# Field-Emission Triode of Low-Temperature Synthesized ZnO Nanowires

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Abstract—A field-emission triode based on the low-temperature (75 °C) and hydrothermally synthesized single-crystalline zinc-oxide nanowires (ZnO NWs) grown on Si substrate with a silicon dioxide (SiO<sub>2</sub>) insulator was fabricated for the controllable field-emission device application. Field-emission measurement reveals that the ZnO NWs fabricated on the Si substrate exhibit a good emission property with the turn-on electric field and threshold electric field (current density of 1 mA/cm<sup>2</sup>) of 1.6 and 2.1 V/ $\mu$ m, respectively, with a field enhancement factor  $\beta$  of 3340. The field-emission properties of the ZnO NW-based triode exhibit the controllable characteristics. The well-controlled field-emission characteristics can be divided into three parts: gate leakage region, linear region, and saturation region. Therefore, this study provides a low-temperature field-emission triode fabrication process that is compatible with the Si-based microelectronic integration, and the field-emission measurements also reveal that the emission behavior can be well controlled by adopting the triode structure.

*Index Terms*—Field-emission triode and device, hydrothermal method, nanowires (NWs), ZnO.

#### I. INTRODUCTION

URRENT trends in nanotechnology that include one-dimensional (1-D) nanostructures such as nanowires (NWs), nanotubes, and nanobelts as an important class play a prominent role in the potential applications of photonic, electrooptical, and electronic devices because of their unique physical and chemical properties [1]–[4]. In particular, these high-aspect-ratio 1-D nanostructures have been extensively studied in vacuum microelectronic devices, including the field-emission display (FED), electron sources, and high-power RF amplifier for their low turn-on electric field and high electron emission efficiency [3]–[5]. The main challenges of the FED are a large-area display, high productivity, high brightness, low cost, and low-power consumption. From this point of view, a triode-type FED device with a low driving voltage, high resolution, and controllable electron emission characteristics is the candidate for the next generation of FED devices.

ZnO with a wide bandgap (3.4 eV) and large exciton binding energy (60 meV) has drawn much attention for the possible applications in phosphors, transparent conducting films for solar cells, ultra-violet (UV) laser devices, and flat-panel

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displays [6]–[9]. Recently, the ZnO NW emitters have been reported as demonstrating good emission properties with high stability, low-threshold electric field, and high-emission current density [9], [13]. The ZnO NWs could be synthesized by various procedures [9]–[12]; however, it is hard to fabricate the NW-based FED devices because of the high synthesis temperature which limits the type of substrate materials to be used and the integration processes for a final device structure. Thus, a hydrothermal method is a suitable process for the FED fabrication because of the catalyst-free-growth, low cost, low reaction temperature, large area and uniform production, environmental friendliness, and the process compatibility to the VLSI and plastic electronics.

Although the field-emission triode based on the carbon nanotubes (CNTs) have been developed [14], [15], the device based on ZnO NWs is seldom discussed. In this paper, the hydrothermal method is adopted to fabricate the ZnO NWs in the field-emission triode device at 75 °C, and the controllable field-emission characteristics were investigated.

# II. EXPERIMENTS

The fabrication procedure for the ZnO-based triode fieldemission device is shown in Fig. 1. The details of the fabrication process are summarized as follows: a gate oxide of SiO<sub>2</sub> is deposited by plasma-enhanced chemical vapor deposition (PECVD), and gate electrodes of aluminum (Al) are deposited by electron beam evaporator. The cathode active region is electrically insulated from the Al gate by a  $0.5-\mu$ m-thick SiO<sub>2</sub> layer. The emitter regions were defined by photolithography and buffer oxide etch (BOE). Then, an ultrathin ZnO seeding film ( $\sim 70 \text{ Å}$ ) was deposited on the substrate by RF sputtering (13.56 MHz) under Ar as sputtering gas at a pressure of 20 mTorr to prepare the well-aligned ZnO NWs by the hydrothermal method. Then, the photoresistance (PR) layer was stripped, and the substrate was put into an aqueous solution (Milli Q, 18.2 M $\Omega$  · cm) of zinc nitrate hexahydrate  $(\text{Zn} (\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}, 0.01 \text{ M})$  and diethylenetriamine (HMTA,  $C_6H_{12}N_4$ , 0.01 M) in a sealed vessel at 75 °C for 30 min [16]. After the NWs were hydrothermally grown on the substrate, the triode device was complete. The surface morphologies were confirmed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700I, Japan). The test scheme corresponding to the field-emission properties is illustrated in Fig. 1(b). A Keithley 237 current-voltage analyzer was used for measuring the field-emission characteristics at a base pressure of  $1 \times 10^{-6}$  torr at room temperature, and a power supply was adopted for the control of the gate bias  $(V_q)$ . A copper electrode probe that acts as an anode with the tip diameter of 500  $\mu m$ 

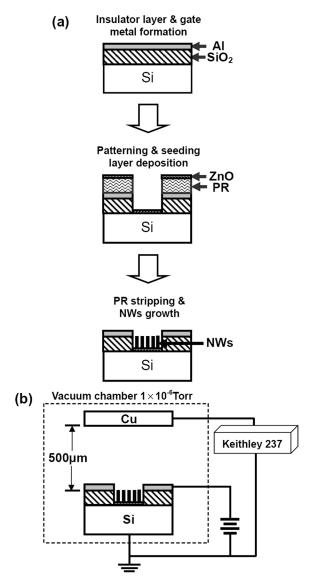


Fig. 1. Schematic description of fabrication processes of field-emission triode.

was placed at a distance of 500  $\mu m$  from the tips of the NWs. The distance between cathode and anode was adjusted by a precision vernier with an accuracy of  $\pm 0.1~\mu m$ .

## III. RESULTS AND DISCUSSION

The SEM image of the fabricated ZnO-based triode structure is shown in the inset of Fig. 2(a), indicating that the cathode active region is  $100 \times 100~\mu\text{m}^2$ , and the distance between the two active regions is  $500~\mu\text{m}$ . The gate region here is  $2 \times 2~\text{mm}^2$ . The rectangular islands of ZnO NWs are successfully and selectively grown on the ZnO seeding areas, but no NWs are grown on the gate region. Fig. 2(a) is the enlarged image of the triode device, in which well-aligned ZnO NWs with a diameter of 50 nm and a number density of  $3.4 \times 10^{10}~\text{cm}^{-2}$  are uniformly grown on the ZnO seeding layer. The cross-sectional SEM image of ZnO NWs on the substrate is shown in Fig. 2(b), indicating that the ZnO NWs were directly grown on the substrate with an average length of 500 nm. The polycrystalline ZnO seeding film with the distinct orientation results in the nonvertical random distribution of ZnO NWs.

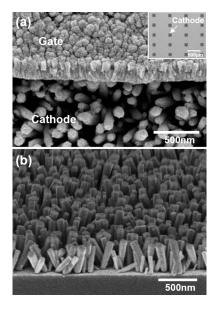


Fig. 2. (a) FE SEM microphotographs of the triode near the gate edge. The inset is the  $4 \times 5$  array triode with the ZnO NW islands grown inside gate holes. (b) Cross-sectional FE SEM image of ZnO NWs on the substrate.

The relationship between emission current density (J) and applied electric field  $(E_a)$  of the ZnO NW-based triode for different gate bias  $(V_q)$  is shown in Fig. 3(a). The threshold electric field  $E_{\rm th}$  (at a current density of 1.0 mA/cm<sup>2</sup>) is 2.1 V/ $\mu$ m under the zero gate bias. As  $V_g$  increases to 10 V, J is depressed to 36  $\mu$ A/cm² under the  $E_a$  of 2.1 V/ $\mu$ m. While  $V_g$  increases to 18 V,  $E_{\rm th}$  slightly decreases to 2.0 V/ $\mu$ m, but J abruptly increases to 12 mA/cm<sup>2</sup> under  $E_a$  of 2.2 V/ $\mu$ m. The corresponding Fowler–Norheim (F-N) plots  $\left[\ln\left(J/E_a^2\right)\right]$  versus  $E_a^{-1}$  are depicted in the inset of Fig. 3(a), and the field-enhancement factor  $\beta$  can be calculated from the slope of the F-N plot by adopting the work function of ZnO (5.37 eV) [9]. As shown in the figure, the F-N plot under a  $V_q$  of 10 V is deviated from the F-N fitting and that under  $V_q$ of 0 and 18 V are obeying the fitting with the same slope. The calculated  $\beta$  value of a ZnO NW-based triode under a  $V_q$  of 0 V is 3340. The relationships between  $J, V_q$ , and  $\beta$  values are unusual, and they will be discussed next.

The characteristic plots of J versus  $V_q$  at various values of  $E_a$ are shown in Fig. 3(b), indicating that a controllable behavior could be divided into three parts: gate leakage region (region 1), linear region (region 2), and saturation region (region 3). After applied electric field, the electron can be emitted from ZnO NW emitters under  $V_g$  of 0 V. J decreases with an increase in  $V_g$ in region 1. With an increase of  $V_q$  from 0 V, the electric field gradient near the ZnO NW emitters will increase due to the short emitter-gate spacing, but some emitted electrons might be trapped by the gate, which results in a lower J and leads to the deviation from the F-N fitting at a  $V_q$  of 10 V [see Fig. 3(a)]. As  $V_q$  is continuously increased up to 14 V, J abruptly increases at the linear region (region 2). The linear intercept on the  $V_q$ -axis is the linear region threshold voltage  $V_{g\rm th}$ . It is believed that, at region 2, the induced electric field gradient is large enough to accelerate the electrons; consequently, the emitting electrons gain momentum while passing through the gate without being trapped. It is well known that the  $\beta$  value depends only on the

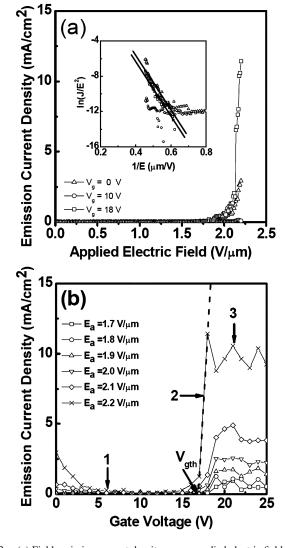


Fig. 3. (a) Field-emission current density versus applied electric field curves under the gate voltages of 0, 10, and 18 V, respectively. The inset is the corresponding F-N plots. (b) Field-emission current density versus gate voltage  $(J-V_g)$  curves under the various applied electric field.

geometry, structure, tip size, and number of emitters on the substrate; thus, the  $\beta$  value should be constant under various gate voltages. However, there is a large deviation from the F-N fitting at  $V_g$  of 10 V, as indicated in the inset of Fig. 3(a). It is suggested that the gate trapping is the main mechanism; the electrons are emitted under the F-N mechanism but are trapped by the gate, which results in the low current density and the large deviation from the F-N fitting under a  $V_g$  of 10 V. The high emission current of the triode operated in region 3 is assumed to be due to the short gate-tip spacing, small gate aperture, and high aspect ratio of the ZnO NWs. Moreover, the fact that the J saturates (region 3) as the  $V_g$  is larger than 18 V is due to the space-charge effect of the semiconductor emitters [17].

The field-emission characteristics also could be observed in the variation of small-signal transconductance  $(g_m)$ . Fig. 4 depicts the relationships between  $g_m$  and  $V_g$  of the ZnO NW-based field-emission triode. The  $g_m$  is defined as

$$g_m = \left. \frac{dI_e}{dV_g} \right|_{V_a}$$
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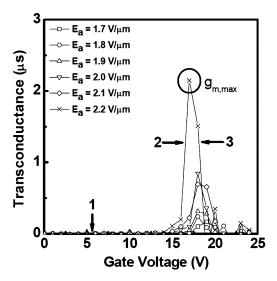


Fig. 4. Relation of transconductance versus gate voltage of the field-emission triode.

It should be noted that  $g_m$  is nearly zero below  $V_{g{
m th}}$  because  $I_e$  is very small in the gate leakage region. It goes through a maximum at the point of inflection of linear region to the saturation region in the  $I_e$ - $V_g$  curve, and then decreases. The ZnO NW-based triode exhibits a high  $g_m$  of 2.2  $\mu$ S under the applied electric field of 2.2 V/ $\mu$ m and a low operating gate bias of 17 V, which is the optimized operation of the field emission triode. Then decreasing values of  $g_m$  in the saturation region are due to the space-charge effect.

# IV. CONCLUSION

A field-emission triode based on low-temperature hydrothermally grown ZnO NWs was successfully fabricated. The ZnO NW-based triode emitter was design with a  $100 \times 100~\mu\text{m}^2$  cathode active region. This device exhibits gate-controllable behavior and emits electrons at a  $V_{g\text{th}}$  value of 14 V and J up to 12 mA/cm² under  $V_g$  of 18 V and  $E_a$  of 2.2 V/ $\mu$ m. The triode also displays a high  $g_m$  of 2.2  $\mu$ S at a low operating  $E_a$  of 2.2 V/ $\mu$ m and  $V_g$  of 17 V. Thus, this field-emission triode with controllable transistor characteristics may be appropriate for field-emission display applications.

### REFERENCES

- [1] X. Hu and C. T. Chan, "Photonic crystals with silver nanowires as a near-infrared superlens," *Appl. Phys. Lett.*, vol. 85, pp. 1520–1522, 2004.
- [2] Y. J. Chen, Q. H. Li, Y. X. Liang, T. H. Wang, Q. Zhao, and D. P. Yu, "Field emission from long SnO<sub>2</sub> nanobelt arrays," *Appl. Phys. Lett.*, vol. 85, pp. 5682–5684, 2004.
- [3] S. Hofmann, C. Ducati, B. Kleinsorge, and J. Pobertson, "Direct growth of aligned carbon nanotube field emitter rays onto plastic substrates," *Appl. Phys. Lett.*, vol. 83, pp. 4661–4663, 2003.
- [4] O. J. Lee and K. H. Lee, "Fabrication of flexible field emitter arrays of carbon nanotubes using self-assembly monolayers," *Appl. Phys. Lett.*, vol. 82, pp. 3770–3772, 2002.
- [5] V. V. Zhinov, E. I. Givarfizov, and P. S. Plekhanov, "Field emission from silicon spikes with diamond coatings," *J. Vac. Sci. Technol. B*, vol. 13, pp. 418–421, 1995.
- [6] C. X. Xu, X. W. Sun, C. Yuen, B. J. Chen, S. F. Yu, and Z. L. Dong, "Ultraviolet amplified spontaneous emission from self-organized network of zinc oxide nanofibers," *Appl. Phys. Lett.*, vol. 86, pp. 011118–011120, 2005.

- [7] S. Fujihara, A. Suzuki, and T. Kimura, "Ga-doping effects on electrical and luminescent properties of ZnO:(La,Eu)OF red phosphor thin films," *J. Appl. Phys.*, vol. 94, pp. 2411–2416, 2003.
- [8] T. Miyata, Y. Minamino, S. Ida, and T. Minami, "Highly transparent and conductive ZnO:Al thin films prepared by vacuum arc plasma evaporation," J. Vac. Sci. Technol. A, vol. 22, pp. 1711–1715, 2004.
- [9] S. Y. Li, P. Lin, C. Y. Lee, and T. Y. Tseng, "Field emission and-photofluorescent characteristics of zinc oxide nanowires synthesized by a metal catalyzed vapor-liquid-solid process," *J. Appl. Phys.*, vol. 95, pp. 3711–3716, 2004.
- [10] B. P. Zhang, K. Wakatsuki, N. T. Binh, Y. Segawa, and N. Usami, "Low-temperature growth of ZnO nanostructure networks," *J. Appl. Phys.*, vol. 96, pp. 340–343, 2004.
- [11] J. J. Wu and S. C. Liu, "Low-temperature growth of well-aligned ZnO nanorods by chemical vapor deposition," *Adv. Mater.*, vol. 14, pp. 215–218, 2002.
- [12] L. Vayssieres, K. Keis, A. Hagfeldt, and S. Lindquist, "Three-dimensional array of highly oriented crystalline ZnO microtubes," *Chem. Mater.*, vol. 13, pp. 4395–4398, 2001.
- [13] Y. B. Li, Y. Bando, and D. Golgerg, "ZnO nanoneedles with tip surface perturbations: Excellent field emitters," *Appl. Phys. Lett.*, vol. 84, pp. 3603–3605, 2004.
- [14] C. L. Tsai, C. F. Chen, and C. L. Lin, "Field emission from well-aligned carbon nanotips grown in a gated device structure," *Appl. Phys. Lett.*, vol. 80, pp. 1821–1822, 2002.
- [15] I. T. Han, H. J. Kim, Y. J. Park, N. Lee, J. E. Jang, J. W. Kim, J. E. Jung, and J. M. Kim, "Fabrication and characterization of gated field emitter arrays with self-aligned carbon nanotubes grown by chemical vapor deposition," *Appl. Phys. Lett.*, vol. 81, pp. 2070–2072, 2002.
- [16] C. Y. Lee, S. Y. Li, P. Lin, and T. Y. Tseng, "ZnO nanowires hydrother-mally grown on PET polymer substrates and their characteristics," *J. Nanosci. Nanotechnol.*, vol. 5, pp. 1088–1094, 2005.
- [17] C. W. Lu and C. L. Lee, "Direct current circuit simulation model for a field emission triode," *J. Vac. Sci. Technol. B*, vol. 16, pp. 2876–2880, 1998.



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