Field emission from randomly oriented ZnO nanowires

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(Received 14 December 2006; accepted 30 May 2007; published 29 June 2007)

Randomly oriented zinc oxide (ZnO) nanowires with different diameters were synthesized on a large scale on silicon substrates through a simple physical evaporation method. The nanowires exhibit stable and uniform electron field emission, and the turn-on field reduces with the diameter decreasing. The perfect field emission ability of the ZnO nanowires may be related to their rough surface and sharp curvature. Considering the efficient synthesis method and their excellent field emission characteristics, the authors expect that the randomly oriented ZnO nanowire films could have a promising industrial prospect as economic emitters for flat panel displays. © *2007 American Vacuum Society.* [DOI: 10.1116/1.2752517]

I. INTRODUCTION

Many nanostructured materials have been considered as efficient field emitters for field emission displays (FEDs) and related vacuum microelectronics. The reduced sizes of the nanomaterials result in high local electric fields, and large electron emission currents can be achieved. Carbon nanotubes have been considered to be one of most promising candidates for FED applications,[1] and wide band-gap nanostructures, such as GaN, AlN, and SiN, have been also investigated.[2–4] However, the field emission of these materials undergoes irreversible degradation under oxygen ambient. As a wide band-gap oxide semiconductor, ZnO nanostructures are promising materials due to their inherent properties of thermal stability, oxidation resistance, and high chemical stability. To date, field emission from kinds of ZnO arrays, such as nanowires, nanoneedles, nanopins, and nanotubes has been observed, and these results suggest that nanostructured ZnO has great potential application in FEDs.[5–8] However, the synthesis of ZnO arrays is difficult to control and grow uniformly on a large scale, and the field emission ability of the ZnO arrays is usually influenced by screening effect. In the present article, we provide one method to synthesis large-area randomly oriented ZnO nanowires on silicon substrates via a simple physical vapor deposition method, and we also investigate the field emission from the randomly oriented ZnO nanowires in detail.

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II. METHODS

Large-area ZnO nanowires were synthesized through a thermal evaporation process of pure zinc powders. A glass slice with zinc powders was put into a horizontal tube furnace, meanwhile, a cleaned (100) silicon wafer was placed downstream from the vapor for collection of the products. The source temperature was raised to about 500 °C and hold for a certain time with an argon flow. We can control the mean diameters of the nanowires by adjusting these synthesis parameters. The summary of four batches (namely, sample A–D) and the corresponding experimental conditions is presented in Table I. During the growth process, the temperature around the silicon substrate was intentionally kept below 500 °C for practical consideration.

The morphology and microstructure of the samples were studied using field emission scanning electron microscopy (FESEM: DB-235 focused ion beam system) and high-resolution transmission electron microscopy (HRTEM: Tecnai F30). The phase purity was characterized using x-ray diffractometer (XRD) with Cu $K\alpha$ radiation and the composition analysis was performed using energy-dispersive x-ray

TABLE I. Growth conditions of sample A ~ D.

Sample	Growth temperature (°C)	Pressure (MPa)	Flow rate (SCCM)	Growth time (min)
A	500	0.03	135	100
B	500	0.04	120	130
C	500	0.05	100	160
D	500	0.06	100	200

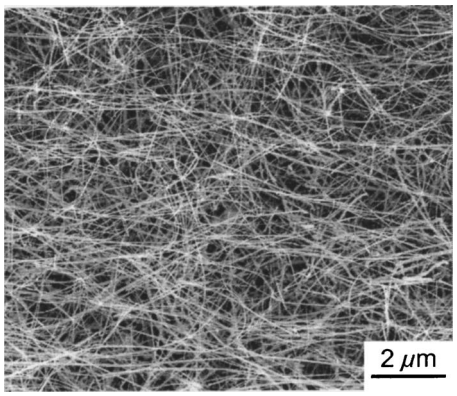

FIG. 1. Typical SEM image of randomly oriented ZnO nanowires grown on the silicon substrate.

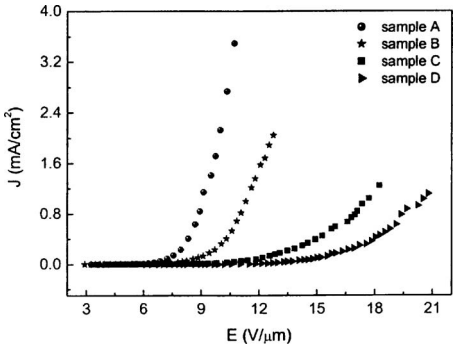

FIG. 3. Emission current density J of the samples A–D plotted as a function of applied electric field E, the distance between the anode and cathode is 100 μm.

spectroscopy. Field emission measurements were performed in a vacuum chamber with a pressure of 10^{-7} Pa at room temperature. The cathode was the as-grown ZnO nanowires on the silicon substrate and the anode was a stainless steel plate. Voltages up to 5 kV were applied between the anode and the cathode, and the emission current-voltage (V-I) data were measured repeatedly at different anode-cathode distances.

III. RESULTS AND DISCUSSION

Figure 1 shows a typical FESEM image of the samples, the ZnO nanowires are randomly aligned and quite uniformly cover the entire substrate surface. The representative length of the ZnO nanowires is around 10 μm. The diameter could be controlled by the growth conditions, and the nominal mean diameters of sample A–D are ~15 (diameter distribution of 6–22 nm), ~28 (diameter distribution of 12–39 nm), ~57 (diameter distribution of 45–80 nm) and ~312 (diameter distribution of 280–336 nm), respectively. X-ray diffraction analyses on all the samples show that the as-grown products are consisted of pure ZnO phase with hexagonal structure. Figure 2 is the typical XRD pattern.

We can study the effects of lateral sizes of the wires on their field emission characteristics with these ZnO samples (sample A–D). The field emission current density (J) from the samples as a function of the applied electrical field (E) is shown in Fig. 3. The emission data were all recorded with a fixed cathode-anode distance of 100 μm and the voltage was increased from 1 to 5 kV with a sweep step of 50 V. For all the samples, as E rises so do the emission current density J, and no saturation of J is evident under the highest applied electrical field. To compare with other emitters, we evaluate the turn-on field (E_{ton}) and threshold field (E_{thr}) of our samples. E_{ton} and E_{thr} are arbitrarily defined as the electrical fields under which an emission current density of 0.1 μA/cm^2 and 1 mA/cm^2 can be observed, respectively. Table II lists the values of E_{ton} and E_{thr} for all the samples as well as their mean diameters (ϕ_m) showing that the larger the mean diameter of the nanowires the higher the values of their E_{ton} and E_{thr}. The field emission characteristics are theoretically evaluated by the simplified Fowler-Nordheim (FN) equation $J=(A\beta^2E^2/\phi)\exp(-B\phi^{3/2}/\beta E)$,[9] where β is the field enhancement factor, ϕ is the work function of the emitter which is 5.3 eV for ZnO,[10] A and B are constants with the value of 1.56×10^{-10} A V^{-2} eV and 6.83×10^3 V eV$^{-3/2}$ μm^{-1}. The field enhancement factors β could be derived from the slope of $In(J/E^2)\sim(1/E)$, and the values of β are estimated to be 1203, 1153, 1014, and 675 for sample A–D, respectively. It clearly demonstrates that sample A has the largest β value. This phenomenon is readily understandable since the field enhancing factor is expected to increase with decreasing radius of curvature of the emitting tip, which is in turn related to the diameter of the ZnO nanowires, it is natural that smaller diameter of ZnO nanowires have larger field enhancing factor and thus smaller turn-on field. Unlike those aligned nanowires,[6] it is not reasonable to attribute the large emission current from our samples only to the tip emission, given the random orientation of the nanowire axes. To further clarify the emission sites, a typical

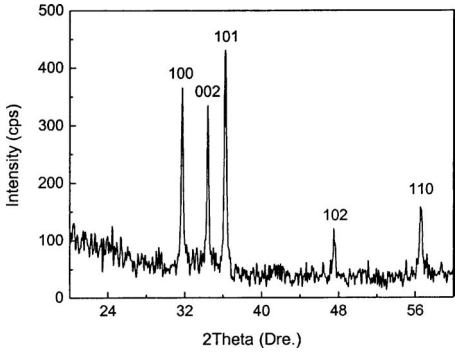

FIG. 2. Typical XRD spectrum of randomly oriented ZnO nanowires.

TABLE II. Correlation between the average diameters (ϕ_m) of the samples and their turn-on field (E_{ton}) and threshold field (E_{thr}).

	Sample A	Sample B	Sample C	Sample D
ϕ_m (nm)	15	28	57	312
E_{ton} (V/μm)	4.6	4.7	6.1	8.8
E_{thr} (V/μm)	9.0	11.3	17.5	20.3

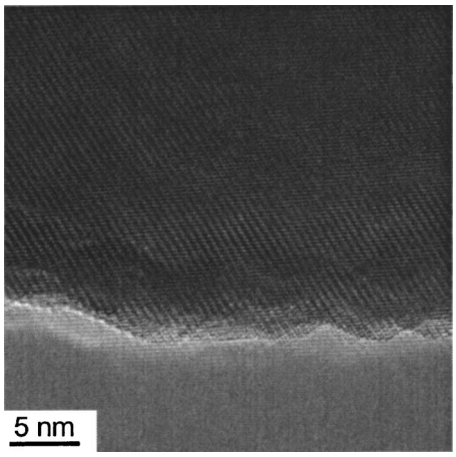

FIG. 4. HRTEM image of the ZnO nanowire side surface shows ridges with typical dimension of 3–5 nm.

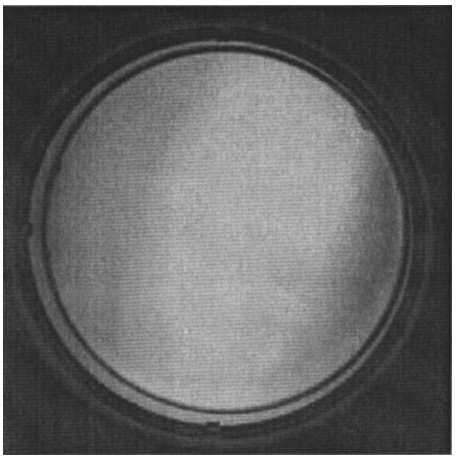

FIG. 6. Cathodoluminescence image of a phosphor fluorescence screen irradiated by the electrons emitted from sample A.

high-resolution TEM image of the ZnO nanowires is shown in Fig. 4. The surface of the nanowire is not smooth but having ridges with about 3–5 nm in size. The high local electric field adjacent to these small features can lead to large emission. The smaller diameter of the ZnO nanowires has larger aspect ratio that might be responsible for the increase of their field enhancing factors and their low turn-on/threshold fields. The high and uniform coverage of the nanowires on the silicon surface provides a large number of such edge-shaped emitters. They can sustain the observed high emission current without any saturation. We therefore believe that these surface ridges of the ZnO nanowires could behave as peculiar field emitters and contribute to the excellent field emission ability of the ZnO nanowire films.

Figure 5(a) shows the curves of emission current I versus applied voltage V from sample A collected with different anode-cathode distances (100–300 μm). Relatively smooth and consistent I-V curves were obtained with different anode-cathode distances, indicating the robustness of the emission process from the ZnO emitters. Figure 5(b) shows the corresponding F-N plots of sample A [I vs V shown in Fig. 5(a)]. Although ZnO is a semiconductor, the F-N theory, which was developed based on the metal field emitters, can still be used here since the F-N plot in Fig. 5(b) can be well fitted by straight line indicating that the electron emission form the randomly oriented ZnO nanowires is a barrier-tunneling quantum process (F-N tunneling).

Besides the low turn-on and threshold fields, an ideal field emitter should exhibit uniformly distributed emission. Figure 6 shows the cathodoluminescence image of a phosphor fluorescence screen irradiated by the electrons emitted from sample A, and the image was recorded using a charge-coupled device camera and the applied cathode-anode voltage was 5 kV. The luminescence of the screen is very bright, and most importantly, it is extremely homogeneous. The bright and homogeneous luminescence from the phosphor fluorescence screen indicates the high and uniform electron current emitted from the ZnO nanowires. From the engineering standpoint, the uniform emission is crucial to the application of nanomaterials as cold cathode emitters in future flat panel displays.

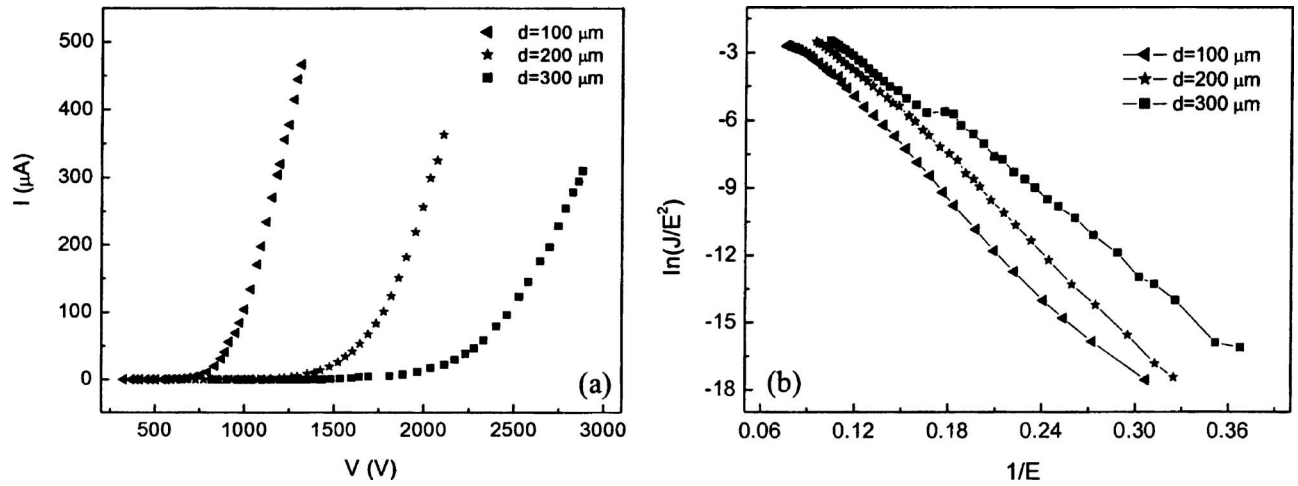

FIG. 5. (a) Field emission curves of sample A measured at different anode-sample distances; (b) FN plots corresponding to (a).

In summary, large-scale randomly oriented ZnO nanowires were fabricated using a very simple physical evaporation method, and the diameter control of the nanowires was achieved by varying the growth conditions. The field emission characteristics of the nanowires depend on their mean diameter. The sample of a smaller mean diameter has lower threshold emission field and higher field emission current density. The excellent field emission properties might relate to their rough surfaces and sharp curvatures. The above results suggest that these randomly oriented ZnO nanowires have great potential applications in flat panel displays. In addition, compared with the fabrication of ZnO arrays, we believe that the simple and efficient synthesis method of the random ZnO nanowire emitters will satisfy more the industrial requirements such as low cost, quality control, and large scale.

ACKNOWLEDGMENTS

This project is financially supported by the National Natural Science Foundation of China (No. 50502005) and Beijing Natural Science Foundation (No. 1062008). One of the authors (Y.Q.C.) is supported by the Beijing Novel Program.

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