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A two-step route to synthesize highly oriented ZnO nanotube arrays

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Abstract

Large-scale and highly oriented ZnO nanotube arrays are synthesized on transparent conductive glass substrates by a two-step route. First, ZnO nanorod arrays were prepared by electrochemical deposition from an aqueous solution of zinc nitrate. Then, hollow ZnO nanotubes were obtained by the selective dissolution of the electrodeposited ZnO nanorods in potassium hydroxide solution. Field emission scanning electron microscopy (FESEM) and X-ray powder diffraction (XRD) have been used to characterize the morphology and structure of the derived products. The effect of the concentration of alkali, dissolution time, and temperature on the formation process and morphologies of ZnO nanotube arrays has been discussed.

Keywords: ZnO nanotube; Electrodeposition; Selective dissolution

1. Introduction

In recent years, one dimensional ZnO nanostructures in highly oriented and ordered arrays have been demonstrated to be of crucial importance for the development of novel devices, such as room-temperature UV lasers, light-emitting diodes, solar cells, gas sensor and so on [1–6]. Especially, great interests have been focused on the controllable synthesis and application of the ZnO nanotube arrays owing to its special hollow structure and larger surface area. Several approaches have been developed for fabricating ZnO nanotube arrays. The most direct route to prepare ZnO nanotube arrays is the template-assisted method, in which the nanochannels of anodic aluminum oxide membrane were filled by the electrochemical deposition method [7]. However, the ordered arrays may be destroyed when the template is removed. Another popular strategy is a solvothermal method, which were performed under high pressure in an autoclave [8–10]. But, in these approaches, control of the size and wall thickness during the growth of nanotube remains complex and difficult. Recently, electrochemical deposition method has been to adopted to prepare ZnO nanotube arrays on transparent conductive substrates by a two-step route, which could be conducted at atmospheric pressure and at near room temperature [11–14]. Though extensive efforts have been made to fabricate ZnO nanotube arrays, it is still a challenge to realize large-scale growth of ZnO nanotube arrays with controllable sizes and dimensions.

In this paper, a two-step route has been used to fabricate large-scale ZnO nanotube arrays on indium doped tin oxide (ITO) glass substrates. The first step consists in the electrodeposition of ZnO nanorod arrays in an aqueous solution of zinc nitrate. In the second step, the core of electrodeposited ZnO nanorods is selectively etched in a KOH solution. The effects of KOH concentrations, time, and temperature on the formation process and morphologies of ZnO nanotubes have been investigated. It is expected that these ZnO nanotube arrays on conducting ITO substrates might be convenient for the fabrication of electrical devices such as dye-sensitized solar cells, sensors, and electroluminescent devices.

2. Experimental

The ZnO nanotube arrays were synthesized by a two-step route. Firstly, ZnO nanorod arrays were grown by cathodic electrochemical deposition from an aqueous solution containing 5 mM of zinc nitrate. Zinc sheets (99.99% purity) and ITO glass substrates (pretreated by sonication in absolute

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ethanol and distilled water successively and dried in air at 40 °C) were used the anode and cathode, respectively. The deposition temperature was fixed at 70 °C by a water bath. The deposition current was fixed at 0.9 mA. The effective deposition area on cathode is 1 cm^2 in all experiments. After 4 h of electrodeposition, ZnO nanorod arrays on the ITO glass were obtained. Subsequently, the products were rinsed with distilled water several times and dried at room temperature. Then, the products with the ZnO nanorod arrays were immersed in KOH solution of concentration in the range from 0.09 M to 0.36 M for time periods ranging from 0.5 to 4 h. The temperature of the solution was varied from 30 to 90 °C.

The surface morphology of ZnO nanorods and nanotubes was analyzed by a field emission scanning electron microscope (FE-SEM, Hitachi S-4800). The crystal structure of nanorods and nanotubes was characterized by using X-ray diffraction (XRD, AXS D8-Advance with Cu KR radiation).

3. Results and discussion

Fig. 1a displays the typical FE-SEM micrographs of ZnO nanorod arrays electrodeposited on ITO-coated glass substrate. It can be seen that large-area arrays of uniform ZnO nanorods with well defined hexagonal cross-sections have been grown on the ITO substrate. The nanorods are about 400 nm in diameter, and their *c*-axes are perpendicular to the substrate. The sizes of the nanorods can be readily controlled by tuning the electrochemical parameters [15]. After dissolution in 0.18 M KOH solution for 2 h at 70 °C, we obtained hexagonal ZnO nanotubes (Fig. 1b). By the formation of hexagonal holes along the axes of the nanorods, the sizes of the ZnO nanotubes are similar with that of the nanorods. The high-magnification image of the tubes reveals that the inner/outer wall surfaces are quite smooth and the wall thickness is uniform in ~60 nm.

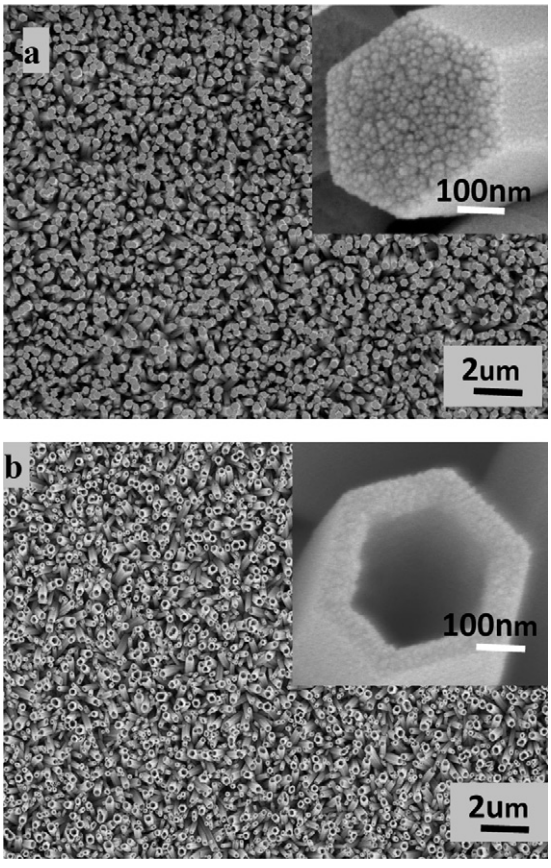

Fig. 1. SEM images of ZnO nanorod arrays electrodeposited on ITO-coated glass substrate (a) and ZnO nanotubes by selective dissolution of the rods in 0.18 M KOH solution for 2 h at 70 °C (b).

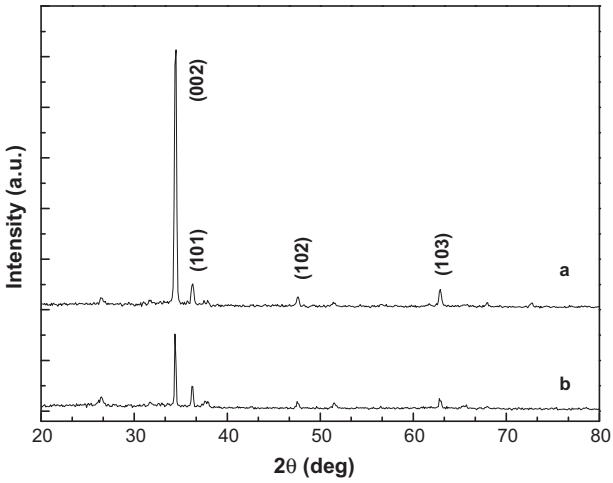

Fig. 2. XRD patterns of ZnO nanorod arrays (a) and ZnO nanotube arrays (b).

Fig. 2 illustrates the X-ray diffraction pattern of ZnO nanorods and ZnO nanotubes. All these diffraction peaks can be indexed as hexagonal wurtzite structures of ZnO, and no peaks for other impurities were detected in the spectra. The sharp and intense peaks (0 0 2) indicate that both ZnO nanorods and ZnO nanotubes are oriented perfectly with their *c*-axis being perpendicular to the ITO substrates, but the intensity of the (0 0 2) diffraction peak in ZnO nanotube arrays was much weaker than that of ZnO nanorod arrays.

From the chemical view of point, this selective etching mechanism has been proposed to explain the formation of ZnO nanotubes [13,14]. It is known, ZnO is an amphoteric oxide which can be dissolved with acid or alkali. In alkali solutions, this chemical equation can be described below:

$$ZnO + 2OH^- \rightarrow ZnO_2^{2-} + H_2O$$

To form the tubular morphology, the dissolution of ZnO nanorods must be a preferential etching process. As there were no other assistant reagents in the etching solution, the preferential etch should be related with intrinsic characters of the ZnO nanorods. One hand, the {0 0 0 1} plane has higher surface energy and is metastable, which leads to the preferential etch in the {0 0 0 1} plane. On the other hand, more defects existed in the center part of nanorods, and led to the preferential etch in the center part of the nanorods.

In order to study the formation process of ZnO nanotubes, the time, KOH concentration and temperature dependence of