# Influence of morphologies on the field emission performance of oriented ZnO nano-arrays\*

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**Abstract:** Different morphologies of comb-like ZnO and oriented ZnO nano-arrays such as ZnO nanoneedles and ZnO nanorods were synthesized by using flexible thermal evaporation method via simply adjusting the temperature and oxygen content. The ZnO nanorods arrays have the lowest turn-on field, highest current density and the largest emission efficiency owning to its good contact with the substrate and relatively weaker field screening effects. The experiments show that the morphologies and orientation of one-dimensional (1D) ZnO nanomaterials have considerable effects on the turn-on field and the emission current density, and the nanoarray also contributes to electrons emission. The results could be valuable for the application of ZnO nanorod arrays as cathode materials in field emission based devices.

 Key words:
 ZnO; oriented; nanorods; field emission; morphology

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## 1. Introduction

ZnO has become one of the few dominant nanomaterials for nanotechnology<sup>[1]</sup>, for it exhibits a wide application in sensors<sup>[2]</sup>, actuators<sup>[3]</sup>, solar cells<sup>[4]</sup> and biomedical sample iences<sup>[5]</sup>. Recently, increasing interest of ZnO has been put on the application in field emitter because of its low electron affinity, high aspect ratio and oxide resistibility<sup>[2, 6]</sup>. Many reports have revealed that ZnO nanostructure with sharp tips have good field emission properties<sup>[7–9]</sup>, such as tetrapods<sup>[10]</sup>, nanoneedles<sup>[11]</sup>, nanorod<sup>[12]</sup>, nanowires<sup>[8, 13]</sup> and nanocones<sup>[14]</sup>. These works verify that ZnO has a potential application in field emission, however it is difficult to control key factors that affect its field emission properties. Generally the electron emission is very sensitive to the shape of emitters and the structure of the device. So it is necessary to investigate the influence of emitters' morphologies on their field emission properties.

In this work, a simple method, thermal evaporation, has been introduced to synthesize different ZnO nanostructures. Just by controlling the temperature and oxygen flux, different morphologies of ZnO have been obtained. The effect of temperature and oxygen content on morphology was investigated in detail. Furthermore, the field emission properties of all those as-prepared ZnO nanomaterials were characterized and disample used systematically.

## 2. Experimental

The experiment was carried out in a horizontal electronic resistance furnace. As an evaporation source, the Zn (99.9%)

powder was spread around on a ceramic boat positioned at the center of the furnace. A silicon wafer coating with 100 nm gold, was placed 5 cm far away from the source along the down airflow. The furnace was quickly heated to the desired temperature at a rate of 30 °C/min and then a certain amount of oxygen and argon gas was introduced. While argon acted not only as a delivering gas during thermal evaporation and but also a protection gas during the heating up and cooling down. After 30 min reaction, the system was shut down and cooled down to room temperature. Some white products were found on both the boat and the substrate. ZnO samples A, B, C and D were synthesized at various temperature and oxygen flux, which is shown in Table 1.

The morphologies of the as-grown ZnO samples were investigated by scanning electron microscopy (SEM, Hitachi-S3000N), X-ray diffraction (XRD, D/Max- $\gamma$ A, CuK $\alpha$  radiation), high-resolution transmission electron microscopy (HRTEM, JOEL JEM-2010F) and fluorescence spectrophotometer (PL, Hitachi F-4600). The cathode was the as-prepared ZnO samples on silicon wafer and the anode was an indium tin oxide (ITO) coated glass with green phosphor powders printed on it. They were separated by a spacer of 1000  $\mu$ m in height. Field mission properties of the samples were measured in a vacuum chamber under a pressure of  $2 \times 10^{-4}$  Pa at room temperature. The current–voltage (I-V) characteristics were

Table 1. Parameters u	ised for s	synthesizing	ZnO.
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Sample	А	В	С	D
Temperature (°C)	500	500	550	550
Oxygen flux (SCCM)	1	3	1	3

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Fig. 1. SEM image of ZnO nanostructures synthesized at various temperatures. (a) Sample A, nanoneedles. (b) Sample B, comb-like. (c) Sample C, nanorods. (d) Sample D, nanorods.



Fig. 2. (a) XRD patterns of sample C. (b) HRTEM image of a single nanorod of sample C.

recorded by Agilent digital multimeter (34401A).

### 3. Results and discussion

The SEM images of ZnO samples with different morphologies synthesized at various conditions are shown in Fig. 1. As shown in Fig. 1(a), ZnO nanoneedles obtained at 500 °C were randomly stretched upward and they are  $\sim 50$  nm in diameter and  $\sim 4 \,\mu\text{m}$  in length. However there are many comb-like ZnO nanostructures in Fig. 1(b), scattering on the substrate and the diameter of each tooth is about 30 nm. Sample C (Fig. 1(c)) and D (Fig. 1(d)) are nanorods. Both of them are perfect dimensional uniformity and vertical to the substrates. But sample D is more dense and thinner than sample C.



Fig. 3. PL spectra of ZnO nanorod of sample C at room temperature.

The theory of vapor-liquid-solid (VLS) mechanism explained the synthesis of ZnO nanostructures. Au acting as catalyst, Zn vapor combined with O2 and then dissolved into Au particle to form a liquid alloy droplet, which is a preferred site for deposition<sup>[15]</sup>. There existed more Zn vapor with the enhancement of temperature, for the melting point of Zn is about 419 °C. In addition, Zn vapor is more active and easier to combine with  $O_2$ . Thus the growth rate speeds up in higher temperature. So the samples synthesized at 550 °C are bigger than that at 500 °C. Since the amount of the O<sub>2</sub> in the reaction chamber was limited, when the amount of O2 increased, more ZnO nuclei may be formed for further growth. Furthermore, the Zn concentration decrease, therefore the growth rate slow down<sup>[16]</sup>. This explains why ZnO are more dense and thinner in higher oxygen concentration. It could be concluded that the morphology of ZnO nanostructures is very sensitive to the synthesis temperature and oxygen flux.

Further insight into the detailed structure was gained by TEM. A typical TEM image of sample C is shown in Fig. 2(a). The high resolution image of a single nanorod shown in Fig. 2(b) revealed the atomic structure of ZnO nanorods of sample C, indicating that the ZnO nanorods contain no defects such as dislocations and stacking faults in the examined area. The lattice fringe of the ZnO nanorods is about 0.32 nm, corresponding to the (001) fringes perpendicular to the growth direction, which is consistent with that of the bulk wurtzite ZnO crystal.

The wurtzite structure of sample C was confirmed by XRD analysis (JCPDS Care No. 89-1397). The XRD pattern reveals that the lattice constants of ZnO nanorods are a = b = 0.3253 nm and c = 0.5213 nm. The overwhelmingly high intensity of (002) reflections peak, which full width at half-maximum is only 0.015°, clearly imply that each ZnO nanorod is perfectly oriented synthesized<sup>[17]</sup>. This *c*-axis preferential growth of ZnO crystals is well known for the lowest surface energy of (001) ZnO basal planes. Except that, no other diffraction peak corresponding to Zn or other impurity was detected.

As shown in Fig. 3, besides a strong narrow peak centered at 380 nm (3.27 eV) in UV band, there appears a weak broad green-yellow band (visible emission) at 494 nm (2.52 eV) and two small peak at 450 nm (2.77 eV) and 470 nm (2.65 eV) for all nanostructures. The UV emission band is the recombination of free excition due to a near-band-edge (NBE) transition of wide band gap of  $ZnO^{[18-21]}$ . And the visible emission is



Fig. 4. Field emission current density versus electric field (J-E) for ZnO nanostructures, and the insert is the corresponding FN plots.

the radial recombination of photo generated holes with electrons, decreasing with the increase of oxygen content<sup>[22]</sup>. The comb-like ZnO and nanoneedle have higher intensity in visible emission than ZnO nanorods. Yang *et al.* believed the intensity of the green band was size-dependent, the intensity increases as the wire diameter decreases<sup>[23]</sup>. The blue emission peaks of 450 nm and 470 nm in comb-like ZnO and nanoneedle are attributed to the O vacancies and Zn interstitials<sup>[24]</sup> which are the centers of electrons capture<sup>[25]</sup> and may influence the electric current.

The field emission current density versus the electric field (J-E) curves and corresponding Fowler–Nordheim (F–N) plots are shown in Fig. 4. Defined as electric field required for  $10 \ \mu \text{A/cm}^2$  current density, the turn-on electric fields of samples A, B, C and D are 2.61, 2.25, 1.81 and 2.05 V/µm, respectively. The turn-on field of ZnO nanorods is lower than that of ZnO nanoneedles and comb-like ZnO, because vertical tips of nanorods greatly evaluate the electric field around it, therefore the electrons are easier to be extracted out. The turn-on field of sample D is a little higher than sample C, for narrow space between ZnO nanorods may shield electric field<sup>[26]</sup>. Although the turn-on field varies slightly with morphologies, they are rather low on the whole. The reason may come from the excellent electric contact with Au coated Si substrate. Unlike turnon field, the current density shows large variations in different samples. The maximum emission current densities of nanoneedles and comb-like are 0.86 mA/cm<sup>2</sup> and 0.64 mA/cm<sup>2</sup>, much lower than that of nanorods (sample C is 2.7 mA/cm<sup>2</sup> and D is 2.45 mA/cm<sup>2</sup>). The lowest current density of comb-like ZnO is due to a lot more O vacancies, which are the capture center of electrons. Furthermore, electrons are usually convenient to be extracted out from the tips. If the nanostructures are towards the substrate, electrons are more probable to transport to the anode. As can be seen in Fig. 1, most of ZnO nanoneedles are towards all directions and all tips of comb-like ZnO lie horizontally on the substrate, which result in few electrons being captured by anode. Whereas, nanorods ZnO vertical erect on the substrate, implying most of the nanorods contribute to the electron emission. But the close space between adjacent ZnO nanorods in sample D also shield the electron field, thus reduce its field enhancement and field emission current<sup>[24]</sup>.

The F-N plot exhibits approximately straight lines, indi-

cating that the emission electrons come from barrier tunneling electrons extracted by electric field. According to F–N law, the relationship between current density (J) and the applied field (E) can be described as

$$J = \frac{AE^2}{\phi} \exp \frac{-B\phi^{\frac{3}{2}}}{\beta E},\tag{1}$$

where  $\phi$  is the work function of the emitting material, A and B are constants,  $1.56 \times 10^{-10} \text{ A} \cdot \text{V}^{-2} \cdot \text{eV}$  and  $6.83 \times 10 \text{ V} \cdot \text{eV}^{-3/2} \cdot \text{m}^{-1}$ , respectively. As the work function of ZnO is 5.3 eV, we can figure out the field enhancement factors  $\beta$ are 3260, 4042, 6382 and 5052, respectively. The higher the enhancement factor, the greater the field around the tips and the electrons are easier to emit. So the local field is closely related to the shape of the emitters and their density. The results demonstrated that the improvement of field emission properties owns a lot to the morphologies.

#### 4. Conclusion

In summary, three types of ZnO nanostructures, nanoneedles, comb-like and nanorods, were successfully synthesized by thermal evaporation. The experiments reveal that higher temperature and sufficient oxygen help to form more nuclei for further growth. The synthesis condition influence the ZnO morphology, especially the orientation and the array, to a large extent. In addition, they have great impacts on the field emission ability. ZnO nanorod arrays exhibiting excellent field emission properties are perpendicular to the substrate and have proper space between adjacent nanorods. The as-fabricated single crystal oriented ZnO nanorods have potential application in field emission and other photoelectric devices.

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