Materials Letters 206 (2017) 162–165

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Enhanced field emission of ZnO nanoneedle arrays via solution etching at room temperature

Huanming Ma [a,*], Zhiwei Qin [a], Zaide Wang [a], Mashkoor Ahmad [b], Hongyu Sun [c,*]

[a] CITIC Dicastal Wheel Manufacturing Co., Ltd, Qinhuangdao 066011, China
[b] Nanomaterials Research Group, Physics Division, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Islamabad 44000, Pakistan
[c] Department of Micro- and Nanotechnology, Technical University of Denmark, Kongens Lyngby 2800, Denmark

ARTICLE INFO

Article history:
Received 23 April 2017
Received in revised form 29 June 2017
Accepted 3 July 2017
Available online 3 July 2017

Keywords:
ZnO nanoneedle arrays
Crystal growth
Solution method
Field emission

ABSTRACT

ZnO nanoneedle arrays (ZnO nns) were synthesized by a facile two-step solution-phase method based on the etching of pre-synthesized ZnO nanowire arrays (ZnO nws) with flat ends at room temperature. Field emission measurement results showed that the turn-on electronic fields of ZnO nns and nws were 2.7 and 5.3 V μm^{-1} at a current density of 10 $\mu A\ cm^{-2}$, and the field enhancement factors were 4939.3 for ZnO nns and 1423.6 for ZnO nws. The enhanced field emission properties in ZnO nns were ascribed to the sharp tip geometry.

1. Introduction

One-dimensional (1D) nanomaterials show fascinating physical and chemical properties, which allow the applications in electronic/photonic devices, energy conversion and storage [1]. A wide range of 1D nanostructures have been synthesized by catalyst-assisted gas-phase deposition, template methods, oriented-attachment route, chemical/electrochemical etching, and standard photolithography techniques, etc [2]. As a typical direct wide band gap (3.37 eV) semiconductor, zinc oxide (ZnO) has been extensively studied due to its unique properties and potential applications in energy and bionanotechnology [3–8]. For many devices application especially in field electron emission, 1D arrays with sharp tips are highly needed [9,10]. Currently, gas-phase deposition at elevated temperature is mainly employed to yield ZnO nanoneedles randomly dispersed on substrate or ordered nanoneedle arrays (ZnO nns) [11–17]. In those works, high energy consumption and expensive equipment are inevitable, which contradict with the state-of-art concept of green synthesis, and hinder the large scale applications [18]. In this work, we report a two-step solution-phase method to synthesize ZnO nns based on the solution etching of pre-synthesized ZnO nanowire arrays (ZnO nws) with flat tips at room temperature. Thanks to the sharp tip geometry, ZnO nns show improved field emission properties. This work represents a facile way to synthesize ZnO nns with enhanced properties.

2. Experimental

The synthesis of ZnO nanoneedle arrays was realized by the growth of ZnO nanowire arrays and subsequent etching at room temperature. Firstly, a piece of clean zinc foil was suspended in a mixed solution containing 5% formamide and $Zn(NO_3)_2{\cdot}6H_2O$. The reaction was maintained at 70 °C for 18 h to yield ZnO nanowire arrays. Secondly, the sample was rinsed with deionized water and then immersed in KOH (8 M) aqueous solution at room temperature (~25 °C) for 8 h. The samples were examined by powder X-ray diffractometer (XRD; Bruker Model D8), scanning electron microscopy (SEM; Hitachi-S5500, 5 kV), and transmission electron microscopy (TEM; FEI-Tecnai G^2 T 20, 200 kV). Photoluminescence (PL; Hitachi F-4500) measurements were performed at room temperature by employing the 325 nm line of a He – Cd laser as the excitation source. The field emission tests were conducted in a homemade ultrahigh vacuum chamber with a pressure lower than 5×10^{-7} Pa. The emission current verses applied electric field was recorded by a Keithley 485 picoammeter.

3. Results and discussion

Fig. 1a shows a low-magnification SEM image of the aligned ZnO nws with flat tips over the substrate. The length of nanowires

* Corresponding authors.
E-mail addresses: mahuanming@dicastal.com (H. Ma), hyltsun@gmail.com (H. Sun).

http://dx.doi.org/10.1016/j.matlet.2017.07.014
0167-577X/

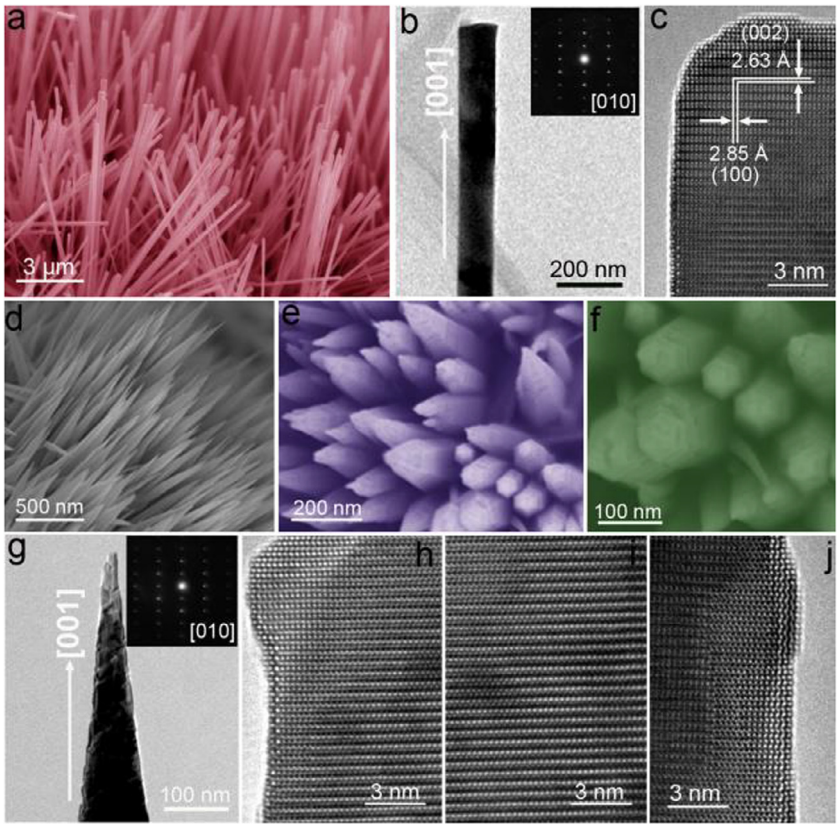

Fig. 1. Morphology and structure of (a–c) ZnO nws and (d–j) ZnO nns.

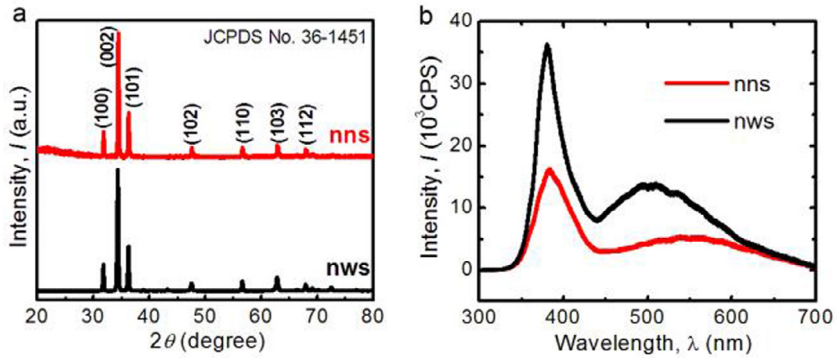

Fig. 2. (a) XRD spectra and (b) room temperature PL spectra of ZnO nns and nws.

is in the range of 6–8 μm, and the average diameter is ~150 nm. Bright-field TEM image of a single ZnO nanowre (Fig. 1b) confirms the flat tip character. HRTEM image (Fig. 1c) of the nanowire illustrates 2D lattice fringes with spacings of 2.63 and 2.85 Å, which are corresponding to the (0 0 2) and (1 0 0) planes of hexagonal ZnO. The HRTEM results and the selected-area electron diffraction (SAED) pattern (Fig. 1b inset) show that the growth direction of the nanowire is along [0 0 1]. After immersing the ZnO nws in KOH aqueous solution, the products change into 1D needle-like arrays with sharp tips (Fig. 1d). The average diameters of the tip and root of needle are sub-10 nm and 120–150 nm, respectively. The length of nanoneedles decrease to 4–6 μm (not shown here), which is due to KOH etching effect. Enlarged SEM image (Fig. 1e, f) shows the fine surface morphology of the ZnO nns and the surface of each nanoneedle is coarse. The needle morphology is also confirmed by TEM image (Fig. 1g). SAED pattern (Fig. 1g inset) and HRTEM images (Fig. 1h–j) indicate the products still keep [0 0 1] as the growth direction after etching treatment. It is interesting to find that spiral-like hexagonal steps, which are related to the possible etching trace, are clearly identified on each nanoneedle (Fig. 1f). Similar spiral morphologies with exposed hexagonal steps or terraces have been reported in the growth of ZnO nanostructures, illustrating the important role of screw dislocations effect [19]. On the contrary, our results show the ZnO spiral structures can also be obtained during etching. Recent works show that 1D growth can be driven by intrinsic screw dislocation, which have been demonstrated both in the gas-phase and solution-phase synthesis [20,21]. Due to the defect strain fields, atoms around the screw dislocation are active and have higher energy [22]. We therefore hypothesize that the opposite process corresponding to the screw dislocation driven 1D growth, i.e., preferable etching or dissolving, could be responsible for the formation of needle-like