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# Measuring the Work Function at a Nanobelt Tip and at a Nanoparticle Surface

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**ABSTRACT**

**The work function at the tips of individual ZnO nanobelts has been measured by an electromechanical resonant method using in-situ transmission electron microscopy. The work function of the ZnO nanobelts is ∼5.2 eV, which shows no significant dependence on the geometrical size. Using a ZnO nanobelt as a carrier beam, the work function of a single nanoparticle of a different material has also been measured.**

One-dimensional oxide nanostructures are stimulating a great deal of interest because of their novel properties, diverse functionalities, surface cleanliness, and chemical/thermal stability.[1−9] Among those oxides, zinc oxide (ZnO) is a semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, which is suitable for short-wavelength optoelectronic devices at room temperature. ZnO nanobelts and nanowire have shown interesting electronic, chemical, photoluminescence, and lasing properties.[4,10−12] The field-emission property for well-aligned ZnO nanowire arrays has been reported,[13] demonstrating a promising application of semiconductor nanowires as field emitters for flat panel display.

Following the Fowler−Nordheim (F−N) theory,[14] an important physical quantity in electron field emission is the surface work function, which is well documented for elemental materials. For the emitters such as ZnO nanowire arrays, most of the electrons are emitted from tips of the nanowires, and it is the local work function that matters to the properties of the field emission. However, the work function measured based on the F−N theory is an average over the large scale of emitting materials. So it is necessary to measure the local work function at the tip of individual emitter. Gao et al.[15] have measured the work function at the tips of carbon nanotubes by an in-situ transmission electron microscopy (TEM) technique. The measurement relies on the mechanical resonance of the carbon nanotube induced by an externally applied oscillating voltage with tunable frequency.[16] In this paper, we report the measurements of work functions at the tips of individual ZnO nanobelts using the in-situ TEM technique. The work function at the tips of the ZnO nanobelts is ∼5.2 eV, which shows little dependence on their dimension. This result provides an experimental basis for the work function of ZnO nanostructures and is important for understanding their field emission characteristics.

Figure 1a is a typical scanning electron microscopy (SEM) image of the as-prepared ZnO nanobelts produced at a high yield. The lengths of the ZnO nanobelts are in the range of several tens to several hundreds of micrometers. A transmission electron microscope (TEM) image, as shown in Figure 1b, reveals the high structural uniformity of the ZnO nanobelts. The selected area electron diffraction pattern (inset in Figure 1b) indicates that the nanobelt grows along [0001] and is enclosed by $\pm(2\bar{1}\bar{1}0)$ and $\pm(01\bar{1}0)$ facets.[1]

The measurement of work function at the tip of a single ZnO nanobelt was carried out in-situ at 200 kV in a Hitachi HF-2000 FEG TEM. A specimen holder was built for applying a voltage across a nanobelt and its counter gold electrode, as reported in detail elsewhere.[17,18] The nanobelts to be used for measurements are directly imaged under TEM. Figure 2 is a setup for work function measurement. One end of the nanobelt was electrically attached to a gold wire, and the other end faces directly against the gold ball. Because of the difference in the surface work function between the ZnO nanobelt and the counter Au ball, a static charge $Q_0$ exists at the tip of the nanobelt to balance this potential difference.[19] The magnitude of $Q_0$ is proportional to the

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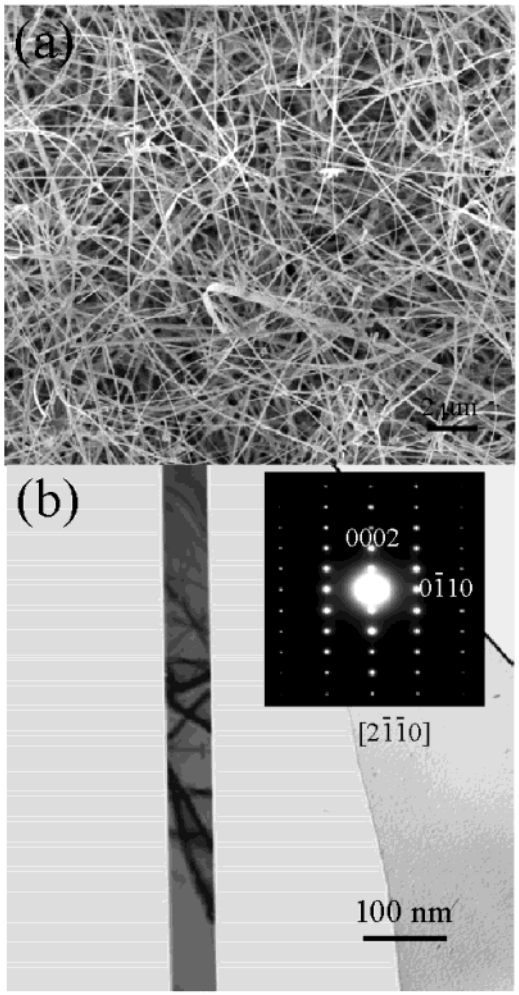


**Figure 1.** (a) SEM image of the as-grown ZnO nanobelts. (b) TEM image of the ZnO nanobelt; the inset is its electron diffraction pattern, which indicates the nanobelt growing along [0001].

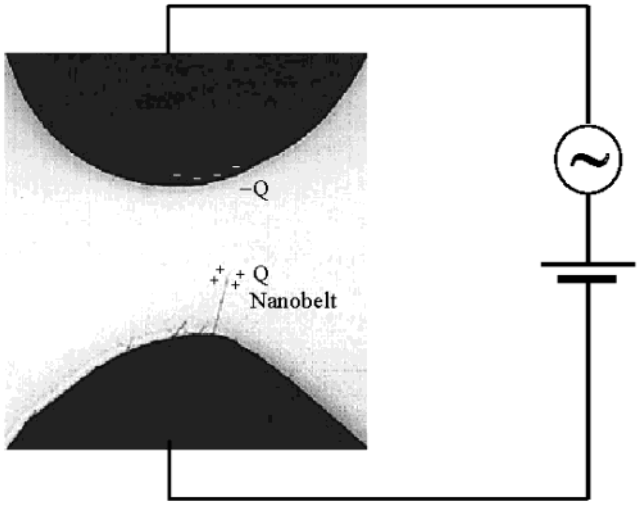


**Figure 2.** Experimental set up for measuring the work function at the tip of a ZnO nanobelt.

difference between work function of the nanobelt tip (NBT) and the Au electrode, $Q_0 = \alpha\ (\phi_{Au} - \phi_{NBT})$, where $\alpha$ is related to the geometry and distance between the nanobelt and the electrode.

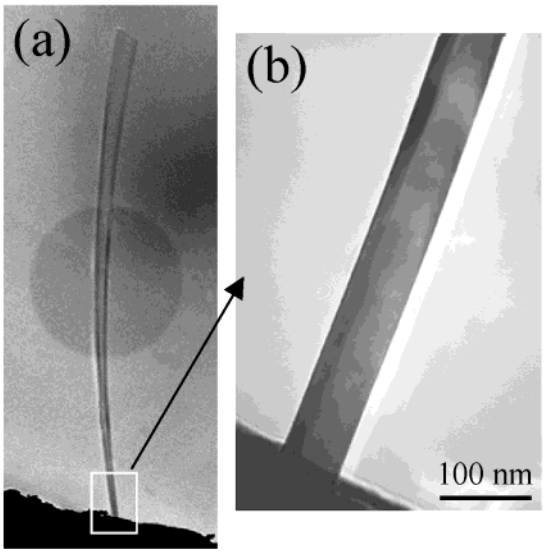


**Figure 3.** (a) TEM image of a fixed ZnO nanobelt at mechanical resonance as induced by an oscillating voltage at $f = 0.576$ MHz and $V_{ac} = 3.0$ V. (b) TEM image recorded from the root of the nanobelt, showing the projected geometry of the nanobelt.

The measurement is based on the mechanical resonance of the nanobelt induced by an externally alternative electric field. Figure 3a shows the attached ZnO nanobelt can be regarded as a vibration cantilever clamped at one end. Experimentally, a constant voltage $V_{dc}$ and an oscillating voltage $V_{ac}\cos 2\pi ft$ are applied to the nanobelt (Figure 2), where $f$ is the frequency and $V_{ac}$ is the amplitude. Thus, the total induced charge on the nanobelt is

$$Q = Q_0 + \alpha e\ (V_{dc} + V_{ac}\cos 2\pi ft) \tag{1}$$

The force acting on the nanobelt is proportional to the square of the total charge on the nanobelt

$$\begin{aligned} F &= \beta[Q_0 + \alpha e\ (V_{dc} + V_{ac}\cos 2\pi \mathrm{ft})]^2 \\ &= \alpha^2\beta\{[(\phi_{Au} - \phi_{NBT} + eV_{dc})^2 + e^2{V_{ac}}^2/2] + \\ &\quad 2eV_{ac}(\phi_{Au} - \phi_{NBT} + eV_{dc})\cos 2\pi ft + e^2{V_{ac}}^2/2\cos 4\pi ft\} \end{aligned} \tag{2}$$

where $\beta$ is a proportional constant. In eq 2, the first term is constant and it causes a static deflection of the ZnO nanobelt. The second term is a linear term, and the resonance occurs if the applied frequency $f$ is tuned to the intrinsic mechanical resonance frequency $f_0$ of the ZnO nanobelt, as shown in Figure 3a. According to vibration theory and considering the rectangular cross-section of the nanobelt,[20] mechanical resonance could be along the thickness or width direction at frequencies given by

$$f_T = \frac{1.875^2 T}{8\pi L^2}\sqrt{\frac{E_T}{3\rho}} \tag{3a}$$

$$f_W = \frac{1.875^2 W}{8\pi L^2}\sqrt{\frac{E_W}{3\rho}} \tag{3}$$

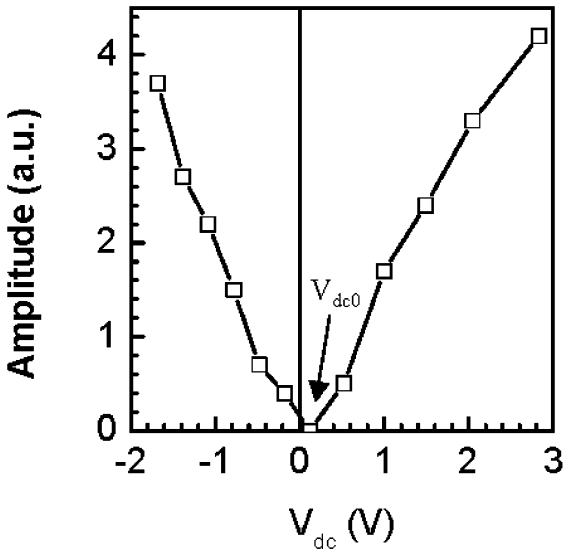


**Figure 4.** Plot of vibration amplitude of a ZnO nanobelt as a function of the applied direct current voltage, from which the offset voltage $V_{dc0} = 0.12$ V.

respectively, where $T$ is the thickness of the nanobelt, $W$ its width, $L$ its length, $\rho$ the volume density, and $E$ the bending modulus of the nanotube. The last term in eq 2 is the second harmonics. The most important result of eq 2 is that, for the linear term, the resonance amplitude $A$ of the nanobelt is proportional to $V_{ac}(\phi_{Au} - \phi_{NBT} + eV_{dc})$.

The principle of the measurement is as follows. We first set $V_{dc} = 0$ and tune the frequency $f$ to get the mechanical resonance induced by the applied oscillating field. Second, under the resonance condition of keeping $f = f_0$ and $V_{ac}$ constant, slowly change the magnitude of $V_{dc}$ from zero to a value $V_{dc0}$ that satisfies $\phi_{Au} - \phi_{NBT} + eV_{dc0} = 0$. At this moment, the resonance amplitude $A$ becomes zero although the external AC voltage is still in effect. Therefore, the work function at the tip of ZnO nanobelt is $\phi_{NBT} = \phi_{Au} + eV_{dc0}$, while $\phi_{Au} = 5.1$ eV.[21] Figure 4 is a plot of the vibration amplitude $A$ of the nanobelt as a function of the applied direct current voltage $V_{dc}$, from which the value for $V_{dc0}$ is determined. The dual-mode resonance of the nanobelts has been observed experimentally, as defined by eqs 3a and 3b.[22] It is important to point out that it does not matter which resonance direction/frequency one chooses, either along the thickness or width direction, the measured $V_{dc0}$ remains the same.

To investigate the dependence of the work function of ZnO nanobelts on the size of their cross-section, i.e., the width $W$ and thickness $T$ of the nanobelts, we measured the geometrical size of the nanobelts from which the work function was measured. Using the projected dimension measured from the TEM image and the orientated angle determined from the corresponding electron diffraction pattern, the geometrical parameters of the nanobelts are obtained.[22] The experimental results are summarized in Table 1. The work function at the tip of the ZnO nanobelt is around 5.2 eV and shows no significant dependence on the cross-section size of the ZnO nanobelts.

**Table 1.** Work Functions of the ZnO Nanobelts with Different Cross-Section Size

| nanobelt | width $W$ (nm) | thickness $T$ (nm) | work function $\phi$ (eV) |
|---|---|---|---|
| 1 | 78 | 43 | 5.22 |
| 2 | 51 | 39 | 5.23 |
| 3 | 55 | 35 | 5.18 |
| 4 | 41 | 20 | 5.16 |
| 5 | 34 | 20 | 5.26 |


**Figure 5.** Measurement the work function of an attached carbon particle on the tip of a ZnO nanobelt at $f = 0.349$ MHz and $V_{ac} = 9.0$ V.

To ensure the accuracy of the measurements, the resonance stability and frequency drift of the ZnO nanobelts have been examined prior to and post measurement so that the change in vibration amplitude is solely attributed to the effect of $V_{dc}$. The sensitivity of this measurement is excellent because the full width at half-maximum for the resonance peak is $\Delta f/f_0 = 0.2\%$. Furthermore, the influence of surface condition on work function is important. In our experiments, the surfaces of the ZnO nanobelts are clean, atomically sharp, and without any sheathed amorphous phase. [1]

This resonant method can also be applied to measure the work functions of other materials, such as the case shown in Figure 5. A carbon particle of diameter ~300 nm is attached at the tip of a nanobelt. Since the induced charges are accumulated mainly at the surface of the carbon particle, the measured work function should be for the surface of the particle. Using the same technique as demonstrated above, the mechanical resonance of the nanobelt gives a work function of 5.05 eV, which is consistent with that of carbon ($\phi_C = 5.0$ eV).[23] This demonstrates a technique for measuring the work function of a single nanoparticle.

In conclusion, the work functions at the tips of individual ZnO nanobelts have been measured by an electromechanical resonant method using in-situ TEM. The work function at the tip of a ZnO nanobelt is ~5.2 eV, which shows little dependence on the geometrical size. This quantity is important in the interpretation of the field emission properties of nanobelts. Using a ZnO nanobelt as a carrier beam, the work functions of a nanoparticle of a different material on the tip of the nanobelt has also been measured.

**Experimental Section.** The synthesis of ZnO nanobelts is based on thermal evaporation of source materials under controlled conditions without the presence of catalyst. The commercial ZnO powder (purity: 99.99%; mp 1975 °C) was loaded on an alumina boat and positioned at the center of an alumina tube inside a high-temperature furnace. After evacuating the tube to $2 \times 10^{-3}$ Torr, thermal evaporation was conducted at 1350 °C for 1 h under the pressure of 200−300 Torr and Ar carrier gas flow rate of 50 sccm. During evaporation, the products were deposited onto an alumina plate placed at the downstream of the alumina tube. The local growth temperature was ∼800 °C.

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