

High-current field emission from a vertically aligned carbon nanotube field emitter array

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Arrays of vertically aligned carbon nanotubes (CNTs) were grown on a patterned sputtered cobalt film by chemical vapor deposition from ethylenediamine at 900 °C. Each square array comprises a moderate density of nanotubes with an average height of 90 μm covering a total area of $3.6 \times 10^{-3} \text{ cm}^2$. Field emission measurements were carried out on individual arrays at pressures below 10^{-8} mbar. The spacing between the anode and the top of the CNT array is 935 μm and a total current of 2 mA could be obtained at 2.5 kV. A Fowler–Nordheim plot of the I – V data shows an unusually high field enhancement factor at lower fields. At an average field strength of 1.925 V/ μm , the corresponding emission current density is 130 mA/ cm^2 . This emission current was found to be very stable, with short-term fluctuations (5 Hz measurement bandwidth) of no more than $\pm 1.5\%$, while the current drifted less than 1.5% over a test period of 20 h. © 2001 American Institute of Physics. [DOI: 10.1063/1.1412590]

Carbon nanotubes (CNTs) have attracted considerable attention as cold field emission sources due to their slender geometry and small tip radii. Rinzler *et al.*¹ reported field emission from a single nanotube, while de Heer *et al.*² demonstrated field emission from a film of aligned CNTs. Area emitters are of interest in flat-panel displays and in devices requiring large total currents. In several studies of field emission from CNTs emission current densities ranging from typically 0.1 up to values as large as 4 A/ cm^2 have been reported.^{2–9} However the experimental conditions under which such results are obtained vary considerably, and high reported current densities are often associated with small array areas. The practical current density is known to fall off sharply with an increase in cathode area.¹⁰ Zhu *et al.*⁷ reported current densities of 0.5 A/ cm^2 at >16 V/ μm fields from single-walled CNTs, while more recently Sohn *et al.*⁹ reported current densities of 80 mA/ cm^2 from an area of $4 \times 10^{-5} \text{ cm}^2$, achieved at 3 V/ μm from multiwalled CNTs. In the present work, an emission current of 2 mA was obtained from a $3.6 \times 10^{-3} \text{ cm}^2$ array, corresponding to an average current density of greater than 0.5 A/ cm^2 achieved at a field of only 2.67 V/ μm .

Various synthesis techniques based on a chemical vapor deposition (CVD)/metal catalyst process can be used to obtain vertically aligned CNTs, some of which involve prior substrate preparation or patterning.^{2,6,9} A simpler technique would be to use a thin metal catalyst film which transforms into small metal particles as the result of substrate heating in the CVD reactor. Such a technique has been used to fabricate field emission arrays,⁸ albeit with poorer uniformity than that achievable with porous substrates.⁶ In our work, CNT arrays were grown by catalytic decomposition of ethylenediamine

($\text{C}_2\text{H}_8\text{N}_2$) using a cobalt catalyst. Patterns 600 μm square of 5 nm thick cobalt were fabricated on a gold-coated p -type silicon substrate of 3–10 $\Omega \text{ cm}$ resistivity by sputtering and a lift-off process. The intended purpose of the 20 nm sputtered gold coating on the silicon was to provide a metallic contact on which to grow the CNTs. However it turned out that at a CVD temperature of 900 °C, the gold film formed into islands. Energy-dispersive x-ray analysis of the top of the CNT array shows the presence of only carbon and cobalt but no trace of gold, and it could be safely concluded that the gold was not incorporated into the CNT array. The silicon wafer was placed in the middle of a 50 mm diam CVD quartz tube reactor of 1100 mm length. The tube was purged with nitrogen to prevent oxidation of the cobalt film. When the temperature reached 900 °C, ethylenediamine was carried into the quartz tube by nitrogen bubbled through a bottle containing ethylenediamine at a flow rate of 500 ml/min. After reaction for 30 min, the reactor was cooled down to room temperature in nitrogen ambient. The CNT array attained a height of 90 μm and is comprised of vertically aligned multiwalled CNTs with diameters ranging between 80 and 250 nm that form the main structure of the array (Fig. 1). However many smaller CNTs with diameters of 10–60 nm are found to interweave among the larger vertical CNTs. Transmission electron microscope images reveal multiwalled nanotubes with a bamboo-like structure (Fig. 2). The majority of the tips are closed, although some of the smaller-diameter nanotubes are open ended. Cobalt particles are distributed along the length of the CNT and are sometimes present as small particles at the ends of much larger closed and bulbous tips.

A planar diode configuration was adopted for the field emission measurements. A silicon die with the CNT array was attached to the cathode plate, while a similar silicon die attached to the anode plate presents a smooth anode surface.

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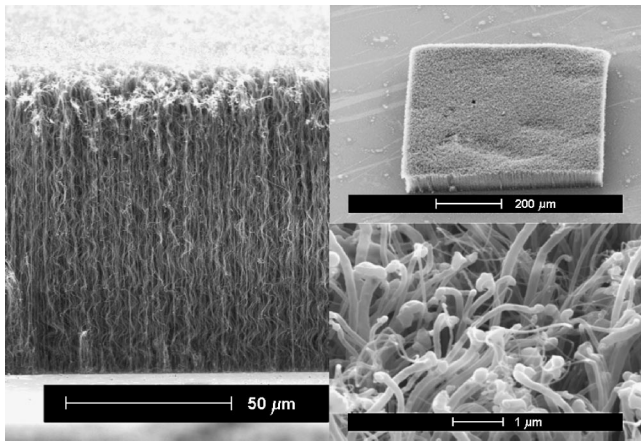


FIG. 1. Side view of a CNT array. The top inset shows an overview of the array, and the bottom inset shows details of the surface.

Ceramic spacers define the anode to cathode spacing, and also provide a heat conduction path from the otherwise isolated anode to the mounted cathode plate. The spacing between the anode and the top of the CNT array is $935 \pm 10 \mu\text{m}$. The assembly was placed in an ultrahigh vacuum (UHV) chamber, baked and evacuated for over 24 h. Measurements were carried out at vacuum levels better than 10^{-8} mbar.

A current–voltage (I – V) measurement was first carried out on the pristine CNT array with a maximum voltage of 2.5 kV, corresponding to an average “planar” field of $2.67 \text{ V}/\mu\text{m}$ (Fig. 3). The emission current reached 1.38 mA at 2.20 kV before a sudden drop. The current increased again on a lower curve segment, and a second current drop from 1.62 mA occurred at 2.42 kV, before rising again, apparently following the same lower curve segment. These two current spikes are associated with localized destruction of the CNT array which was readily apparent in a subsequent scanning electron microscope (SEM) examination of the array surface, as discussed below. Repeated measurements of the I – V curve, which were carried out only up to 2.20 kV to avoid the possibility of further localized destruction, followed the lower curve segment. For comparison with other reported

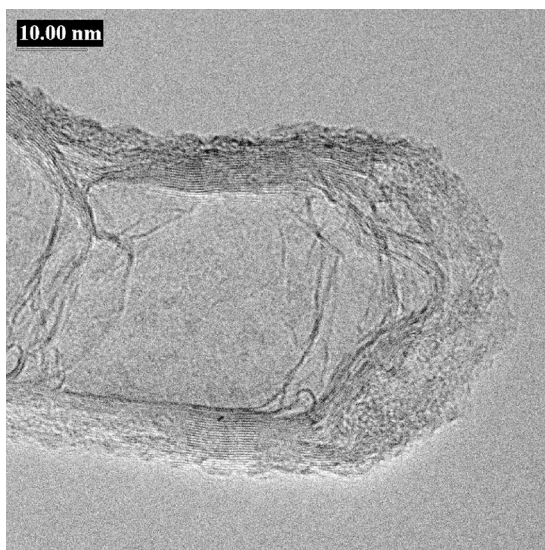


FIG. 2. Transmission electron micrograph of the CNT tip.

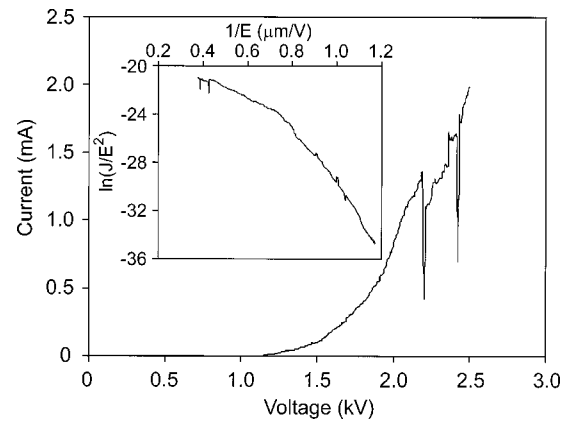


FIG. 3. Emission I – V data. The inset shows the $\ln(J/E^2)$ vs $1/E$ plot.

works, the so-called “turn-on” field to produce a current density of $10 \mu\text{A}/\text{cm}^2$ is around $1 \text{ V}/\mu\text{m}$, while the “threshold field” to produce $10 \text{ mA}/\text{cm}^2$ is $1.23 \text{ V}/\mu\text{m}$. Current of 2.0 mA at 2.5 kV corresponds to a current density of $555 \text{ mA}/\text{cm}^2$ averaged over the area of the entire array. This relatively high current density achieved at a low average field is due to the moderate sparseness of the emitting tips (spacing of the order of a micron) which reduces the effect of shielding by neighboring tips.¹¹

Following the conventional approach adopted in reporting field emission data from CNTs, the Fowler–Nordheim equation, $J = (AE^2/\phi)\exp(-B\phi^{3/2}/E)$ where J is the current density, $A = 1.54 \times 10^{-6} \text{ A eV V}^{-2}$, $B = 6.83 \times 10^9 \text{ eV}^{-3/2} \text{ V m}^{-1}$, and $\phi = 5.0 \text{ eV}$, and E is the local field at the emitting tip, is used to plot the emission data. The local field is expected to vary markedly over an ill-defined CNT array surface, but to first order approximation we will assume that an average value of E is related to the “planar” anode to cathode spacing via $E = \gamma E_0 = \gamma(V/d)$ where γ is the field enhancement factor. A cautionary note by Zhirnov *et al.*¹⁰ in the interpretation of such data should be borne in mind. The Fowler–Nordheim plot shows a reduction in slope at fields beyond $1.3 \text{ V}/\mu\text{m}$ ($J = 40 \text{ mA}/\text{cm}^2$), yielding an unusually high field enhancement factor of $\gamma = 17\,300$ for $E_0 < 1.3 \text{ V}/\mu\text{m}$ and $\gamma = 3000$ for $E_0 > 1.3 \text{ V}/\mu\text{m}$. Such dual-slope behavior has previously been observed.^{3,5} The origin of the field emission is not clear without observing the emission pattern, but, at low fields, is likely to come from the weave of smaller CNTs rather than the larger vertical CNTs since the latter have closed tips with diameters ranging from 100 to 250 nm. At higher fields, however, the larger tips may be expected to contribute to the total emission current.

Emission current stability tests were subsequently carried out on the same array at an anode voltage of 1.80 kV. The current started off at 0.20 mA, increased over a period of around 30 min and finally stabilized at 0.46 mA (Fig. 4). The short-term current fluctuation is about $\pm 1.5\%$ based on a measurement bandwidth of 5 Hz. The emission current remained fairly constant over the following 20 h, dropping by about 1.5% over this period of time. It is noted that current of 0.46 mA falls on a point that is higher than the value of 0.38 mA at 1.80 kV recorded on the original I – V sweep of the pristine CNT array. On the other hand, the starting current of 0.20 mA would be in line with the lower curve segment of the original I – V sweep. For comparison with other reported

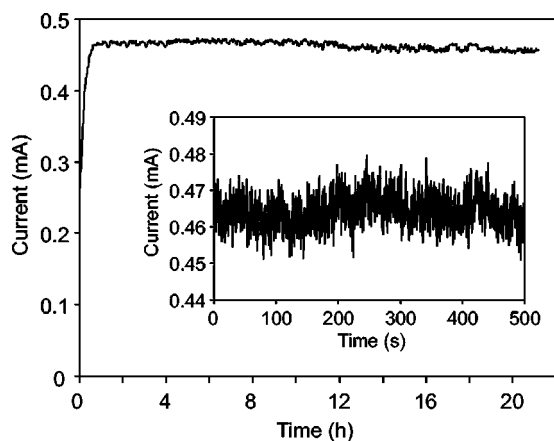


FIG. 4. Emission current over 21 h (5 mHz bandwidth). The inset shows the short-term stability measured with the 5 Hz bandwidth.

ment (Fig. 3) after the CNT array was damaged. Further I - V sweeps at the end of the 20 h run show consistent I - V characteristics that are in accordance with the higher emission current previously recorded. The good performance of the stability is attributed to the averaging effect of a large emission area and the UHV conditions under which the measurements were carried out. Other experiments carried out at 10^{-5} mbar oxygen and argon pressures show considerably poorer performance.

SEM inspection of the CNT array after the stability test showed no visible changes to the array except at two locations where discharge damage is apparent. The damage was sustained during the initial I - V ramp to 2.5 kV, where two glitches in the I - V curve were recorded. Each of these glitches is associated with the damage craters observed. The craters have a diameter of around 20–30 μm where the

CNTs have apparently evaporated to a considerable depth. A few CNTs remain within the crater but they have collapsed due to the loss of support by surrounding CNTs. A small bunch of melded nanotubes was found stuck on the anode.

In summary, we have fabricated aligned CNT arrays that are capable of providing large current densities over a relatively large emitting surface at modest electric fields. The anomalously high field enhancement factor at low fields cannot be attributed to the tip geometry of the larger vertically aligned CNTs with closed tips of large curvature. It is thought that the weave of smaller nanotubes is responsible for the bulk of the emission at lower fields. Investigation of the emission pattern will be needed to elucidate the nature of field emission from such arrays.

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- ¹A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tomanek, P. Nordlander, D. T. Colbert, and R. E. Smalley, *Science* **269**, 1550 (1995).
- ²W. A. de Heer, A. Chatelain, and D. Ugarte, *Science* **270**, 1179 (1995).
- ³P. G. Collins and A. Zettl, *Appl. Phys. Lett.* **69**, 1969 (1996).
- ⁴Q. H. Wang, T. D. Corrigan, J. Y. Dai, R. P. H. Chang, and A. R. Krauss, *Appl. Phys. Lett.* **70**, 3308 (1997).
- ⁵J.-M. Bonard, J.-P. Salvetat, T. Stöckli, W. A. de Heer, L. Forró, and A. Châtelain, *Appl. Phys. Lett.* **73**, 918 (1998).
- ⁶S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tomblor, A. M. Cassell, and H. Dai, *Science* **283**, 512 (1999).
- ⁷W. Zhu, C. Bower, O. Zhou, G. Kochanski, and S. Jin, *Appl. Phys. Lett.* **75**, 873 (1999).
- ⁸Y. J. Yoon and H. K. Baik, *J. Vac. Sci. Technol. B* **19**, 27 (2001).
- ⁹J. I. Sohn, S. Lee, Y.-H. Song, S.-Y. Choi, K.-I. Cho, and K.-S. Nam, *Appl. Phys. Lett.* **78**, 901 (2001).
- ¹⁰V. V. Zhirnov, C. Lizzul-Rinne, G. J. Wojak, R. C. Sanwald, and J. J. Hren, *J. Vac. Sci. Technol. B* **19**, 87 (2001).
- ¹¹O. Gröning, O. M. Küttel, Ch. Emmenegger, P. Gröning, and L. Schlapbach, *J. Vac. Sci. Technol. B* **18**, 665 (2000).