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Field emission from well-aligned zinc oxide nanowires grown at low temperature

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Field electron emission from vertically well-aligned zinc oxide (ZnO) nanowires, which were grown by the vapor deposition method at a low temperature of 550 °C, was investigated. The high-purity ZnO nanowires showed a single crystalline wurtzite structure. The turn-on voltage for the ZnO nanowires was found to be about 6.0 V/μm at current density of 0.1 μA/cm^2. The emission current density from the ZnO nanowires reached 1 mA/cm^2 at a bias field of 11.0 V/μm, which could give sufficient brightness as a field emitter in a flat panel display. Therefore, the well-aligned ZnO nanowires grown at such low temperature can promise the application of a glass-sealed flat panel display in a near future. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1518810]

One-dimensional wide band-gap nanowires have attracted much interest because of their remarkable physical and chemical properties.[1,2] Among those wide band-gap nanowires, the zinc oxide (ZnO) nanowire, which has a wide band-gap of 3.37 eV and a large exciton binding energy of 60 meV presents substantial interest for practical applications such as ultraviolet/blue emission devices, piezoelectric devices, acousto-optical devices, and chemical sensors.[3] The ZnO nanowire has been synthesized by various techniques using arc discharge, laser vaporization, pyrolysis, electrodeposition, physical vapor deposition, and chemical vapor deposition.[4–7] Recently, electronic and optical devices fabricated by various semiconductor nanowires were reported.[8–10] Moreover, ultraviolet lasing action was observed in well-aligned ZnO nanowire arrays synthesized by the carbon thermal reduction vapor transport method.[3] However, there were rare reports on field emission properties for wide band-gap semiconductor nanowires.[11,12] Carbon nanotubes (CNTs) have been proved as promising material for a field emitter due to their high mechanical stability, high aspect ratio, and high conductivity.[13–16] In addition, some wide band-gap semiconductors, such as gallium nitride (GaN), aluminum nitride, and ZnO nanowires were also investigated as electron field emitters because they have negative electron affinity, high mechanical strength, and chemical stability. The field emission from hexagonal GaN pyramids or surface plasma-etched GaN films was studied by some research groups.[17,18] However, the field emission from semiconductor nanowires is still not sufficiently studied. Therefore, it was necessary to evaluate the field emission properties for semiconductor nanowires systematically.

In this letter, we report field electron emission properties from well-aligned single crystalline ZnO nanowires grown on silicon (Si) substrate using a metal vapor deposition method at a low growth temperature of 550 °C. The electron emission from as-grown ZnO nanowires reveals high emission current density of ~1 mA/cm^2 at an applied field of less than 11 V/μm. It is sufficient for the application of flat panel displays.

Our synthesis was based on nanosized cobalt (Co) catalyst particles dispersed on an *n*-type Si substrate. In order to form nanosized Co particles, we employed didodecyldimethylammonium bromide (DDAB) and sodium borohydride ($NaBH_4$) as a cationic surfactant and a reducing agent, respectively.[19] In a typical process, the DDAB was dissolved in toluene with concentration of 10 wt %, and then dissolved cobalt chloride ($CoCl_2 \cdot 6H_2O$) to the DDAB/toluene solution (concentration of Co^{2+}:0.005 M). With strong stirring, the $NaBH_4$ aqueous solution (5 M) was added to the toluene solution to a molar ratio of $[BH_4]/[Co^{2+}]=3:1$. The average diameter of Co nanoparticles was about 6–8 nm. The nanometer-sized Co particles in toluene were dispersed onto the Si substrate of 10×10 mm^2 in size and then dried at room temperature. Before the ZnO nanowire growth, the Co nanoparticles were sulfurized in H_2S ambient (being diluted by nitrogen gas) at 400 °C for 60 min. The Co nanoparticles deposited on the Si substrate were put with the face down direction on a quartz boat filled with a metal zinc powder (100 mesh, 99.998%, SIGAMA-ALDRICH). The quartz boat was then loaded in a horizontal quartz tube with an inner diameter of 20 mm. After loading the quartz boat, the quartz tube was heated up to 550 °C under a constant flow of argon (flow rate: 500 sccm, heating zone: 200 mm). The reaction time was 60 min, and a vertical distance between the zinc source and the catalyzed Si substrate was about 3–5 mm. After the reaction, a white wax-like material was deposited on the surface of Si substrate. The as-deposited product was characterized by scanning electron microscopy (SEM) [Hitachi S-4700], transmission electron microscopy (TEM) [Hitachi H-9000 NAR], energy-dispersive x-ray spectroscopy (EDX) [Hitachi S-4700], and x-ray diffraction (XRD) [Rigaku DMAX PSPC MDG 2000].

Figure 1 shows SEM images of the nanowires synthe-

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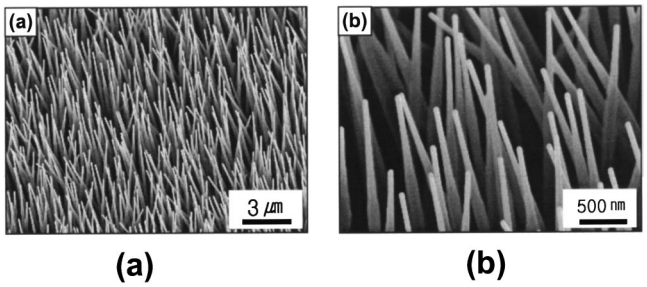

FIG. 1. SEM image of well-aligned nanowires grown on *n*-type silicon substrate (a) and a magnified SEM image of well-aligned nanowires (b).

sized at 550 °C for 60 min. Vertically aligned nanowires with a high density were grown on the Si substrate, as shown in Fig. 1(a). A magnified top view of nanowire array reveals that a high-purity nanowire has a sharp tip, as shown in Fig. 1(b). The synthesized ZnO nanowire indicates the average length of 13 μm and the typical diameter of 50 nm, revealing that the average aspect ratio is estimated to be larger than 250. In our experiment, we have also successfully synthesized high-crystalline ZnO nanowires at higher growth temperature (600–750 °C). Higher growth temperature leads to the higher crystalline ZnO nanowire that possesses higher growth rate and larger diameter.

XRD peaks demonstrate that the produced nanowires show a high-quality wurtzite ZnO structure, as shown in Fig. 2(a). EDX analysis also indicates that the nanowires consist of the ZnO composition clearly, as shown in Fig. 2(b).

The crystallinity of ZnO nanowire was also evidenced by high-resolution TEM and electron diffraction characterization, as shown in Fig. 3. The growth of ZnO nanowire follows *c*-axial direction ($c=5.13$ Å). The inset shows a low-dimensional TEM image of a ZnO nanowire tip that has sharp morphology. It results in the advantage of acquiring a large field enhancement in field emission process.

The *n*-type Si substrate was used as a cathode-conducting layer. Field emission experiments were prepared in a vacuum chamber with a 2×10^{-7} Torr at room temperature. The distance between an indium tin oxide anode and a tip of ZnO nanowire was 230 μm. The measured emission area was 28 mm^2. Emission current was monitored with a Keithley 6517A and recorded at intervals of 0.5 s. The emission current-voltage characteristics were analyzed by using the Fowler–Nordheim (FN) equation for the field emission:

$$J=A(\beta^2V^2/\phi d^2)\exp(-B\phi^{3/2}d/\beta V),$$

where J is the current density, $A=1.56\times10^{-10}$ (AV^{-2} eV), $B=6.83\times10^{9}$ ($VeV^{-3/2}$ Vm^{-1}), β is a field enhancement

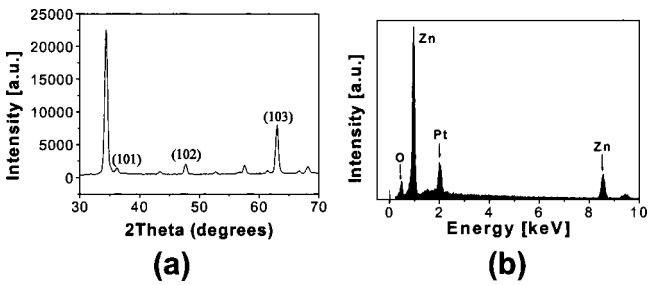

FIG. 2. XRD diffraction (a) and EDX spectra (b) of ZnO nanowires on the substrate.

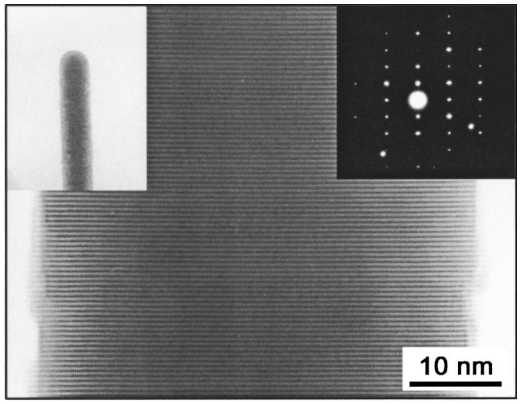

FIG. 3. High-resolution TEM image of a single crystalline ZnO nanowire that has a crystal face direction of [2110]. Inset shows that the ZnO nanowire has a sharp morphology.

factor, ϕ is the work function, $E=(V/d)$ is the applied field, d is a distance between the anode and the cathode, and V is the applied voltage.[20]

Figure 4 illustrates the emission current density from well-aligned ZnO nanowire array grown on the Si substrate as shown in Fig. 1(a). The bias voltage sweeps were conducted several times and the plot shows the initiatory four sweeps. After measuring four times, the current was well stabilized due to the field annealing effect. After a few sweeps, the structure of ZnO nanowire tip seemed to reach a stable configuration and the current intensity was kept constant for each given applied field. The turn-on voltage was about 6.0 V/μm at current density of 0.1 μA/cm^2. The emission current density reached about 1 mA/cm^2 at an applied field of about 11.0 V/μm (so-called threshold field). This threshold voltage was higher than that of CNTs. Nevertheless, the emission current value from ZnO nanowires could produce sufficient brightness for flat panel displays.[21] The FN plot usually presented in the literature is also shown in the inset of Fig. 4. It exhibits a linear behavior in a measurement range, and thus the emission is indeed caused by a vacuum tunneling. The field enhancement factor β can be calculated from the slope of the FN plot if the work function of the emitter is known. The measurement value for the work function of ZnO nanowire was about 5.3 eV.[22] From the inset

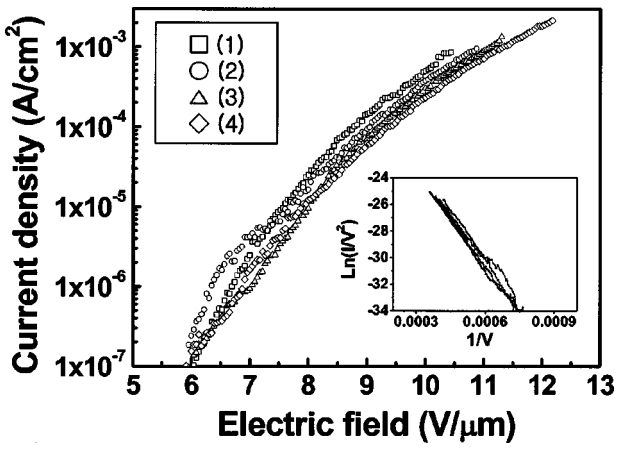

FIG. 4. Emission current density from ZnO nanowires grown on silicon substrate at 550 °C. The inset reveals that the field emission follows FN behavior.

of Fig. 4, the calculated β value was about 847, which is enough for various applications of field emission, even though it was much lower than that of CNTs. The average β of ZnO nanowire is related to the geometry, structure, and density of nanowires grown on the substrate. The ZnO nanowires grown at higher temperatures exhibit a higher crystalline structure and lower density, resulting in a high field enhancement factor. We could find a higher emission current density from ZnO nanowires grown at higher growth temperatures.

In summary, vertically well-aligned ZnO nanowires, which have a single crystalline wurtzite structure, were grown at a low temperature of 550 °C. The turn-on voltage for ZnO nanowires was about 6.0 V/μm and the emission current density was about 1 mA/cm^2 at an applied field of about 11.0 V/μm. This is a sufficient emission current as a field emitter in flat panel displays, even though the threshold voltage for field emission is still higher than that of CNTs. It is suggested that well-aligned ZnO nanowires grown at a low temperature can promise the applicaton of glass-sealed field emission displays.

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