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Field emission and room temperature ferromagnetism properties of triangle-like ZnO nanosheets

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ABSTRACT

Triangle-like ZnO nanosheets have been synthesized via conventional thermal evaporation method at a low temperature of 550 °C using CuO as catalyst. The obtained samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDX) and photoluminescence (PL) spectra. The great influences of Cu catalyst on the morphology of the obtained ZnO nanostructures were investigated. The field emission measurements confirmed that the ZnO nanosheets possessed good performance with a turn-on field of 3.1 V μm^{-1} and a field enhancement factor of ~3250, which have promising application as a competitive cathode material in FE microelectronic devices. Room temperatures ferromagnetism has been observed in the triangle-like ZnO nanosheets, although the products consist of only nonmagnetic elements.

1. Introduction

Semiconductor nanostructures materials have stimulated intensive interest due to their particular physical and chemical properties and their applications in nanotechnology. Field emission is one of the important applications of one-dimensional nanostructure materials. It is of great commercial interest in vacuum microelectronic devices such as field emission displays, X-ray sources, parallel-electron-beam microscopes, vacuum microwave amplifiers, etc [1,2]. The field emission properties of various zinc oxide (ZnO) nanowires such as well-aligned, randomly oriented, tetrapod-like, and gallium doped ZnO nanowires had been widely investigated [3–8]. But as we know, ZnO nanostructure arrays are arranged tidily and densely, with the field shielding effect existing, which may have an obvious effect on decreasing the field emission properties. To improve the field emission properties of ZnO film, it is necessary to synthesize a ZnO nanostructure arrays with suitable tip morphology and distribute evenly and sparsely. Recently, Yu et al. [9] have firstly synthesized the "ultra long" ZnO nanostructures including nanobelts, nanocombs and hierarchical ZnO dendrites. Adding CuO/Cu into the reaction source is of critical importance for these ultra long ZnO nanostructures. It is a simple but effective way to control the morphology and density of the ZnO nanostructures. Exploring the catalysing mechanism of Cu in synthesis of ZnO nanostructures is a challenging work.

The prospects of integrating intrinsic magnetic and electronic functionalities into a single material have provoked intense interest towards developing wide band gap diluted magnetic semiconductor (DMS) system with room temperature (RT) ferromagnetism [10–12]. Nanostructure DMSs are expected to have a longer coherence time, which may provide a pathway for increasing the spin lifetime for practical spintronics applications [13]. It is interesting to research the ferromagnetism properties of various ZnO nanostructures.

In this work, ZnO nanostructures were fabricated using conventional thermal evaporation method at a low temperature of 550 °C. Powder mixture of pure Zn, CuO and graphite was employed as the source material. The field emission measurements confirmed that the ZnO nanostructure films had a lower turn-on field, lower threshold field, and uniform electron field emission with high emission spot density. Room temperatures ferromagnetism has been observed in the triangle-like ZnO nanosheets, although the products consist of only nonmagnetic elements.

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2. Experimental

In our experiments, all the growth was performed in a conventional horizontal tube furnace at atmospheric pressure. A quartz boat loaded with a mixed source of high-purity Zn powder, graphite powder and CuO powder was pushed to the center of the tube. A piece of single crystal silicon substrate was then placed over the quartz boat as a substrate, 5 mm above the source powder. Meanwhile, argon at a flow rate of 800 sccm was introduced into the deposition system. After the heating process under a temperature of 550 °C lasted about 90 min, the furnace was cooled down to room temperature at the rate of 5 °C/min under the same argon flow. A layer of white products was found on the surface of silicon substrate (sample 1). To investigate the effect of CuO in the growth of ZnO nanostructures, sample 2 was prepared at the same condition except without CuO powder in the source material.

The obtained zinc oxide triangle-like nanosheets were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDX) and photoluminescence (PL) spectra. Field emission (FE) properties were measured with diode structure in a vacuum chamber at a pressure of $5.00 \pm 0.01 \times 10^{-5}$ Pa at room temperature, the sample (as a cathode) was separated from a phosphor/ITO/glass anode by Teflon spacers with thickness of 400 μm. The magnetic properties were investigated using a physical property measurement system (PPMS) at 300 K.

3. Results and discussion

The morphologies of as-prepared products were examined by SEM. Fig. 1(a) gives the general morphologies of the ZnO triangle-like nanosheets (sample 1). It can be seen that there are large percentage of the products with interesting triangle structures covering the surface of the substrate on a large scale. The transverse width and longitudinal length of the as grown triangle-like nanosheets ranges from 0.5–1 to 1.5–2.5 μm, respectively. Carefully observation reveals that nearly all the orientation of the triangles is upturned. Inset of Fig. 1(a) shows a typical sharp tip of the triangle, these tip structures are very effective to improve the field emission properties. To compare, a SEM micrograph of ZnO nanowires (sample 2) is shown in Fig. 1(b). Inset is the corresponding high magnification SEM image of a single nanowire with 200 nm in diameter. Compare with the bushy nanowire structures, the effective emitting points of the ZnO triangle-like nanosheets film will be increased greatly.

The transmission electron microscopy (TEM) image of a single triangle-like nanosheet with a width of about 1 μm shown in Fig. 2(a) indicates that the nanosheets are single-crystalline nature. The high-resolution (HR) TEM image of the nanosheet indicated by the rectangle in Fig. 2(a) is shown in Fig. 2(b). The selected area electron diffraction pattern recorded on the sheet (inset) indicates that the nanosheet grow along [0 0 0 1] direction. Combining the HRTEM image and SAED pattern, it can be measured that the d spacing is 0.26 nm, which agree well with the *d* spacing of (0 0 0 2) of wurtzite hexagonal ZnO. Energy dispersive X-ray spectroscopy analysis of the samples 1, shown in Fig. 2(c), reveals the average elements (Zn, O and Cu) concentration of the ZnO nanosheets. The average atomic concentration ratio of Zn:Cu measured from ten nanosheets was 0.93:0.07. It can be clearly seen that the two elements Zn and O are uniformly distributed over the whole area; with the content of O being a little higher than that of Zn. Cu is randomly distributed in the ZnO nanosheets with a much lower content. The relatively high O content may be a result of the combined contributions of O in the surface oxide layer of the Si substrate and that in copper oxide nanoparticles, together with diffusion and adsorption of oxygen on the nanoflake after exposure to air.

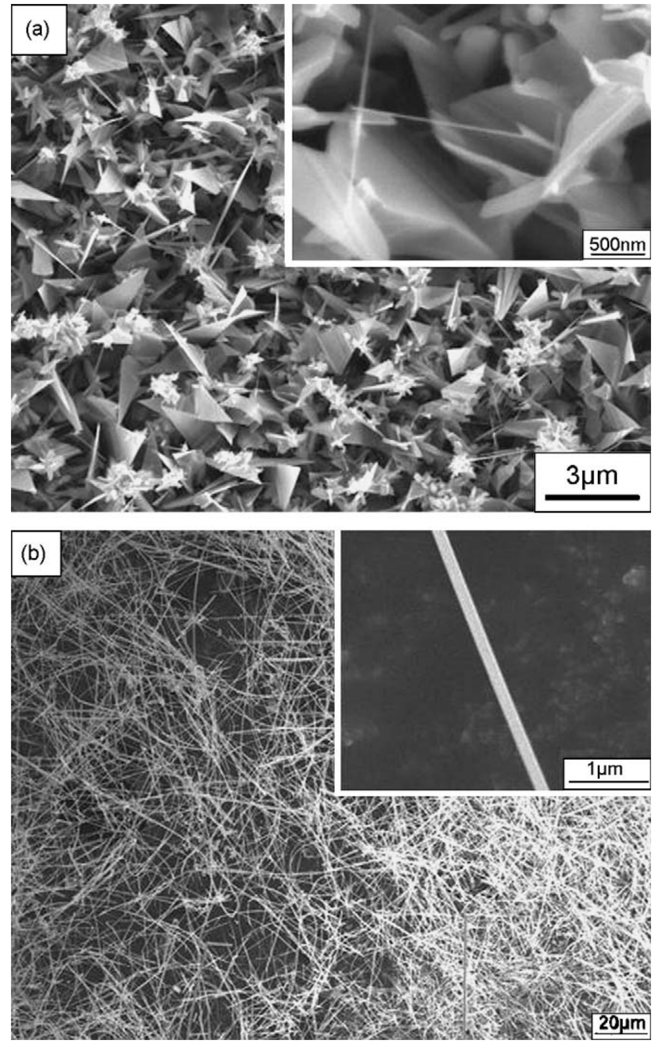

Fig. 1. (a) SEM image of the as-fabricated ZnO nanosheets grown on silicon substrate (sample 1, with CuO as catalyst), inset is SEM image of a typical sharp tip of the triangle flake. (b) SEM image of ZnO nanowires (sample 2, without CuO as catalyst), inset is SEM image of a single nanowire.

In our experiments, CuO powder was added into the reactant mixture powder, which is supposed to play a critical role in the formation of triangle-like ZnO nanosheets [14,15]. The growth mechanism of triangle-like nanosheets was thought to be the growth and coalescence of nanobranches process [16]. In this reaction process, the Cu particles were suggested to act as storage capacitors of the zinc source [9]. First, ZnO nanorods stems nucleate and grow along [0 0 0 1] direction via the mechanism of solid–liquid–solid process. Second, the nanobranches mucleate and grow at the expense of the nanorods stem. The Cu particles evaporated in the atmosphere would deposit on the newly grown stem and act as new nucleation sites for the growth of nanobranches perpendicular to the growth direction of the stem. At the same time, some Cu atoms would precipitate to the surface layer of the stem and result in the distortion of the lattice. Third, the nanobranches are driven by the distortion energy to grow parallel along the axial direction of the stem and lead to the widening growth of the nanobranches. The geometrical coalescence between two neighbored branches would happen when the branches met each other. Such widening and geometrical