Characterization of the field emission properties of individual thin carbon nanotubes

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(Received 5 April 2004; accepted 29 June 2004)

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 drawn 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 showing metallic behavior, i.e., field emission. The Fowler–Nordheim plot, is approximately a linear curve. The functions t(y) and v(y) were calculated by Good and Mueller10 and can be approximated by t(y)=1+0.1107y1.33 and v(y)=1−y1.69. The function y is expressed as

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

with the permittivity of free space \( \varepsilon_0 \). Of importance is the tunneling parameter \( d \),

\[ d = \frac{e h F}{4 \pi^2 m \phi t(y)} = c_4 F \sqrt{\frac{\phi}{t(y)}} \quad (3) \]

The current density as function of the energy E is given by

\[ J(E) \approx \frac{4 \pi \text{med}}{h^3} \frac{\exp(E/d)}{1 + \exp(E/k_B T)} \quad (4) \]

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 \( I=2\pi R^2 J \). The field at a sharp conducting tip is \( F=\beta U \), with the extraction voltage \( U \) and the field enhancement factor \( \beta \), 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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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. 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 in a scanning electron microscope (SEM, Philips), equipped with nanomanipulator (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 of about 1000 K in vacuum for 10 min to re-activate the carbonization process. The sample was then mounted to a tungsten support tip with a radius of 100 nm, a length of 100 nm, and a thickness of 2 nm. The tip was fixed to an anode area and amounted to 4.9 nm. When calculated numerically, the field enhancement factor is 8.4 × 106 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:

$$v(y) = a_1 - a_2 \times y^2$$

The current density can now be expressed as

$$J = \frac{e^2}{b_1^2 \phi} \exp \left\{ \frac{a_2 c_2 c_3^2}{\sqrt{\phi}} \exp \left\{ -a_1 c_2 \phi^{3/2} \right\} \right\}.$$  (5)

Fitting this equation to the voltage–current data gives the values $\beta$ = 8.1 × 106 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-
respectively. 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 $K_B T=0.044$ 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, we have used a numerical generated energy spectrum 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 $k_B T=0.043$ 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 $k_B T$ 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 $b=-\alpha d\phi^{3/2}/\beta$ yields \cite{16,17}

$$\phi = -\frac{b_1}{a_1} \frac{bd}{a_2c_4V} = -\frac{3}{2} \frac{b_1}{a_1} \frac{bd}{V} = -1.64 \frac{bd}{V}$$

(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 $5.1\pm0.1$ 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 $5.1\pm0.2$ 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.\cite{18} A mechanism that predicts a smaller work function for small nanotubes\cite{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 $5.1\pm0.1$ 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.

The authors thank A. S. Teh, M. H. Yang, N. L. Rupesinghe, G. A. J. Amarutunga, and T. van Rooij for experimental help and O. Groening for discussions. This work was supported by FEI Company, the Dutch Ministry of Economic Affairs, the EPSRC and the EC.

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