

# Field emission from ZnO nanofibers fabricated by electrospinning

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ZnO nanofibers were fabricated by electrospinning. The samples were characterized by Field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and Raman technique. Field emission scanning electron microscopy (FE-SEM) shows that the obtained ZnO nanofibers were randomly aligned on the substrates. XRD and Raman patterns show that the ZnO nanofibers is the wurtzite structure. The turn on electric field of the ZnO nanofibers for generating a current density of  $10 \mu\text{A}/\text{cm}^2$  is  $14 \text{ V}/\mu\text{m}$  and the current density is over  $1 \text{ mA}/\text{cm}^2$  at an applied field of about  $18.9 \text{ V}/\text{mm}$ . The corresponding Fowler–Nordheim plot shows a linear behavior. The possible emission mechanism is discussed.

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## 1. Introduction

One-dimensional nanostructures of wide band-gap semiconductors have been considerably studied on field emission properties due to the small size and large aspect ratio, as well as their related novel physical and chemical properties [1]. Field emission from 1D nanostructures has been widely studied for their significance in both fundamental research and technical applications.

Zinc oxide (ZnO) nanomaterials are promising semiconductor materials for applications in photonic and electronic devices, such as dye-sensitized solar cells [8], photodiodes [9], nanolasers [10], and gas sensors [11], its also has been regarded as one of the most promising candidates for field emission applications because they are characterized by a high aspect ratio in combination with high thermal stability, easily tuned electronic property wide direct band gap ( $\sim 3.37 \text{ eV}$ ), large exciton binding energy  $60 \text{ meV}$ , and oxidation resistance. So far, different methods have been employed to prepare ZnO nanostructures, such as chemical vapor deposition (CVD) [2], hydrothermal [3], thermal evaporation [4, 5], pulsed laser deposition [6], electrochemical deposition [7], electrospinning [12, 13].

Among them, the electrospinning has been proved as an efficient and inexpensive way to fabricate inorganic nanofibers in recent years [14-16]. The fibers prepared by electrospinning have good orientation, large specific surface area, large aspect ratio and dimensional stability. Using this method we can obtain nanofibers with diameters ranging from less than  $10 \text{ nm}$  to over several micrometers that depend on the applied-voltage and the

distance between two electrodes, the viscosity of precursor, the conductivity of polymeric fluids.

In this paper, we report the field emission behaviour of ZnO nanofibers prepared by electrospinning method. To our knowledge, this is the first report on ZnO nanofibers field emission properties.

## 2. Experimental

All chemicals were analytical grade purity and used as purchased without further purification. The ZnO nanofibers used in this study were synthesized via electrospinning. In brief,  $0.2 \text{ g Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and  $0.25 \text{ g PVA}$  were mixed with  $4 \text{ ml}$  deionized water, followed by magnetic stirring for  $4 \text{ h}$  at  $60 \text{ }^\circ\text{C}$  in water bath. The prepared solution was loaded into a plastic syringe equipped with a stainless needle. The needle was connected to a high-voltage power supply that is capable of generating dc voltages up to  $60 \text{ kV}$ . A plate of aluminium foil as the collection screen was placed at a distance of  $20 \text{ cm}$  from the needle tip to silicon wafers were held on the screen to be used as substrates. Then the electric voltage of  $25 \text{ kV}$  was applied between the stainless needle and the collector. The electrospinning process was finished in air and the deposition was conducted for  $1 \text{ h}$  so that dense mats were obtained. The as-spun composite nanofibers on silicon wafers were left in air for about  $24 \text{ h}$ . Then these samples were annealed in air for  $1 \text{ h}$  at  $600 \text{ }^\circ\text{C}$ .

The images of the as-prepared product were obtained on a HITACHI S-4800 field emission scanning electron microscope (FE-SEM). X-ray diffraction (XRD) patterns of the nanofibers were recorded using a Rigaku

D/Max-III C (Cu K<sub>α</sub> radiation). Raman spectra were measured at room temperature using the 532 nm of an Ar<sup>+</sup> laser as the exciting light source (JY-HR800). The field emission measurements were carried out in a vacuum chamber with a base pressure of 1×10<sup>-4</sup> torr at room temperature. A probe with about 2 mm diameter was used as the anode and the prepared ZnO sample as the cathode. The distance of the cathode-anode was fixed at 100 μm. The emission current was measured with a cylinder-plane geometry structure and a 2 MΩ resistor was inserted in the series for safety. A dc voltage from 0 to 2500 V was applied to the sample at a step of 50 V.

### 3. Result and discussion

Fig. 1 shows SEM images of ZnO nanofibers. The diameter of fibers was greatly decreased with increasing the annealed temperature. The as-prepared composite fibers (Fig. 1 (a)) exhibits a very long and straight fibrous morphology. The surface of fibers is smooth and uniform. The diameters is range from 100 nm to 200 nm. After being calcined at 600 °C as shown in Fig. 1 (b), the hybrid fibers surface shrunk and became porous due to the decomposition of PVA and crystallization of ZnO. The average diameters of nanofibers is 50 nm, which is smaller than the as-prepared fibers due to complete removal of PVA from the as-prepared fibers.

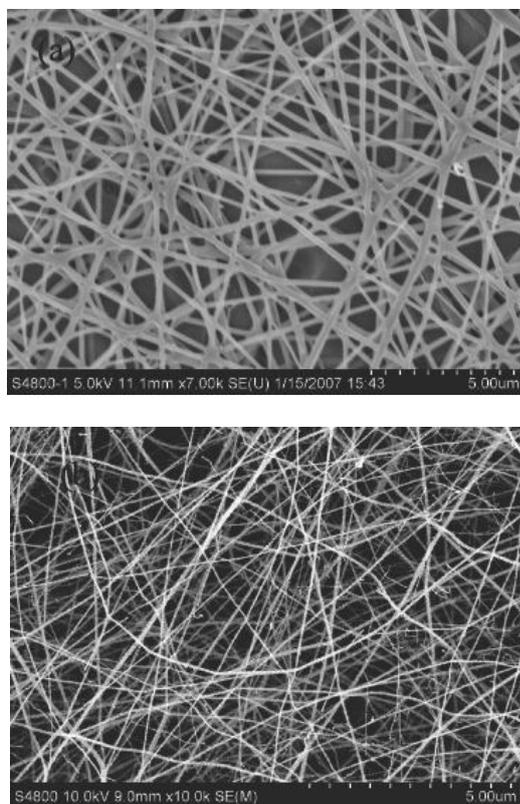


Fig. 1. SEM images of ZnO nanofibers. (a) as-prepared and (b) annealed at 600 °C.

Fig. 2 shows the XRD pattern of ZnO nanofiber annealed at 600 °C. The peaks at  $2\theta=31.9^\circ$  (100),  $34.6^\circ$  (002),  $36.5^\circ$  (101),  $47.7^\circ$  (102),  $56.8^\circ$  (110),  $63.1^\circ$  (103),  $66.5^\circ$  (200),  $68.1^\circ$  (112),  $69.2^\circ$  (201) observed in this samples are indicative of the wurtzite ZnO structure with the lattice constants of  $a = 3.250\text{Å}$  and  $c = 5.207\text{Å}$ . (according to JCPDS No. 36-1451 for ZnO), which revealed excellent crystal quality of the ZnO nanofibers. No impurities peak were found in this pattern.

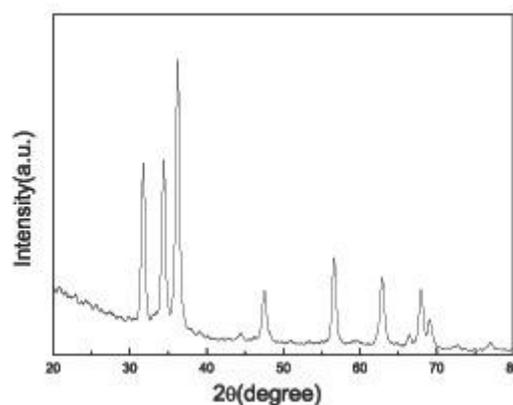


Fig. 2. XRD pattern of ZnO nanofibers annealed at 600 °C.

Raman spectroscopy is an effective method used to study materials structure and composition. The hexagonal ZnO crystal has a wurtzite structure of space group  $C_{6v}^4(P6_3mc)$  with two formula units per primitive cell, which gives six Raman-active phonon modes at 101 ( $E_2$  low), 381 ( $A_1$  TO), 407 ( $E_1$  TO), 437 ( $E_2$  high), 574 ( $A_1$  LO), and  $583\text{ cm}^{-1}$  ( $E_1$  LO) of first order, respectively.

The Raman spectrum of ZnO nanofibers is shown in Fig. 3. The Raman spectrum shows a strong and very sharp  $A_1(\text{LO})$  mode peak, which is an indication of high crystal quality. This result is consistent with the XRD. In backscattering configuration with the incident light normal to the sample surface used herein, only the  $A_1(\text{LO})$  modes are predicted to be observable according to Raman selection rule in the first order spectra.

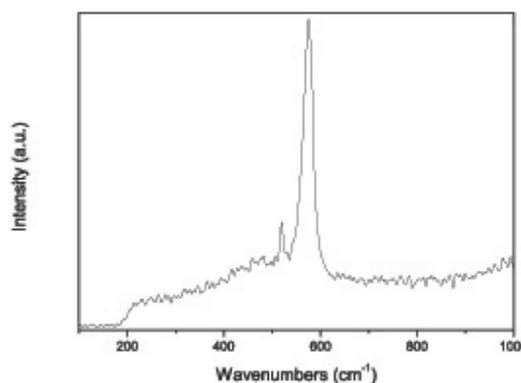


Fig. 3. Raman spectrum of ZnO nanofibers annealed at 600 °C.

The curve of field emission current density  $J$  versus the applied electric field  $E$  for the grown ZnO nanofibers is shown in Fig. 4. The electric field  $E$  is defined as the applied voltage divided by the cathode–anode distance. The turn-on electric field is defined as the electric field  $E$  applied at which the current density  $J$  can reach  $10 \mu\text{A}/\text{cm}^2$ . The current density  $J$  is defined as field emission current divided by the effective emission area. The effective emission area is the size of the cross sectional area of the anode tip. It can be seen that ZnO nanofibers have a turn-on electric field of  $14 \text{ V}/\mu\text{m}$  at the current density of  $10 \mu\text{A}/\text{cm}^2$  its maximum current density is over  $1 \text{ mA}/\text{cm}^2$  at the electric field of  $18.9 \text{ V}/\mu\text{m}$ .

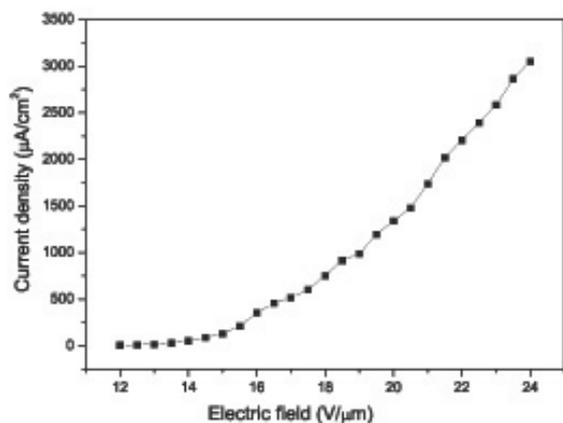


Fig. 4.  $J$ - $E$  relations of the field emission characteristics of ZnO nanofibers annealed at  $600 \text{ }^\circ\text{C}$ .

Fig. 5 shows the corresponding Fowler-Nordheim (F-N) plot. The plot is approximately a straight line, which implies that the emission mechanism is likely of the F–N tunneling type [17]. It is well known that field emission current strongly depends on the electrical field enhancement factor ( $\beta$ ) that follows Fowler–Nordheim formula [18]

$$J = \frac{A\beta^2 E^2}{\phi} \exp\left(\frac{-B\phi^{3/2}}{\beta E}\right)$$

where  $J$  is the current density,  $E$  the applied field,  $\phi$  the work function of ZnO ( $5.37 \text{ eV}$ ),  $\beta$  the field enhancement factor,  $A=1.56 \times 10^{-10} (\text{A V}^{-2} \text{ eV})$  and  $B=6.83 \times 10^3 (\text{V eV}^{-3/2} \mu\text{m}^{-1})$ , while  $\phi$  is the work function and  $E$  is the applied electric field ( $\text{V}/\text{mm}$ ), the field enhancement factor  $\beta$  can be written as

$$\frac{-B\phi^{3/2}}{k}$$

where  $k$  is the slope of F-N plot which can be calculated from the F-N plot. Here, in our calculation, the value of the work function  $\phi$  is  $5.3 \text{ eV}$  and  $\beta$  is calculated to be about  $750$ .

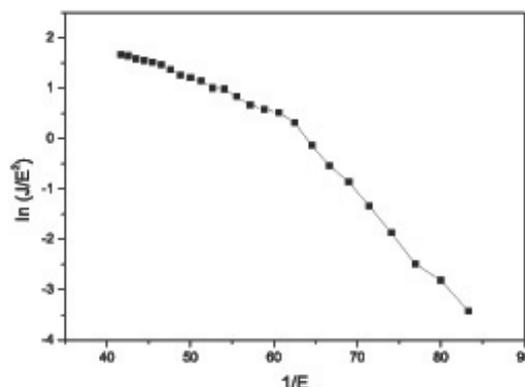


Fig. 5. F-N plots for field emission characteristics of ZnO nanofibers annealed at  $600 \text{ }^\circ\text{C}$ .

### 3. Conclusion

In summary, ZnO nanofibers were grown on Si substrate by electrospinning. FESEM measurement shows that the ZnO nanofibers are randomly aligned on the substrate with a diameter of  $100\text{--}200 \text{ nm}$ . The obtained ZnO nanofibers are of the wurtzite ZnO structure. ZnO nanofibers have a turn-on electric field of  $14 \text{ V}/\mu\text{m}$  at the current density of  $10 \mu\text{A}/\text{cm}^2$  its maximum current density is over  $1 \text{ mA}/\text{cm}^2$  at the electric field of  $18.9 \text{ V}/\mu\text{m}$ . The fact that the F-N plots of the nanofibers are linear implies that the emission mechanism is likely of the F–N tunneling type.

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