

The effects of gas exposure and UV illumination on field emission from individual ZnO nanowires

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Abstract

Individual ZnO nanowires grown on a Pt tip were exposed to O₂ and H₂ in the course of field emission. O₂ exposure was found to suppress field emission, while H₂ reduced the turn-on voltage and increased the emission current. Upon UV (250–400 nm) illumination, the emission current increased almost immediately by about two orders of magnitude, but takes a much longer period, depending on the vacuum level, to fall to its original value following illumination. These phenomena can be accounted for with reference to mechanisms responsible for the sensitivity of metal oxides to oxidizing and reducing gases.

ZnO nanowires have found various applications such as chemical sensors, field effect transistors, laser diodes and nanoactuators [1–3]. The interest in ZnO nanowires is mainly derived from the material's wide direct bandgap (~3.37 eV) with large exciton binding energy of ~60 meV and piezoelectric properties, and the nanowire's high sensitivity to surface chemistry and UV illumination.

Field emission (FE) studies on ZnO nanowires have largely been limited to ZnO nanowire films [4–7] with only a few preliminary studies on single or quasi-single ZnO nanowire field emitters [8–10]. Previous FE studies conducted on ZnO nanowire films only reported performance characteristics such as turn-on voltage and emission-current stability, and were limited in their ability to elucidate the underlying physics of FE since the measurements represent the collective behaviour 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 behaviour and work-function of their specific multipod ZnO nanowires [8, 9]. However, there are more interesting properties of ZnO nanowires, such as chemical and optical sensitivity, that have not been investigated in the context of field emission.

In this paper, we report the effects of O₂ and H₂ exposures and UV illumination on the FE properties of individual ZnO nanowire emitters grown directly on sharp Pt tips. Exposure

to O₂ and H₂ was found to affect the emission turn-on voltage and emission current significantly. UV illumination was also found to greatly influence the FE current. These effects can be accounted for by mechanisms known to be responsible for gas sensitivity in ZnO. This study attempts to link the chemical and optical sensitivity of ZnO nanowires to their FE properties which may lead to new applications of ZnO nanowires as FE-based UV or gas sensors.

The ZnO nanowire was grown directly from Zn on an electrochemically sharpened Pt tip through an autocatalytic mechanism [11]. Direct growth of ZnO nanowires on Pt tips gives much better mechanical adhesion and electrical contact as compared to attachment methods, and permits higher flashing temperatures and field-emission currents. Two-point current–voltage (*I*–*V*) measurements show that the ZnO–Pt contact is nearly ohmic, possibly due to a zinc or zinc-alloy interface. A 250 nm thick Zn film was first evaporated on the Pt tip before annealing it in a tube furnace at 600 °C in ambient air for 2 h. The Pt tip was then spot-welded on a standard tungsten-filament stand to form a field emitter and loaded into a FE characterization system [12–14]. FE studies were subsequently performed at vacuum levels of ~10⁻⁹ mbar. Field-emission microscopy (FEM) was carried out to ensure that the emission was dominated by a single emitter.

ZnO nanostructures comprising nanowires and nanoflakes were found to cover the entire Pt tip and shank after oxidation (figure 1(a)). The nanowires had diameters ranging from a few

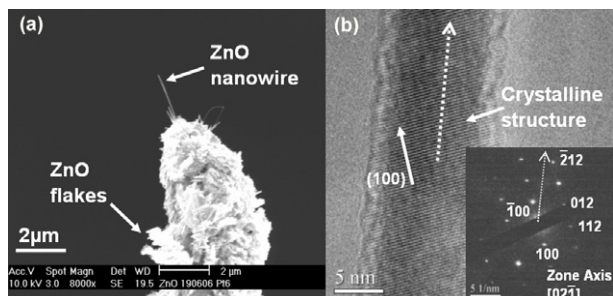


Figure 1. (a) SEM image of a single ZnO nanowire grown on a sharp Pt tip. (b) HRTEM image of a single ZnO nanowire. The inset shows the SAED pattern at the base of the nanowire. Zone axis of the diffraction pattern is deduced to be $[02\bar{1}]$.

nanometres up to a few tens of nanometres, and lengths of up to a few micrometres. For this particular growth process, we found that the number of ZnO nanowires protruding from the apex of the Pt tip depended very much on the diameter of the underlying Pt tip. Tips with diameter less than $2\ \mu\text{m}$ often gave rise to only one or two ZnO nanowires on the tip as shown in figure 1(a). Thus, by controlling the electrochemically etched tip diameter, we were able to reliably fabricate single ZnO nanowire field emitters. Transmission electron microscope (TEM) images show that the surface of the film on the tip is full of granular structures from which most of the ZnO nanowires and nanoflakes emerged. The nanowires are seen to be single-crystalline. Since we do not know the axial direction of these nanowires with respect to the electron beam, it is difficult to deduce the growth direction confidently. For the particular nanowire shown in figure 1(b), the apparent growth direction was found to be between $(\bar{3}12)$ and $(\bar{2}12)$. But as the nanowire is not necessarily perpendicular to the electron beam, the actual growth direction may be anywhere between this and the beam direction, $[02\bar{1}]$. Of the three likely fast growth directions for ZnO, $[1\bar{1}0]$, $[100]$ and $[001]$, only $[1\bar{1}0]$ lies in this range and is thus the most likely growth direction for this nanowire.

Figure 2(a) shows the FE I - V curves right after flash-cleaning for 10 s at 800°C . The turn-on voltages (V_{on}) for an emission current of 1 nA during voltage sweep-up and sweep-down are also indicated in the figure. V_{on} at 10^{-10} mbar vacuum after annealing was about 1730 V. The emitter was then exposed to O_2 at a pressure of 10^{-6} mbar for 5 min. Taking note that the monolayer formation time at 10^{-6} mbar is only around 1 s, such an exposure should result in high coverage of O_2 molecules on the ZnO surface. An I - V voltage sweep was executed only when the vacuum returned to the 10^{-9} mbar level after dosing since the emission-current at 10^{-6} mbar was too noisy for any meaningful analysis. Figure 2(b) shows the I - V behaviour after exposure to the first dose of O_2 . V_{on} of the sweep-up path was found to have increased significantly from 1730 V before exposure to 2060 V after exposure. However, V_{on} reduced back to 1740 V during voltage sweep-down due to desorption of the physisorbed O_2 molecules from the ZnO surface by the emission-current or intense electric field. Subsequent exposures to O_2 resulted in a permanent V_{on} increase to 1920 V as shown in figure 2(c) which suggests that increasing amounts of O_2 have been ionisorbed to occupy the surface-vacancy states after the end of each cycle of O_2 exposure and voltage sweep.

On the other hand, subsequent exposures to H_2 gas and voltage sweeps increased the adsorption of H_2 molecules on the ZnO nanowire surface which finally led to the reduction of V_{on} to 1490 V as shown in figures 2(d) and (e). The difference between the emission currents post- O_2 and post- H_2 exposures is up to two orders of magnitude as evident from figures 2(c) and (e) at an anode bias of 2200 V.

Adsorbates are known to modify the electron affinity of an emitting surface, which in turn changes the FE properties significantly [15, 16]. Upon exposure to the gases, the molecules behave as loosely bound adsorbates that invariably affect the turn-on voltage. However, from what is known of the mechanisms responsible for metal-oxide gas sensitivity, we believe ionosorption of O_2 and H_2 on the entire ZnO nanowire surface would also affect the emission current. O_2 and H_2 are well known to be oxidizing and reducing agents, respectively, for metal-oxide gas sensors. O_2 or H_2 ionisorbed on a metal-oxide surface creates a doubly charged layer on the surface which induces conduction band bending. The field penetration caused by this space charge could extend up to 100 nm beneath the surface. For the case of a metal-oxide nanowire whose diameter is of the order of 100 nm, the entire Fermi level across the nanowire will be shifted according to the coverage of ionisorbed species [17–19]. In other words, O_2 or H_2 ionosorption would change the carrier concentration and induce band bending in the ZnO nanowire. If the nanowire is field emitting, these changes would affect the FE properties significantly.

After a few cycles of O_2 exposure and voltage sweep (figure 2(c)), a significant amount of O_2 molecules should have been ionisorbed on the metal-oxide nanowire to form surface acceptor states. This reduces the carrier density by capturing free electrons and induces band bending in the sub-surface region. These effects depress FE since the decrease in the electron concentration at the conduction band reduces the electron supply for tunnelling, and in addition, the bending up of the conduction band increases the effective tunnelling width (W_2) or, equivalently, lowers the tunnelling probability as compared to that of the inherently n-type ZnO nanowire (W_1) as illustrated in figure 3(b).

On the other hand, significant amounts of H_2 would have ionisorbed on the nanowire surface after a few cycles of H_2 exposure and voltage sweep (figure 2(e)). At room temperature, these hydrogen atoms can react with adsorbed oxygen ions to form hydroxyl groups which function as surface donor states and release electrons to the underlying substrate [18]. This increases the electron concentration and bends the conduction band downwards which reduces the effective tunnelling-width (W_3) for FE, as illustrated in figure 3(c). These effects finally lead to the enhancement of the FE process.

For UV illumination studies, a 75 W ozone-free xenon-arc lamp with a parabolic reflector was used as the light source. The light was focused directly on the field emitter in 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. The ZnO nanowire emitter was biased at constant voltage (2 kV) to yield an initial FE current of around

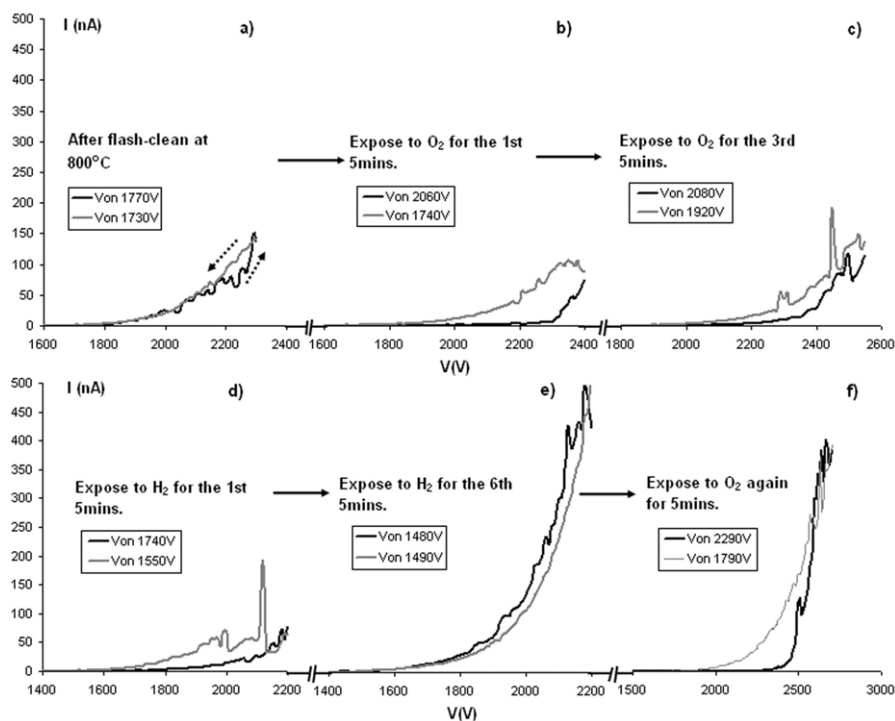


Figure 2. Field emission I - V curves of ZnO nanowire emitter. (a) After annealing at 800°C for 10 s. Voltage is first swept-up (black line) from 0 to 2300 V at steps of 10 V/10 ms before being swept-down (grey line) to 0 V to form a closed loop. (b) ZnO nanowire emitter after first dosage of 5 min O_2 exposure at 10^{-6} mbar. (c) After three dosages of 5 min O_2 exposure at 10^{-6} mbar. (d) After first dosage of 5 min H_2 exposure at 10^{-6} mbar following (c). (e) After six dosages of H_2 exposure at 10^{-6} mbar. (f) After exposure to O_2 again at 10^{-6} mbar.

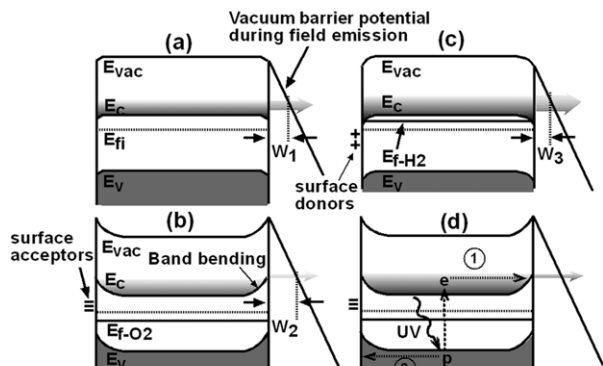


Figure 3. (a) Band diagram of inherently n-type ZnO nanowire across nanowire diameter with intrinsic Fermi level (E_{fi}). The vacuum barrier at the emitter tip and tunnelling width (W) during FE is also incorporated at the right side of the band diagrams. (b) Band diagram after multiple cycles of O_2 exposure and voltage sweep. Ionisorbed oxygen molecules act as surface acceptors which induce band bending and lowering of Fermi level ($E_{f-\text{O}_2}$). The tunnelling width is indicated as W_2 . (c) Band diagram after multiple cycles of H_2 exposure and voltage sweep. Ionisorbed hydrogen molecules produce surface donors which induced band bending and lifting of Fermi level ($E_{f-\text{H}_2}$). The tunnelling width is indicated as W_3 . (d) UV generation of electron-hole pairs on ZnO nanowire. Photo-excited electrons could then participate in FE tunnelling (1) whereas photo-excited holes could react with surface acceptors and release the oxidizing agents (2).

5 nA. Upon UV illumination, the emission current increased immediately and then fluctuated around the new current level which was up to two orders of magnitude higher than initial current level, as shown in figure 4(a). Upon termination of

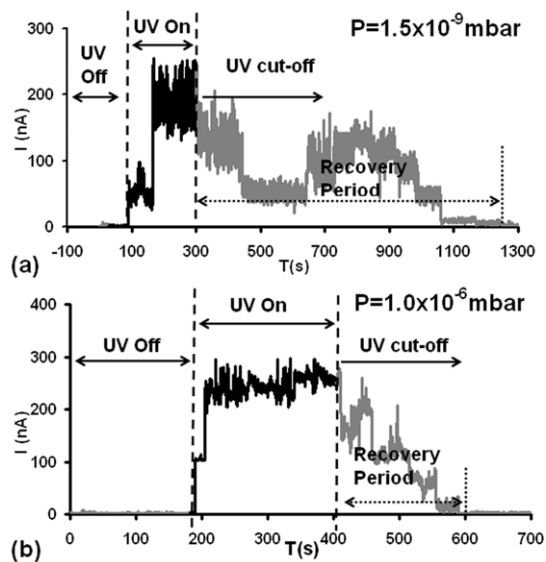


Figure 4. Emission current of ZnO nanowire at constant anode bias of 2000 V. (a) The emission current upon UV illumination and UV cutoff at pressure of 1.5×10^{-9} mbar. (b) The emission current upon UV illumination and UV cutoff at pressure of 1.0×10^{-6} mbar.

UV illumination, the emission current reduced gradually, in contrast to the rapid increase upon illumination. The time taken for the emission current to reach its original current level was about 13 min at a vacuum level of 10^{-9} mbar. However, the recovery period reduced to about 3 min at a pressure of 10^{-6} mbar (by admitting ambient air), as shown in figure 4(b).

The response of the emission current to the UV illumination is thought to be similar to the photoresponse of single ZnO nanowire diodes and field-effect transistors [20–24]. Upon UV illumination, electron–hole pairs are created by absorption of UV photons which have energy greater than the bandgap of the ZnO nanowire (3.37 eV), as illustrated in figure 3(d). These charge carriers can reach the ZnO nanowire surface quickly and easily due to the small diameter of the ZnO nanowire which is comparable to the Debye length (10–100 nm) of the space-charge layer. Photo-excited electrons can then participate in the field-tunnelling process (indicated as process 1 in figure 3(d)) whereas photo-excited holes can react with surface oxygen ions (indicated as process 2 in figure 3(d)) and eventually release them from the surface [17]. Thus, the increase in the electron concentration in the conduction band and the reduction of oxygen ions on the ZnO surface finally lead to a significant increase in FE current. The gradual recovery of emission current after UV termination suggests low re-ionosorption rate of oxidizing agents, such as CO₂ and H₂O typically found in UHV environments, at a pressure of 10^{−9} mbar [25]. Higher pressure implies a higher rate or, equivalently, a shorter recovery period.

In summary, we studied the FE properties of individual ZnO nanowires grown directly on Pt tips. Exposure to O₂ depresses FE whereas exposure to H₂ enhances FE significantly. Upon UV illumination, the emission current increases immediately and could eventually rise by about two orders of magnitude. When the UV is cut off, it takes much longer for the emission current to fall to its original value which is believed to be due to the slow reabsorption of oxidizing agents on the ZnO nanowire. The recovery period is shorter at higher pressure. The mechanisms underlying metal-oxide sensing have been used to account for these observations. The effect could be due to the change of carrier concentration and tunnelling width upon ionosorption of the respective gas molecules. The high sensitivity of FE current to gas exposure and UV illumination could be used in new applications such as FE-based gas and UV sensors.

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