Hot Nanotubes: Stable Heating of Individual Multiwall Carbon Nanotubes to 2000 K Induced by the Field-Emission Current

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Field emission (FE) electron spectroscopy from an individual multiwalled carbon nanotube (MWNT) is used to measure quantitatively stable temperatures at the apex, T_A, of up to 2000 K induced by FE currents ≈ 1 μA. The high T_A is due to Joule heating along the length of the MWNT. These measurements also give directly the resistance of the individual MWNT which is shown to decrease with temperature, and explain the phenomenon of FE-induced light emission which was observed simultaneously. The heating permits thermal desorption of the MWNT and, hence, excellent current stability.

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Carbon nanotubes (CNTs) are currently one of the most intensively studied research subjects in physics because their intrinsic properties such as nanometric dimensions, high aspect ratio, good thermal and electrical conductivity, and high Young's modulus may open many applications in industry and nanoscience. One of the most immediate has been shown to be for field emission (FE) electron sources [1], for example, for flat panel displays for which prototypes have already been built [2]. The mastering of CNTs for FE applications passes by in-depth FE characterization studies that relate the dependence of emission current, I_{FE}, on voltage, temperature, energy, and time, to the CNT bulk and surface structural and electronic properties [3]. One of the most useful tools in this research is field emission energy spectroscopy (FEES) [4], whereby the total energy distributions (TEDs) of the emitted electrons are measured. The TEDs give direct information on the electronic structure at the surface near the Fermi level, E_F, the tunneling barrier, and, most importantly for this work, the temperature at the apex emission zone, T_A. In this article we present TEDs which show conclusively and quantitatively that individual multiwall carbon nanotubes (MWNTs) heat to very high temperatures during FE for currents in the μA range. Furthermore, we show that the TEDs give an excellent measurement of the resistance of individual MWNTs. Finally, we show that the high temperatures are accompanied by the previously observed light emission from the MWNTs [5,6] and which is thus definitively explained as incandescence.

The MWNTs were grown by chemical vapor deposition (CVD) directly on Ni tips that had been previously electrochemically etched in an HCl solution. The CVD consisted of the decomposition of acetylene mixed with 80% N_2 at 870 K. By this method, they are securely mechanically and electrically bound to the substrate. The MWNTs were straight [see Fig. 1(a)], with diameters $\sim$30 nm and lengths $\sim$40 μm. The multiwall character of the MWNTs was confirmed by transmission electron microscopy (TEM) on samples fabricated by exactly the same procedure [see Fig. 1(b)]. A fairly large number grew on the end of the Ni tip but the FE measurements are specific to individual ones (see below). The FE experiments were carried out in an ultrahigh vacuum system with a base pressure $\sim 7 \times 10^{-11}$ Torr. The Ni tip was held in a W spiral to allow *in situ* cleaning by standard Joule heating to $\sim$1200 K. A circular cathode loop placed in front of the tip was used to heat the tip at up to 1600 K by electron bombardment. The emission patterns were measured on a multichannel plate (mcp) placed at $\approx$35 mm from the tip. I_{FE} was measured by (i) the total current leaving the tip, (ii) letting the emission strike a polarized metal plate connected to a picoammeter, and (iii) integrating the TEDs. The TEDs were measured with a hemispherical electron energy analyzer through a probe hole in the same UHV system. Mechanical displacements of the tip and electrostatic deflection allowed a precise centering of the emission pattern on the probe hole or over the mcp. T_A versus the current in the heating spiral was determined by optical micropyrometry on the Ni tip apex.

It is important to explain that, though many MWNTs are present on the Ni tip, the FE experiments are specific to an individual one. This is, first, because I_{FE} is a strongly exponential function of field and, hence, only a few MWNTs that protrude furthest to the anode or who have a sharper apex radius will emit. Second, the radial projection geometry of FE means that even if several MWNTs emit they are in general projected at different angles and can be

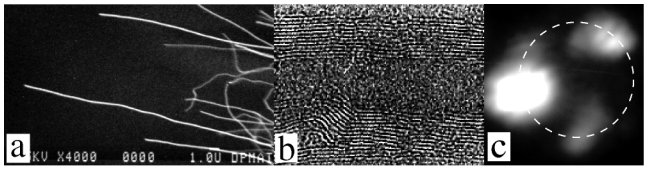

FIG. 1. (a) Scanning electron microscope image of the MWNT sample grown by CVD used in this experiment. (b) TEM image of a MWNT grown by the same method. (c) FE pattern. The bright areas follow approximatively a circle and correspond to one MWNT. The TEDs presented correspond to the bright spot.

distinguished with ease in the FE pattern and at the probe hole which subtends an angle of only 4°. The FE pattern is shown in Fig. 1(c). There is a rough circle of emission which, as we discuss below, is due to one MWNT. After several cycles of heat treatment, another emission spot occurred corresponding to a different MWNT which had distinct TEDs.

Before the full high temperature treatment to remove nanometric adsorbate structures, we found poor current stability above 10 nA, highly curved Fowler-Nordheim (FN) plots, distinct and irreproducible peaks in the TEDs that cannot be interpreted directly by a standard free electron model, and shifting of the peaks to lower energy roughly linear with the field similar to [7] (see below). These effects are known for TEDs from deposited molecules or adsorbed structures [8]. After the high temperature treatment (≈1600 K), I_{FE} had excellent stability up to the μA range, the FE patterns were smoother, and the TEDs were reproducible and approached the standard asymmetric peak from a metallic tip (see below). This study was carried out on the cleaned MWNT.

The formula for the TED of FE from a free electron gas [9] is the product of a field-dependent transmission probability and the Fermi-Dirac distribution [4]. Ignoring the energy independent prefactors, it is

$$I(E) \propto e^{E/d}/(1 + e^{E/(k_B T)}). \qquad (1)$$

E is measured with respect to E_F and $d(\mathrm{eV}) \approx F_0/\sqrt{\phi} \approx 0.2$ eV. F_0 is the applied field (~0.3–0.7 V/Å), and ϕ is the work function in eV. The TEDs are asymmetric peaks of width ~0.3 eV at room temperature. The slope on the low energy side is $\sim 1/d$ and the high energy side is positioned approximately at E_F with a slope $\sim(1/d - 1/k_B T) \sim -1/k_B T$ at 300 K. In general, the experimental measurements of TEDs from metallic emitters deviate somewhat from this formula [4], but they do permit an excellent measure of E_F and the temperature. We have found agreement within 20 K between optical pyrometer measurements and fits to (1) in the 1000 to 1300 K range and better than 0.05 eV for E_F for emission from W and Pt emitters in the same experimental setup.

A series of TEDs from the brightest FE zone at various I_{FE} are shown in Fig. 2. In agreement with previous work on clean MWNTs [10], we find that the form of the TEDs follows Eq. (1) to first order. The series shows two main characteristics as I_{FE} is increased. First, the TEDs widen on both sides and, second, they shift to significantly lower energy. From Eq. (1) the first characteristic can be explained by the increase in the slope of the tunneling barrier with field and the temperature at the emission zone. The second characteristic means that E_F at the emission zone shifts to lower energy. We have determined T_A and E_F against I_{FE} by fitting the TEDs to Eq. (1) (see Fig. 3). T_A increases from 300 K ($I_{\mathrm{FE}} < 1$ nA) to 2000 K ($I_{\mathrm{FE}} = 1.2$ μA) and the position of E_F displaces to lower energy roughly linear with I_{FE}. It is essential not to confuse this shift with the field shifting of TEDs in the

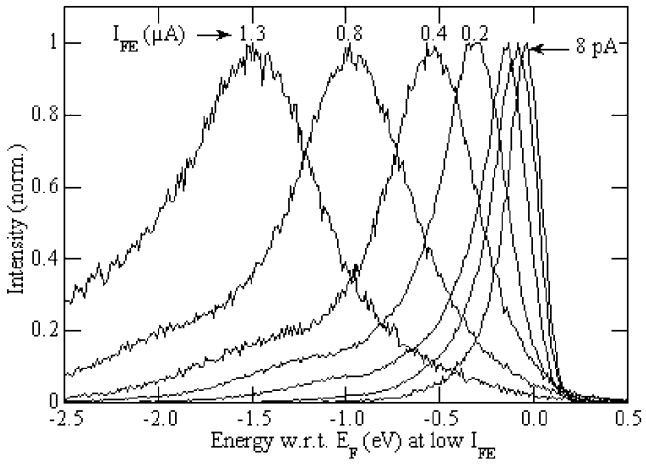

FIG. 2. TEDs for different emission voltages and currents.

presence of the nanometric adsorbed structures mentioned above. In that case, the shift is roughly linear in voltage [7,8], while here the shift is linear in I_{FE} and exponential in voltage (see Fig. 3). The direct interpretation of this data is that the peaks shift because of a simple resistive IR drop along the tube and T_A rises because of Joule heating along the MWNT. TED series at two other spots of the FE pattern were also measured. Another spot on the circle of emission shown in Fig. 1(c) gave TEDs with precisely the same T_A and E_F versus I_{FE}. A third series corresponding to an FE spot outside the original circle (see above) had much lower T_A and E_F shifts indicating that it was from a separate MWNT.

Five additional proofs of the high T_A are presented. (i) First, TEDs were measured at a fixed-emission voltage while the temperature of the tip was varied at up to 1300 K with the heating spiral. The TEDs increased in width on the high energy side in accordance with Eq. (1), and the values of T_A found by fitting were close to those measured by simultaneous pyrometry. (ii) The second proof is the FN plot of the probe hole current plotted in Fig. 4. At

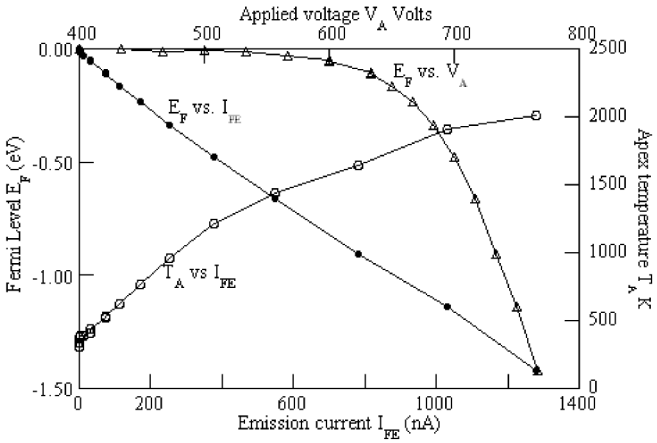

FIG. 3. T_A and E_F against I_{FE} found by fitting the TEDs with Eq. (1). E_F is also plotted against voltage to show its an exponential dependence.

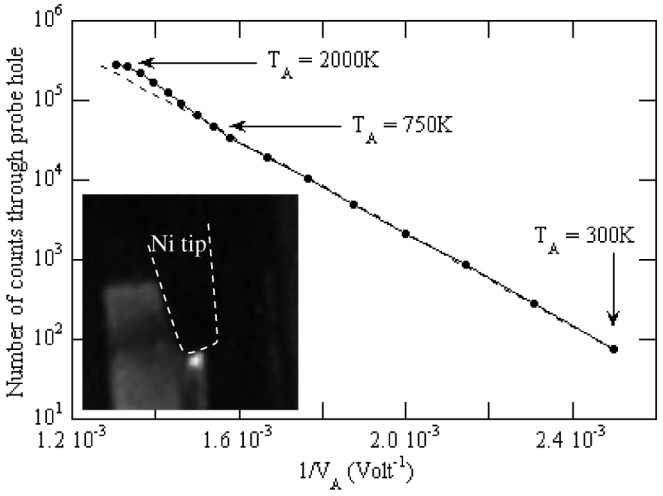

FIG. 4. FN plot of the current through the probe hole found by integrating the TEDs. The inset is a photo of the light spot that occurs at high I_{FE}.

lower voltages it follows very well the linear FN equation of $ln(I/V^2) \propto -1/V$. However, at the higher voltages I_{FE} increases abruptly and significantly above the FN line at $T_A \approx 750$ K. This is the direct consequence of the well-known increase of $I_{FE} \propto T^2$ [4]. (iii) Third, we show that the I_{FE}-induced heating can be used to thermally remove absorbates allowed to accumulate by long term exposure to the vacuum. In Fig. 5 we see that the current from the adsorbed MWNT is extremely unstable without cleaning but becomes very stable after I_{FE} was raised to 1 μA during 10 s. In fact I_{FE} is even more stable at higher values because the hot nanotube prevents readsorption (see Fig. 5), as is well known for Schottky emitters. (iv) Fourth, we have carried out a numerical simulation of the Joule heating along the MWNT using

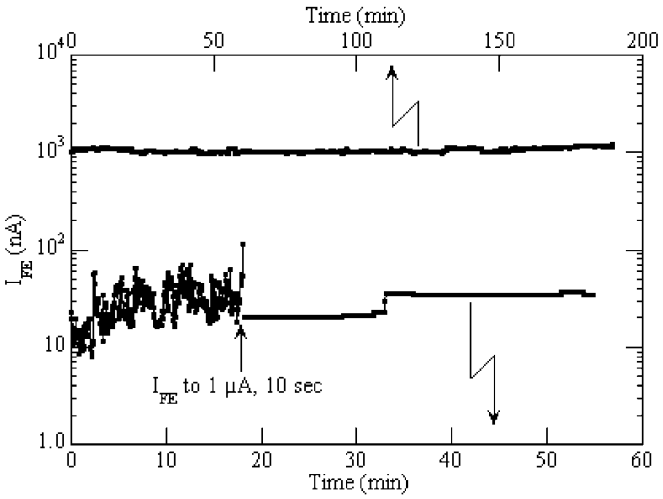

FIG. 5. Current stability before and after thermal desorption of the MWNT by raising I_{FE} to 1 μA during 10 s. Also shown is the even better stability at 1 μA.

the experimental I_{FE}, MWNT shape, and resistance found in this experiment. The simulation gave $T_A \sim 1500$ K, sufficiently close to that found in the experiments. Note that ~ 1 μW of power is dissipated in the nanometric scale MWNT. These results will be presented elsewhere.

A final proof (v) is that we observed light emission by eye and by optical microscopy from a point precisely at the end of the Ni base tip starting at $I_{FE} \sim 0.6$ μA ($T_A \sim 1500$ K) and which increased in intensity as I_{FE} was raised. A photo of the point light emission is inserted in Fig. 4. Light emission from MWNTs during FE has been previously observed [5,6]. Both incandescence [5], but without any proof of heating, and fluorescence from apex resonant states have been proposed [6]. Because of the association with high T_A, the light emission here is clearly an incandescence effect, also because no resonancelike tunneling states are detectable in the TEDs after the high temperature cleaning. In fact, we can use Planck's law to calculate that at the observation distance of 20 cm we should see $\sim 10^5$ photons/s, well within the sensitivity of the human eye.

From the E_F versus I_{FE} plot, the resistance $R(T)$ of the MWNT is ≈ 1 MΩ. Furthermore, the slope decreases by $\approx 40\%$ from 300 to 2000 K indicating a drop in $R(T)$. Numerical simulations must be made to determine $R(T)$ because of the temperature gradient along the MWNT. The value of R and the temperature behavior are similar to those found previously for CVD MWNTs [11]. The decrease in R with temperature has been attributed to different conduction mechanisms, such as hopping along thermally activated defect sites [12], and demands in-depth studies for its elucidation.

The stable high T_A found raises an interesting point for FE in general: To the authors' knowledge this is the first example in FE literature, which dates back to before the turn of the century, of observations of FE-induced stable heating of the emitter body to any temperature above ambient, let alone to 2000 K. We propose that this is because of two parameters of MWNTs that differ from those of metal emitters and which lead to I_{FE} runaway and thus emitter breakdown. First, the resistance of metals increases roughly linearly with temperature which means a positive heating feedback once I_{FE}-induced heating starts. Second, a combination of high temperature and field permits the well-known mechanism of field-driven sharpening of tips by surface diffusion which in turn increases the field and, hence, creates positive feedback for I_{FE}. This creates an extremely unstable situation, and metal FE tips generally breakdown at high I_{FE} without warning. In contrast, the resistance of this MWNT was shown to decrease substantially with temperature which gives a negative feedback to heating and, second, surface diffusion is much slower for covalent carbon which inhibits the field-driven sharpening.

In summary, the principal result we wish to emphasize from this work is that FE currents can heat nanotubes to very high stable temperatures and FEES can be used to measure this temperature quantitatively. We argued that

it is due to the intrinsic decrease in the MWNT resistance with temperature and low surface diffusion. Several other important conclusions can be drawn. (i) FEES can be used to measure the MWNT resistance quantitatively. The measure at 2000 K is the highest temperature in the literature. (ii) Strong evidence was presented that the phenomenon of light emission from MWNTs during FE is due to Joule heating. (iii) The widths of the TEDs, which is $\sim$0.3 eV at low I_{FE} in agreement with [3,7], are much larger at the higher I_{FE} ($\approx$1 eV) due to the increase in T_A and F_0. (iv) The heating is important for technological applications because it provides a method to heat treat and thus improve the structure along the tubes and at the surface. This means, for example, that the CNT surfaces can be cleaned and recrystallized without external heating which could be very important for FE devices in particular flat displays. Also the heating likely controls the maximum current that can be drawn from a nanotube before its destruction. (v) The heating explains the excellent current stability in the μA range.

In conclusion, it will be interesting to examine this heating effect in single wall nanotubes. Furthermore, hot nanotubes may provide a nanometric-scale source of light and heat for interesting applications in nanoscience.

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[1] See, for example, W. de Heer, A. Châtelain, and D. Ugarte, Science **270**, 1179 (1995).
[2] W. B. Choi *et al.,* Appl. Phys. Lett. **75**, 3129 (1999).
[3] For a recent review, see J.-M. Bonard, H. Kind, T. Stöckli, and Lars-Ola Nilsson, Solid State Electron. **45**, 893 (2001), and references therein.
[4] See J. W. Gadzuk and E. W. Plummer, Rev. Mod. Phys. **45**, 487 (1973); L. W. Swanson and A. E. Bell, in *Advances in Electronics and Electron Physics,* edited by L. Marton (Academic, New York, 1973), Vol. 32, p. 193.
[5] A. G. Rinzler *et al.,* Science **269**, 1550 (1995).
[6] J.-M. Bonard *et al.,* Appl. Phys. A **69**, 245 (1999).
[7] M. J. Fransen, T. L. van Rooy, and P. Kruit, Appl. Surf. Sci. **146**, 312 (1999); J. L. Shaw and D. Y. S. Hsu, in Proceedings of the 14th International Vacuum Microelectronics Conference, Davis, 2001 (to be published).
[8] L. W. Swanson and L. C. Crouser, Surf. Sci. **23**, 1 (1970); S. T. Purcell *et al.,* Phys. Rev. B **49**, 17 259 (1994).
[9] R. D. Young, Phys. Rev. **113**, 110 (1959).
[10] A. Takakura, K. Hata, Y. Saito, K. Matsuda, T. Kona, and C. Oshima, in Proceedings of the 47th International Field Emissions Symposium, Berlin, 2001 (to be published).
[11] Seung-Beck Lee *et al.,* Microelectron. Eng. (to be published).
[12] T. W. Ebbesen *et al.,* Nature (London) **382**, 54 (1996).