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Stable field emission from hydrothermally grown ZnO nanotubes

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Zinc oxide nanotube arrays were prepared by hydrothermal reaction in ammonia and zinc chloride solutions, and the field emission properties were tested. The turn-on field of the field emission was extrapolated to be about $7.0 \text{ V}/\mu\text{m}$ at a current density of $0.1 \mu\text{A}/\text{cm}^2$. Meanwhile, the emission current densities reached $1 \text{ mA}/\text{cm}^2$ at a bias field of $17.8 \text{ V}/\mu\text{m}$. The field enhancement factor β was estimated to be 910. The field emission of the zinc oxide nanotubes showed good stability. The variation of emission current density was less than 10% during a 24 h test under a field of $15 \text{ V}/\mu\text{m}$. © 2006 American Institute of Physics. [DOI: 10.1063/1.2206249]

Field emission (FE) of zinc oxide (ZnO) nanostructures has received great attention due to its potential applications in vacuum microelectronic devices such as field emission displays, x-ray sources, microwave devices, etc. Nanostructured ZnO is a wide band gap semiconductor, which has high melting point and excellent chemical stability. Moreover, the band bending of wide band gap semiconductors, which usually favors the FE by lowering the surface barrier and bring more electrons to the bottom of conduction band, is often quite dramatic under high fields.¹ It can also exhibit negative electron affinity through heavy *n*-type doping.^{2,3} Hence, good FE performance is expected from ZnO nanostructures. In fact, FE of ZnO tips sharpened by chemical etching was reported early in the 1970s.⁴ The FE from *n*-type ZnO thin film has been observed by Cheung *et al.* in 2003.⁵ To date, FE has been observed from various ZnO nanostructures, such as nanowires, nanoneedles, nanopins, and nanofibers.^{6–10} In addition, ZnO nanostructures exhibit strong endurance to oxygen ambient compared with carbon nanotubes.¹¹ For tubular nanostructures of ZnO, the large thickness ratio of the wall to the diameter implies good FE performance similar to the large aspect ratio of carbon nanotubes. Previously, FE from a single ZnO microtube has been performed by Cheng *et al.*¹²

In the past years, various approaches have been developed to synthesize ZnO nanostructures by means of catalyst-assisted vapor-phase transport,^{6,13} metal-organic vapor-phase deposition,^{14,15} aqueous thermal decomposition,^{16–18} and porous template method.¹⁹ In this letter, we present a simple aqueous solution approach to fabricate ZnO nanotubes with

stable FE performance. This method involves only two chemical agents, so that it can effectively avoid the contaminations occurred in other complicated chemical reactions. Meanwhile, the nanotubes can be aligned on a conductive substrate and utilized directly as field emitters.

ZnO nanotubes were fabricated by a hydrothermal decomposition method on a copper plate substrate. The reaction solution was prepared by mixing 2 ml ammonia (25%) and 40 ml zinc chloride solution (ZnCl_2 , 0.1M) in a bottle with autoclavable screw cap. Then a copper plate substrate, cleaned with acetone and de-ionized (DI) water in the ultrasonic cleaner, was immersed into the reaction solution. The bottle was then heated at a constant temperature of 95°C for 70 min in an ordinary laboratory oven. Subsequently, the bottle was cooled down to 35°C . After thoroughly washing with DI water and drying in air, a white layer of product was deposited on the substrate.

The morphology of the sample was examined by scanning electron microscopy (SEM). Energy dispersive x-ray (EDX) spectra measured by a SEM attachment were used to characterize the elemental composition of the product. The crystal structure of the sample was characterized by x-ray diffraction (XRD) using $\text{Cu } K\alpha_1$ line. The field emission measurement was carried out inside a bell jar which was pumped down to $\sim 10^{-6}$ Torr. The cathode was the ZnO nanotubes on a metal substrate and the anode was the indium tin oxide glass. The distance between cathode and anode was 0.1 mm separated by a polytetrafluoroethylene film spacer with an aperture of 5 mm in diameter for electron emission. The stability of field emission and the dependence of the emission current on the applied voltage were recorded automatically by a field emission detection system. The current data was acquired by varying the applied voltage between the cathode and anode from 800 to 1800 V (corresponding to a field strength of $8\text{--}18 \text{ V}/\mu\text{m}$) with a step of 20 V. The

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FIG. 1. (a) SEM image of the ZnO nanotubes grown on Cu plate by hydrothermal method. The left corner inset shows the top view of a single nanotube. (b) XRD pattern of the hydrothermally grown nanotubes. The inset is the EDX spectrum.

measurement of stability of FE was continued for 24 h at a field of $15 \text{ V}/\mu\text{m}$. All the measurements, including FE, were carried out at room temperature.

Figure 1(a) shows the SEM image of the product. It can be seen that the nanostructures possess tubelike shape with a hexagonal cross section and the nanotubes are predominantly aligned perpendicularly to the substrate. The nanotubes show homogeneous size with about 500 nm in diameter, 50 nm in wall thickness, and $3 \mu\text{m}$ in length. The formation of tubular structure is due to the nucleation in the initial stage followed by the nanorod growth and chemical aging subsequently.^{17,18,20}

Figure 1(b) shows the XRD pattern of the sample. It can be seen that all of the diffraction peaks match the hexagonal ZnO structure with lattice constants of $a=3.242 \text{ \AA}$ and $c=5.176 \text{ \AA}$, in agreement with the values reported in literatures. From the XRD pattern, the intensity of (0002) peak is still quite strong, indicating that the tubes are not completely tubular, i.e., the tubes (or some of them) are tubes at the top but rods at the bottom. However, FE will not be degraded, because such a structure (half-tube half-rod) enjoys both enhancement of sharp edges at the top and good conduction at the bottom.¹⁰ The EDX spectrum of the sample is shown in the inset of Fig. 1(b), where except the peaks corresponding to Zn and O, no trace amount of other impurities, such as Cl,

FIG. 2. Field emission characteristics in J - E (curve A) and $\ln(J/E^2)-(1/E)$ (curve B) plots of the ZnO nanotubes. The straight line is a linear fit to the $\ln(J/E^2)-(1/E)$ plot.

could be seen in the detection limit of the EDX. The contents of Zn and O are determined to be 49.4 and 50.6 at. %, respectively, which is close to the stoichiometry.

Figure 2 shows the FE current density J as a function of the applied field E in J - E plot (curve A) and $\ln(J/E^2)-(1/E)$ plot (curve B). From Fig. 2, the turn-on field is extrapolated to be about $7.0 \text{ V}/\mu\text{m}$ at a current density of $0.1 \mu\text{A}/\text{cm}^2$. Meanwhile, the emission current densities reach about $1 \text{ mA}/\text{cm}^2$ at a bias field of $17.8 \text{ V}/\mu\text{m}$.

The FE current-voltage characteristics can be expressed by a simplified Fowler-Nordheim equation,²¹

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

where J is in the unit of A/cm^2 , E is in the unit of $\text{V}/\mu\text{m}$, ϕ is the work function of the emitter, which is 5.3 eV for ZnO, A and B are the constants with values of $1.56 \times 10^{-10} \text{ A V}^{-2} \text{ eV}$ and $6.83 \times 10^3 \text{ V eV}^{-3/2} \mu\text{m}^{-1}$, respectively, and β is the FE enhancement factor that is introduced to quantify the degree of enhancement of any tip over a flat surface, i.e., β represents the true value of the electric field at the tip compared to its average macroscopic value. For nanostructural ZnO, the value of β is related to the geometry, crystal structure, and nanostructure density.^{6,10} From the slope of $\ln(J/E^2)-(1/E)$ plot, the estimated field enhancement factor β is 910 for the ZnO nanotubes.

FIG. 3. The emission current density J of ZnO nanotubes as a function of the operation time T at $15 \text{ V}/\mu\text{m}$. The straight line is a guiding line for the viewer.

TABLE I. Key performance parameters of some ZnO nanostructure/thin film field emitters reported in the literature and this work. The turn-on field and on field are at current densities of $0.1 \mu\text{A}/\text{cm}^2$ and $1.0 \text{ mA}/\text{cm}^2$, respectively, unless otherwise stated.

ZnO emitter	Turn-on field (V/ μm)	On field (V/ μm)	β	Stability: testing time and fluctuation	Reference
Nanopins	1.92	5.9	657	...	6
Nanoneedles	2.4	7 at $2.4 \text{ mA}/\text{cm}^2$	2.3×10^6	...	8
Microtube	5.6 at $1 \mu\text{A}/\text{cm}^2$	20.2 at $11 \text{ mA}/\text{cm}^2$	...	...	12
Nanowires	8.0	17	900	...	22
Nanorods	3.6 at $10 \mu\text{A}/\text{cm}^2$	11.2	...	30 min, <10%	23
Nanoscrews	3.6 at $10 \mu\text{A}/\text{cm}^2$	11.2 at $1.2 \text{ mA}/\text{cm}^2$	...	30 min, <10%	24
Fibrous thin film	1.4 at $10 \mu\text{A}/\text{cm}^2$	3.6	2.18×10^4	...	25
Tetrapod nanoneedles	1.8 at $1 \mu\text{A}/\text{cm}^2$	3.9	...	8 h, <3%	26
Nanotubes	7	17.8	910	24 h, <10%	This work

Figure 3 shows the variation of the emission current density of ZnO nanotubes within 24 h of testing. No obvious degradation of current density was observed and the emission current fluctuation was less than 10% at $15 \text{ V}/\mu\text{m}$ in 24 h. The stable FE behavior is suggested to be related to the uniform height of the vertical aligned nanotube arrays, which guarantees a uniform field distribution across the device under test.

For comparison, Table I tabulates the key performance parameters of the ZnO field emitters reported in the literature. One can see that our ZnO nanotube emitter is comparable to other nanostructured ZnO emitters. Although with a slightly higher turn-on field, the FE stability of our hydrothermal ZnO tubes is better than any other ZnO nanostructures listed in Table I, except for tetrapod nanoneedles,²⁶ as it is hard to compare with different testing time. It is worth mentioning that this good stability of FE shown in Fig. 3 demonstrates that ZnO nanotube fabricated by hydrothermal method could be a promising candidate of practical FE devices.

In summary, aligned ZnO nanotube arrays were prepared on Cu substrate by aqueous solution decomposition method. The turn-on field of field emission was extrapolated to be about $7.0 \text{ V}/\mu\text{m}$ at a current density of $0.1 \mu\text{A}/\text{cm}^2$, and the emission current density reached $1 \text{ mA}/\text{cm}^2$ at about $17.8 \text{ V}/\mu\text{m}$. The field enhancement factor β was estimated to be 910. The dependence of emission current density on the operation time demonstrates the good stability of the ZnO nanotube emitter. The stable FE behavior is attributed to the uniform height of the vertical aligned nanotube arrays. This method provides a simple and low-cost approach to fabricate field emitters. Furthermore, the substrate size can be scaled up easily for flexible design of field emission display panels and light sources. It would probably provide an economic way to meet the industrial requirements of low-cost processing techniques for the large-scale production of nanomaterials with acceptable FE performance and engineered surface functionality arising from the solution chemistry.

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