The Growth of ZnO Nanostructures Prepared by Anodization in Combination with Hydrothermal Method on the Zn Sheet

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Abstract

ZnO nanostructures prepared by anodization in combination with hydrothermal method using Zn metal plate in water vapor were investigated. In the first step, the Zn nanoporus were fabricated by electrochemical anodization in a HF/Methanol/H_2O electrolyte system. Ultrasonic wave was used to clean the surface of ZnO nanoporus in the medium of water after the completion of the anodization. After drying in air, in the second step, the nanostructures were converted by hydrothermal. The ZnO nanostructures were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD patterns show the ZnO hexagonal wurtzite structure. SEM images indicate that the ZnO structures depend on preparation temperatures. The density of ZnO nanostructures increase as the times increases. The growth of ZnO nanostructures was observed to be times dependence

Keywords: ZnO: Nanostructure: Anodization: Hydrothermal

Introduction

Zinc oxide, with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photostability, is a multifunctional material [1,2]. In materials science, zinc oxide is classified as a semiconductor in group II-VI, whose covalence is on the boundary between ionic and covalent semiconductors. This wide band gap semiconductor (of 3.37 eV at room temperature) may have numerous possible applications, particularly in the form of thin films, nanowires, nanorods, or nanoparticles. It can be used in optoelectronic and electronic devices, as well as in the field of electrochemistry for the production of chemical sensors, photocatalysts [3], and solar cells [4]. The uses of ZnO as a photocatalytic degradation material for environmental pollutants has also been extensively studied, because of its nontoxic nature, low cost, and high activity. However, such photocatalytic degradation can only proceed under UV irradiation because of its wide band gap. All kinds of novel morphologies of ZnO nanobelts [5], nanowires[6], nanotubes[7], and nanocombs [8]. The properties of ZnO are strongly dependent on its structure, including the morphology, aspect ratio, size, orientation, and density of crystal. Development of a synthesis route capable of producing ZnO nanomaterials with controlled size and morphology is important due to their potential applications as smart and functional materials. Anodizing is an electrolytic passivation process used to increase the thickness and density of the natural oxide layer on the surface of metal parts. Besides increasing corrosion and wear resistance, anodizing is a very cost-effective method to produce uniform and adhesive oxide films on metals. Anodic deposition is a process that combines simplicity, cost-effectiveness, and ease in morphology control [9]. Anodic films can also be used for a number of cosmetic effects, either with thick porous coatings that

can absorb dyes or with thin transparent coatings that add interference effects to reflected light. Recently, much interest has been drawn toward the anodization method as it enables the preparation of nanostructured metal oxides with unique physical and chemical properties [10]. Hydrothermal technique is a promising alternative synthetic method because of the low process temperature and very easy to control the particle size. The hydrothermal process have several advantage over other growth processes such as use of simple equipment, catalyst-free growth, low cost, large area uniform production, environmental friendliness and less hazardous. The low reaction temperatures make this method an attractive one for microelectronics and plastic electronics [11]. This method has also been successfully employed to prepare nano-scale ZnO and other luminescent materials. The particle properties such as morphology and size can be controlled via the hydrothermal process by adjusting the reaction temperature, time and concentration of precursors.

Materials and Methods

In the first step, preparation Zn sheets (2Pcs high purity 99.9% pure Zinc Zn sheet plate for science) were used as substrate for the anodization. Prior to the anodization, pieces (radius 1.5 cm) of the Zn sheet were ultrasonicated in acetone, 2-propanol and methanol for 15 min, then washed with water and dried under nitrogen. Anodization was performed in an appropriate electrochemical cell, made of teflon, at ambient temperature [12]. The working area was 7.06 cm^2 and the distance between the anode (Zn sheets) and the cathode (Pt mesh) was set at 5 cm. The Zn sheets were anodized at 9.7 V for 10 min and the anodization was conducted in mixed electrolyte of water, hydrofluoric acid (48%) and methanol (99.9%). The HF concentration is 1 wt.% and the methanol volume fraction is 30% or 50%. The reaction time ranges from30 s to 30 min. Finally, the white ZnO thin films were deposited on the Zn sheets, thoroughly washed with deionized water to eliminate remainder, and dried in air at room temperature. The morphologies of ZnO films were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). In the second step, the synthesis method of nanostructure was basically the same as in previous works [13,14]. A commercial, ZnO powder (commercial; a mixture of crystalline hexagonal wurtzite structurex) was used as a starting material. In a typical synthesis, 0.8 g of ZnO powder was crushed with 25 mL of 0.6 g/L of NaOH aqueous solution were putt into a teflon- lined stainless autoclave and then heated at 200 °C for 20 h. Repeat again, but the concentration of NaOH aqueous solution is 0.8 g/L, 1.0 g/L, 1.2 g/L, 1.4 g/L, 1.6 g/L and 1.8 g/L. The samples were cooled down to room temperature. The treated samples were washed thoroughly with DI water and 0.1 mol/L HCl aqueous solutions until the pH value of the washing solution lower than 7 and dried at 60 C. The structural and chemical natures of the obtained materials were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM).

Results and Discussion

The Zn sheet substrates before anodization process and Zn sheet is anodization using code Zn sheet anodization. The samples were synthesized by hydrothermal under different the concentration of NaOH aqueous solution is 0.6, 0.8 g/L, 1.0 g/L, 1.2 g/L, 1.4 g/L, 1.6 g/L and 1.8 g/L using code ZnHC0.6, ZnHC0.8, ZnHC1.0, ZnHC1.2, ZnHC1.4, ZnHC1.6 and ZnHC1.8. The crystal structures were used for comparisons purpose. Figure 1 represents the X-ray diffraction patterns of as-synthesized samples. XRD patterns of the hydrothermal treated sample dried at 200 °C displayed clear and sharp diffraction patterns at the 20 h values 31.7, 34.4, 36.2, 47.5, 56.6, 62.8 and 69.1 corresponding to the (hkl) planes (100), (002), (101), (102), (110), (103) and (201), which are directly indexed to the hexagonal wurtzite phase of

ZnO (quite analogous to those of bulk ZnO) with the lattice parameters a = 0.3249 nm and c = 0.5205 nm and P63mc space group (JCPDS data: 01-089-0511). The intensity of the diffraction patterns directed the high crystallinity of the ZnO sample.

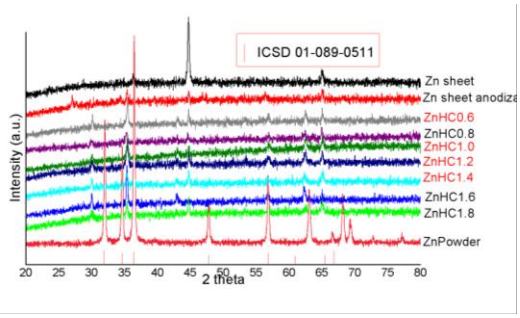
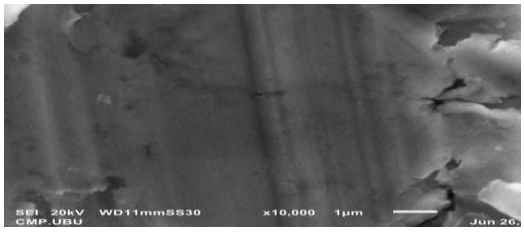
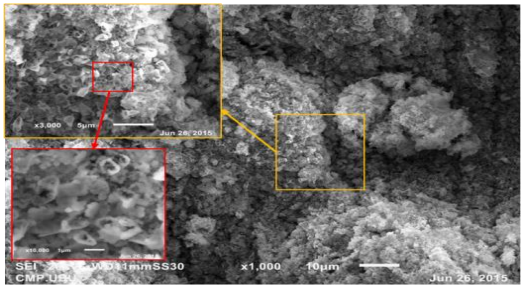


Figure 1 XRD patterns of The Zn sheet substrates before anodization process using code Zn sheet and Zn sheet is anodization using code Zn sheet anodization. The samples were synthesized by hydrothermal under different the concentration of NaOH aqueous solution is 0.6g/L, 0.8 g/L, 1.0 g/L, 1.2 g/L, 1.4 g/L, 1.6 g/L and 1.8 g/L using code ZnHC0.6, ZnHC0.8, ZnHC1.0, ZnHC1.2, ZnHC1.4, ZnHC1.6 and ZnHC1.8



(a)



(b)

Figure 2 (a) shows the SEM images of the Zn sheet substrates before anodization process and (b) after anodization process.

The surface and internal morphologies of the prepared ZnO samples were investigated by SEM. Figure 2(a) represents the SEM images of the Zn sheet substrates before anodization process and (b) after anodization process. From these SEM images, morphologies of the samples can be obviously found on the surface of the nonporous.

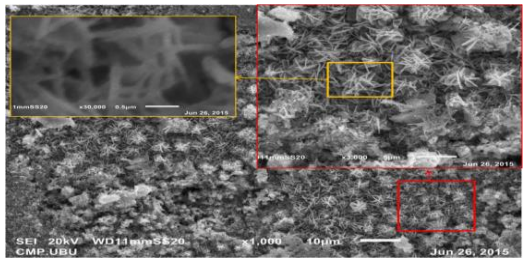


Figure 3 show the SEM images of morphologies of the sample under preparation at a concentration of 1.2 g/L

We chose to study morphologies of the sample under preparation at a concentration of 1.2 g/L because all the conditions are not different crystals. The surface and internal morphologies of the samples were investigated by SEM in Figure 3. The morphologies can be obviously found on the surface of the nano/microstructure flower-like ZnO.

Conclusions

In summary, ZnO nanoporous were successfully fabricated by anodization and the morphologies of the nano/microstructure flower-like ZnO. The ZnO nanostructure has a hexagonal wurtzite structure with the lattice parameters a = 0.3249 nm and c = 0.5205 nm and P63mc space group.

Acknowledgments

This work is supported by Program of Physics, Faculty of science, Ubon Ratchathani University. The authors gratefully thank them.

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