Field Emission of Individual Carbon Nanotubes in the Scanning Electron Microscope

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The field emission of individual multiwall carbon nanotubes grown by chemical vapor deposition was measured in a scanning electron microscope. By using a sharp anode, we were able to select one nanotube for measurements in carefully controlled conditions. Single nanotubes follow the Fowler-Nordheim law, and the dependence of the field enhancement with interelectrode distance and nanotube radius is in good agreement with the recent model of Edgcombe and Valdré. Our results suggest that only nanotubes with the highest field enhancement factors, i.e., at least 8× higher than those of the average nanotube population, contribute to the emitted current in usual large area measurements.

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Carbon nanotubes [1] are at present the most intensively studied material in electron field emission. One of the advantages of nanotube film emitters is their low turn-on field [2] coupled with deposition techniques that permit the realization of highly homogeneous films when observed in scanning electron microscopy (SEM). Figure 1(a) displays such a film of multiwall carbon nanotubes (MWNTs) grown by hot-filament chemical vapor deposition over nanosupported Ni catalysts [3], and the high resolution transmission electron microscopy (TEM) micrograph of Fig. 1(b) shows that the nanotubes are straight and well graphitized. The field emission *I-V* curve of Fig. 1(c) has been acquired under typical conditions for large area measurements (e.g., in a flat panel display) and confirms the good emission properties of such films with an onset field of 2 V/μm. Interestingly, the corresponding emission image reveals that the actual density of emitters is low ($\sim 10^4$ cm^{-2}) when compared to the areal density of nanotubes (at least 10^8 cm^{-2}). Why is such a tiny proportion of emitters participating in the field emission? Are these emitters representative of the overall nanotube population or do they represent special cases? To address these issues, we have measured the field emission from individual nanotubes in a SEM on the nanotube film characterized in Fig. 1. We consider more than 40 emitters and compare the extracted onset voltages and field enhancement factors with Fowler-Nordheim (FN) theory and recent models. Individual nanotubes follow the FN law, but the extracted field enhancement factors are low when compared to those obtained in the large area measurements of Fig. 1. We suggest that the emitters that contribute to the emitted current in large area measurements (e.g., in a display) represent only a very small proportion of exceptionally long and/or narrow nanotubes.

Figure 2(a) displays a typical experimental configuration. The nanotube film is mounted on the sample holder of the SEM while the position of the sharp anode is fixed. Since both film and anode are imaged by the electron beam of the SEM, this permits the selection of the nanotube (or nanotubes) to be measured by positioning them in front of and in the same plane as the anode, as well as a precise adjustment of the interelectrode distance. During SEM observation, care has been taken to minimize contamination effects and to systematically blank out the electron beam during the measurements.

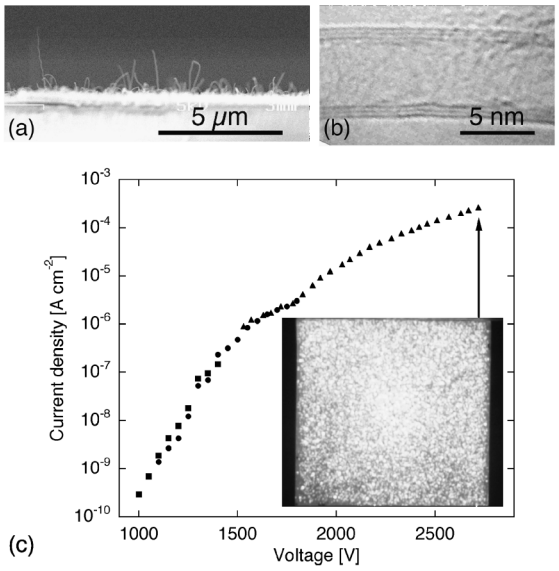

FIG. 1. (a) Typical SEM and (b) TEM micrographs of multiwall carbon nanotubes grown by hot filament chemical vapor deposition over nanosupported Ni catalysts. (c) *I-V* curve taken at $d = 500$ μm over an effective emitting area of 1.88 cm^2 ($\gamma = 1800$). The slight dip is due to different acquisition protocols (dc as compared to pulsed applied voltage, indicated by different symbols) and to the fact that the different parts of the curve have been acquired in sweeping the voltage down, leading to a slight degradation for the high current part. The corresponding emission image in the inset was taken at 2800 V (emitter density of 10^4 cm^{-2}).

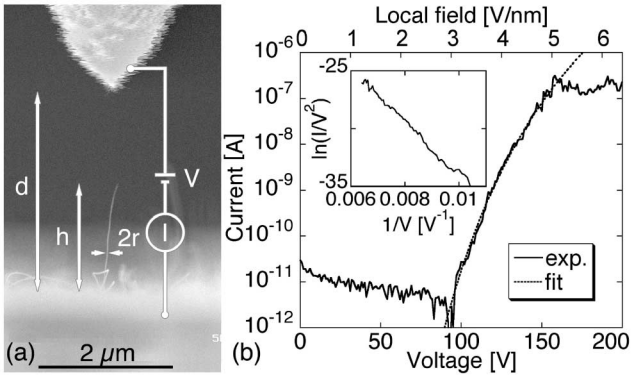

FIG. 2. (a) SEM micrograph of a nanotube of length $h = 1.4\ \mu$m and radius $r = 7.5$ nm with the sharp anode positioned at a distance $d = 2.65\ \mu$m. (b) Corresponding I-V curve with the best fit to the FN law ($\gamma = 90 \pm 15$; $A = 5 \times 10^{-16}$ m^2) in the dotted line. The FN plot is given in the inset.

A typical I-V curve for the nanotube of Fig. 2(a) is shown in Fig. 2(b) [4]. A field emitted current is detected from 91 V on, and increases then monotonically with the voltage with a strong saturation around 150 V. No significant differences were detected when the voltage was ramped up or down. These characteristics are comparable to other measurements on individual nanotubes by scanning anode field emission microscopy [5,6], where a sharp tip is scanned over the film at a constant height of a few μm (but where the emitters cannot be simultaneously imaged, making a direct comparison between the dimensions of the emitter and its field emission properties more difficult).

The most surprising result of Fig. 2 is probably the high voltage needed for emission. The onset voltage (voltage needed to extract a current of 1 nA) of 115 V is only 16× smaller than the voltage necessary to extract ~1 nA from each emitter of the large area measurements of Fig. 1 (1950 V for a current density of 10 μA cm^{-2}), while the distance between the substrate and the anode is 190× smaller. Given the fact that only one long nanotube is measured, one would expect a far lower field. How can these relatively high values be explained?

We use the FN law [7], which has proven useful in describing field emission from carbon-based electron emitters [5], to interpret the above measurements. The FN law gives a relation between the emitted current I [A] and the local field at the emitter surface F [V/m]. F is usually related to the applied voltage V as $F = \gamma V/d$, where d is the interelectrode distance and γ quantifies the ability of the emitter to amplify the applied field V/d and is named the field enhancement factor. In this frame, the FN law (with image charge correction) is written as [7,8]

$$I = A\frac{1.5 \times 10^{-6}}{\phi}\left(\frac{V}{d}\right)^2 \gamma^2 \exp\left(\frac{10.4}{\sqrt{\phi}}\right) \times \exp\left(-\frac{6.44 \times 10^9 \phi^{1.5} d}{\gamma V}\right), \quad (1)$$

where A has the dimension of an area [m^2] and ϕ is the work function in [eV]. Equation (1) shows that, for typical values encountered in carbon-based film emitters ($A = 10^{-14\pm1}$ m^2, $\phi = 4.9 \pm 0.1$ eV [5]), one obtains a current of $I = 1$ nA at $F = 3.3 \pm 0.4$ V/nm.

The easiest way to determine A and γ from the measurements is to trace a FN plot, i.e., to plot $\ln(I/V^2)$ versus $1/V$. The I-V curve should appear as a linear function with a slope ($-6.44 \times 10^9 \phi^{1.5} d/\gamma$) that depends on d, ϕ, and γ. Since d is known from the experimental configuration, γ can be determined by taking a reasonable value for ϕ (e.g., 5 eV for carbon-based emitters [5]).

The FN plot for the measurement presented in Fig. 2(b) shows that the FN law describes well the field emission from single nanotubes. The FN plot yields a straight line at low currents on every measured nanotube, but deviations were systematically observed at higher currents [9]. The field enhancement factor obtained from the FN plot is $\gamma = 90 \pm 15$: The local field obtained with this value is also given in the upper scale of Fig. 2(b) and is in the expected range as we obtain 1 nA at 3.8 V/nm.

From the large area measurement of Fig. 1, we obtain a field enhancement factor of $\gamma = 1800$ over an area of 1.88 cm^2 at $d = 500\ \mu$m, and the voltage needed to extract 1 nA per emitter (10 μA cm^{-2}) is ~1950 V. For the individual tubes measured in this study, the onset voltage needed for emission is high (between 47 and 185 V), but the field enhancement we deduce from the measurements is quite low ($30 \leq \gamma \leq 260$). However, the obtained values seem reasonable, since the local fields at the onset of emission are comparable (typically 4 V/nm for the individual tubes as on Fig. 2 and 6 V/nm for the film on Fig. 1). While the agreement is encouraging, we have to keep in mind that the field (and, hence, the emitted current) estimated in the two configurations cannot be directly correlated as the emitter density is not exactly known and varies with the emitted current. On the other hand, γ does not depend on the emitter density and can be directly used for comparing single emitters and emitter arrays.

We therefore need a reliable model to estimate the field enhancement factor. For a cylinder of height h terminated by a half-sphere of radius r, Edgcombe and Valdré have recently shown from detailed simulations that $\gamma_0 = 1.2 \times (2.5 + \frac{h}{r})^{0.9}$ [10]. Furthermore, γ will increase significantly when the gap between the emitter apex and the counterelectrode becomes small (i.e., for $d \leq 1.25h$) [11]. From Fig. 6 of Ref. [11], we obtain by fitting that $\gamma = \gamma_0 \times [1 + 0.013 \times (\frac{d-h}{d})^{-1} - 0.033 \times (\frac{d-h}{d})]$. We use, hence, in the following,

$$\gamma = 1.2\left(2.5 + \frac{h}{r}\right)^{0.9}\left[1 + 0.013\left(\frac{d-h}{d}\right)^{-1} - 0.033\left(\frac{d-h}{d}\right)\right]. \quad (2)$$

We do not take into account the shape of the anode when we determine γ, but simulations indicate that the

shape of the anode does not have a significant influence on the obtained value of γ, as the radius of curvature of the nanotube is much smaller than that of the anode.

We show in Fig. 3 the observed variation of γ and onset voltage (1 nA of emitted current) with $d - h$ for an individual nanotube, along with the dependences predicted by Eq. (2) (the measured values of γ are higher than predicted by a factor of 2, which we discuss below). The increase of γ at low $d - h$ is well reproduced by the model, and shows that γ levels off when $\frac{d-h}{d} \geq 0.2$, i.e., when $d \geq 1.25h$.

The value of γ predicted by Fig. 3 at d typical for large area measurements (~ 230 for this tube, and in the range 30–240 for the 40 nanotubes we measured) are far lower than the one obtained from Fig. 1 ($\gamma = 1800$), leading to onset voltages that are far higher. To further underline that fact, we present in Fig. 4(a) *I-V* curves of a MWNT and a single-wall nanotube (SWNT) rope (acquired on a film prepared from commercial laser ablation material) of comparable length acquired at similar d. The onset voltage is lower by a factor 6 for the SWNTs, while $\gamma = 515$ for the SWNTs as compared to 100 for the MWNT. The latter difference cannot be due to the slight difference in $\frac{d-h}{d}$ between the two measurements, and is, hence, due only to the difference in emitter radius. In fact, the difference in γ suggests that $r = 1.6$ nm for the SWNT rope, which is entirely in the expected range. We use again Eq. (2) in Fig. 4(b) to extrapolate γ and onset voltages to large d, and see that the difference between the two emitters persists at distances comparable to the one used in Fig. 1. We note also that the values of γ (and onset voltage) at large d remain far lower (respectively higher) than the ones obtained from Fig. 1 (indicated by squares in Fig. 3).

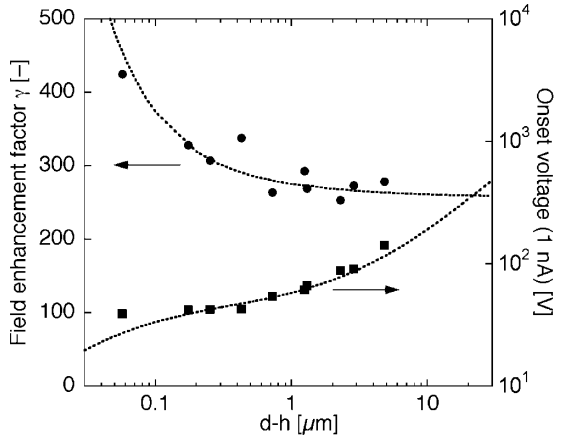

FIG. 3. γ (derived from the FN plots, circles) and onset voltage (1 nA, squares) as a function of $d - h$ for a nanotube of $h = 3.2$ μm length and $r = 17$ nm radius. The dotted lines give the dependence of both parameters as predicted by Eq. (2), taking $\gamma = 230$ at large d and $F = 3.2$ V/nm for the field needed to extract 1 nA.

This suggests strongly that the γ of the emitters in large area measurements are even higher than for the SWNTs of Fig. 4. We argue therefore that field emission is a very selective process with a highly nonlinear behavior, which implies that only a small proportion of emitters (those with the highest γ [5]) contribute to the current when a large area is sampled. The emitting tubes will

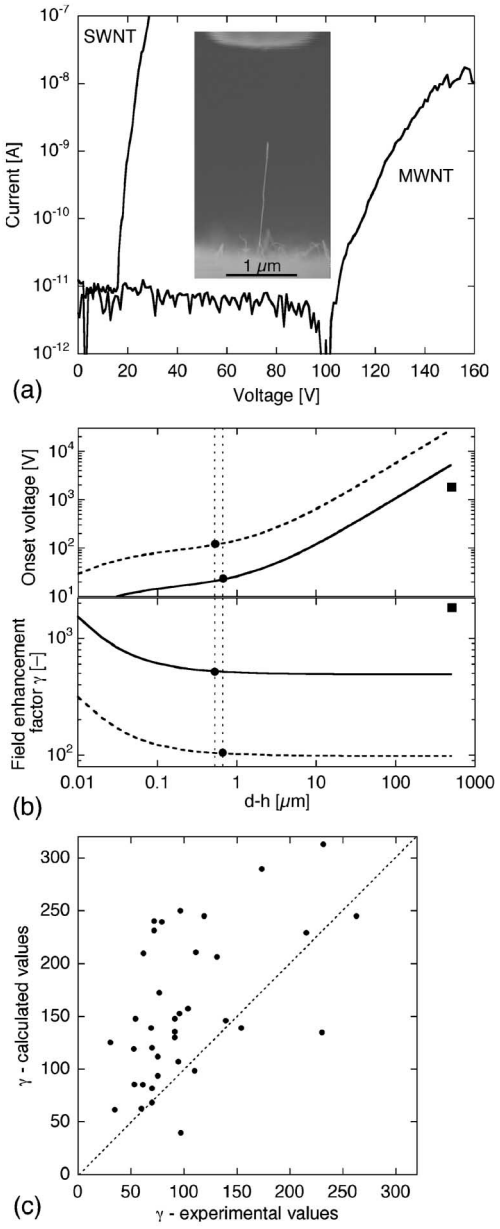

FIG. 4. (a) *I-V* curves acquired on a SWNT rope ($h = 1.6$ μm, $d = 2.13$ μm) and on a MWNT ($h = 1.7$ μm, $d = 2.35$ μm, $r = 8$ nm, shown in the inset). (b) Dependence of γ (lower graph) and onset voltage (upper graph) as a function of $d - h$ as predicted by Eq. (2) for the two emitters (SWNTs: plain lines; MWNT: dotted lines) with the measured values shown by circles. The squares indicate the values extracted from the large area measurements of Fig. 1. (c) Predicted versus measured field enhancement factor for the 40 emitters considered in this study.

consequently be long, of small diameter and without nanotubes in their vicinity that may screen the applied field. It follows therefore that the enhancement factor measured in large area measurements is representative of only a very small population of nanotubes. Figures 3 and 4 suggest that the field enhancement factor of the emitting nanotubes has to be at least 8× higher than the nanotubes considered here (be it through higher length and/or smaller radius) to obtain the γ and onset voltage values observed during large area measurements. In fact, it is quite probable that none of the nanotubes we observed in the course of this SEM study would have significantly contributed to the emitted current in a large area measurement.

Finally, it has to be pointed out that the model of Edgcombe and Valdré reproduces well the relative behavior of γ with $d - h$ (Fig. 3) and with r (Fig. 4), but yields absolute values that overestimate γ for most tubes by typically a factor 2, as is shown in Fig. 4(c). We see several reasons for this discrepancy. First, the presence of neighboring tubes will lead to a decrease of the effective γ because of shielding effects, especially if the tubes are of comparable height and/or at lateral distances smaller than h. Second, it is possible that conventional FN theory (derived for field emission from a flat surface at 0 K) is not directly applicable to highly curved surfaces such as the tip of a nanotube [12], and that in some cases the FN law overestimates the effective enhancement. Third, the work function may be lower than 5 eV, as evidenced by Semet *et al.* who deduced $\phi = 4$ eV from SAFEM measurements [6]. Last, the shape of the tip of the nanotube is probably not equivalent to a hemisphere of radius r on a cylindrical post as assumed by the model. Indeed, simulations show even small changes in the shape of the tip can lead to large variations of γ: A small hemispherical protuberance of 1.5 nm radius on top of a nanotube of 7.5 nm radius will increase γ by more than a factor of 2, and a blunt tip can significantly lower γ. The difference between calculated and measured values are probably due to a combination of these factors, and further investigations are in progress to clarify this issue.

In conclusion, we measured the field emission of individual carbon nanotubes with a sharp anode in a SEM, which allowed us to characterize precisely the measurement geometry. The emitting nanotubes followed the FN law at low emitted currents, with estimated field enhancement factors that are far lower than the ones obtained in usual large area characterization. The field enhancement extracted from measurements performed at varying interelectrode distance, as well as on nanotubes of similar height but different radius, follow the model of Edgcombe and Valdré. We conclude that the nanotubes emitting in usual large area measurements (e.g., in a display) represent only a very small proportion of exceptionally long and/or narrow nanotubes with field enhancement factors that are at least 8× higher than those of the average nanotubes present on the film.

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