Characterization of the field emission properties of individual thin carbon nanotubes

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Electron emission measurements were conducted on individual carbon nanotubes. The nanotubes had a closed end and their surfaces were thoroughly cleaned. It is shown conclusively that *individual* carbon nanotube electron emitters indeed exhibit Fowler–Nordheim behavior and have a work function of 5.1 ± 0.1 eV for the nanotubes under investigation, which had diameters of 1.4 and 4.9 nm. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1786634]

Electron emission from carbon nanotubes has drawn the attention of many scientists since the initial reports in 1995,[1,2] triggering investigation into a wide range of possible applications, such as field emission displays,[3] cathode ray lamps,[4] x-ray sources,[5] and electron sources for electron microscopes.[6] But, despite the large scientific and industrial interest for carbon nanotubes, the emission mechanism is not yet fully understood. The literature contains a large number of reports on films containing a multitude of carbon nanotubes that emit electrons under the presence of an electric field. Often a voltage–current characteristic is given, which hardly provides any information about the related physical processes. First, the nanotubes in the film may be covered by adsorbed species, which have a strong influence on the emission efficiency. Second, the emission is usually not dominated by the average nanotube, but by a few special nanotubes in the film.[7] For an understanding of the relation between the physical parameters of a carbon nanotube and its emission properties, it is, therefore, imperative to measure individual nanotubes and to ensure that the surface of the nanotube is thoroughly cleaned. In this letter, measurements conducted under such conditions, are described allowing conclusions to be draw on the emission mechanism.

A carbon nanotube emits electrons under the influence of a large electric field at the tube end. Often it is assumed that the emission process can be described by that of a sharp tip showing metallic behavior, i.e., field emission. The Fowler–Nordheim theory[8,9] describes the field emission process in terms of a tunneling current density J through a potential barrier between a metal surface and vacuum[10]

$$J=\frac{e^3F^2}{8\pi h\phi\, t^2(y)}\exp\left\{-\frac{8\pi\sqrt{2m}\,\phi^{3/2}}{3heF}v(y)\right\}=c_1\frac{F^2}{\phi\, t^2(y)}\exp\left\{-c_2\frac{\phi^{3/2}}{F}v(y)\right\} \quad (1)$$

with work function ϕ, electron mass m, electric field F, Planck's constant h, the electron charge e, and the functions $t(y)$ and $\nu(y)$. A plot of $\log(J/F^2)$ versus $1/F$, the so-called Fowler–Nordheim plot, is approximately a linear curve. The functions $t(y)$ and $v(y)$ were calculated by Good and Mueller[9] and can be approximated by,[10] $t(y)=1+0.1107y^{1.33}$ and $v(y)=1-y^{1.69}$. The function y is expressed as

$$y=\frac{1}{\phi}\sqrt{\frac{e^3F}{4\pi\varepsilon_0}}=c_3\frac{\sqrt{F}}{\phi} \quad (2)$$

with the permittivity of free space ε_0. Of importance is the tunneling parameter d,

$$d=\frac{ehF}{4\pi\sqrt{2m\phi}\,t(y)}=\frac{c_4F}{\sqrt{\phi}\,t(y)}. \quad (3)$$

The current density as function of the energy E is given by:[10]

$$J(E)\cong\frac{4\pi\, med}{h^3}\frac{\exp(E/d)}{1+\exp(E/k_BT)}. \quad (4)$$

Here, k_B is the Boltzmann constant and T is the temperature. The Fowler–Nordheim equation is valid for low temperatures only and a correction factor is needed to include a temperature effect, but in the temperature range of our measurements (up to 900 K) this effect can be neglected. The Fowler–Nordheim theory was derived for a surface that appears flat as "seen" from the electrons; a correction may be needed for surfaces with an extremely large curvature.[11] An additional correction may furthermore be necessary in the case of nanotubes since the density of states is not energy independent around the Fermi level as in "real" metals.[12] The main question is now, whether or not a "pure" Fowler–Nordheim model applies, or whether correction factors are needed, or other emission mechanisms should be accounted for. We will design our experiment with the goal to answer this question.

The total current I is the product of J and the emitting surface A, which is often taken as a half sphere with radius of curvature R, thus $I=2\pi R^2J$. The field at a sharp conducting tip is $F=\beta U$, with the extraction voltage U and the field enhancement factor β, which depends on the shape of the emitter and extractor geometry. The field enhancement factor of a carbon nanotube mounted on a support tip can be calculated numerically. For the geometry as shown in Fig. 1(a), the potential was calculated for cylindrical symmetry inside a large casing (10 mm) using Munro's Electron Beam Soft-

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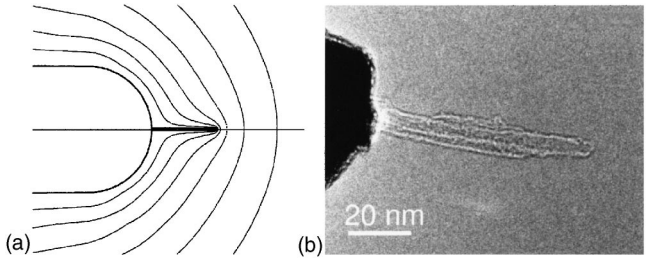

FIG. 1. Carbon nanotube electron source on a support tip. (a) Numerical calculations on the field enhancement factor. A nanotube with a length of 100 nm, a radius of 2 nm, and mounted on a tip with a radius of 100 nm, has a field enhancement factor of 1.7×10^{7} m^{-1}. Equipotential lines every 50 mV are also shown. (b) Bright field transmission electron microscopy image of a carbon nanotube with a closed end on a tungsten support tip. The image was taken deliberately out-of-focus to enhance the contrast.

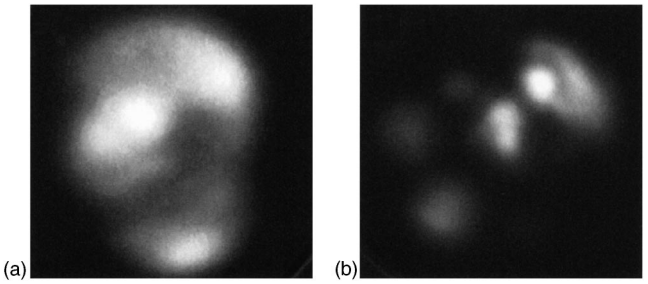

FIG. 2. Emission patterns of individual carbon nanotube electron emitters. (a) Emission pattern of the closed nanotube 1. (b) Emission pattern of an open nanotube.

ware. The axial potential was differentiated to obtain the electric field strength as function of the axial position for a potential difference between the anode and the cathode of 1 V. The field enhancement factor was directly obtained from the maximal field strength at the nanotube end.

Thin carbon nanotubes were grown on an oxidized silicon substrate by thermal chemical vapor deposition, as described elsewhere.[13] The sample contained mainly thin nanotubes (one to four walls) lying flat on the substrate. Individual nanotubes were mounted on tungsten tips in a highly controlled manner[14] in a scanning electron microscope (SEM, Philips), equipped with nano-manipulator (Omicron). Transmission electron microscopy (TEM, FEI company) images of six nanotube electron sources revealed that always a short and thin nanotube had been mounted, with lengths of 25–110 nm and radii of 1–4.4 nm. It was also found that the majority of the nanotubes had a closed end, see Fig. 1(b).

The field emission properties were measured in an ultrahigh vacuum system with a base pressure of 2×10^{-10} Torr. A fresh nanotube was always heated first to the carbonization temperature[12] of about 1000 K in vacuum for 10 min to remove adsorbed species and impurities from the tube. The effect of the cleaning procedure was checked by recording the emission pattern with a microchannel plate and a phosphor screen. Figure 2(a) shows that nanotube 1 produces the typical emission pattern of a thin nanotube with a closed cap.[15] This pattern was highly stable with time. In contrast, the patterns of nanotubes that were not sufficiently cleaned showed one or more spots that fluctuated with time. A few nanotubes displayed an emission pattern with separate spots, fluctuating with time [Fig. 2(b)], even after repeated heating to the carbonization temperature. These patterns were assigned to the emission patterns of nanotubes with an open end.

The emitted current of nanotube 1 was measured as function of the extraction voltage at room temperature shortly after the cleaning procedure [Fig. 3(a)]. The data follow a straight line in the Fowler–Nordheim plot [Fig. 3(b)], which indicates a field emission process. At low currents a few data points do not fit, on account of a small leakage current in the measurement system. Fitting the Fowler–Nordheim equation (assuming a work function of 5 eV) to this data gave a value of the field enhancement factor $\beta=8.0\times10^{6}$ m^{-1}; the tube radius was extracted from the emitting area and amounted to 4.9 nm. When calculated numerically, the field enhancement factor is 8.4×10^{6} m^{-1} for a tube with a radius of 5 nm and a length of 25 nm, which are typical values of our emitters.

The Fowler–Nordheim equation can be simplified by evaluating the functions $t(y)$ and $v(y)$. For the current range of our measurements, $t(y)$ varied between 1.041 and 1.054, and we will approximate it by $t(y)=b_1=1.05$. The function $v(y)$ showed a variation between 0.6 and 0.71. It is not precise to approximate it by a constant, but we can use a slightly different function:[16,17] $v(y)=a_1-a_2\times y^2=0.958-1.05y^2$. The current density can now be expressed as

$$J=c_1\frac{F^2}{b_1^2\phi}\exp\left\{a_2\ c_2c_3^2\frac{1}{\sqrt{\phi}}\right\}\exp\left\{-a_1\ c_2\frac{\phi^{3/2}}{F}\right\}. \qquad (5)$$

Fitting this equation to the voltage–current data gives the values $\beta=8.1\times10^{6}$ m^{-1} and $R=4.5$ nm (for $\phi=5.0$ eV). These values differ only slightly from the values obtained using the full Fowler–Nordheim equation, 1% and 9%, re-

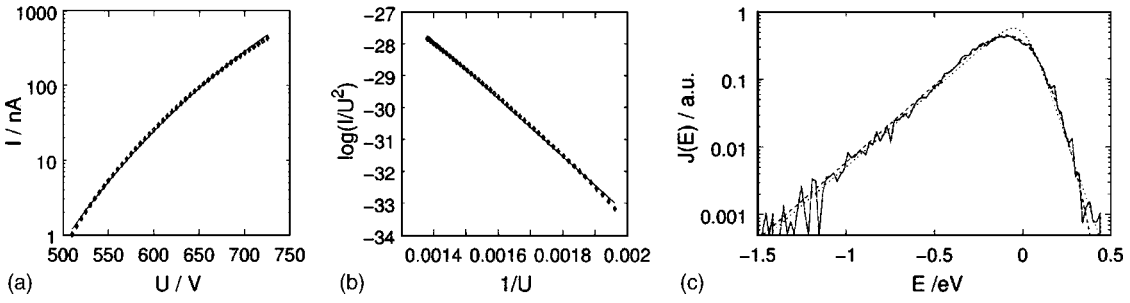

FIG. 3. Field emission measurements of carbon nanotube 1 at room temperature. (a) The emitted current as function of the extraction voltage and a fit of the Fowler–Nordheim theory (line). (b) Fowler–Nordheim plot with a slope of -9.0×10^{3} and a linear fit (line). (c) Energy spectrum recorded at an extraction voltage of 552.8 V, room temperature, and an emitted current of 11 nA (line). Fit with the Fowler–Nordheim theory (dotted line). Numerically generated energy spectrum taking into account the limited resolution of the spectrometer (dashed line).

spectively. Thus, the approximations of the functions $t(y)$ and $v(y)$ are justified.

The energy spectrum of the emitted electron beam of nanotube 1 was measured with a hemispherical energy analyzer (VSW) and is shown in Fig. 3(c). Fitting to Eq. (4) gives the values $d=0.19$ eV and $K_BT=0.044$ eV. The energy spectrum cannot be fitted perfectly to the Fowler–Nordheim model, since a broadening effect occurred due to the limited resolution of the spectrometer. To estimate the broadening effect on the energy spectrum, a numerically generated energy spectrum with $d=0.19$ eV and $T=300$ K was convoluted with a Gaussian function with a sigma of 0.1 eV as the upper limit of the resolution. As can be seen in Fig. 3(c), this spectrum fits well with the measurement. Fitting this curve gives the parameters $d=0.19$ eV and $k_BT=0.043$ eV. Since the numerically generated data do not result in a larger value of d, it can be concluded that indeed the true value of d has been obtained from our measurement. The value of d as calculated with Eq. (3) using $\beta=8.1\times10^6$ m^{-1}, $\phi=5.0$ eV, and $U=552.8$ V equals 0.19 eV, consistent with the measurement. The fitted value of kT resembled a temperature of 507 K, while the measurement was performed at room temperature. This difference of 200 K is attributed to the broadening effect.

The data of the Fowler–Nordheim plot and the energy spectrum can be combined, in order to determine the value of the work function from the field emission measurements. The slope of the Fowler–Nordheim plot $b=-a_1c_2\phi^{3/2}/\beta$ yields[16,17]

$$\phi=-\frac{b_1}{a_1}\frac{bd}{c_2c_4V}=-\frac{3}{2}\frac{b_1}{a_1}\frac{bd}{V}=-1.64\frac{bd}{V} \tag{6}$$

with d and V from the energy spectrum. For our data ($b=-9.0\times10^3$, $d=0.19\pm0.1$ eV, $U=553$ V) Eq. (6) gives a value of the work function of 5.1 ± 0.1 eV, equal to the value of graphite. The same result was obtained for a second set of data points obtained at a later point in time and with an energy spectrum recorded at a current of 90 nA. The measurements on another nanotube (No. 2) revealed a much smaller radius, $R=1.4\pm0.2$ nm, $\beta=1.2\times10^7$ m^{-1} and $b=-5.9\times10^3$ from current–voltage characteristics. The energy spectrum gave $d=0.26\pm0.2$ eV ($I=100$ nA, $U=491$ V). The result is a work function of 5.1 ± 0.2 eV. Our data are consistent with the finding of another group, showing that most carbon nanotubes have a value of the workfunction of 4.9 eV.[18] A mechanism that predicts a smaller work function for small nanotubes[17] does not appear in our data.

We show that carbon nanotube electron sources show Fowler–Nordheim behavior using as only parameters, the extraction voltage, the geometry of the emitter and the work function. The work function is 5.1 ± 0.1 eV, even for small diameter (2–4 nm) nanotubes. As a result, the behavior of carbon nanotubes electron sources can now be calculated numerically, which will help the future design of electron emission devices. Our data demonstrate the need for measurements on samples with a known geometry and the importance of a good cleaning procedure.

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