



Low-temperature fabrication of porous and transparent ZnO films with hybrid structure by self-hydrolysis method

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ABSTRACT

Porous, transparent and controllable ZnO nanoparticulate films were fabricated by self-hydrolysis of zinc salts in its crystalline water without any additions at 65 °C by an evaporating acetone solvent. The crystallite size of ZnO nanoparticles was about 30 nm, and the thickness of the nanoparticle film was controllable by simply changing the coating times. ZnO nanoparticulate films in thickness of 500 nm showed a high transmittance (>90%) in the visible range and widen bandgap (3.35 eV). The *c*-axis oriented ZnO nanoarray film was fabricated by a subsequent heterogeneous nucleation and growth in an aqueous solution. As-grown ZnO hybrid films showed a good transmittance (>85%) in the visible range.

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1. Introduction

ZnO is used in a wide range of functional devices, nanostructure varistors, UV absorbers, gas sensors, dye-sensitized solar cells and industrial additives due to its wide band gap (3.37 eV) with large exciton binding energy (60 meV) [1,2]. The properties of ZnO thin films are currently of great commercial and scientific interest. Presently, low-temperature solution deposition, which has advantages such as simplicity, reproducibility, cost effectiveness, and suitability for producing large-area thin films, is attracting considerable attention. A ZnO template-assisted technique has been used to fabricate nanorods [3–5], nanotubes [6,7], nanocolumns [8] and nanowires [9,10] with well-crystallized and oriented ZnO arrays in an aqueous solution. It has been reported that ZnO nanoparticles template layers were prepared by a sol-gel technique using zinc acetate dihydrate, cetyltrimethylammonium hydroxide (CTAOH) as catalyst and surfactants and ethanol as solvent [11] or using zinc acetate dihydrate, 2-methoxyethanol and MEA (or diethanolamine, DEA) by thermal decomposition at a high temperature of 550 °C [12–14]. ZnO nanoparticles were also prepared from zinc acetate dihydrate in an alcoholic solution under basic conditions [10,15–17]. For the previously reported methods, high-temperature pre-treatment was necessary. Additionally, electrodeposition [18,19], sputtering technique [5,8], radio frequency sputtering technique [20] and pulsed laser ablation (PLA) [21] and pulsed laser deposition (PLD) [22] were reported to prepare ZnO seed layers.

In the present study, transparent ZnO nanoparticles layer was obtained by self-hydrolysis of zinc salts and evaporating acetone solvent on the glass substrate in oven at 65 °C. Also, the *c*-axis oriented

ZnO nanowhisker arrays were fabricated by subsequent heterogeneous nucleation and growth in an aqueous solution at 88 °C without any expensive catalyst or high-temperature treatment. The formation mechanism and optical properties were investigated in detail.

2. Experimental details

The starting materials were zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99%), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), hexamethylenetetramine (HMT, $\text{C}_6\text{H}_{12}\text{N}_4$, 99%) and polyethylenimine (PEI, $(\text{C}_2\text{H}_5\text{N})_n$, branched mean molecular weight of 600, 99%). All chemicals (Wako Pure Chemical Industries, Ltd., Japan) were used as received without further purification. Slide glass (Matsunami Micro Slide Glass, 48 × 28 × 2 mm) was used as the substrate.

0.01 M zinc acetate dihydrate was well dissolved in acetone by stirring. Prior to the coating process, the glass substrate was carefully cleaned by deionized water, ethanol and acetone in the ultrasonic cleaner. After dried in an oven and UV irradiation for 10 min, 0.5 ml coating solution was kept on the cool glass substrate, and then dried in an oven at 65 °C for 10 min. The coating process was repeated for desired times (1 time, 2 times and 5 times), respectively. It should be pointed out that during the repeating processes, heated substrate at 65 °C for 10 min was taken out of the oven and cooled to room temperature for 20 min; then the cooled substrate was put back in the oven, the 0.5 ml coating solution was kept on the substrate at the same time. The surface of substrate changed from wet to dry in the oven due to the quick evaporation of acetone. The derived samples were named as 0.5 ml-derived, 1.0 ml-derived or 2.5 ml-derived film according to the amount of coating solution, respectively. The derived substrates were immersed in a 200-ml solution of zinc nitrate hexahydrate, hexamethylenetetramine and polyethylenimine for deposition of ZnO

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nanowhiskers by heterogeneous nucleation and growth at 88 °C for 1 h [23]. The initial concentration of Zn^{2+} was fixed to 0.1 M. Finally, the substrates were washed repeatedly and dried for characterization.

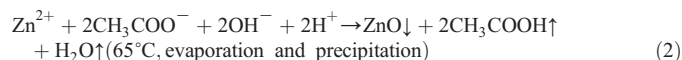
The crystalline phase and orientation of products were identified using X-ray diffraction (XRD; RINT-2100 V, Rigaku) with $CuK\alpha$ radiation (40 kV, 30 mA) at a scan rate of 2°/min. The morphology and microstructure were observed using a field emission scanning electron microscope (FE-SEM; JSM-6335FM, JEOL Ltd.) with an accelerating voltage of 5 kV and emission current of 12 μ A. The optical property of products was measured in the wavelength range 200–850 nm by a spectrophotometer (UV-VIS-NMR-V670, JASCO, Japan).

3. Results and discussion

3.1. The formation of ZnO nanoparticles film

A series of experimental data showed the thickness of ZnO nanoparticles layer depended on the amount of coating solution. Each 0.5 ml zinc acetate dihydrate–acetone solution resulted in about 100 nm in thickness of ZnO nanoparticles layer. Fig. 1 shows the FE-SEM image and XRD patterns of ZnO nanoparticles derived from 2.5 ml acetone solution. Uniform ZnO particles were formed in Fig. 1a. The diffraction peaks in Fig. 1b at $2\theta \approx 31.90^\circ$, 36.46° are in good agreement with the JCPDS card (No. 36-1451) for a typical wurtzite-type ZnO crystal except the broaden diffraction peak at about $2\theta \approx 29^\circ$, which originated from the glass substrate. The estimated crystallite size is about 30 nm using the Scherrer formula ($D = K\lambda/\beta\cos\theta$) by

the Bragg's angle at $2\theta \approx 31.90^\circ$ and its full width of the diffraction line ($10 \bar{1}0$) at half of maximum intensity. The formation of ZnO nanocrystals can be supposed as the following: zinc acetate dihydrate was dissolved in acetone at room temperature as Eq. (1). When the coating solution was transferred into the oven at 65 °C, higher vapor pressure of acetone introduced simultaneous evaporation of acetone and water, and precipitation of ZnO crystal as described in Eq. (2). Resultantly, self-hydrolysis of the zinc salt seems to occur by use of the crystalline water itself.



Here it is noticed that if the glass substrate was preheated before loading the acetone coating solution, self-hydrolysis of zinc salts in itself crystalline water and dehydrate reaction happened together. Broaden diffraction peaks of ZnO were detected together with anhydrous zinc acetate diffraction peak (See the supporting Fig. S1). The intensity of anhydrous zinc acetate diffraction peaks increased with an increasing of aging time (the prolonging of aging time resulted in the increasing of substrate temperature) of loading acetone solution from 0 s to 25 s. Additionally, in the case of ethanol solution, ZnO nanoparticles didn't form. The difference may be due to the vapor pressure (acetone: 24.7 kPa/20 °C; ethanol: 5.33 kPa/20 °C) and the function group (acetone: carbonyl group; ethanol: hydroxyl group). Thus, acetone as a solvent with a high vapor pressure played an essential role during the formation of ZnO nanocrystals.

3.2. The formation of ZnO nanowhisker films

Fig. 2 shows the FE-SEM images of ZnO nanowhiskers film on 0.5 ml and 2.5 ml acetone solution-derived bottoms, respectively. ZnO nanowhiskers were formed on the substrate. In the case of 0.5 ml-derived bottom, the cross-sectional view in Fig. 2b shows ZnO nanowhiskers in average length of about 1.4 μ m grew on a nanoparticles layer, which has about 100 nm in thickness as shown between both dash lines. The delaminated part as shown in Fig. 2c clearly clarifies the nanoparticles layer from the bottom. In the case of 2.5 ml-derived bottoms, smaller ZnO nanowhiskers in diameter grew on the glass substrate in Fig. 2d. The cross-sectional view (Fig. 2e) and magnification images (Fig. 2f) clarified there are nanoparticles layer in thickness of about 500 nm between ZnO nanowhiskers layer in average length of about 0.7 μ m and glass substrate as shown in Fig. 2e. The density of ZnO nanowhiskers, estimated according to the top-view images shown in Fig. 2(a,d) was about 40 and 135 nanowhiskers per square micrometer, respectively. The thickness and diameter of ZnO nanowhiskers are controllable by simply varying the deposition temperature or deposition time using an aqueous solution deposition technique [16,24].

Fig. 3 shows the XRD patterns of as-grown ZnO hybrid films with the 0.5 ml and 2.5 ml solution-derived bottoms, respectively. All of the diffraction peaks are in good agreement with the JCPDS card (No. 36-1451) for a typical wurtzite-type ZnO crystal. A significantly higher intensity of the 0002 diffraction peak indicates that as-grown ZnO films were preferentially oriented along the *c*-axis direction (grown along the direction perpendicular to the (0001) crystallographic face). The relative weaker intensity of the 0002 diffraction peak in Fig. 3b shows a smaller ZnO crystal size. Because 2.5 ml coating solution results in a large amount of ZnO nanoparticles being well dispersed on the surface.

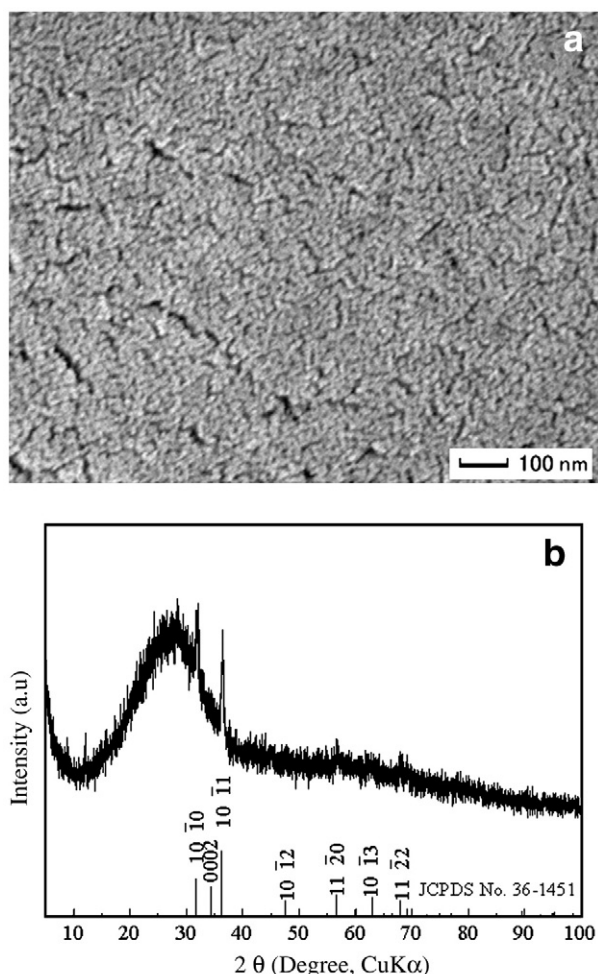


Fig. 1. FE-SEM images (a) and XRD pattern (b) of 2.5 ml-derived ZnO particulate films.

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