed voltages. The structural evolution on deposition time was carefully investigated with XRD and SEM measurements. The growth mechanism was discussed and assigned to a combined growth process: the competitive growth between lateral overgrowth and nanovoid formation. The cause for structural evolution is closely related to the deposition potential, which gradually decreases with the electrodeposition time. Our understanding could be helpful for understanding the growth and corresponding properties of ZnO films as well as their nanostructures.

Acknowledgements

We thank Mr. M.K. Tang and Dr. Amy X.Y. Lu for experimental assistance. This work was financially supported by the National Natural Science Foundations of China (Nos. 61008029 and 51102049), Program for New Century Excellent Talents in University (No. NCET-10-0345), and Shanghai Pujiang Program (No. 11PJ1400900).

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