Effect of Synthesis Conditions on the Growth of ZnO Nanorods via the Solution Deposition Method

C.M. Zhang, T. Meng, S.Y. Yao, S. Huang, D.D. Wang
Beijing Institute of Graphic Communication
Beijing 102600, China

***Abstract*—The ZnO nanorod films were synthesized using zinc acetate-sodium hydroxide aqueous solutions under different synthesis conditions. The effect of synthesis conditions on structural properties and morphology of ZnO films was investigated using field emission scanning electron microscopy and X-ray diffraction. The results demonstrated that the morphology of ZnO films was determined by the concentration of the precursors. The predominatant c-axis growth of hexagonal lattice was observed, which confirmed that high-quality ZnO nanorod films were obtained. At last, the mechanism of formation of varying morphologies was discussed.**

Keywords-ZnO nanorod film; solution deposition; morphology

I. INTRODUCTION

With the rapid developments in nanoscience and nanotechnology, there has been great interest in ZnO nanomaterials because ZnO is a Ⅱ-Ⅵsemiconductor with a wide and direct band gap(3.37eV) and an exaction-binding-energy of about 60meV. [1-2] As a result, it is useful for light-emitting devices, solar cells, gas sensors and laser diodes, etc.[3-6] ZnO is also environmentally friendly, stable, indefinitely and can be synthesized easily and inexpensively into different shapes, such as rods, wires, flowers, ribbons and pillars.[7] For the development of novel devices, the fabrication of ZnO nanorod films with highly oriented, aligned and ordered arrays is of critical importance, and the well-controlled synthetic procedures of ZnO nanorod films have been the focus of crystal synthesis.

Over the past few years, oriented arrays of ZnO nanorods or nanowires have been synthesized with various methods. The low-temperature aqueous solution deposition was frequently employed and is attracting considerable attention because it is easy to handle, low temperature (60-100 ºC), less expensive, and environmentally amicable.[8] With this kind of method, well-aligned ZnO nanorod films have been successfully synthesized in zinc salt aqueous solutions using different chelating agents, such as hexamethylenetetramine (HMT), dimethylamineborane (DMAB), and ethane-1,2-diamine(EN). Recently, zinc nitrate and sodium hydroxide solution without any surfactants was reported to synthesize ZnO with different shapes such as stars, nultipods, spikes and nanorods, and the system of zinc acetate and sodium hydroxide solution was also used to fabricated bunch-shaped nanowires.[9-11] In the present work, we selected the zinc acetate and sodium hydroxide system, and employed the aqueous solution deposition method to synthesize the nanorod films. The influence of the molar ratio of Zn^{2+} to NaOH in the morphologies and the structures of the films was studied.

II. EXPERIMENTAL DETAILS

Firstly, a textured ZnO seed layer was prepared on a glass substrate. The glass substrate was spin-coated with 0.0025M zinc acetate dehydrate-ethanol solution, and then was transferred in muffle for treatment at 400 ºC for 30 min. Then the aqueous solution containing $Zn(CH_3COO)_2$ and NaOH with different molar ratios was prepared at ambient temperature by stirring for 20min. Subsequently, pretreated glass substrates were submerged in the aqueous solutions. Then the solution was heated to 65°C and the growth time was 6 hours. Finally, as-deposited substrates were taken out and washed with deionized water and ethanol, and then dried at room temperature.

The morphology of ZnO films were examined by using a field emission scanning electron microscope (FESEM; S4800, Hitachi). The crystalline phase of products was identified by X-ray diffraction (XRD; D8 ADVANCE, Bruker) using Cu Ka radiation (λ= 0.15406 nm).

III. RESULTS AND DISCUSSIONS

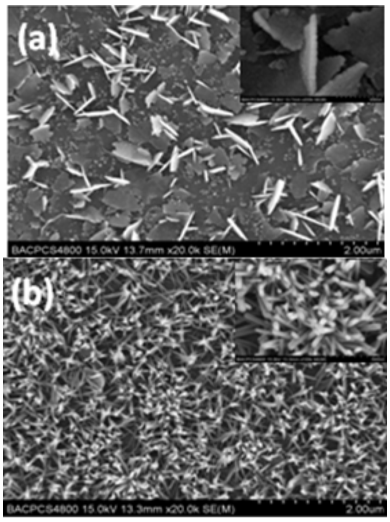

FIGURE I. FE-SEM IMAGES OF ZnO FILMS GROWN UNDER DIFFERENT MOLAR RATIO OF NaOH to Zn^{2+}: (a)6:1, (b)8:1.

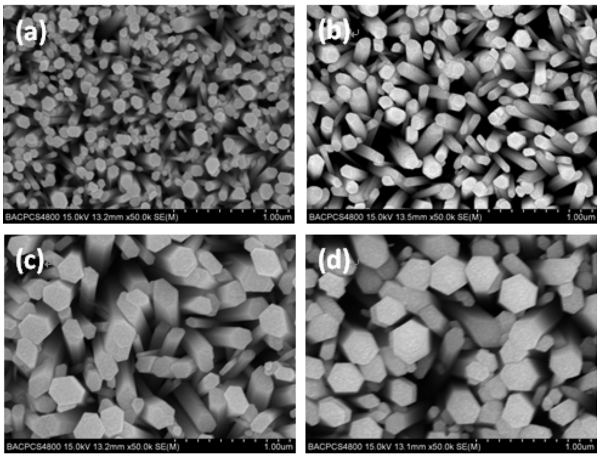

FIGURE II. FE-SEM IMAGES OF ZnO FILMS GROWN UNDER DIFFERENT MOLAR RATIO OF NaOH to Zn^{2+}: (a)10:1,(b)12:1, (c)16:1,(d)20:1.

In this study, ZnO films were grown in aqueous solution of zinc acetate dehydrate and sodium hydroxide. NaOH provides the hydroxide ions (OH^-) to the solution. The initial concentration of OH^- in the solution had a great influence on the growth of ZnO films. So a set of samples were grown on the pre-treated substrates under the condition of different molar ratio between NaOH and $Zn(CH_3COO)_2{\cdot}2H_2O$, in order to investigate the effect of the concentration of NaOH on the structures of ZnO films. In the precursory solution, the initial zinc concentration was 0.05M, which was kept as a constant and the molar ratio of NaOH to $Zn(CH_3COO)_2{\cdot}2H_2O$ changed from 6:1 to 25:1.

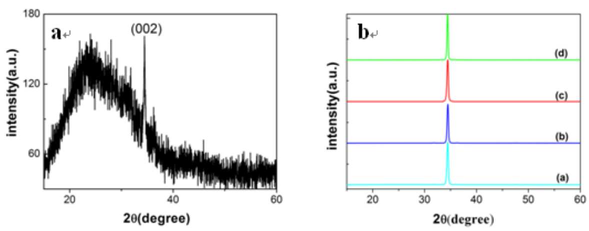

FIGURE III. (a) XRD PATTERN OF ZnO FILMS PREPARED UNDER THE CONDITION THAT THE MOLAR RATIO OF NaOH TO Zn^{2+} WAS 8:1. (B) XRD PATTERN OF ZnO FILMS GROWN UNDER DIFFERENT MOLAR RATIO OF NaOH TO Zn^{2+}: (a)10:1,(b)12:1, (c)16:1,(d)20:1.

Figure1-2 showed the morphological evolution of ZnO films as growth conditions vary with the molar ratio. When the molar ratio was 6:1, randomly distributed nanosheets were observed on the surface of the substrate (Figure1 (a)). The size of the nanosheet was about 300nm and the thickness was about 25nm. The magnified view (inset image) showed that the surface of the nanosheet was rough and was aggregated by nanoparticles. However, for samples under higher molar ratio (Figure1 (b)), the low density nanorod film was obtained and the rod diameter was about 35nm. Then with the further increasing of the molar ratio (Figure2), dense nanorod arrays formed and the diameter of the nanorod increased from 60nm to 200nm. When the molar ratio reached 25:1, there was no ZnO nanorod on substrate, and even the ZnO seed film on substrate was dissolved by OH^-. The result displayed a broad scope of the molar ratio allowable for rod growth in this system and the diameter of nanorod can be adjusted by the molar ratio of NaOH to Zn^{2+}. Most top ends of ZnO nanorods was well faceted and flat hexagonal symmetry, illustrating the nanorods grow along c-axis direction.

Figure3 showed the XRD diffraction pattern of ZnO films prepared with different molar ratio. For all the samples, the significantly high intensity of (002) diffraction peak was observed, indicating that ZnO were preferentially oriented along the c-axis direction as well.

In this work, the possible reaction process for the growth of ZnO film can be described as the following equation[10]:

$$Zn(CH_3COO)_2{\cdot}2H_2O \rightarrow Zn^{2+} + 2CH_3COO^- + 2H_2O \quad (1)$$

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

$$Zn(OH)_2 + 2OH^- \rightarrow [Zn(OH)_4]^{2-} \quad (3)$$

$$[Zn(OH)_4]^{2-} \leftrightarrow ZnO + 2OH^- + H_2O \quad (4)$$

Zinc acetate dehydrate provides Zn^{2+} ions required for growing ZnO nanorod and NaOH produces OH^- in water solution. When the molar ratio of NaOH to Zn^{2+} changed from 10:1 to 20:1, the form of zinc ion in the solution should be predominantly $[Zn(OH)_4]^{2-}$ (Eq.2,3). $[Zn(OH)_4]^{2-}$ can be adsorbed on the positively charged (0001) plane of ZnO seeds on the substrate. Then the crystal structure of ZnO was gradually constructed by dehydration between OH^- present on the (0001) plane and the OH^- ligands of the hydroxyl complexes (Eq.4).[12] It is well known that that the crystal ZnO was the polar crystal, and polar faces ((0001) and $(000\bar{1})$ faces) with surface dipoles are thermodynamically less stable than nonpolar faces, often undergo rearrangement to minimize their surface energy and also tend to grow more rapidly. So ZnO tends to grow as an one-dimensional nanostructure along the c-axis with (0001) and form the rod shape.During the growth of ZnO, the supersaturation was the key driving force. The Zn^{2+} ion and NaOH concentrations should be varied to create the degree of supersaturation.[11-12] If the molar ratio of NaOH to Zn^{2+} was higher than the optimal, ZnO cannot form on the substrate, and even the ZnO seeds were etched away (Eq.3); if too low, most of the zinc ions precipitated out of solution (Eq.2), and the low concentration of $[Zn(OH)_4]^{2-}$ was not benifical for the growth of nanorods. When the molar ratio was 6:1, a large amount of $Zn(OH)_2$ appeared in the solution, and $Zn(OH)_2$ can be tansformed to ZnO by dehydration and hence nucleation of ZnO occurred. Then the nuclei aggregated to nanosheet.[9] With the increasing of the molar ratio, the equilibrium shifted to left (Eq.3) and less ZnO precipitated out by homogeneous nucleation. As a result, the solution became favorable for rod growth and the nanorods were synthesized. With the further increasing of the molar ratio, the higher concentration of

$[Zn(OH)_4]^{2-}$ improved the growth rate of ZnO rod and prompted precursors to accumulate together, which result in high density of nanorod and the increase of the rod diameter.

IV. CONCLUSIONS

A system deriving from $Zn(CH_3COO)_2 \cdot 2H_2O$/NaOH was demonstrated as suitable to prepare ZnO nanorod arrays on the ZnO-coated glass substrate. The preparing conditions such as precursor concentration, the molar ratio of NaOH to Zn^{2+} have a great influence on the morphology of ZnOnanorods. The predominant c-axis growth of hexagonal lattice was observed, which confirmed that high-quality ZnO nanorod films were obtained. At last, the mechanism of formation of varying morphologies was discussed in detail.

ACKNOWLEDGMENTS

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