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Morphological Studies of ZnO Nanostructures Deposited on Nanoporous Anodic Alumina Membrane by Rapid Dip Coating Technique

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Abstract:*Inthiswork,differentmorphologiesofzincoxide(ZnO)nanostructureshavebeenfabricatedbya simpleandrapid dip coating method.Inthis method ZnO nanostructuresare deposited from sol-gel of zinc acetateusing dip coating onto Porous Anodic Alumina Membrane (PAAM).Afterthermalannealinginoxygenat600°Cfor30 min,the ZnO nanoparticles are uniformly agglomerated into, almost, 1D nanorods array. When the starting precursor is zinc nitrate and the annealing was carried out for 10 h at the same conditions, the ZnO nanoparticles are uniformly agglomerated into, almost, nanoseeds (nanocolloidal particles).*

Keywords:*PAA membrane; ZnO; nanostructures; dip coating; SEM; EDX.*

I. Introduction

Recently, ZnO attracted a great interesting as anenvironmental friend semiconductor with a wide band gap (3.3 eV) and large excitation binding energy [1]. ZnO nanostructures offer significant potential in many applications,such as photocatalysts, optical coatings, solar cells, electrical devices, chemical and gas sensors, and active medium in UV semiconductor lasers[2-7]. A variety of methods have been developed for the fabrication of ZnO nanostructures including laser evaporation [8], sol-gel deposition using spin coating and dip coating [9], arc discharge [10], chemical vapor deposition [11], and electrodeposition [12]. However, sol-gel deposition using spin coating and dip coating is an effective and simple method for the fabrication of ZnO nanoarrays via the template- based growth [13, 14]. The sol-gel deposition using dip coatingis one of the versatile and low-cost techniques for the deposition of ZnOnanostructures[14].Porous Anodic AluminaMembrane (PAAM) is characterized by regularly arranged hexagonally arrayed nanopores with pore diameters ranging from 5 to 400 nm, pore heights from a few tens of nm to over 100 mm,and pore density in the range of 10^{10} to $10^{12}cm^{-2}$[15]. In addition, PAAM possesses highchemical and thermal stability. Moreover, the pore structure in the oxide layer could be easily controlled, by optimizing the anodizing factors, for the growth of nanoarrayed structures [16, 17]. These unique properties, simplicity, low-cost, and high-throughput make PAAM ideal template for the fabrication of periodic ZnO nanostructures.PAAM has been used for synthesized a variety of ZnO nanostructures including small quantum-sizedparticles, nanowires, and nanofibres [18, 19]. However, this method faced some challenges such as morphology control and high cost of the deposition method.

From the applications point of view, the propertiesof high aspect ratios and small sizes of ZnO nanowires are expected to improve the luminescence efficiency of the electro-optical devices and the sensibility of the chemical sensors [20]. In addition, ZnO nanowires are reported to show n-type semiconductor behavior due to the native defects such as oxygen vacancies and zinc interstitials [18]. Moreover, well-aligned ZnO nanorods are important for Dye-sensitized solar cells (DSSCs) because the electronic mobility of ZnO nanorods is about 2–3 orders of magnitude faster than that in TiO_2nanoparticles film [4]. So, it is important to have a new strategy to fabricate ZnO nanostructures with controlled morphologies on the top surface of PAAMs. Here, we

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synthesized ordered ZnO nanorods, and colloidal ZnO nanoparticles by varying the precursor electrolyte and the annealing time at 600°C. In addition, morphologies and chemical compositions are studied by FE-SEM and EDX.

II. Experimental procedure

2.1 Preparation of PAAM

The PAAM was prepared by a two-step anodization process [15]. High-purity aluminum foils (99.999%) were de-greased using acetone and alcohol and then rinsed in distilled water.Electropolishing process was carried out in acidic solutionfor 5 min at 5 A to reduce roughness of the Al surface. The anodization was performed in 0.3 M oxalic acid solution under a constant DC voltage of 40 V at 9°C. The alumina (Al_2O_3) layer that formed during the first anodization was removed with a mixture of phosphoric acid (6 wt%) and chromic acid (2 wt%) at room temperature for 3 h. The second anodization was performedunder the same conditions for 10 minto grow highly ordered PAAM. The PAAM pores were widened and the barrier layer was thinned by chemical etching in 6% H_3PO_4 solution for 75 min.

2.2 Fabrication of ZnO nanostructure within the PAAM

ZnO nanostructures were deposited on the top surface of the PAA using dip coating by two different methods. In the first method,0.45 g zinc acetate dehydrate ($Zn(CH_3COOH).2H_2O$ (99.99%) was solved in 20 ml methanoland 0.25ml acetyl acetone mixture at room temperature. The prepared solution was mixed using amagnetic stirrer for 4 h at 50 °C until atransparent solution was obtained. Then, the solution was aged for 24 h.PAAM was immersed in the prepared ZnO sol – gelat 65 °C for 12 h and then annealed at 600°C for 30 min. In the second method, Zn $(NO_3)_2.6H_2O$ was dissolved in deionized water to form 0.01 M and then urea was added to the solution at molar ratio of about 1: 20. After that, the PPAM was immersed in the solution at 80 °C for 24 h (nanotubes) and 48h (nanowires). Then the coated PAAMs were dried at 150°C for 1 h and then at 650 °C for 10 h. The samples were kept inside the furnace until room temperature reached.

2.3. Sample Characterization

The surface morphology was studied using field-emission scanning electron microscopy (FE-SEM, ZEISS SUPRA 55 VP and ZEISS LEO Gemini Column). The chemical compositional analysis was carried out using energy dispersive X-ray (EDX; Oxford Link ISIS 300 EDX).

III. Results and discussion

3.1. PAAM morphology and chemical composition

Figure 1(a) illustrates a top view SEM image of PAAM anodized for 10 min and pore widened for 45 min. The inset shows a cross-sectional SEM image of the membrane. The figure shows a typical hexagonal nanoporous Al_2O_3 array with an interpore distance of ~ 100 nm, pore diameter of ~ 79 nm, and pore density of ~ 1.12×10^{11} cm^{-2}.

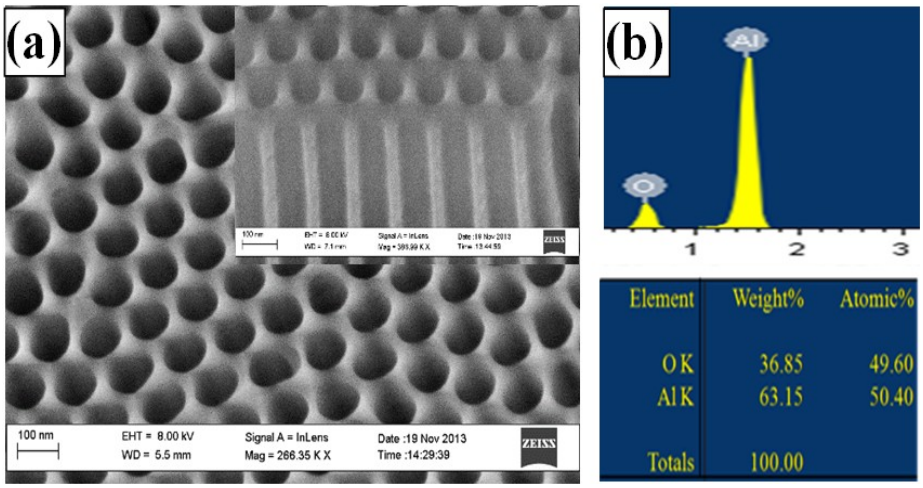

Figure 1.(a) Top view and cross-sectional view SEM images of PAAM**. (b)**Qualitative and quantitative EDX analysis of the PAAM.

Qualitative and quantitative analyses of the chemical composition of the fabricated PAAM are shown in Figure 1(b). The EDX pattern reveals that only signals from O and Al can be detected, and the quantitative analysis for the PAAM is 52% Al and 48% O. But the chart in Figure 1(b) indicates that the Al signal not only

comes from the alumina nanoporous structures but also from the Al substrate. In addition, no trace of C, Cr or S is detected in the EDX pattern, indicating that the nanowires are pure Al_2O_3.

3.2. ZnO nanostructure morphology and chemical composition

Figure 2 shows SEM images of PAAM (a) after the deposition of Zn into the pores by dip-coating technique using Zn acetate and (b) after annealing in air at 600°C for 30 min. Figure 2 (a) shows a densely and uniform Zn deposition inside the pores of the PAAM with 100% filling factor. As shown from the enlarged inset, it is reasonable that the nanotubes are first formed in the wall area of the pores and then extended to the center area gradually, until the pores were filled completely to form nanorods. As indicated in the enlarged part, there are very small nanopores at some pores. After 30 min annealing at 600°C, randomly distributed ZnO nanorods are illustrated in Figure 1(b). The rod diameter is around 22 ± 3 nm and the height is ranged from 100 to 150 nm.

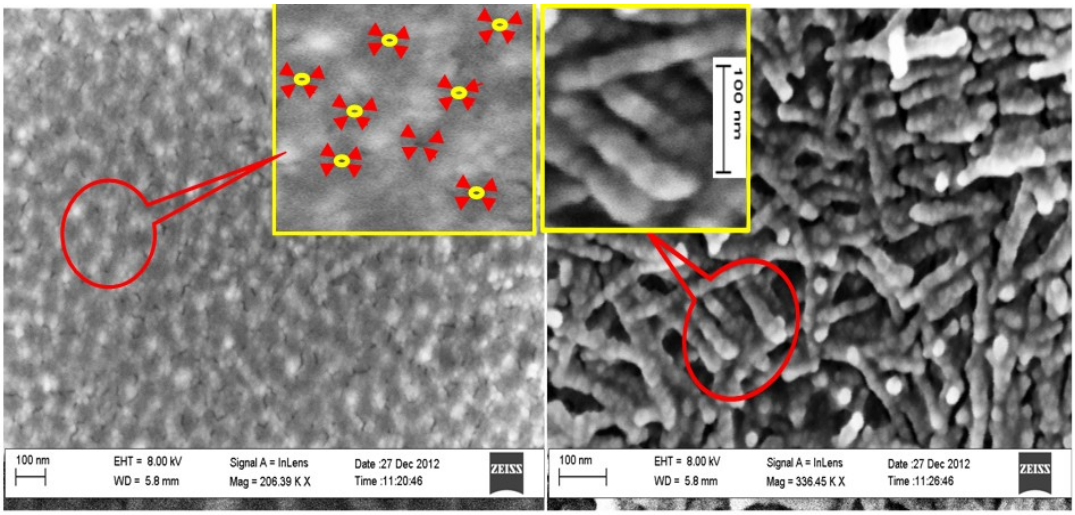

Figure 2 SEM images of PAAM (a) after the deposition of Zn into the pores by dip-coating technique using Zn acetate precursor and (b) after annealing in air at 600°C for 30 min.

To confirm the chemical composition of the fabricated structure after 30 min annealing, Figure 3 shows the EDX pattern and reveals that only signals from O and Zn can be detected. The quantitative analysis is 80% for Zn and 20% for O for ZnO. In addition, no traces are detected in the EDX pattern, indicating that the nanorods are pure ZnO.

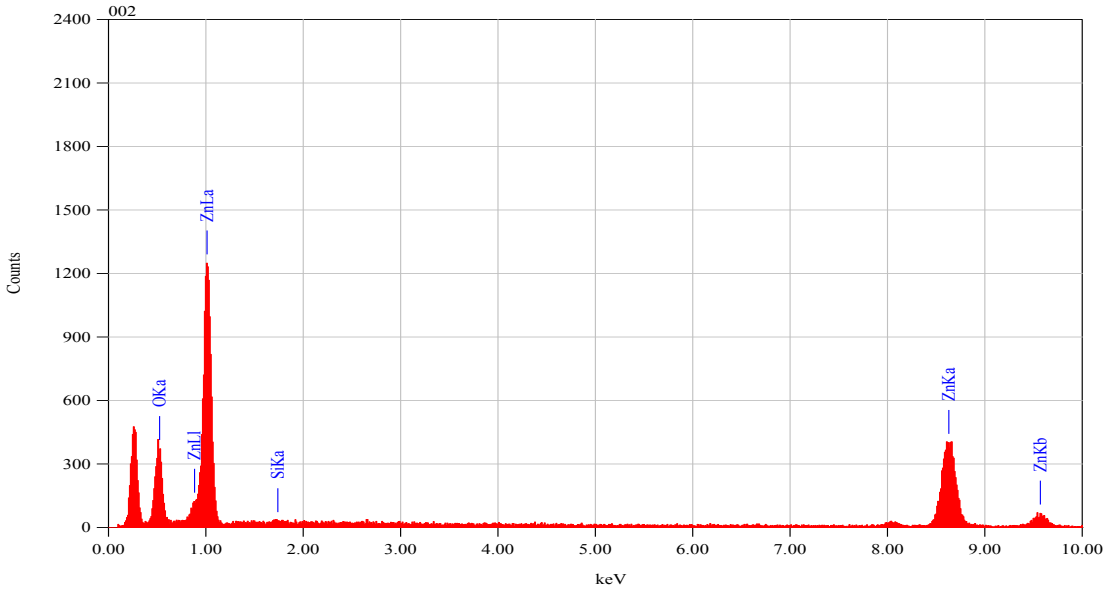

Figure3. EDX spectrum of ZnO nanorods.

Figure 4 shows SEM images of PAAM after the deposition of Zn into the pores by dip-coating technique. 0.01 M $Zn(NO_3)_2.H_2O$ was used as a precursor and annealing was carried out at for 10 h at 650°C.

As shown in this figure, ZnO nanoparticles are aggregated at the top surface of the PAAM. It is reasonable that the ZnO nanoparticles were deposited in the top surfaces of the walls of the pores.Then the deposited nanoparticles were agglomerated and extendedgradually, until the pores were almost completely covered. The particles sizes are estimated to be less than 10 nm.

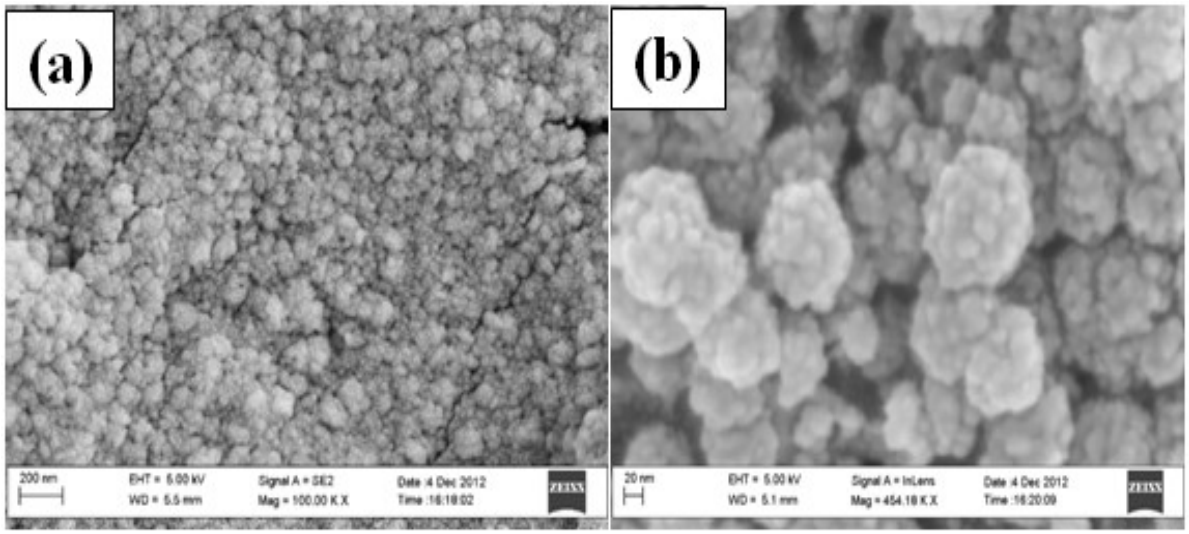

Figure 4. SEM images at two different magnifications of PAAM after the deposition of Zn into the pores by dip-coating technique using 0.01 M $Zn(NO_3)_2$ precursor after annealing at 650^oC for10 h.

IV. Conclusion

1D - ZnO nanorods have been successfully fabricated on the Al substrate when the starting precursor is Zinc acetate. The deposition of the Zn nanorods inside the pores of PAAM was carried out by the dip coating technique and followed by 30 min annealing in air at 600^oC. When the starting precursor is Zinc nitrate and the annealing was carried out for 10 h at the same conditions, the ZnO nanoparticles are uniformly agglomerated into, almost, nanoseeds or nanocolloidal particles.

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