Field emission properties of individual zinc oxide nanowire field emitter

K. S. Yeong and J. T. L. Thong[a)]
Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576, Singapore

(Received 24 September 2007; accepted 7 April 2008; published 7 May 2008)

The authors report the field emission (FE) properties of individual ZnO nanowire field emitters. ZnO nanowire field emitter directly grown on a Pt tip showed a much better field emission current delivery than the attached nanowire emitters due to better contact properties. The emission current and field emission microscopy pattern of the ZnO nanowire are strongly influenced by adsorbates. After thermal-field desorption of adsorbates from the emission tip, the *I-V* curve shows a complex behavior that is different from that of the adsorbate-covered tips or ideal FE. For completeness, the effects of O_2 and H_2 gas exposure, and UV illumination on the FE current are also discussed.
 [DOI: 10.1116/1.2919146]

I. INTRODUCTION

Field emission (FE) studies on ZnO nanowires have largely been limited to ZnO nanowire films[1–4] with only a few preliminary studies on single or quasisingle ZnO nanowire field emitters.[5–7] FE studies conducted on ZnO nanowire films only reveal performance characteristics, such as turn-on voltage and emission-current stability, but are limited in their ability to elucidate the underlying physics of field emission since the measurements represent the collective behavior of thousands of different field-emitting nanowires. It is thus necessary to examine individual ZnO nanowire field emitters in order to understand the FE properties of the nanowire in greater detail. To this end, Ramgir *et al.* measured the current-voltage behavior and work function for their specific multipod ZnO nanowires.[5,6]

In this study, we report the FE properties of ZnO nanowire emitters, comprising either one, or just a few nanowires, directly grown on sharp Pt tips. Directly grown ZnO nanowire field emitters on Pt tips were found to have much better FE capabilities than ZnO nanowires that had simply been attached to Pt tips due to the better contact properties of the ZnO–Pt interface in the former. The FE properties are discussed in the context of the current-voltage (*I-V*) characteristics, field emission microscopy (FEM) patterns, and the effects of adsorbate dynamics on the FE current. Previously, we reported the marked effects of exposures to oxygen and hydrogen, and UV illumination on the FE current,[8] and these findings will be related to those of the current work.

II. FIELD EMITTER FABRICATION

ZnO nanowire field emitters were initially fabricated through an attachment method, where a single ZnO nanowire (derived from the same growth process) was selected, manipulated, attached, and finally, anchored on the Pt tip by electron-beam induced carbonaceous/contamination coating [Fig. 1(a)]. The attachment process was performed *in situ* in a scanning electron microscope (SEM) chamber with the aid of nanomanipulators, in a manner commonly used to fabricate single one dimensional nanostructure field emitters. However, these emitters were found to yield low maximum emission currents, beyond which the emitter is destroyed. The possible causes of such undesirable characteristics will be discussed in Sec. III.

In an alternative approach, we fabricated ZnO nanowire field emitters by direct growth of ZnO nanostructures through a self-catalyzed mechanism[9] on electrochemically sharpened Pt tips. A Zn film of 250 nm thickness was first evaporated onto a sharpened Pt tip before annealing in a tube furnace at 600 °C in ambient air for 2 h. ZnO nanostructures comprising nanowires and nanoflakes were found to cover the entire Pt tip and shank after oxidation [Fig. 1(b)]. The nanowire diameters range from a few nanometers up to a few tens of nanometers with lengths of up to a few microns. For this particular growth process, we found that Pt tips with tip radii of less than 1 μm often gave rise to only one or at most two prominent ZnO nanowires on the tip, whereas Pt tips of larger radii gave rise to multiple ZnO nanowires [Fig. 1(c)]. Transmission electron microscope (TEM) images show that the surface of the oxidized film on the tip was full of crystalline granular structures from which most of the ZnO nanowires and nanoflakes emerged [Fig. 1(d)]. TEM analysis of individual ZnO nanowires [Figs. 1(b) and 1(c)] suggests a growth along the $[1\bar{1}0]$ direction [Fig. 1(e)]. The ZnO nanowire–covered Pt tip was then spot welded on a standard tungsten-filament base to form a field emitter before loading into a UHV FE characterization system described elsewhere.[10] Unless otherwise noted, FE studies were subsequently performed at vacuum levels of $\sim 10^{-9}$ mbar or better. FEM imaging was carried out to ensure that the emission was dominated by a single emitter. All the FEM pattern and *I-V* characteristics should have originated from the small radius and high aspect ratio ZnO nanowires but not the underlying smooth and blunt Pt tip (diameter of ~ 1 μm) since the turn-on voltage for FE of the bare Pt tip is more than the maximum voltage, 10 kV that we can supply.

[a)]Author to whom correspondence should be addressed; Tel.: 6565162270; electronic mail: elettl@nus.edu.sg

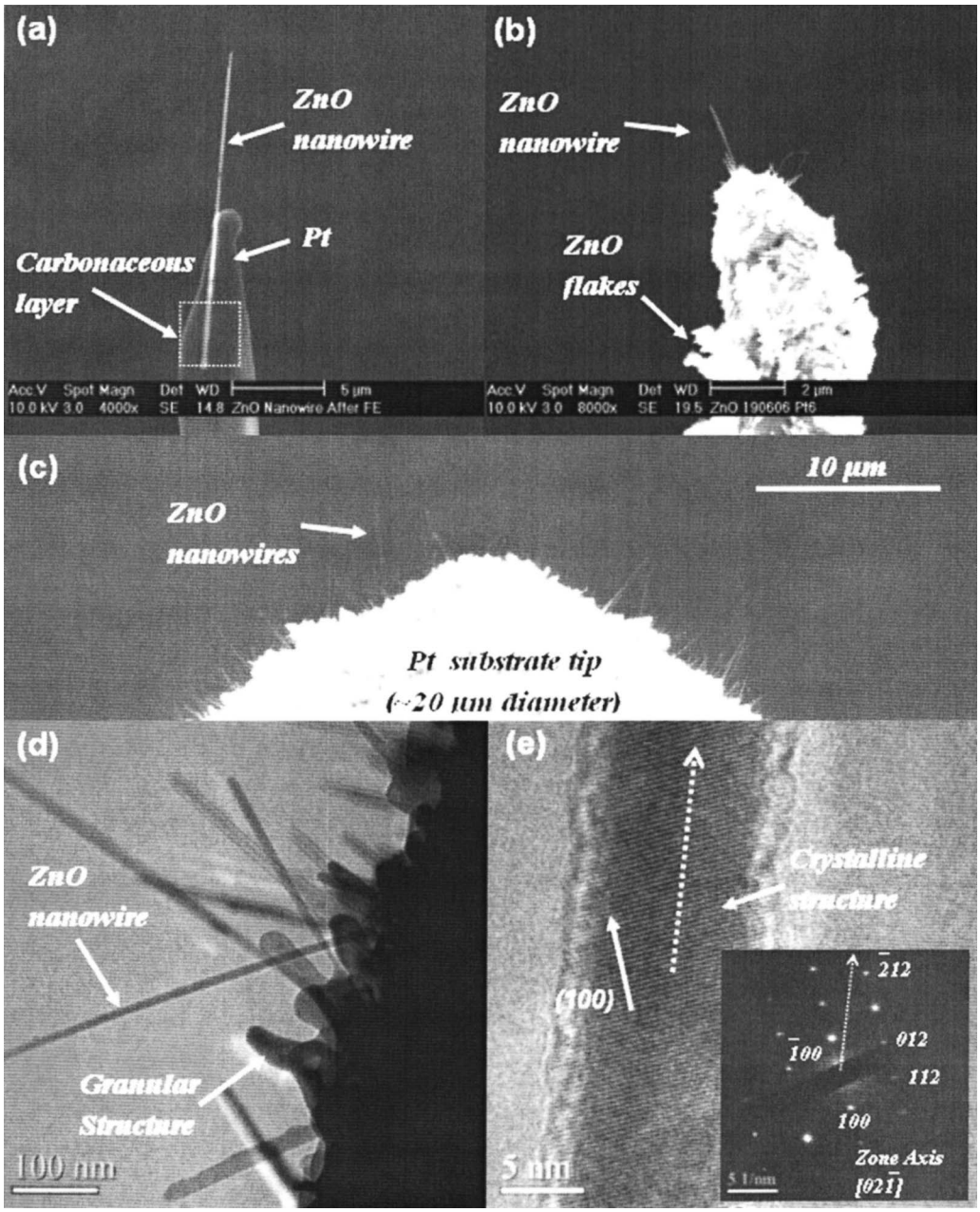

FIG. 1. (a) SEM image of a single ZnO nanowire field emitter attached on a Pt sharp tip. (b) SEM image of a single ZnO nanowire field emitter grown on a Pt sharp tip. (c) SEM image of ZnO nanowires field emitter grown on a Pt blunt tip. (d) TEM image of Pt tip shown in (b). (e) HRTEM image of a single ZnO nanowire shows that it is a single-crystal nanowire. The inset shows the selected area electron diffraction pattern at the base of the nanowire.

III. RESULTS AND DISCUSSION

In this study, we found that ZnO nanowire emitters grown directly on Pt tips yielded much better FE performance compared to attached ZnO nanowire field emitters. The attached ZnO nanowire emitters showed much lower emission current delivery capability. Attempts to increase the emission by increasing the bias often resulted in the destruction of the field emitter at emission currents of less than a few hundred nanoamperes. On the other hand, directly grown nanowire emitters can easily deliver emission currents of up to several microamperes without blowing up. The difference is likely to originate from the interface between the ZnO nanowires and the Pt tip. Apart from providing stronger physical adhesion, the direct-growth method also provides better electrical contact at the interface which translates ultimately into a significantly higher emission current capability.

Pristine ZnO is n-type semiconductor with work function of $\phi_{ZnO}=5.3$ eV and is well known to form a Schottky contact with Pt ($\phi_{Pt}=6.1$ eV).[11–13] Thus, in the case of the attached ZnO nanowire emitter, the lower emission capability is believed to be due to (1) a Schottky junction between the ZnO nanowire and Pt tip, which is reverse biased under field emission conditions (Pt negative with respect to the ZnO), implying a low electron supply across the junction to the

emission tip, or (2) a thin carbonaceous coating, originating from electron-beam induced deposition, with work function (ϕ_c) of about 5.1 eV, similar to ZnO's, forming a desirable Ohmic-like contact to the ZnO nanowire allowing electron to bypass the Pt–ZnO nanowire Schottky junction. However, the typically poor conductivity of the carbonaceous layer causes resistive heating at high emission current. The resulting temperature rise at the anchor may vaporize the carbonaceous layer and thus destroy the emitter.

In the case of the directly grown ZnO nanowire emitter, the Zn is likely to have alloyed with the Pt during the oxidation process, and any residual metallic Zn forms an Ohmic contact to the ZnO since the work function of metallic Zn, ϕ_{Zn}=4.3 eV, is smaller than ϕ_{ZnO}. The Ohmic contact ensures sufficient electron supply from the Pt tip to the ZnO nanowire tip for field emission. Thus, the provision of both good electrical and physical contacts allows the directly grown ZnO nanowire emitter to support higher emission currents. As such, the ZnO nanowire field emitters characterized hereafter were those directly grown on Pt tips.

A. Effects of adsorbate dynamics

In this section, a single ZnO nanowire field emitter [shown in Fig. 1(b)] was used for the study. The *I-V* measurement was conducted at the chamber base pressure of around 8×10^{-10} mbar. Pristine field emitters are covered with adsorbates as they are exposed to air. *I-V* sweeps of the pristine ZnO nanowire showed huge current fluctuations along the sweep as a result of field/emission-current induced adsorbate dynamics of loosely bound adsorbates.

A flash anneal at a temperature around 800 °C eliminated the huge current fluctuations, indicating that most of the loosely bound adsorbates can be desorbed by flash cleaning. Typical *I-V* characteristics from a closed-loop voltage-sweep after flash cleaning are shown in Fig. 2. The *I-V* characteristics remain largely unchanged even after multiple voltage sweeps in the low-current region indicated in Fig. 2. Emission-current disturbances (small current deviations which disrupt the otherwise smooth curve of the *I-V* measurement) started to appear in the intermediate current region and often transformed into huge current fluctuations in the high emission current region along the voltage sweep-up path. However, the emission current in the voltage return path exhibited much less disturbance. The Fowler–Nordheim (FN) plots of both voltage paths are shown in the inset of Fig. 2. The FN plot of the voltage sweep-up path is a curve instead of a straight line, as observed for the voltage sweep-down path. The observation is consistent with the study of Zhang *et al.* on ZnO nanowire film emitters.[14]

The current disturbances and current fluctuations are due to the dynamics of adsorbates on the emission surface, such as desorption, adsorption, and diffusion, activated by the FE current and electric field.[15–18] During the voltage sweep-up, the increasing emission current will induce greater adsorbate diffusion and, finally, desorption of some loosely bound adsorbates at high emission current as is evident from the current disturbances and current fluctuations. On the voltage return path, since most of the relatively loosely bound adsorbates had been desorbed, the decreasing emission current experienced much less disturbance except sporadically which may be due to the arrival of residual gas molecules on the emission tip. The downward curve of the FN plot along the sweep-up path at high emission current could be due to the desorption of adsorbates, which led to a depression in the FE current.

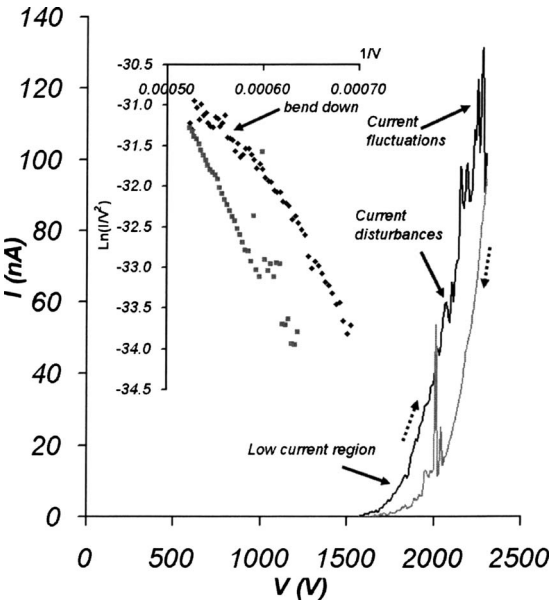

FIG. 2. *I-V* behavior of single ZnO nanowire field emitter shown in Fig. 1(b). Voltage is swept-up (black line) from 0 to 2260 V at 10 V/100 ms step size before sweep-down (gray line). The inset shows the respective FN plots.

B. FEM patterns

Figure 3 shows a FEM pattern of a single ZnO nanowire field emitter right after flash cleaning at 800 °C by resistive heating. The FEM pictures were extracted from a FEM video recorded during a closed-loop voltage sweep. The extent of the emission area falls within a circular pattern, which resembles that from a rounded ZnO nanowire tip. The emission pattern consists of randomly distributed and irregularly shaped emission spots that seem to populate the edge of the circular pattern. The spatial distribution of the emission spots and their relative brightness change as the emission current

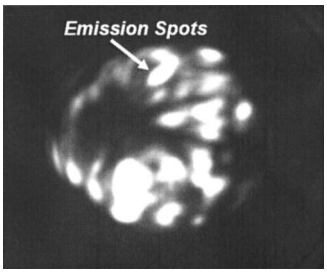

FIG. 3. FEM pattern of single ZnO nanowire field emitter taken at phosphor screen bias of 2500 V.

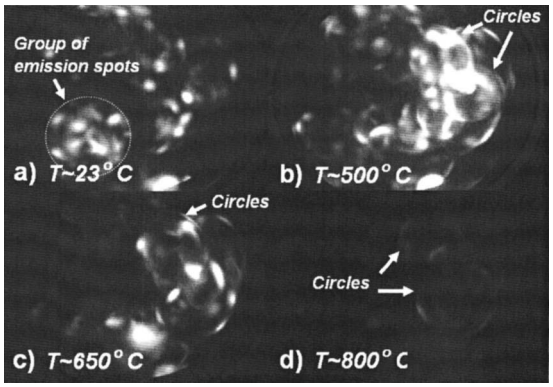

FIG. 4. (a) FEM pattern of multiple ZnO nanowire emitter at room temperature. (b)–(d) FEM patterns at elevated tip temperatures.

increases, and changes coincide with the emission-current disturbances and fluctuations. Thus, the emission spots were likely to have originated from surface adsorbates or clusters of surface atoms which dominate the FE process. These emission spots survived even after thermal annealing up to 1000 °C, which suggests that they were strongly bound to the ZnO surface.

Desorption of these adsorbates, however, is possible through thermal-field activation, as shown in Fig. 4. To show the process clearer, the FEM pattern was taken from the field emitter with multiple ZnO nanowires shown in Fig. 1(c). The FEM pattern [Fig. 4(a)] consists of multiple groups of emission spots originating from individual field-emitting ZnO nanowires. As the tip temperature of the field-emitting ZnO nanowires was increased, the dynamics of the emission spots or adsorbates/surface atoms increased as they gained higher thermal energy. At temperatures higher than 500 °C, thermal-field desorption started to take place as is evident from the reduction in the number of emission spots. One interesting observation is that some of the emission spots appear to run around a circular path, which gave rise to partially lightened circles, as shown in Figs. 4(b)–4(d). We believe these are direct FEM images of field-emitting adsorbates moving around the periphery of a rounded nanowire tip before desorption. At a temperature of 800 °C, most of the emission spots have disappeared as most of the adsorbates have been desorbed.

After thermal-field desorption to clean the ZnO nanowire surface, the *I-V* behavior of the ZnO nanowire emitter significantly changed as compared to the relatively linear FN plot of an adsorbate-covered ZnO nanowire, as shown in Fig. 5(a). The emitter right after thermal-field cleaning showed a complex *I-V* behavior such as highly curved and multiple linear segments on the FN plot, as shown in Figs. 5(b)–5(d). It is a challenge to identify the cause of such *I-V* behavior one by one since FE from a semiconductor is well known to be much more complicated than that from metal,[19–21] in addition to the high sensitivity of the electronic properties of the metal-oxide nanowire to the chemical environment. Possible explanations for these observed *I-V* behavior/FN plots are as follows.

(1) Increasing field penetration into the adsorbate-free semiconducting nanowire field emitter will result in a sudden emission-current increment at a point when the bending of conduction band is great enough to cross over the Fermi level.[19] This might be an explanation for the *I-V* behavior shown in Fig. 5(d), which shows a sudden increase in the emission current toward the upper end of the FN plot. An adsorbate-covered ZnO field emitter has a much higher resistance to field penetration since the adsorbates usually ionosorb on the metal-oxide surface and form a space-charge layer that reduces field penetration. The ZnO nanowire emitter could thus exhibit metallic behavior and show a relatively linear FN plot, as shown in Fig. 5(a).
(2) Field-assisted readsorption or diffusion of adsorbates on the adosrbate-free emission surface that causes an immediate and significant change in emission current. The effect of adsorbates on the FE current is expected to be significant based on the sensitivity of metal-oxide nanowires to chemical species. Oxidizing or reducing residual gas molecules,[22] such as CO_2, CO, and H_2, which ionosorb on the metal-oxide nanowire surface, even in small amounts, could result in a change in the carrier concentration or electron affinity and induce band bending near the surface due to the creation of a space-charge layer.[23] Depending on the type of residual gas molecules that dominate the repopulation of the emission surface, the *I-V* behavior will be changed accordingly during the voltage sweeps. The *I-V* behavior shown in Figs. 5(b) and 5(c) might originate from such events.

The above effects could also take place concurrently and complicate the analysis. However, oxidizing and reducing gases have been shown to significantly affect the FE current of ZnO nanowire field emitters. The results of the effects of oxidizing and reducing gas exposure, and UV exposures to ZnO nanowire field emitter, which have been reported,[8] will be summarized in the following sections to provide a more complete picture of the FE properties of ZnO nanowire field emitter.

C. The effects of O_2 and H_2 exposures on the *I-V* characteristics

Multiple dosages of O_2 exposure of up to 1×10^{-6} mbar from a base pressure for 5 min/dose were found to significantly increase the FE turn-on voltage (V_{on}) or, equivalently, reduce field emission, whereas multiple dosages of H_2 exposure of up to 1×10^{-6} mbar for 5 min/dose lowered the turn-on voltage, as shown in Fig. 6(a). Adsorbates are known to modify the electron affinity of an emitting surface that, in turn, changes the FE properties appreciably.[24] However, for these particular metal-oxide nanowire emitters, we believe ionosorption of O_2 and H_2 on the entire ZnO nanowire surface will also affect the FE properties as well, based on the mechanisms responsible for metal-oxide gas sensitivity.

O_2 molecules ionosorbed on the metal-oxide nanowire create surface acceptor states. This reduces the carrier density by capturing free electrons and induces band bending in the subsurface region.[25–27] These effects depress FE since the

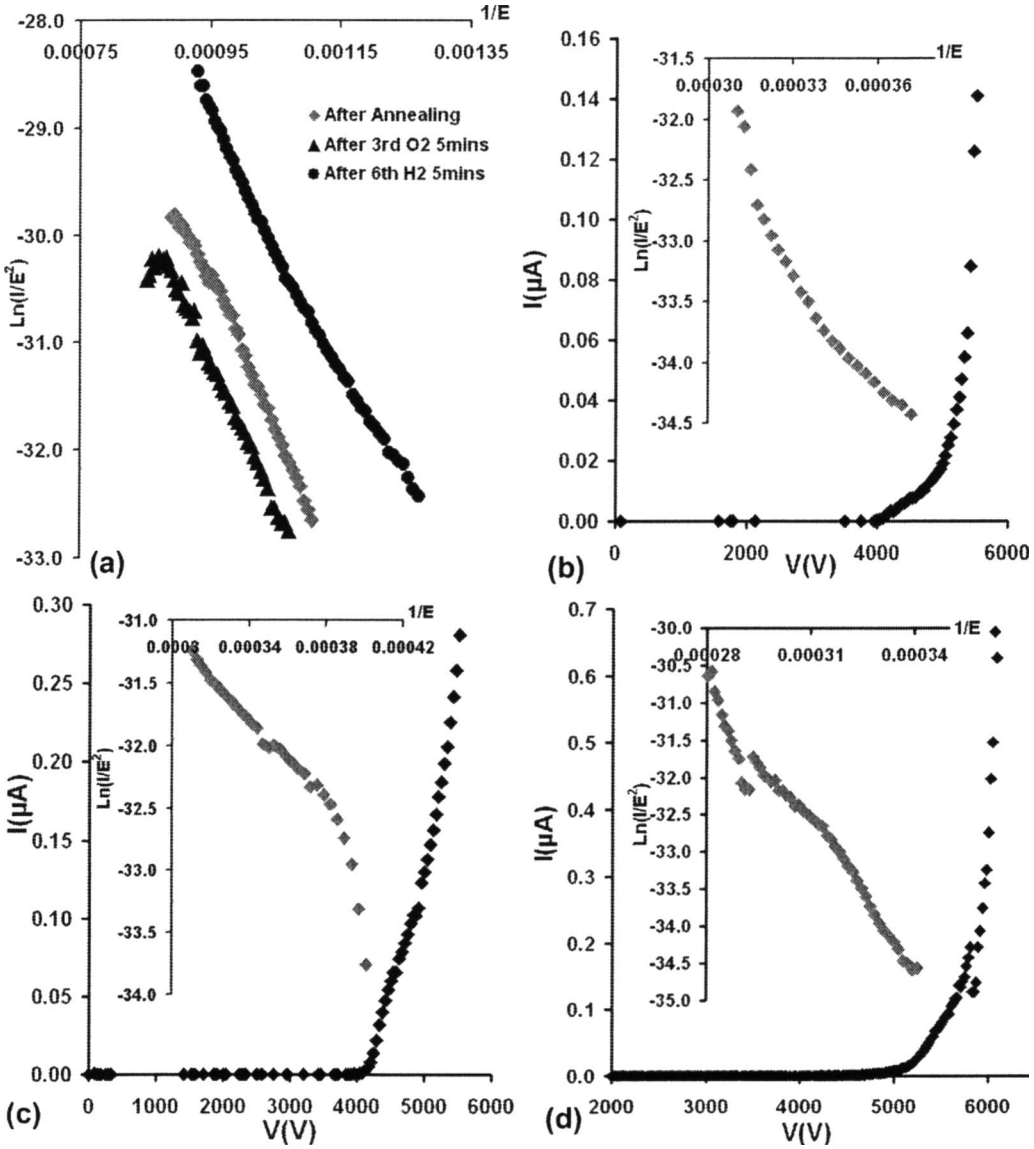

FIG. 5. (a) FN plots of ZnO nanowire right after thermal annealing at 800 °C for 10 s, after 3 doses of exposure to O_2 with 5 min/dose at 10^{-6} mbar and after 6 doses of exposure to H_2 with 5 min/dose at 10^{-6} mbar. [(b)–(d)] Different *I-V* behaviors of the adsorbate-free ZnO nanowire emitter after thermal-field desorption.

decrease in the electron concentration at the conduction band would reduce the electron supply for tunneling, and in addition, the bending up of the conduction band increases the effective tunneling width or, equivalently, lowers the tunneling probability as compared to that of inherently *n*-type ZnO nanowire. On the other hand, H_2 ionosorbed on the nanowire surface reacts with adsorbed oxygen ions at room temperature to form hydroxyl groups which function as surface donor states and release electrons to the underlying substrate.[26] This increases the electron concentration and bends the conduction band downward, which reduces the effective tunneling width for FE. Finally, these effects lead to the enhancement of the FE process.

D. The effect of UV illumination

For UV illumination studies, a xenon arc lamp with an ellipsoidal reflector (Newport Oriel PhotoMax, 75 W ozone-free Xe arc lamp 400 cd/mm^2 brightness) was used as the light source. The light was directly focused on the field emitter at 10 cm distance away from the UHV chamber through a sapphire window. A 400 nm long pass filter was used for background tests (which showed no influence from visible light illumination) to ensure that all the measurable effects were due to the UV spectrum (250–400 nm) of the light source. Upon illumination with above-bandgap UV light, the emission current of a ZnO nanowire field emitter was found to increase immediately and then continued to fluctuate around a new current level of up to two orders of magnitude higher than the initial current level, as shown in Fig. 6(b). Upon termination of UV illumination, the emission current gradually reduced to its initial current level. The recovery period was found to significantly depend on the vacuum level. The response is thought to be similar to the photoresponse of single ZnO nanowire diodes and field-effect

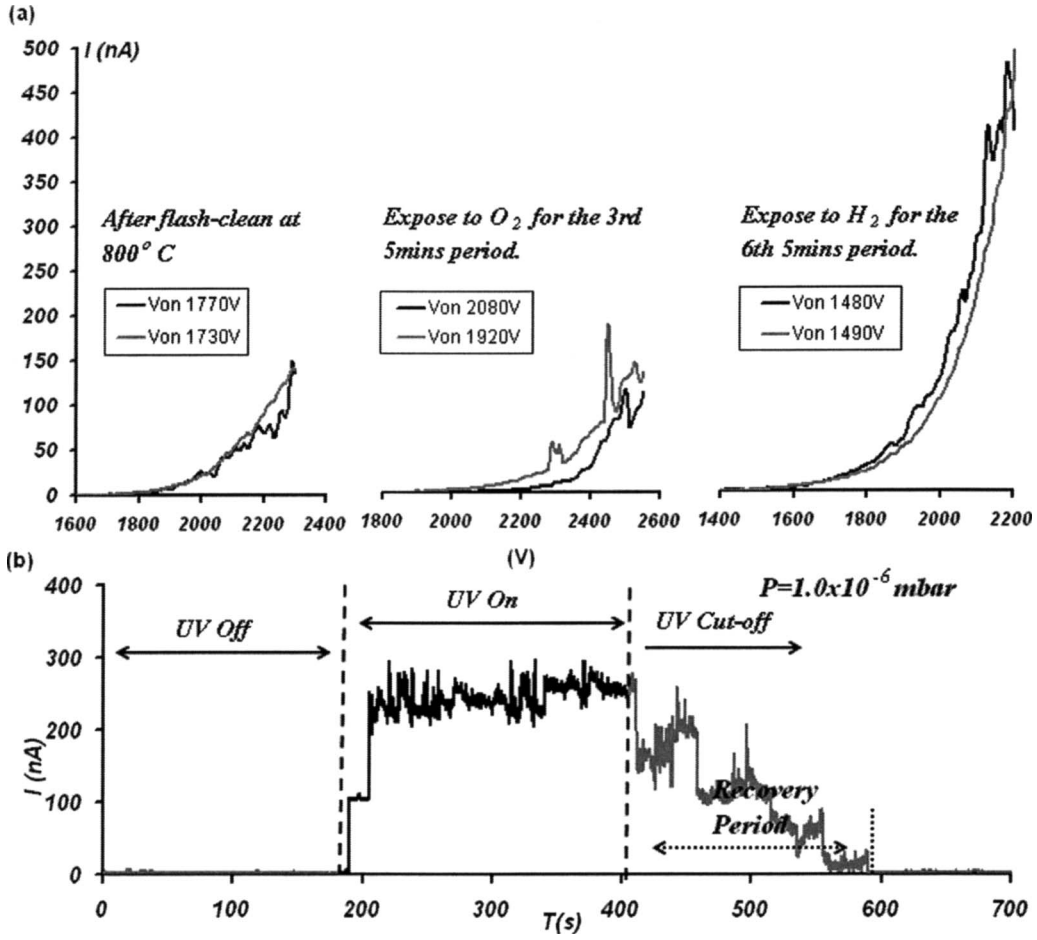

FIG. 6. (a) *I-V* curves of ZnO nanowire emitter after annealing at 800 °C for 10 s (left), after O_2 exposure (center), and after H_2 exposure (right). Voltage was swept-up (black) at 10 V/10 ms before being swept-down (gray). V_{on} is anode bias at 10 nA FE current. (b) The FE current at constant anode bias of 2000 V before UV illumination, during UV illumination and post-UV illumination at vacuum level of 1.0×10^{-6} mbar.

transistors.[12,28–31] Absorption of UV photons generates electron-hole pairs that are able to reach the nanowire surface easily due to its small diameter (comparable to the Debye length of ~10–100 nm of the space-charge layer). Photoexcited electrons can then participate in the field-tunneling process, whereas the photoexcited holes can react with surface oxygen ions and eventually release them from the surface.[25] Thus, the increase in the electron concentration in the band and the reduction in oxygen ions on the ZnO surface finally leads to a significant increase in the FE current.

IV. CONCLUSIONS

In summary, we studied the FE properties of individual ZnO nanowires directly grown on Pt tips. Directly grown ZnO nanowire field emitters showed a much better field emission current delivery than attached nanowire emitters due to the better contact properties. The emission current and FEM pattern of the ZnO nanowire were strongly influenced by adsorbates. After thermal-field desorption of adsorbates from the emission tip, the *I-V* curve showed a complex behavior that is different from that of adsorbate-covered tips or ideal FE. Exposure to O_2 depressed FE, whereas exposure to H_2 significantly enhanced FE due to the change in the carrier concentration and FE tunneling width. The emission current increased by about two orders of magnitude upon UV illumination but decreased much more gradually after UV cutoff in a manner which depends on the readsorption rate of adsorbates.

[1]B. Debasish, S. H. Jo, and Z. F. Ren, Adv. Mater. (Weinheim, Ger.) **16**, 2028 (2004).
[2]S. H. Jo, J. Y. Lao, Z. F. Ren, R. A. Farrer, T. Baldacchini, and J. T. Fourkas, Appl. Phys. Lett. **83**, 4821 (2003).
[3]R. C. Wang, C. P. Liu, J. L. Huang, S. J. Chen, Y. K. Tseng, and S. C. Kung, Appl. Phys. Lett. **87**, 013110 (2005).
[4]C. J. Lee, T. J. Lee, S. C. Lyu, Y. Zhang, H. Ruh, and H. J. Lee, Appl. Phys. Lett. **81**, 3648 (2002).
[5]Niranjan S. Ramgir, Imtiaz S. Mulla, K. Vijayamohanan, Dattatray J. Late, Ashok B. Bhise, Mahendra A. More, and Dilip S. Joag, Appl. Phys. Lett. **88**, 042107 (2006).
[6]Niranjan S. Ramgir, Dattatray J. Late, Ashok B. Bhise, Imtiaz S. Mulla, Mahendra A. More, Dilip S. Joag, and K. Vijayamohanan, Nanotechnology **17**, 2730 (2006).
[7]Dong LiFeng, Jun Jiao, David W. Tuggle, Jeremy M. Petty, Stephen A. Elliff, and Michael Coulter, Appl. Phys. Lett. **82**, 1096 (2003).
[8]K. S. Yeong, K. H. Maung, and J. T. L. Thong, Nanotechnology **18**, 185608 (2007).
[9]H. Y. Dang, J. Wang, and S. S. Fan, Nanotechnology **14**, 738 (2003).
[10]K. S. Yeong and J. T. L. Thong, J. Appl. Phys. **99**, 104903 (2006).
[11]Sang-Ho Kim, Han-Ki Kim, and Tae-Yeon Seong, Appl. Phys. Lett. **86**, 112101 (2005).

[12]Y. W. Heo, L. C. Tien, D. P. Norton, S. J. Pearton, B. S. Kang, F. Ren, and J. R. LaRoche, Appl. Phys. Lett. **85**, 3107 (2004).
[13]K. Ip, Y. W. Heo, K. H. Baik, D. P. Norton, S. J. Pearton, S. Kim, J. R. LaRoche, and F. Ren, Appl. Phys. Lett. **84**, 2835 (2004).
[14]H. Z. Zhang, R. M. Wang, and Y. W. Zhu, J. Appl. Phys. **96**, 624 (2004).
[15]K. Ashihara, H. Nakane, and H. Adachi, J. Vac. Sci. Technol. B **16**, 1180 (1998).
[16]Ch. Kleint, Surf. Sci. **25**, 394 (1971).
[17]Ch. Kleint, Surf. Sci. **200**, 472 (1988).
[18]L. W. Swanson, Surf. Sci. **70**, 165 (1978).
[19]R. Gomer, *Field Emission and Field Ionization* (American Institute of Physics, New York, 1993).
[20]Fursey George, in *Field Emission in Vacuum Microelectronics*, ed by I. Brodie and P. Schwoebel (Kluwer, New York, 2005).
[21]R. H. Fowler and L. Nordheim, Proc. R. Soc. London, Ser. A **119**, 173 (1928).
[22]N. Saitou and S. Yamamoto, Appl. Surf. Sci. **5**, 374 (1980).
[23]P. B. Weisz, J. Chem. Phys. **21**, 1531 (1953).
[24]W. P. Dyke and W. W. Dolan, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic, New York, 1956), Vol. 8, Chap. III, pp. 90–182.
[25]Kolmakov Andrei and Martin Moskovits, Annu. Rev. Mater. Res. **34**, 151 (2004).
[26]D. Kohl, Sens. Actuators **18**, 71 (1989).
[27]H. T. Wang, B. S. Tang, F. Ren, L. C. Tien, P. W. Sadik, D. P. Norton, S. J. Pearton, and Jenshan Lin, Appl. Phys. Lett. **86**, 243503 (2005).
[28]Keem Kihyun, Hyunsuk Kim, Gyu-Tae Kim, Jong Soo Lee, Byungdon Min, Kyoungah Cho, Man Young Sung, and Sangsing Kim, Appl. Phys. Lett. **84**, 4376 (2004).
[29]Michael. S. Arnold, Phaedom Avouris, Zheng Wei Pan, and Zhong L. Wang, J. Phys. Chem. B **107**, 659 (2003).
[30]Q. H. Li, Q. Wan, Y. X. Liang, and T. H. Wang, Appl. Phys. Lett. **84**, 4556 (2004).
[31]J. B. K. Law and J. T. L. Thong, Appl. Phys. Lett. **88**, 133114 (2006).