Quantifying temperature-enhanced electron field emission from individual carbon nanotubes

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The electron field emission properties of individual multiwalled carbon nanotubes have been examined using a combined STM-TEM microscope. The measured electron emission, for low emission currents, can be fitted with a standard Fowler-Nordheim model. For higher electron emission, above 10 μA for an individual carbon nanotube, we observe a significantly increased emission current leading to a nonlinear Fowler-Nordheim plot. The nonlinearity is caused by thermally enhanced electron emission due to Ohmic heating of the carbon nanotube. This is verified by modeling the electron field emission current. In addition to the influence of radiative cooling and the temperature dependence of the nanotube resistivity, we clearly show that a consideration of the temperature change due to the electron emission process itself, known as the Nottingham effect, is crucial to obtain good agreement with the experimental data.

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I. INTRODUCTION

Extensive research in the area of electron field emission from carbon nanotubes has, in recent years, resulted in the development of flat panel displays,[1] new lighting elements[2,3] and compact x-ray sources.[4] Many studies so far have been carried out on films of carbon nanotubes,[5] since it is easy to achieve high electron emission from these structures. However it is difficult to understand the details of the field emission mechanism from studying large films of carbon nanotubes since it is impossible to know the exact number of nanotubes that are actually contributing to the total emission current which is measured. Comparison between experimental results on films of multiwalled nanotubes (MWNT) and individual MWNT suggest that it is only a few longer tubes in the films that align in the presence of the applied electric field and provide the main contribution to the field emission current.[6] This has been confirmed in measurements showing the strong spatial inhomogeneity of emission from thermal-CVD MWNT films.[7]

Measurements on individual carbon nanotubes[6,8–11] therefore provide a cleaner method for determining the physical mechanisms occurring during field emission and the reasons for emitter failure or emitter degradation in the experiments. Here, we report field emission experiments on individual MWNT using a combined transmission electron microscope (TEM) and a scanning tunneling microscope (STM). The experimental results reveal a nonlinear Fowler-Nordheim behavior that is explained as a result of a strong Ohmic heating during high current electron emission that changes the temperature of the emitter tip. Deviations from Fowler-Nordheim behavior have been reported on a number of occasions from nanotube films or individual nanotubes, but this is normally the observation of a *decrease* in the slope of the Fowler-Nordheim plot when the applied field is increased.[5,12–14] This has recently been explained in terms of a two-process model involving first tunnelling from a metallic region into a semiconducting region under the influence of the external electric field, followed by tunnelling from the semiconducting region into vacuum under the Coulomb field of the additional electron produced in the first process.[15] The finite size of the semiconducting region at the tip is then seen to be the cause of the "knee" frequently observed in the Fowler-Nordheim plots, with a decrease in the gradient at high applied electric fields. We have also observed similar results from films of MWNT (Refs. 12 and 16) but concluded that the knee in this case is correlated to the Ohmic heating of the MWNT followed by thermal alteration of the MWNT leading to a change in the electron emission behavior.

In the results presented here, we clearly observe a strong *increase* of the emission current, giving an increasing Fowler-Nordheim gradient at high applied electric fields. Although this effect has been shown previously,[8,17] the present experimental data clearly show the nonlinearity of the increase and allow us to test the model predictions. In addition, the experimental setup that has been used for the measurements allows us to experimentally determine many of the important parameters required for modeling thus providing further constraints and allowing us to clearly identify the most important contributions to the observed behavior. The results, showing a strongly increased current emission at high fields, are explained by modeling the Ohmic heating process taking into account the temperature dependence of the resistivity, the electron cooling effect of the emitter as a result of the high electron emission from the hot surface, known as the Nottingham effect, and the cooling due to thermal radiation. We show that it is essential to include the Nottingham effect in order to obtain a satisfactory agreement with experiment. This important contribution has not been considered in previous models applied to nanotube field emission.

II. EXPERIMENTAL SETUP AND RESULTS

The MWNT are produced by thermal CVD (Refs. 12 and 18) and glued to a Ag wire using conducting epoxy. The Ag wire and STM tip were mounted inside a Philips CM200 Super TWIN FEG with a recently developed STM-TEM holder.[19] A combination of STM and TEM was used previously in pioneering studies of nanotubes by de Heer and co-workers.[9] In our case, the STM is controlled by Nanofac-

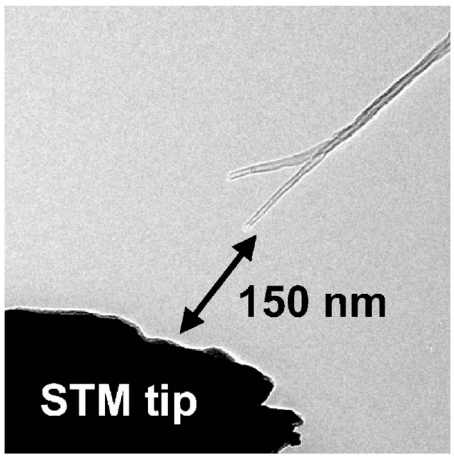

FIG. 1. TEM image of the investigated carbon nanotube. The distance between the STM tip and the carbon nanotube is 150 nm. The diameter of the carbon nanotube tip is 10 nm.

tory electronics and software. This gives the possibility to move the STM tip in three dimensions.[19] The STM tip consisted of a sharp, mechanically cut, Pt/Ir (90/10%) wire. Figure 1 displays a TEM image of an investigated MWNT and the STM tip. In the image we have the STM-tip in the lower left part and the carbon nanotube in the upper right, with a tip diameter of 10 nm. The MWNT extends outside the image to a total length of 1.6 μm. The second nanotube tip that can be seen in the figure is too far away from the STM tip to provide a significant contribution to the field emission signal, as verified by simulations, and cannot explain the observations.

The distance between the MWNT and the STM tip was chosen to be 150 nm and this distance was also monitored during the field emission characterization in order to examine possible influences from electrical field induced alterations in the distance. The resistance of the MWNT was measured by contacting the nanotube with the STM tip and recording the *IV* dependence. The measured value varied between 96–116 kΩ at a few places along the tube and gives an upper limit for the resistance. The corresponding resistivity of the tube is comparable to the resistivity obtained previously for individual iron-filled multiwalled nanotubes.[20] Tarkiainen *et al.* reported resistivities in the range 30–70 kΩ/μm for CVD produced tubes.[21]

The field emission experiments were performed by applying a negative bias to the carbon nanotube and grounding the STM tip. Current starts to be measurable at an applied voltage of approximately 45 V.

Figure 2 shows two sets of sequential data. The applied voltage ranges from 45 V to a maximum of 75 V. The same data is given in a Fowler-Nordheim (FN) plot [Fig. 2(b)].[22] The first scan in this series results in a linearly decreasing FN plot. However for high voltages, close to 75 V, the emission current becomes very noisy. The next scan shows a lower electron emission current but for high applied voltages there is a clear divergence from the linear FN plot. The first, noisy scan can be explained by the presence of adsorbates on the nanotube surface which enhance the field emission current.[23] It has been shown that adsorbates will desorb from nanotubes at elevated temperatures.[8,17,24] If such temperatures are reached due to Ohmic heating then this can explain the large fluctuations in the emission current towards the end of the first scan and also the reduced field emission on subsequent scans. The effect of adsorbates cannot, however, explain the deviation from straight-line behavior observed for high fields on the later voltage scan. Electron emission rates above the extrapolated Fowler-Nordheim line have been shown before[8,17] and attributed to an increased nanotube temperature due to strong Ohmic heating of the carbon nanotube at high emission currents. We have previously demonstrated this strong Ohmic heating in large films of aligned thermal-CVD MWNT.[16] Black-body radiation, corresponding to temperatures in the range 1550–2200 K, was seen to be emitted from the nanotubes under conditions where high field emission currents were measured. These temperatures were in good agreement with measurements of electron energy distributions.[8]

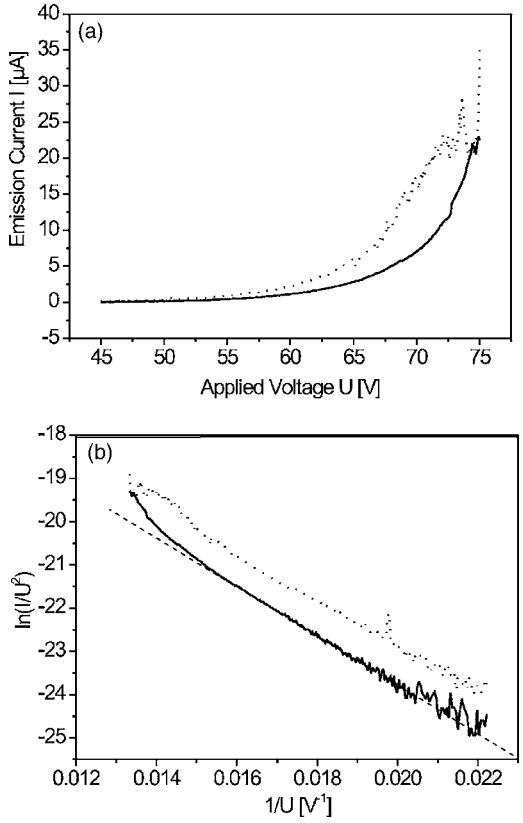

FIG. 2. (a) Measured field emission current as a function of applied voltage for two voltage scans on the same nanotube (first scan, dotted; second scan, full line). (b) The corresponding Fowler-Nordheim plot.

III. MODELING AND COMPARISON WITH EXPERIMENTAL RESULTS

In order to understand our experimental results we have modeled the effect of the emitter temperature on the electron field emission current. We start by calculating the electron emission rate Γ. A number of expressions can be found in the literature for this purpose, derived at different levels of so-

phistication and with slightly different physical assumptions (see, e.g., Refs. 22, 25, and 26). The precise form does not affect the conclusions drawn here. We use the expression[22]

$$\Gamma = \pi r^2 \int \rho(\varepsilon) v(\varepsilon) f(\varepsilon) |T|^2 d\varepsilon, \tag{1}$$

where ε is the electron energy with respect to the Fermi level, $\rho(\varepsilon)$ is the three-dimensional (3D) electron gas density, $v(\varepsilon)$ the velocity of the electrons and $f(\varepsilon)$ is the Fermi function. $|T|^2$ is the square of the tunnelling matrix, which we calculate from the WKB approximation.

$$|T|^2 = e^{-(4/3)\sqrt{(2m/\hbar^2)}[(\phi-\varepsilon)^{3/2}/eF_l]}, \tag{2}$$

where F_l is the local field at the emitter tip ($F_l = \gamma F_{\text{applied}}$) and ϕ is the work function [5 eV (Ref. 27)]. The field enhancement factor, γ, was obtained from fitting the experimental data. From the expressions (1) and (2) it is already clear that the field emission current will be enhanced for elevated temperatures since an increasing fraction of the electrons will be above the Fermi level and will have a thinner barrier to tunnel through. In order to solve the integral in Eq. (1) we have used a second order Sommerfeld expansion. This approximation will break down at high temperatures (on the order of 3000–4000 K) but should be sufficient for the present comparisons. Additional effects which we do not consider here are, e.g., thermionic emission from the walls of the nanotube at elevated temperatures. An estimation of the importance of these effects again suggests that our calculations will not be valid for temperatures above 3000–4000 K.

The model used to calculate the emitter temperature is similar to that presented by Vincent *et al.*[28] and Huang *et al.*[25] The model assumes that the thermal conductance of the nanotube is that of a one-dimensional (1D) object that is connected to a heat sink at one end. The stationary heat equation is, in this case, given by

$$\pi r^2 \kappa \frac{\partial^2 T}{\partial x^2} dx - 2\pi r \sigma (T^4 - T_0^4) dx + I^2 dR = 0, \tag{3}$$

where κ is the thermal conductivity, r is the tube radius (5 nm), σ the Stefan-Boltzmann constant, T_0 the ambient temperature, and I is the electron emission current calculated with Eq. (1). dR is the resistance of a length element dx of the carbon nanotube. The numerical calculation used a discretization length of 16 nm. Reducing this by a factor of 2 did not result in any appreciable difference in the calculated values. The solution of the coupled equations (1) and (3) gives the temperature profile along the tube from which the conductance and emitted current can be calculated. It should be pointed out that κ depends on the temperature and the values reported in the literature range from 3000 W m^{-1} K^{-1} (Ref. 29) down to 25 W m^{-1} K^{-1} (Ref. 30) for MWNTs. However there exists so far no good experimental data for temperatures up to 2500 K which is the temperature range that we are interested in. In our calculations a constant value of 40 W m^{-1} K^{-1} has been used.

The value of R or dR is also temperature dependent.[8] In this calculation we use a form similar to those valid for semiconductor resistivities,

$$R(T) = R_0 e^{E_R/k_B T}. \tag{4}$$

The parameters E_R (=36.6 meV) and R_0 (=24.3 kΩ) are chosen to agree with the experimental findings that the resistance is decreased by 70% when the temperature increases from room temperature to 2000 K.[28] The room temperature resistance was taken to be 100 kΩ.

We have also considered the effect that appears when a large number of electrons leave a hot surface, the Nottingham effect.[31] Electrons leaving the nanotube with energies higher than the Fermi level cool the tip of the MWNT emitter. Conversely, those emitted from below the Fermi level heat the tip. Since in the experiments we measure electron currents up to 20 μA, which is approximately 10^{14} electrons per second, this can be an important effect, as we show below. This effect was not previously included in the calculations by other authors.[25,28] We therefore calculate the mean energy of the emitted electrons,

$$\langle \varepsilon \rangle = \frac{\pi r^2}{\Gamma} \int \varepsilon \rho(\varepsilon) v_x(\varepsilon) f(\varepsilon) |T|^2 d\varepsilon \tag{5}$$

and distribute this energy loss along the carbon nanotube. The results are not significantly changed if the cooling is considered to affect only the tip region of the nanotube. Since the 1D heat equation depends on both Eqs. (1) and (5), it is necessary to iterate the calculations until the change in the emitter temperature converges. The criterion for convergence is a change of less than 2 mK between two iterations, at any point on the tube.

The three-dimensional Fermi gas description yields the correct slope for low emission currents in the FN plot but the absolute magnitude of the emission current is approximately an order of magnitude lower than the experimental value. In order to correctly estimate the effect of Ohmic heating we adjust for this discrepancy by scaling the calculated values to correctly reproduce the experimental currents for low applied electric fields. In Fig. 3(a) we show the results from five different simulations and compare these with the last voltage scan given in Fig. 1 (gray full line). Figure 3(b) shows the corresponding FN plots. The full black line shows the results of the calculation including all the effects discussed above [temperature dependent resistance, thermal conductivity, radiative cooling, electron cooling (Nottingham effect)]. The other lines show the effects of neglecting one or more of these contributions. The black dashed line shows the effect of neglecting the radiative cooling term. The dotted line assumes a constant value of the resistance (100 kΩ) instead of the exponentially varying function [Eq. (4)]. The dashed-dotted line shows the effect of neglecting the electron cooling and the gray dashed line shows the effect of neglecting all cooling mechanisms, including the heat sink at the base of the carbon nanotube. The emitter temperature is shown as a function of the emission current in Fig. 4 for the same simulations as given in Fig. 3.

As expected, the thermal conductivity of the nanotube and heat transport to the room temperature substrate play important roles. Without these, the carbon nanotube very rapidly reaches a temperature beyond 4000 K and is destroyed (gray dashed lines in Figs. 3 and 4). Similar observations have

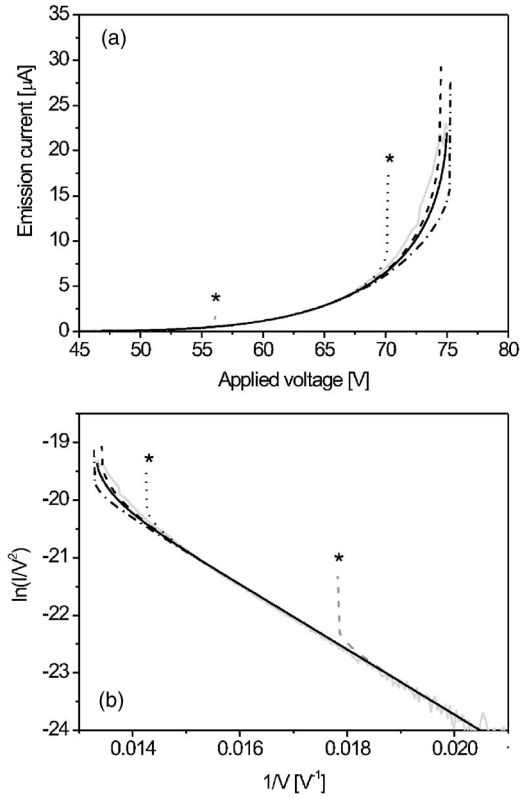

FIG. 3. (a) *IV* data for the third voltage scan of the experimental data (full gray line), and five different simulations. Full line, including thermal conductivity and heat transfer to substrate, temperature dependent resistance, electron cooling, and radiative cooling. Dashed line, neglecting radiative cooling. Dotted line, constant resistance. Dashed-dotted line, neglecting electron cooling. Dashed gray line, no heat transport or cooling considered. (b) The corresponding Fowler-Nordheim plots. The asterisks denote where the emitter tip exceeds a temperature of 4000 K.

been made previously.[25,28] Good agreement with the experimental measurements is obtained when all the cooling effects are considered (full black line). The model line lies slightly below the experimental data but the rate of increase in emission current with increased applied voltage is well reproduced. Clearly, an assumption of constant resistance (dotted line) leads to a too rapid increase in emission current and temperature. The electron cooling term is also important for obtaining the correct form of the experimental curve. Neglecting this leads to a later onset of the deviation from FN behavior (i.e., towards higher applied voltages) and the rate of increase in current beyond this point is too abrupt to provide agreement with experiment. Interestingly, the main influence of the Nottingham effect for temperatures up to approximately 2500 K (emission current of 20 μA) is actually a "heating" due to the emission of electrons from below the Fermi level (see discussion above). This can be clearly seen in Fig. 4 where the neglect of this effect gives significantly lower emitter temperatures for emission currents up to 20 μA. Radiative cooling plays a relatively minor role for the nanotube studied here but serves to reduce the temperature and therefore rate of current increase for high applied voltages/emission currents thus providing better agreement with the form of the experimental curve. It should be noted that the relative importance of radiative cooling compared to the Nottingham effect will depend on the geometrical parameters (length and radius).

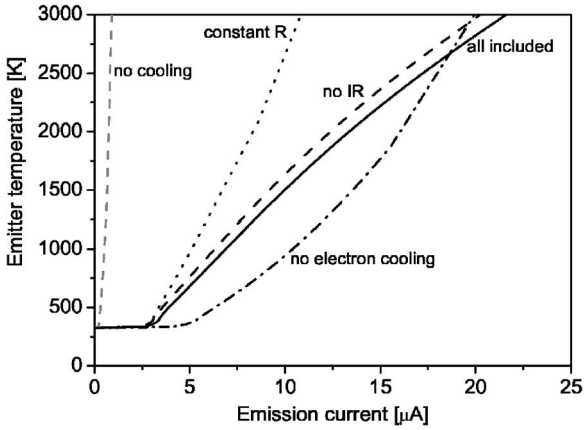

FIG. 4. Calculated carbon nanotube emitter temperature as a function of the electron emission current for the five cases in Fig. 3. The same notation is used as Fig. 3.

The comparison with the simulations clearly shows that the form of the measured experimental data curve (after the thermal removal of adsorbates and "self-annealing") is due to positive feedback as a result of the increased emitter temperature caused by Ohmic heating. However, in order to obtain good agreement with the measured experimental curve it is necessary to account for the temperature dependence of the resistivity, the energy balance on electron emission and, to a lesser extent, radiative cooling. The temperatures obtained from the modeling are also in good agreement with experimental data. For emission currents in the range 10–20 μA we get temperatures ranging from 1500 K up to 2800 K (Fig. 4). This is in reasonable agreement with blackbody radiation measurements from films of nanotubes[16] and also includes the temperature range that has been determined from the measurement of electron energy distributions from individual nanotubes.[8]

IV. CONCLUSION

Field emission data from individual carbon nanotubes have been measured using an STM-TEM. The experiment determined the emission current as a function of the voltage applied to the nanotube tip. After stabilization of the emission current (due to thermal desorption of adsorbates) a strong increase of current, beyond the linearly extrapolated Fowler-Nordheim dependence, was observed for high applied electric fields. The experimental setup allowed the distance of the nanotube tip to the electrode as well as the length and diameter of the individual nanotube to be clearly determined and also gave an upper limit on the resistivity. These parameters were used in simulations of the emission current. Good agreement with the form of the experimental curve could be obtained by modeling the temperature increase in the nanotube, accounting for the temperature dependence of the resistivity and considering the energy bal-

ance on electron emission. Radiative cooling was shown to be a smaller but still significant contribution.

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