

Work function at the tips of multiwalled carbon nanotubes

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The work function at the tips of individual multiwalled carbon nanotubes has been measured by an *in situ* transmission electron microscopy technique. The tip work function shows no significant dependence on the diameter of the nanotubes in the range of 14–55 nm. Majority of the nanotubes have a work function of 4.6–4.8 eV at the tips, which is 0.2–0.4 eV lower than that of carbon. A small fraction of the nanotubes have a work function of ~ 5.6 eV, about 0.6 eV higher than that of carbon. This discrepancy is suggested due to the metallic and semiconductive characteristics of the nanotube. © 2001 American Institute of Physics. [DOI: 10.1063/1.1356442]

The unique geometrical structure of carbon nanotubes (NTs) suggests that they are likely to be ideal field emitters for flat panel displays.^{1,2} Growth of aligned carbon nanotubes is a major advance in the field for patterned field emission devices.^{3–6} Several physical quantities are important for determining the performance of field emission. The turn-on field (ϕ_{10}) and threshold field (ϕ_{thr}) for electron emission, defined as the macroscopic fields needed to produce a current density of $10 \mu\text{A}/\text{cm}^2$ and $10 \text{mA}/\text{cm}^2$, respectively, are in the range of 2–5 and 4–7 V/ μm for carbon NTs.^{7–13} Recent experimental data of Pan *et al.*¹⁴ show that the aligned and opened carbon NTs exhibit superior field emission performances with ϕ_{10} and ϕ_{thr} in the range of 0.6–1 and 2–2.7 V/ μm , respectively. Another important physical quantity in electron field emission is the surface work function, which is well documented for elemental materials. For the emitters such as carbon NTs, most of the electrons are emitted from the tips of the carbon NTs, and it is the local work function that matters to the properties of the NT field emission. The work function measured from the $\ln(J/E^2)$ vs $1/E$ characteristics curve (the Fowler–Nordheim theory),¹⁵ where J is the emission current density and E is the macroscopic applied electric field, is an average over all of the aligned carbon NTs that are structurally diverse in diameters, lengths, and helical angles.

In this letter, we present experimental measurements of tip work functions of individual carbon NTs. Our results indicate that the tip work function of $\sim 75\%$ of the carbon NTs is ~ 0.2 – 0.4 eV lower than that of carbon; these nanotubes are likely to be metallic. The other 25% of the NTs have a tip work function of ~ 0.6 eV higher than that of carbons; these tubes are likely to be semiconductive.

The multiwalled carbon NTs were synthesized by arc discharge and details have been reported elsewhere.¹⁶ The structures of the carbon NTs are uniform and intact. The NTs have closed ends. The measurement of the tip work function of a single carbon nanotube was carried out *in situ* in a transmission electron microscope (TEM) JEOL 100C (100 kV).¹⁷ A specimen holder was built for applying a voltage across a

NT and its counter gold electrode. The detailed experimental set up has been reported elsewhere.¹⁸ The NTs to be used for measurements are directly imaged under TEM. The principle for work function measurement is schematically shown in Fig. 1(a). We consider a simple case in which a carbon nanotube, partially soaked in a carbon fiber produced by arc discharge, is electrically connected to a gold ball. Due to the difference in the surface work functions between the NT and the counter Au electrode, a static charge Q_0 exists at the tip of the NT to balance this potential difference even at zero applied voltage.¹⁹ The magnitude of Q_0 is proportional to the difference between work functions of the Au electrode and the NT tip (NTT), $Q_0 = \alpha(W_{Au} - W_{NTT})$, where α is related to the geometry and distance between the NT and the electrode.

The measurement relies on the mechanical resonance of the carbon NT induced by an externally applied oscillating voltage with tunable frequency.¹⁷ In this case, a constant voltage V_{dc} and an oscillating voltage $V_{ac}\cos 2\pi ft$ are applied onto the NT, as shown in Fig. 1(b), where f is the

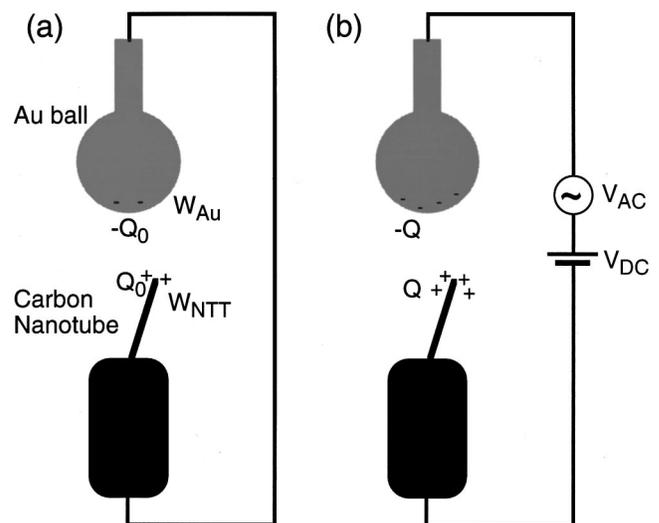


FIG. 1. (a) Schematic diagram showing the static charge at the tip of carbon nanotube as a result of difference in work functions between the nanotube and the gold electrode. (b) Schematic experimental approach for measuring the work function at the tip of a carbon nanotube.

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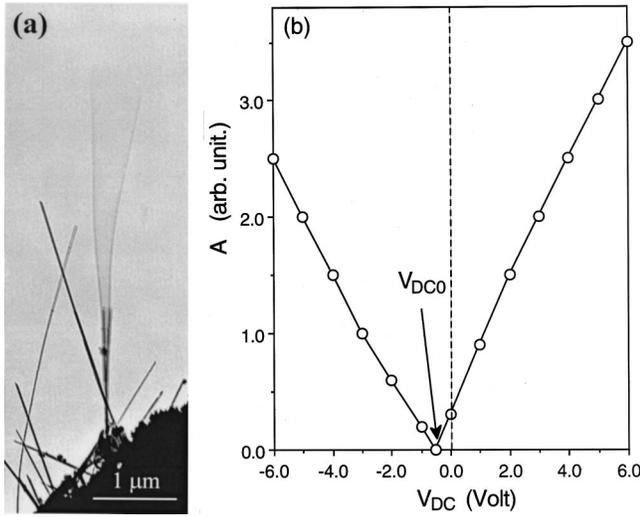


FIG. 2. (a) Mechanical resonance of a carbon nanotube induced by an oscillating electric field. (b) A plot of vibration amplitude of a carbon nanotube as a function of the applied direct current voltage V_{dc} , while the applied frequency of 0.493 MHz and $V_{ac}=5$ V.

frequency and V_{ac} is the amplitude. The total induced charge on the NT is

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

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

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

where β is a proportional constant. In Eq. (2), the first term is constant and it causes a static deflection of the carbon NT; the second term is a linear term, and the resonance occurs if the applied frequency f approaches the intrinsic mechanical resonance frequency f_0 of the carbon NT [Fig. 2(a)]²⁰

$$f_0 = \frac{1.875^2}{8\pi} \frac{1}{L^2} \sqrt{\frac{(D^2 + D_1^2)E_b}{\rho}}, \quad (3)$$

where D is the tube outer diameter, D_1 is the inner diameter, L is its length, ρ is the volume density, and E_b is 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 NT is proportional to $V_{ac}(W_{Au} - W_{NTT} + eV_{dc})$.

Experimentally, we first set $V_{dc}=0$ and tune the frequency f to find the mechanical resonance induced by the applied 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 that satisfies $W_{Au} - W_{NTT} + eV_{dc0} = 0$; the resonance amplitude A should be zero although the oscillating voltage is still in effect. V_{dc0} is the x -axis interception in the $A \sim V_{dc}$ plot [Fig. 2(b)]. Thus, the tip work function of the NT is $W_{NTT} = W_{Au} + eV_{dc0}$.¹⁷

Several important factors must be carefully checked to ensure the accuracy of the measurements.¹⁸ The true funda-

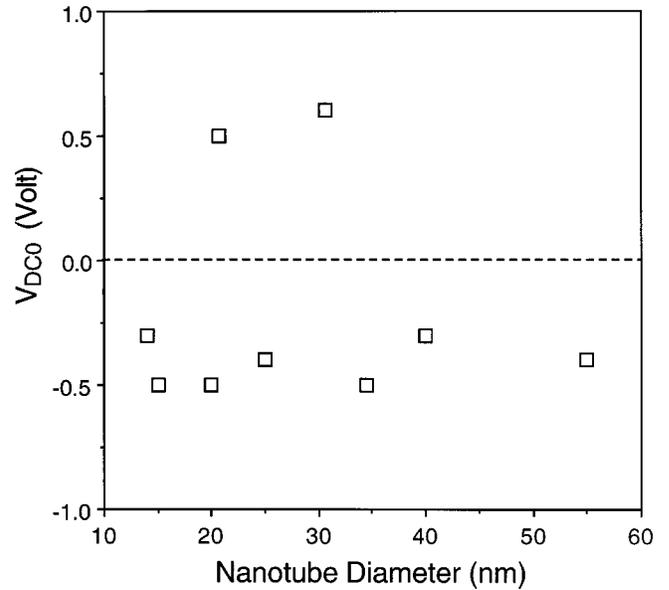


FIG. 3. The experimentally measured V_{dc0} as a function of the outer diameter of the carbon nanotube.

mental resonance frequency must be examined to avoid higher order harmonic effects. The resonance stability and frequency drift of the carbon nanotubes must be examined prior and post each measurement to ensure that the reduction of vibration amplitude is solely the result of V_{dc} . The NT structure suffers no radiation damage at 100 kV, and the beam dosage shows no effect on the stability of the resonance frequency. The sensitivity of this measurement is good because the full width at half maximum for the resonance peak is $\Delta f/f_0 = 0.6\%$.²¹ Figure 3 gives the plot of the experimentally measured V_{dc0} as a function of the outer diameter of the carbon NTs. The data show two distinct groups: -0.3 to -0.5 eV and $\sim +0.5$ eV. The work function shows no sensitive dependence on the diameters of the NTs at least in the range considered here. 75% of the data indicate that the tip work function of carbon NT is 0.3–0.5 eV lower than the work function of gold ($W_{Au} = 5.1$ eV),²² while 25% of the data show that the tip work function is ~ 0.5 eV higher than that of gold. This discrepancy is likely due to the nature of some nanotubes being conductive and some being semiconductive, depending on their helical angles. In comparison to the work function of carbon ($W_C = 5.0$ V),²³ the work function at the tip of a conductive multiwalled carbon NT is 0.2–0.4 eV lower. This is important for electron field emission.

An interesting phenomenon observed in our measurements is that the $A \sim V_{dc}$ curve for some NTs is close to a “Λ” shape (Fig. 4), and the V_{dc} field required to reach zero vibration amplitude is in the order of 10 V or larger. This phenomenon can be interpreted by introducing the tension induced drift in resonance frequency. From Eq. (1), ignoring the small difference between W_{Au} and W_{NTT} , the first term gives $F_0 \approx \alpha^2 e^2 \beta (V_{dc}^2 + V_{ac}^2 / 2)$. If V_{ac} remains constant, and the distance between the NT and the Au electrode is rather small, so that the α and β coefficients are significantly larger and the electrostatic force F_0 is rather strong, the tensile stress in the nanotube increases slightly. The resonance frequency could drift from the true intrinsic resonance fre-

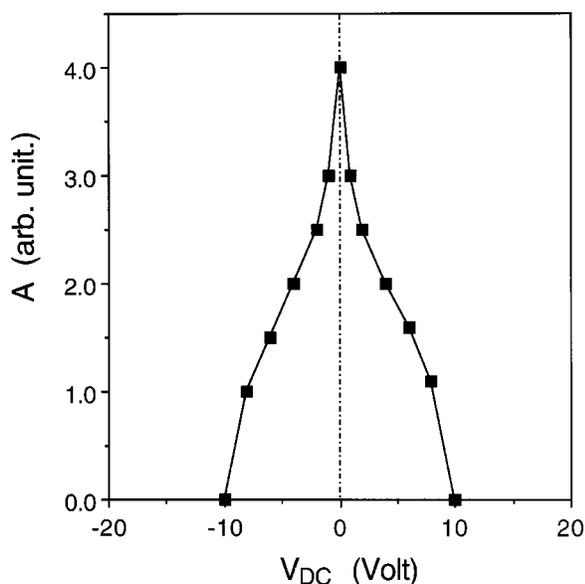


FIG. 4. A plot of vibration amplitude of a carbon nanotube as a function of the applied direct current voltage V_{dc} , while the applied frequency is 0.546 MHz and $V_{ac}=4$ V.

quency f_0 with the increase in V_{dc} . This is analogy to tuning the resonance frequency of a string by applying a tension. The magnitude of the frequency drift is proportional to V_{dc}^2 , thus, the vibration amplitude of the NT would decrease as the resonance frequency drifts away from the applied frequency that is set at the intrinsic resonance f_0 under no tension.

In conclusion, the work function at the tips of individual carbon nanotubes have been measured by an *in situ* TEM technique. The majority of the nanotubes have a work function ~ 0.2 – 0.4 eV lower than that of carbon, and the work function shows little dependence on the diameters of the carbon nanotubes in the range of 14–55 nm. This result provides an experimental basis for the work function of multi-walled carbon nanotubes and is likely important in understanding their field emission characteristics.

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