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Nanostructured ZnO films in forms of rod, plate and flower: Electrodeposition mechanisms and characterization

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ABSTRACT

Uniformity and reproducibility of well-defined ZnO nanostructures are particularly important issues for fabrication and applications of these nanomaterials. In present study, we report selective morphology control during electrodeposition, by adjusting the hydroxyl generation rate and $Zn(OH)_2$ deposition. In presence of remarkably high chloride concentration (0.3 M) and −1.0 V deposition potential, slow precipitation conditions were provided in 5 mM $Zn(NO_3)_2$ solution. By doing so, we have obtained highly ordered, vertically aligned and uniformly spaced hexagon shaped nanoplates, on ITO surface. We have also investigated the mechanism for shifting the morphology from rod/plate to flower like structure of ZnO, for better understanding the reproducibility. For this reason, the influence of various supporting electrolytes (sodium/ammonium salts of acetate) has been investigated for interpretation of the influence of OH^- concentration nearby the surface. From rod to plate and flower nanostructures, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analysis were realized for characterization, also the optical properties were studied.

1. Introduction

Most of the integrated nanodevice applications employing ZnO involve specifically designed nanostructures with their shape, size, orientation etc. For example, nanowire and nanorod structured ZnO films offer remarkably large surface area, which is very important for light harvesting efficiency in solar cell applications [1–7]. On the other hand, nanoplate structured ZnO films are interest of applications like sensors, photocatalytic nanoreactors and nanocontainers etc. Among all the other methods (molecular beam epitaxy [8], chemical vapor deposition [9], hydrothermal synthesis [10], sprays pyrolysis [11], pulsed laser deposition [12] etc.), electrochemical deposition is the most efficient route for tuning the morphology [13–19]. Since the deposition kinetics could be controlled precisely with adjusting the electrolyte solution composition and concentration, as well as the employed electrochemical deposition parameters [14,20–22].

It has been well recognized that it is highly important to obtain well-defined distinct nanostructures (rod, plate etc.) with desired alignment, order, homogenous distribution and reproducibility. For this purpose, a seed layer (which is also ZnO) may be prepared on the surface, prior to ZnO film production. The seed layer could be performed via chemical or electrochemical routes, and it is expected to govern the uniformity and ordering of nanostructures.

In electrochemical synthesis of ZnO, deposition kinetics is controlled with OH^- generation and Zn^{2+} transportation rate from bulk solution to substrate surface. Actually, the precursor (generally $Zn(NO_3)_2$) concentration is crucial for both events, as well as employed electrochemical synthesis parameters like deposition potential etc. Moreover, Tena-Zaere et al. [23] have demonstrated the critical role of the ratio between the electrochemical OH^- generation rate and Zn^{2+} concentration gradient nearby the electrode surface.

Additionally, the capping effect of various ions (present in synthesis bath) has been reported frequently, regarding their impact on preferential growth dimensions of electrodeposited ZnO nanostructures. Moreover, Pradhan and Leung [24,25] have reported the electrosynthesis of 2D nanostructured (wall like) ZnO films. In this study, they explained the mechanism with the capping effect of chloride ions on polar *(002)* surface, under fast ZnO deposition conditions (0.1 M $Zn(NO_3)_2$ + 0.1 M KCl and −1.1 V deposition potential). They have also reported that large fraction of these nanowalls tends to form local groups and decreasing the $Zn(NO_3)_2$

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concentration (from 0.1 to 0.05 M) leads to formation of large quantity of stacked ZnO nanodisks.

In present work, it was emphasized that optimization between precipitation rate and capping effect could be used for fabrication of well-defined ZnO nanoplates as highly ordered and vertically aligned distinct constructions, with high reproducibility. For this purpose, we have slowed down the precipitation rate by reducing both precursor concentration and OH^- generation rate (i.e. nitrate reduction, electrochemically). In the mean time we have increased chloride concentration for favoring the capping effect. Additionally, we have also investigated the mechanism of shifting the morphology from rod/plate to flower like structure of ZnO, for better understanding the reproducibility. For this reason, the influence of various supporting electrolytes (sodium/ammonium salts of acetate) has been investigated, for interpretation of OH^- concentration nearby the surface.

2. Experimental

The electrochemical deposition of ZnO nanostructures was performed in a conventional three-electrode system. ITO coated glass substrate (surface resistivity 8–12 Ω/sqr) was used as a working electrode, where a platinum sheet was the counter and Ag/AgCl (3 M KCl) as the reference. Prior to deposition process, the ITO coated glass substrates were ultrasonically cleaned with 1 M (mol/L) NaOH solution, ethanol and distilled water for 3 min, respectively.

The aqueous deposition bath solution included 5 mM ($Zn(NO_3)_2{\cdot}4H_2O$) as the precursor and various supporting electrolytes (KCl, CH_3COONH_4 and CH_3COONa). The concentration and type of supporting electrolyte were studied for understanding the growth mechanisms leading to different nanostructures. The ZnO films were prepared by employing a constant potential value, i.e. potentiostatically. The deposition temperature was kept constant at 70 °C with the help of water bath. After deposition, ZnO nanostructures were thoroughly rinsed with distilled water and dried at room temperature.

The surface morphologies of prepared ZnO films were characterized by field emission scanning electron microscopy (FE-SEM, Zeiss, Supra 55). The crystallographic properties were investigated with X-ray diffraction (XRD Rigaku, SmartLab). Optical properties were obtained by using ultraviolet-visible (UV–vis) Spectrophotometer (Perkin Elmer, Lambda 25). The charge mobility measurements were realized by Hall measurement system connection (ECOPIA, HMS-3000), for this purpose silver welding were utilized. Electronic properties were investigated and interpreted extensively, by using X-ray photoelectron spectroscopy (XPS). XPS analyses were carried out using PHI 5000 Versa Probe equipped with an argon ion gun and employing Al K alpha monochromatic X-ray ($h\upsilon$=1486.6 eV) source. The electron take off angle was 45°, and the pass energy was 187.85 eV for survey spectra. The binding energies were referenced to the Fermi edge.

3. Results and discussions

3.1. Electrochemical deposition of ZnO nanostructures

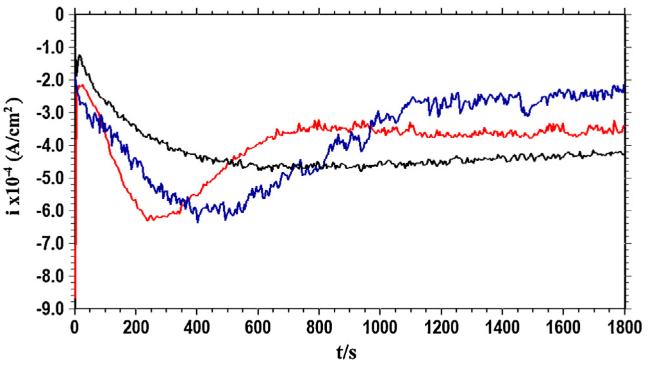

Fig. 1. The choronoamperograms for development of ZnO nanostructure on ITO in different deposition medium (5 mM $Zn(NO_3)_2$ + (red): 0.1 M KCl; (blue): 0.3 M KCl; (black): 10 mM CH_3COONH_4 solutions) under −1.0 V constant potential for 30 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In this present study, the ZnO deposition was carried out potentiostatically (−1.0 V) and chronoamperometric plots were recorded and given in Fig. 1. For the purpose of electrocrystallization, $Zn(NO_3)_2$ precursor and various supporting electrolytes (KCl, CH_3COONH_4 and CH_3COONa) were studied. Basically, the three stages of deposition are electrochemical reduction of nitrate species to generate OH^-, chemical precipitation of Zn^{2+} ions with OH^- and dehydration of $Zn(OH)_2$. Therefore the growth dimensions, thus the morphology could be controlled by tuning the OH^- generation rate and/or transport rate of Zn^{2+} ions to electrode surface.

In 5 mM $Zn(NO_3)_2$ synthesis solution supported by 0.1 M KCl, electrochemical hydroxyl generation rate was very high, at the beginning. Therefore, high cathodic current was measured within the first 300 s. The said cathodic current was due to reduction of NO_3^- ions to yield hydroxide ions, on the ITO surface. These freshly generated OH^- ions will react readily with Zn^{2+} already present at the surface. This precipitation reaction leads $Zn(OH)_2$ deposition on ITO surface and this compound undergoes dehydration soon, thus the nucleation of ZnO particles starts on the electrode surface. In vicinity of the electrode surface, the Zn^{2+} ions are consumed in the $Zn(OH)_2$ precipitation reaction, then migration of Zn^{2+} ions occurs from bulk solution to the electrode surface. Thus, the ZnO deposition rate is controlled by the rate of OH^- generation and diffusion rate along the pathway between electrode surface and bulk solution [26]. As a conclusion, the observed current value is not a direct measure of the ZnO deposition rate; it is the direct measure of OH^- generation rate.

With increasing deposition time, the ITO electrode surface becomes covered with large and small ZnO particles. Also, it was observed that the measured current value gets lower with time. This was indicative for decreasing electrochemical charge transfer rate, which means lesser OH^- generation. After completion of nucleation stage and achievement of steady deposition conditions on the surface, the current value remains quite stable during further growth of ZnO particles.

When the KCl supporting electrolyte concentration was increased to 0.3 M, the nucleation rate decreased remarkably and involved longer period for completion, with respect to studies reported by Skompska et al. [15]. The excess concentration of KCl decreased the electrical resistance through the electrolytic cell, but also influenced negatively the adsorptive interaction of NO_3^- with the electrode surface. The Cl^- concentration is quite higher (three times) and it has smaller size, with respect to NO_3^-, these ions take the advantage in competitive adsorption on the surface. Especially, the adsorption of chloride ions on the positively charged (001) plane of ZnO has dramatic influence on formation of plate morphology. In the meantime, the nitrate reduction (i.e. OH^- generation) rate is altered, since the adsorption of NO_3^- is limited. These two events determine the resulting morphology, as will be discussed in the next coming section.

In synthesis solution supported by 10 mM CH_3COONH_4, the nucleation period cannot be distinguished well. The presence of ammonium and acetate ions altered the deposition kinetics remarkably, due to $[Zn(NH_3)_4]^{2+}$ complex formation and hydrolysis of acetate ions. The influence of these events on the elec-