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One-step method for growing of large scale ZnO nanowires on zinc foil

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ABSTRACT

Large scale ZnO nanowires were grown on the zinc foil substrate by a novel and facile hydrothermal method at low temperature. The obtained ZnO nanowires were characterized by field emission scanning electron microscopy (FESEM), energy dispersive X-ray analysis (EDX), transmission electron microscope (TEM), X-ray diffraction (XRD) and photoluminescence (PL). It is shown that the as-grown ZnO nanowires have a very good crystallinity with hexagonal wurtzite structure. The room temperature PL of the ZnO nanowires is also studied, which exhibited strong ultraviolet (UV) emission at 382 nm. In addition, the possible formation process of these ZnO nanowires at different intervals is presented. The applied method can be used as a promising, simple and fast option for large scale production of ZnO nanowires.

1. Introduction

Recently, various one-dimensional ZnO nanostructures, such as nanowires [1], nanorods [2] and nanotubes [3] etc. have been synthesized due to their outstanding physical properties. Especially, ZnO nanowires are important materials because of their unique structural one-dimensionality, possible quantum confinement effects in two dimensions, and nontoxic. It had been reported that they can possess novel electronic and optical properties with uses as room-temperature ultraviolet lasers [4], photocatalyst [5], biosensor [6], electrodes [7], coatings [8] and solar cell [9]. In addition, their magnetic properties can be modified by intentionally introducing impurities into the lattice [10].

Until now, the vapor-phase techniques such as metal–organic chemical vapor deposition, chemical vapor transport, and pulsed laser deposition are major physical approaches to synthesis ZnO nanowires [11]. Although these methods can produce high-quality, single crystalline wires with lengths of several microns, they generally require expensive equipment, complex process control, and stringent reaction conditions such as high temperature (450–900 °C) and low or high pressure. In addition, the produced nanostructures often showed poor uniformity and low yield [12]. In order to solve this problem, the exploration of novel and facile approaches for ZnO nanowires microstructure never stopped. More recently, besides the gas-phase approach, various synthesis strategies such as flexographic printing [13], laser decomposition [14], thermal oxidation [15], hydrothermal [16] and electrospinning technique [17] etc had been developed. Among which, the hydrothermal method is recognized as a low-cost and powerful one because the solution chemical approaches can allow the growth of ZnO crystals at relatively lower temperatures (60–200 °C), and can be used for large-scale production [18].

Herein, a simple hydrothermal method is put forward for the large scale growth of ZnO nanowires on the zinc foil. The quality of the resulting nanowires has been characterized by FESEM, EDX, TEM, XRD, and PL. The as-grown ZnO nanowires showed a very good crystallinity with hexagonal wurtzite structure. The room temperature photoluminescence of the as-prepared ZnO nanowires exhibited strong UV emission at 382 nm. To better understand the growth process of these ZnO nanowires, products prepared at different intervals were systematically investigated.

2. Experimental section

For the preparation of high density ZnO nanowires at a large scale, a typical easy process was as follows: A piece of zinc foil (99.9% purity, Sigma-Aldrich) with $20 \times 20 \times 0.25$ mm^3 in size was cleaned by sonication in absolute ethanol and deionized water. After that, the zinc foil was placed on the bottom of a Teflon cup (20 mL) in a stainless autoclave and then the cup was filled with ethylenediamine (3.5 mol/L) aqueous solution. Then, the autoclave was maintained at 140 °C for 10 h and cooled down to room temperature naturally. Finally, the obtained film was washed with ethanol, and distilled water, and dried in a desiccator. On drying in air, the resulted zinc substrates were found to be covered with a white layer of ZnO (as shown in Fig. 1a). To better understand the growth process of these ZnO nanowires, products at different

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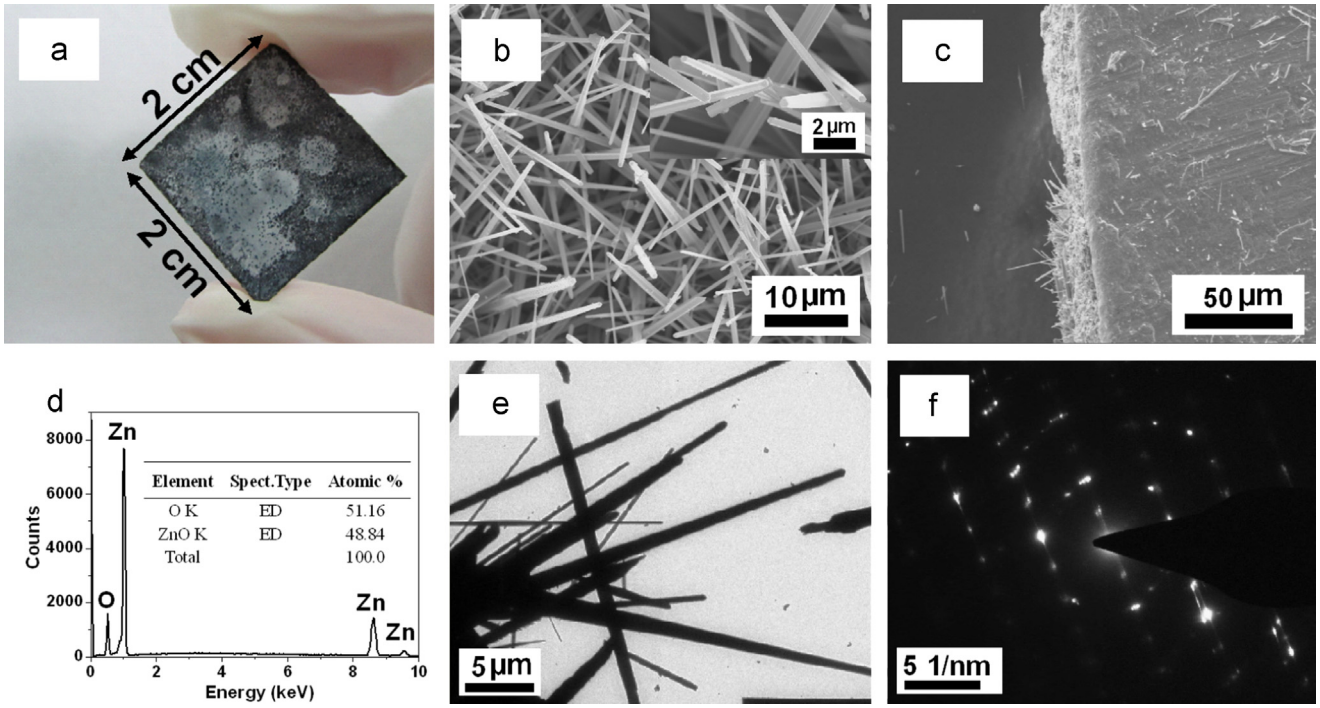

Fig. 1. (a) Digital image of fabricated 2 cm × 2 cm ZnO nanowires on zinc foil. (b) FESEM image of ZnO nanowires at a low magnification. Inset shows the magnified image. (c) The cross-section view of ZnO nanowires thin film on zinc foil. (d) The corresponding EDX pattern of the ZnO nanowires. (e) TEM image of the obtained ZnO nanowires. (f) The selected area electron diffraction pattern of the sample.

intervals such as 2 h, 5 h and 8 h under hydrothermal condition at 140 °C were systematically investigated. The corresponding samples are denoted as ZNW-2, ZNW-5, and ZNW-8, respectively.

FESEM images were taken on a Hitachi S4800 scanning electron microscope equipped with a field emission gun. The chemical composition was determined by energy dispersive X-ray analysis (EDX). The transmission electron microscope (TEM) images were obtained using a JEOL 1200EX TEM operated at 80 kV. Structures of the products were characterized by powder X-ray diffraction using a Philips PW 3710 X-ray powder diffractometer. Photoluminescence was studied on a HITACHI F-7000 fluorescence spectrophotometer with a Xe light as excitation source at 325 nm.

3. Results and discussion

Fig. 1a shows the digital image of fabricated 2 cm × 2 cm ZnO nanowires on zinc foil. Fig. 1b shows the FESEM image of ZnO nanowires at a low magnification. Inset shows the magnified image. It can be observed that ZnO crystals with wire-like structures randomly distributed on the surface of the zinc foil. From the higher magnification, the biggest ZnO nanowires show ~1 μm in diameter. By contrast, the smallest ZnO nanowires show ~300 nm in diameter. In addition, the tip diameters of the ZnO nanowires are slightly smaller than that of the middle. Fig. 1c shows the cross-section view of ZnO nanowires thin film on zinc foil. It can be estimated that the thickness of ZnO nanowires is about 15 μm.

The formation of ZnO after hydrothermal treatment was demonstrated by the elemental signature in the EDX spectrum (Fig. 1d). The EDX spectrum exhibits O, and Zn peaks, and the corresponding atomic percentage are 51.16% and 48.84%, respectively. Moreover, the obtained ZnO nanowires were further investigated using TEM (Fig. 1e). Meanwhile, the selected area electron diffraction pattern of the sample is shown in Fig. 1f.

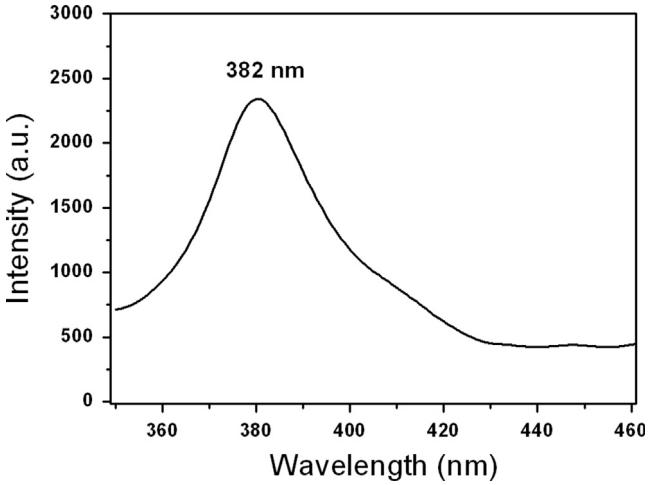

Fig. 2. The room temperature photoluminescent spectrum of ZnO nanowires on zinc foil.

Photoluminescence spectroscopy is an effective technique for evaluating the optical properties of semiconductor materials. Fig. 2 shows a typical room-temperature PL spectrum of the ZnO nanowires excited by 325 nm laser, with a dominant emission peak centered at 382 nm, which corresponds to the UV emission of ZnO with a band gap of 3.24 eV. Generally, the sharp UV emission peak at ~382 nm is attributed to the recombination of free excitons [19]. Meanwhile, there is no other defect emission was observed.

To better understand the growth process of these ZnO nanowires nanostructures, products prepared at different intervals were examined by FESEM. As can be seen in Fig. 3a, the original zinc foil source showed a relatively smooth surface in a large scale. However, worm-like structures were formed based on zinc foil substrate after 2 h hydrothermal reaction as shown in Fig. 3b.