Synthesis and photoluminescence of well aligned ZnO nanotube arrays by a simple chemical solution method

Yuewen Wang Zuolin Cui*

Key Laboratory of Nanomaterials, Qingdao University of Science and Technology, Zhengzhou Road 53, Qingdao 266042, PR China
cuizl@public.qd.sd.cn

Abstract. The oriented ZnO nanotube arrays have been synthesized by a chemical solution method on a silicon wafer coated with ZnO thin films via thermally decomposing zinc acetate at 280°C. The morphologies, phase structure and the photoluminescence (PL) properties were investigated by field-emission scanning electron microscopy (FE-SEM), X-ray diffractometer (XRD), transmission electron microscope (TEM) and photoluminescence (PL) spectrum. It was found that the outer diameters of the ZnO nanotube ranges from 200nm to 300 nm, and the wall thickness is in the range of 30nm to 40 nm. ZnO nanotubes prefer to grow along the c axis. Photoluminescence (PL) spectrum shows a strong UV emission peaks at ~380 nm and a broad green-yellow emission at ~ 580 nm.

1. Introduction

Zinc oxide (ZnO), with a direct band gap of 3.37 eV and a large exciton binding energy of 60 meV[1-3] at room temperature, has received considerable interest due to its many important applications including blue light-emitting diodes (LEDs), field-effect transistors(FET), ultraviolet laser diodes (LD)[4] , and so on. Since the first report of ultraviolet lasting from arrays of ZnO nanorods[5], vast interest has been devoted to the synthesis of vertically aligned one-dimensional (1D) ZnO nanostructure materials (nanorods (NRs), nanowires (NWs), nanotubes (NTs), etc.))[6]. Several methods of synthesizing ZnO nanostructure arrays have been employed, including vapor phase transport (VPT), template-assisted growth, electrochemical deposition, pulsed laser deposition (PLD), motel-organic chemical vapor deposition, thermal vaporization[7-9] However , this vapor phase synthesis methods are very expensive and require high temperature and low press. Therefore, a simple and fast route for the synthesis of well aligned 1D ZnO nanostructure materials on the substrate under ambient conditions has remained a great challenge until now. In this paper, we present a simple method for synthesis of vertically aligned ZnO nanotubes with diameters in the range 200–300 nm and wall thickness in the range of 30–40 nm on silicon substrates that had been pre-covered by a thin ZnO film produced via thermally decomposing zinc acetate at 280°C by a chemical solution method.

2. Experiment·

2.1. Materials

The raw materials included zinc nitrate hexahydrate (Zn(NO3)2·6H2O), zinc acetate dihydrate (Zn(CHCOO)2·2H2O), hexamethylenetetramine((CH2)6N4). All reagents and solvent used in this
experiment were chemical reagent grade. Silicon wafers as substrates were rinsed ultrasonically successively in anhydrous ethanol and distilled water, then dried in the air.

2.2. Preparation
In this work, the preparation process of ZnO nanotube arrays need two steps: in the first step (seed layer deposition) ZnO seed layers were firstly deposited on silicon substrates. In brief, zinc acetate dihydrate (0.005M) was dissolved in anhydrous ethanol with continuous stirring for 30 min. Then, the clean silicon substrates were dipped into this clear solution 10min and drawn out at 2 cm/min and dry in the air, then the second time dipping was carried out. The process was repeated for six times. Subsequently, the substrates were heat-treated at 280°C for 2 h to obtain seed layers. in the second step (nanotube arrays growth), zinc nitrate hydrate (Zn(NO3)2·6H2O) (0.025M) and hexamethylenetetramine (HMT; (CH2)6N4) solution (0.025M) were mixed and stirred to get a uniformly growth solution, then the substrate with ZnO seed layers was horizontally suspended in aforementioned growth solution at 85 °C for 6 h, then the growth solution was cooled down to room temperature naturally. The substrate was pulled out and thoroughly washed with deionized water to remove any residual salt or amino complex on the surface and allowed to dry in air at room temperature.

2.3. Characterization
The morphologies and sizes of the resulting products were determined by field-emission scanning electron microscopy (FE-SEM, JSM 6700F) and transmission electron microscopy (TEM, JEM 2000EX). The crystal structures of the resulting products were characterized by X-ray diffractometer (XRD, Rigaku D-max-γA XRD with Cu Kα radiation, λ=1.54178 Å). Photoluminescence (PL) at room temperature was measured using a He–Cd laser with a wavelength of 325 nm as the excitation source.

3. Results and discussion
X-ray diffraction analysis was carried out to investigate the phases of ZnO nanostructures. A typical XRD pattern of the as synthesized products is shown in figure 1. All of the diffraction peaks in figure 1 can be exactly indexed to the hexagonal ZnO with lattice constants a=0.3249 nm and c=0.5206 nm, which is in good agreement with the literature values (JCPDS 36-1451). No impurity peaks are observed, indicating a high purity of the final products. The much stronger (002) peak indicates that these ZnO nanostructures prefer to grow along the c-axis.

Figure 1. XRD pattern of ZnO nanotube array on the silicon substrate coated with ZnO thin films
The surface morphologies of the ZnO nanotube arrays were characterized by scanning electron micrograph (SEM), as shown in figure 2.

Figure 2 Scanning electron micrographs of ZnO nanotube array on silicon substrates. (a) Top view at low magnification (b) top view at relatively high magnification

Figure 2a is the low magnification image of the ZnO nanotube arrays grown on a silicon substrate coated with a thin film of ZnO, showing the array consists of the nanotubes with diameters of 200–250 nm and most of the nanotubes are perpendicular to the substrate.

The figure 2b reveals a high-magnification SEM image of one ZnO nanotube, showing a perfect hexagonally faceted morphology with a diameter of 200-300nm, and uniform wall thickness of about 30-40 nm

Further structural characterization of the ZnO nanotube was performed by TEM. Figure 3 shows a typical TEM image of an individual ZnO nanotube, the inset of Figure 3 shows the accompanying selected-area electron diffraction pattern (SAED) pattern and reveals that the obtained ZnO nanotube exhibits crystal structure.
To characterize the optical properties of ZnO nanotube arrays, we performed photoluminescence (PL) measurements. As an excitation source for the PL experiment, a He–Cd laser (325 nm) was employed. Figure 4 shows the room-temperature PL spectrum of ZnO nanotube arrays fabricated on the silicon substrate. Two typical emission peaks at ~380 nm and ~580 nm were observed, which were assigned to UV emission and green-yellow emission, respectively. According to the literature, the UV emission with a peak at ~380 nm has been attributed to the near band edge emission of ZnO. The green-yellow emission is a deep-level transition, originating from the recombination of the holes with the electrons occupying the singly ionized oxygen vacancy. The intensity of the deep-level emission is determined by the concentration of the oxygen vacancies in the ZnO crystal.

**Figure 3** a TEM image of an individual the nanotube and related SAED patterns

**Figure 4** Photoluminescence spectrum of the ZnO nanotube arrays at room temperature
4. Conclusion
Well-aligned ZnO nanotube arrays were grown on silicon wafer substrates coated with ZnO film by a simple chemical solution method under mild conditions. The outer diameters of the nanotube range from 200nm to 300 nm, and the wall thickness is in the range of 30–40 nm. The ZnO nanotube is wurtzite structure, which prefers to grow along the c axis. The photoluminescence (PL) spectrum of the ZnO nanotube has a broad and stronger visible emission peak showing the potential application as a visible phosphor.

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