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Field emission from individual multiwalled carbon nanotubes prepared in an electron microscope

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Abstract

Individual multiwalled carbon nanotube field emitters were prepared in a scanning electron microscope. The angular current density, energy spectra, and the emission stability of the field-emitted electrons were measured. An estimate of the electron source brightness was extracted from the measurements. The results show that carbon nanotubes are promising candidates to replace existing sources in high-resolution electron beam instruments.

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Keywords: Carbon nanotubes; Electron microscope; Electron source; Field emission

1. Introduction

Interest in carbon nanotubes (CNTs) [1] has grown rapidly in the past few years. Their unique properties make them promising candidates for a variety of applications, among which their use as field-emission sources for displays [2–5]. Our main interest is in a different application of field emission from CNTs, namely as an electron source for electron microscopes [2,6]. The most important requirements on the source for such instruments are (i) high brightness, (ii) low energy spread, (iii) emission stability and (iv) long-lifetime. Promising results for the energy spread (0.11–0.2 eV) of the field-emitted electrons from CNTs have been found by several groups [2,4,6]. Lifetime and stability measurements have also been reported previously [2,6]. Values for the brightness were not yet reported, however. Here, we report a method to prepare individual multiwalled CNT field emitters and present our investigations on the electron optical properties of these emitters.

2. Sample preparation and characterization

Previously, experiments in our laboratories have used a combination of micro-manipulators and an optical microscope to mount individual multiwalled CNTs onto etched tungsten tips [6]. This is a simple and effective method to produce samples. However, there is not sufficient control over the length and the diameter of the nanotube sample, due to the low resolution of the optical microscope.

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In addition, tips prepared under the optical microscope sometimes had additional nanotubes (not visible in the optical microscope) attached to them.

To improve the preparation method, a piezo-driven nano-manipulator (Omicron) has been built into a scanning electron microscope (SEM, Philips 525M). The system provides manipulation of the CNT sample with respect to the tungsten tip with steps of 50 nm in the x, y and z direction. The piezo elements can be activated during SEM operation, although some interference with the SEM signal is visible. The set-up enables manipulation of objects while watching with a resolution of 10 nm at video frequency and an electron beam energy of 30 keV. In addition, a voltage difference can be applied between the tip and the sample and the current can be measured. Although manipulation of CNTs in a SEM has been reported previously [7], field emission from such samples has not been studied before.

The procedure to mount individual CNTs is very similar to that described in Ref. [6], with the SEM replacing the optical microscope. A nanotube was selected from an ensemble of multiwalled CNTs (grown using the arc discharge method [1]). This nanotube was attached to a sharp tungsten tip using the glue of conducting carbon tape (STR tape from Shinto Paint Co.). To remove the nanotube from the ensemble, the nanotube was either pulled from the ensemble by retracting the tip, or cut by applying a current of over 30 μA. The latter method was found to cut the CNT at the position where it was relatively thin. This allows for control of the length of the nanotube sticking out from the tungsten tip. Finally, the occurrence of field emission from the liberated nanotube was tested by moving it close to a conductive plane (inside the SEM).

Fig. 1 shows several transmission electron microscope (TEM) images of a thin and

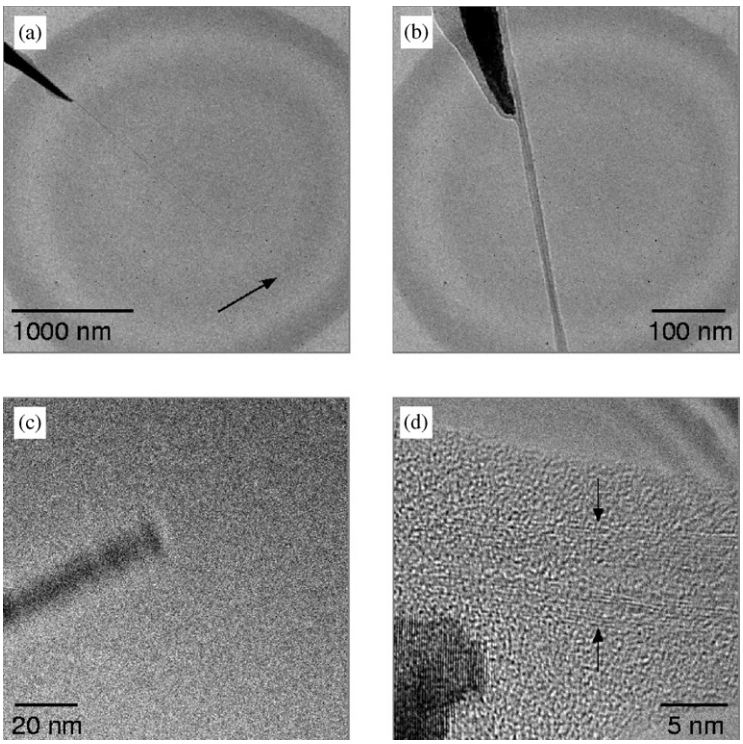

Fig. 1. TEM images of tube #1 for several magnifications. The full length of the tube is visible in (a). The glue and the tungsten tip are visible in (b). The cap of the tube is visible in (c). In high resolution mode the shells of the nanotube become visible, the tungsten tip can also be seen (d).

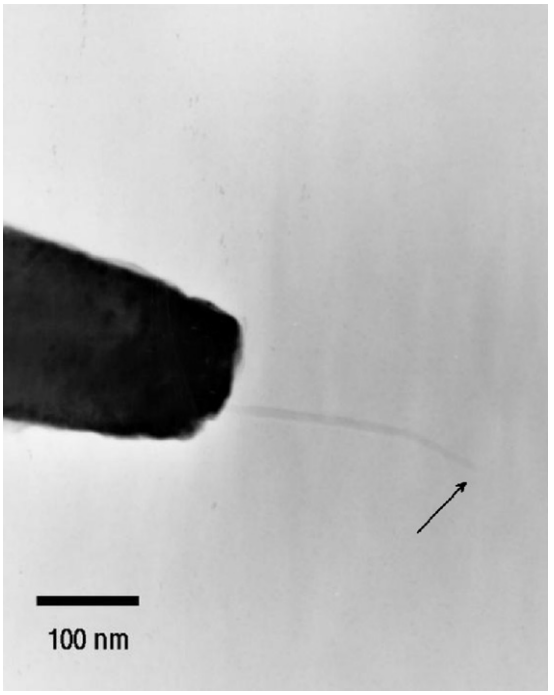

Fig. 2. TEM image of a very thin and short nanotube sample, tube #2 with a tube diameter of 8 nm.

long nanotube, tube #1. The images show that this nanotube has a length $l = 2$ μm, a diameter $d = 8$ nm at the base, a uniform diameter over its length and consists of 10 carbon sheets. The tube end could not be imaged in high resolution mode, probably due to vibrations. But, as seen from Fig. 1(c), the tube diameter at the tube end is 15 nm. This means that the vibrations of the tube end due to the influence of the electron beam and the thermal energy $k_B T$ cannot be larger than 15 nm. Indeed, a simple estimate of the thermal vibration amplitude is $X_{tip} = (4l^3 k_B T/3\pi r^4 Y)^{1/2}$ [8], which for a Young's modulus of $Y = 1$ TPa [1] yields $X_{tip} = 7$ nm. Fig. 2 shows the TEM image of another nanotube sample, were a short and very thin nanotube was chosen.

3. Field emission experiments

Several samples were prepared and transferred into a UHV chamber to characterize their emission properties. Details of our UHV vacuum system are described in Refs. [6,9]. We concentrate here on the results of tube #3, the best tube (low energy spread, high-angular current density) so far. From the SEM image (Fig. 3) we estimated a diameter of 20 nm, and a length of 1.5 μm protruding from the tungsten tip. After a first series of experiments in the UHV chamber with this sample, a second SEM image was taken, to make sure that the tube was still on the tip. Next, the tube was again transferred into the UHV chamber and a second series of experiments was performed, showing the same IV characteristics. Field emission was obtained by applying a negative voltage to the tip. The surrounding vacuum system acted as the grounded anode, at a typical distance of 5 cm. Currents in the range of 0.4–80 nA were extracted for voltages $V = 300$–421 V. The IV characteristics follow the Fowler–Nordheim (F–N) curve [10] and from the slope we found a field enhancement factor $\beta = 1.1 \times 10^7$ m^{-1}, for a value of the work function $\phi = 5$ eV [11], where β is the ratio between the field at the tip surface and the applied voltage.

The electron energy spectra were measured using a hemispherical electron energy analyzer (VSW Class 150). At typical operation conditions, the broadening of the full-width at half-maximum (FWHM) of an energy spectrum due to the resolution of the spectrometer was 0.05 eV [9]. The anode–cathode geometry was the same as for the measurement of the F–N curve. The measured FWHM of the energy distribution ΔE was around 0.2 eV, increasing only mildly to 0.3 eV at high

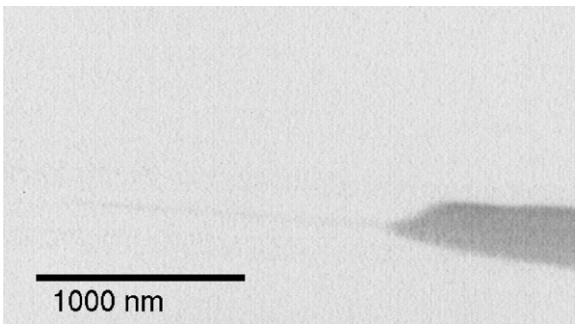

Fig. 3. SEM image of tube #3.

currents (100 nA), see Fig. 4(a). The spectra showed a single main peak with a shape that fitted reasonably well with F–N theory, see Fig. 4(b). A small additional feature at the low-energy side was sometimes observed, containing less than 10% of the signal. The height of this feature depended on the exact alignment of the set-up and fluctuated in time. Moreover, the broadening was in first-order linear proportional to the extraction voltage as expected from the F–N theory. Fitting the main peak of the energy spectrum to the F–N theory [10] results in a value $\beta = 7 \times 10^6$ m^{-1} (again using $\phi = 5$ eV).

This somewhat lower value of β reflects the fact that the energy spectrum is narrower than expected on the basis of F–N theory. This has been observed by others as well [2,4,6]. Such deviations from F–N theory are by no means surprising, since CNT emitters violate many of the assumptions inherent to F–N theory. For instance, the local density of states at the carbon nanotube tip is expected to be highly sensitive to the precise structure of the tip [12]. Nevertheless, F–N theory often serves as a useful reference frame [2,5,6], and we use it here as such.

Despite its importance for electron-optical applications, the angular current density emitted from individual carbon nanotubes has, to our knowledge, not yet been reported. Here, the angular current density was determined by measuring the current collected in a Faraday cup with an opening diameter of 1 mm, at a distance of 20 mm from the emitter. The emitter was aligned with the Faraday cup for maximal current. The alignment was slightly off the prolonged axis of the tungsten tip. The angular current density was found to increase approximately linearly with emitted current, see Fig. 5. The maximum measured value of $\mathrm{d}I/\mathrm{d}\Omega$ was 1.1×10^{-5} A/sr, at a total emitted current of 170 nA. The extraction voltage was 322 V at this current, somewhat lower than in the measurements described above, due to the presence of the grounded housing of the Faraday cup at 20 mm from the emitter. We did not measure at higher currents, since the emission stability decreased above 200 nA. Several other carbon nanotubes were characterized in this way, but all showed a worse performance, i.e. a smaller value of $(\mathrm{d}I/\mathrm{d}\Omega)/\Delta E$.

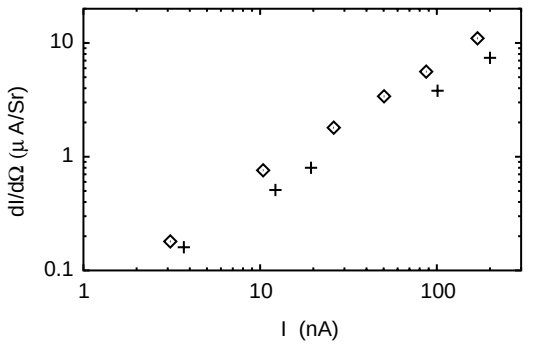

Fig. 5. The angular current density as function of the total emitted current of tube #3. The squares represent a first series of measurements. The plusses represent a second series of measurements taken after re-aligning the emitter.

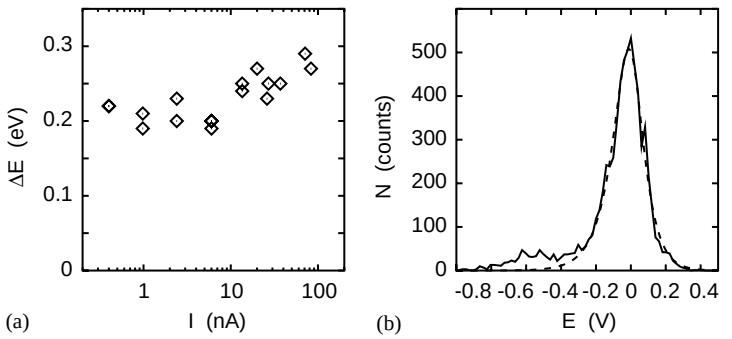

Fig. 4. Measurements of the energy spectrum of tube #3. (a) the energy spread as function of the emitted current. (b) the energy spectrum at a current of 2.4 nA, with a FWHM of 0.20 eV. The dashed line indicates the fit with the F–N theory.

To characterize the lifetime and the stability of the SEM-prepared nanotubes, several tubes were allowed to emit continuously. It was possible to have the samples emit for several weeks, without observable degradation. A period of emission of tube #4 is shown in Fig. 6. Periods of very stable operation over several hours were observed (see inset), sometimes interrupted by sudden changes in the emitted current. It was found that when such a change increased the current much beyond 200 nA, breakdown of the nanotube emitter was likely to occur. To avoid this, an automatic feedback system was set up, that adjusted the extraction voltage whenever a sudden change in emitted current was detected. In this way, the emitted current was kept in the 100 nA range, with only small adjustments in extraction voltage (see the lower graph in Fig. 6). The excellent stability on the 1 h time-scale is similar to, or better than that reported by others [2,5,13], except for the excellent stability during a period of two months reported in Ref. [6].

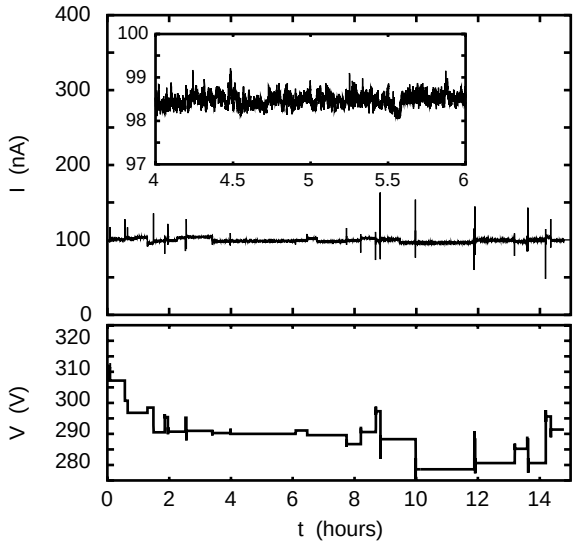

Fig. 6. Emission current measured every second (top) and extraction voltage (bottom) of tube #4 as a function of time. The vacuum level was 5×10^{-11} mbar. The inset shows in detail a period of stable emission in which the current fluctuated less than 0.5%, at constant extraction voltage.

4. Discussion

Unlike many other preparation techniques [5,6,13], our SEM preparation technique allows for reliable and controllable realization of individual nanotube field emitters. To assess the viability of these samples for use as sources in high-resolution electron beam instruments, it is useful to compare their characteristics to those of the most commonly used source in electron microscopes, the ZrO/W Schottky emitter [14,9]. The latter has demonstrated a reduced brightness of $B_r = 1 \times 10^8$ A/m^2 sr V, at a ΔE of 0.5–0.7 eV, a short term current stability better than 1% and a lifetime of over one year. Increasing B_r towards the 10^9 region is expected to be possible [15].

Clearly, carbon nanotubes show promising characteristics for three out of four of the above parameters. B_r is the only parameter for which experimental data was not obtained, since its measurement requires a specially designed set-up not yet available to us. Based on the data presented above, it is possible, however, to give an estimate. One method often used to determine B_r [16] is to measure the angular current density $dI/d\Omega$ and the virtual source size d_v. This d_v is the diameter of the apparent emitting area when the electron trajectories are traced back beyond their origin at the actual emitting surface. Once these parameters are known the reduced brightness can be calculated via $B_r = 4(dI/d\Omega)/\pi d_v^2 V$, with V the electron acceleration voltage. Typically, the virtual source size of an emitter is much smaller than the physical source size and it is determined by the exact geometry of the emitting area [14–16]. An analysis of ray tracing calculations, along the lines of Refs. [14,16], indicates that for a nanotube with a hemispherical cap the virtual source size is around 5% of the tube diameter, while for an open-ended thin cylinder it is approximately equal to the tube diameter. Since we do not know the tip geometry for the CNTs, we use the tube diameter as a conservative estimate for the virtual source size, to obtain a reasonable lower value for the reduced brightness. For our best sample so far (tube #3), with a diameter of 20 nm, this estimation method gives a value of $B_r = 1.1 \times 10^8$ A/m^2 sr V.

The above discussion estimates the value for B_r as emitted by the source, i.e., the *intrinsic* value for the reduced brightness of the source. Two effects can decrease the *effective* value of the reduced brightness in the subsequent electron-optical system. First, tip vibrations can increase the effective virtual source size. For tube #3, it is not expected that this will broaden the virtual source size beyond the tube diameter of 20 nm, since the end of tube #1, which was thinner and longer, could be imaged with a better resolution than 10 nm. More generally, tip vibrations can be reduced by having only a short segment of the nanotube stick out from the tungsten tip. As demonstrated, our SEM-based preparation method is well-suited to produce such shorter samples.

Second, statistical Coulomb interactions among the emitted electrons can also increase the effective virtual source size through trajectory displacement [15]. This can be significant in our present experiments, because the anode is far away (20 mm or more), and the extraction voltage is low. The Coulomb interactions can be strongly reduced in practice by placing the extraction electrode and current-limiting aperture much closer to the nanotube.

5. Conclusion

We have demonstrated SEM preparation of individual carbon nanotube field emitters. These emitters show promising characteristics for use as sources in high-resolution electron beam instruments.

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