Field emission from individual B–C–N nanotube rope

P. Dorozhkin, D. Golberg, Y. Bando, and Z.-C. Dong

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Field emission from individual B–C–N nanotube rope

P. Dorozhkin,[a] D. Golberg,[b] Y. Bando, and Z.-C. Dong
Nanomaterials Laboratory, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

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The field-emission characteristics of individual ropes made of B–C–N nanotubes were measured *in situ* in a low-energy electron point source microscope. The tungsten field emission tip of the microscope was used as a movable electrode, approaching the rope, and acting as an anode during field-emission measurements. The atomic structure and chemical composition of the ropes were analyzed by high-resolution transmission electron microscopy and electron energy-loss spectroscopy. The tubes assembled within the ropes typically revealed open-tip ends, a small number of layers and zigzag chirality. We found that the field-emission properties of the B–C–N nanotube ropes are competitive with conventional C nanotubes, with the expected additional benefit that the B–C–N ropes exhibit higher environmental stability. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1497194]

Carbon nanotubes (NTs), seamless cylinders made of a wrapped graphitic sheet with a diameter as small as a few Å,[1] are highly promising field-emitter materials.[2–8] A practical field-emission (FE) device should have low threshold electric field, high emission current, and good environmental and thermal stability. FE current densities as high as a few A/cm^2 (about 100 times traditional cold cathode materials) and threshold fields of $\sim 2\ V/\mu m$ have been achieved for various C NT emitters,[6] which are already in use in flat panel displays.

NTs in the B–C–N system,[9,10] being structural analogs of C NTs in which alternating B, N, and C atoms assemble in a graphiticlike sheet, are also of special interest as field emitters. Such interest is strongly supported by the recent findings that pure BN and BN-rich B–C–N NTs may be more thermally and chemically stable than their C counterparts.[11] In addition, it is believed possible to smoothly tune the electrical properties of B–C–N NTs from insulating (the case of pure BN NTs)[12] to metallic and/or semiconducting (the case of pure C NTs)[13] by changing only the BN/C elemental ratio. This may be a key advantage of B–C–N NTs as FE devices over C NTs whose FE properties were found to deteriorate over time[14] or under oxidation[15] and whose electrical properties, being a complex function of NT helicity, diameter, number of layers, and cross-sectional shape, can not be easily adjusted.[13]

Recently, a FE experiment on an individual pure BN NT has been reported,[16] where an electrically insulating (expected *a priori*) BN NT surprisingly demonstrated FE currents at relatively low voltages. To date, the experiments on FE properties of B–C–N NT-like materials have been limited to measurements on large-area films with mats of undulating, poorly graphitized chemical vapor deposited (CVD) B–C–N nanofibers.[17] This has motivated us to perform FE measurements on individual B–C–N NTs.

BN-rich B–C–N NTs were produced by reacting C CVD NT templates with B_2O_3 and CuO (or Au_2O_3) at 1700–2000 K in a N_2 flow.[11,18–20] The product was dispersed onto a Cu-coated-C grid and analyzed using a JEOL-3000F high-resolution transmission electron microscope (HRTEM) equipped with a Gatan-766 electron energy-loss spectrometer (EELS). The same product was mounted onto a Ni grid with a hole size $\sim 6\ \mu m$ for FE measurements in a low-energy electron point source (LEEPS) microscope.[21–23] The LEEPS microscope was based on a commercial Omicron ultrahigh vacuum scanning tunneling microscope.[23] The *X*, *Y*, and *Z* movements were performed by both inertial sliders and a piezotube for course and fine W tip positioning. The tips were produced by electromechanical etching of a W wire in

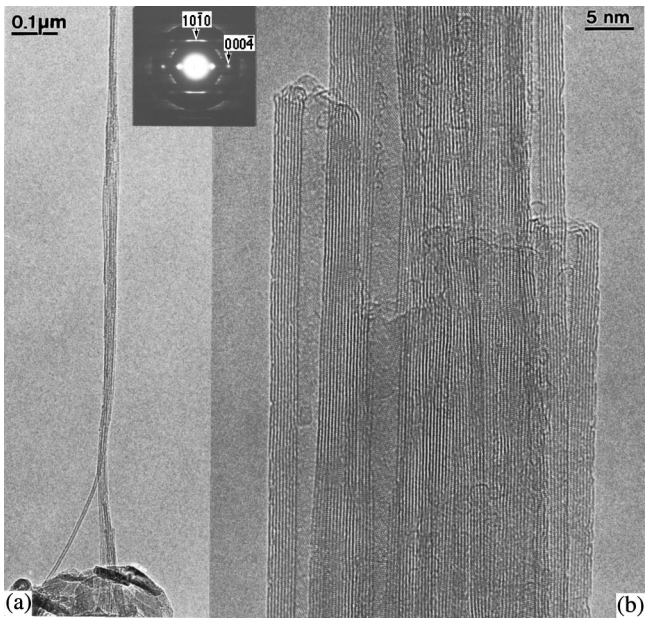

FIG. 1. Low magnification (a) and HRTEM (b) images of nanotube ropes used for FE measurements. The inset in (b) shows a representative diffraction pattern taken from a whole rope using a ~50 nm diameter electron probe and displays zigzag arrangement of the tubular layers. The tube axis is vertical in the diffraction pattern.

[a]Permanent address: Laboratory of Non-Equilibrium Electronic Processes, Institute of Solid State Physics, Chernogolovka, 142432, Russia; electronic mail: pdorozh@issp.ac.ru
[b]Electronic mail: golberg.dmitri@nims.go.jp

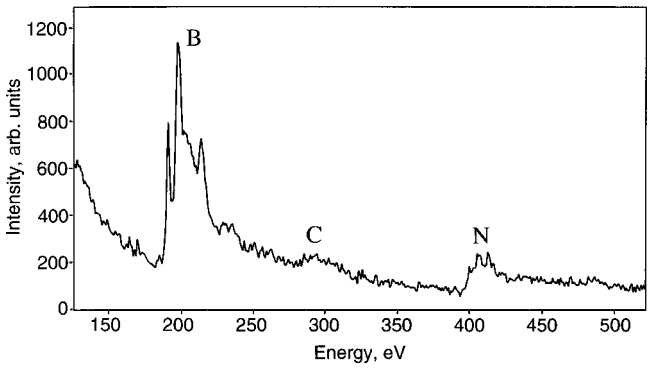

FIG. 2. A representative EELS taken from a nanotube rope with the aid of a ~50 nm diameter electron probe and primarily displaying B and N *K* edges at 188 and 401 eV, and the low intensity C edge at 284 eV. The B/N ratio was calculated to be ~1.0, whereas the C content was estimated to be in the range ~5–6 at. %.

a 2 M NaOH solution. They were subsequently cleaned in a vacuum by Ar^+ sputtering and annealing at 900 K. The electron detector, a one stage multichannel plate combined with a phosphor screen, was placed 7 cm from the sample. The microscope was placed in a vacuum chamber with a working pressure of 10^{-9} Torr.

Figures 1(a) and 1(b) show low magnification and HRTEM images of the NTs. The NTs were self-assembled in ropes composed of dozens of individual tubes and extending up to several μm in length. HRTEM imaging of the ropes and the corresponding diffraction analysis [Fig. 1(b)] allows us to draw conclusions concerning several important features of the product: (i) the rope is constituted of at least several tubes; (ii) the tip ends of the tubes are typically open; (iii) all individual tubular shells in the rope display so-called zigzag arrangement of the graphiticlike sheet. In fact, a diffraction pattern (DP) taken from the whole rope, and shown in the inset of the HRTEM image [Fig. 1(a)], exhibits a diffraction spot distribution typical for the [10-10] graphitic sheet direction lying parallel to the tube/rope axis. Only slight deviations from this highly symmetrical case (within 10°) are visible in the DP.

Figure 2 shows a representative EEL spectrum taken from the whole rope. High intensity *K* edges corresponding to B and N atom excitations, and a low intensity C edge, are observed at 188, 401, and 284 eV, respectively. The C content was estimated to be in the range of ~5–6 at. % for the particular spectrum depicted in Fig. 2. Overall, C contents in the ropes varied in the range of ~2–20 at. % as revealed by quantification of the numerous EEL spectra taken. The cross sections involved in the computation were calculated with the usual σ-*K* hydrogenic model.[9] The fine structure of the edges, characterized by intense π^*-peaks and the shape of the σ^* bands, was typical for sp^2-hybridized B–C–N layered structures.

Figure 3(a) is a LEEPS image of a representative individual B–C–N NT rope, stretched across a hole of the Ni microgrid. An image of the rope after performing FE measurements is given in Fig. 3(b). We first positioned the metal tip of the LEEPS microscope next to the rope, as shown schematically in Fig. 3(c). The tip was then positively biased and acted as an anode for extracting and gathering FE electrons from the rope apex. Figure 3(d) shows consecutive FE

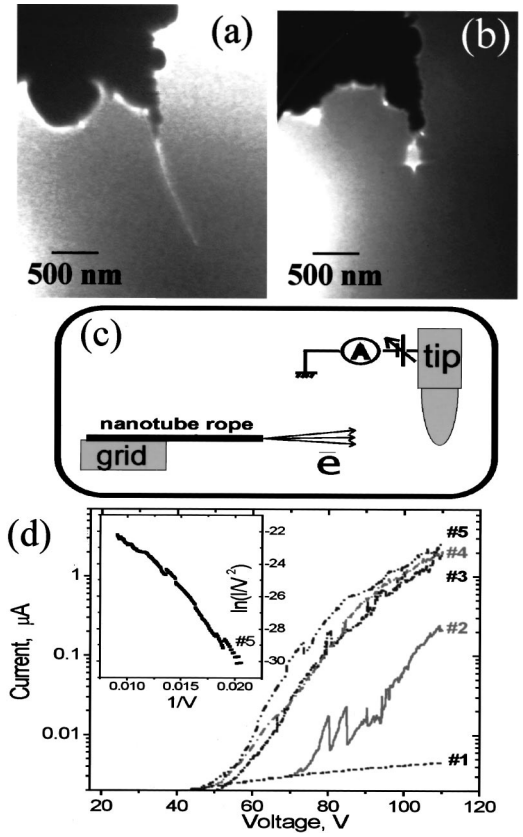

FIG. 3. Low-energy electron point source microscopy images of a nanotube rope before (a) and after (b) FE measurements; (c) the relative position of the NT rope and the microscope tip (anode) during FE measurements; and (d) consecutive $I-V$ curves taken at three distances between the tungsten tip and the rope: curve No. 1—infinitely large distance; curve No. 2—when notable FE current was first recorded; curves Nos. 3–5—consecutive curves taken at a shorter distance. FE current gradually increases while the rope is presumably ''sharpened'' (Nos. 3–5). Inset in (d) shows a representative Fowler–Nordheim plot for curve No. 5.

current–voltage ($I-V$) curves of the rope. Curve No. 1 was taken at a large distance, d, between the microscope tip and the rope, and shows only a small leakage current of the measurement circuit. The tip was then moved closer to the rope until a notable emission current was detected (curve No. 2). Then the tip–rope distance was further decreased and three consecutive $I-V$ curves (Nos. 3–5) were recorded at fixed d.

Curve No. 2 in Fig. 3(d) demonstrated stable emission current up to ~0.011 μA. On reaching this value, the current abruptly dropped down. This happened twice, at 80 and 85 V. Given that the work function of the apex of the field emitter was constant, the drop of the emission current (and corresponding increase of the FE threshold voltage) can only be the result of a decrease in the local field near the tip. This could be caused by a tip burnback, which increases the distance between the emitting tip and the anode, thus reducing the field F at constant bias voltage V, or a reduction in the field enhancement factor, β, reflecting the tip sharpness.[24] Comparing the rope images before and after the measurements [Figs. 3(a) and 3(b)] one can see a substantial decrease in the rope length. The fact that no other abrupt changes in the emission current were detected implies that the two current jumps resulted mainly from the rope shortening. After the reduction in length of the rope its current-carrying char-

acteristic substantially improved: The FE current could easily reach values of a few μA (see curve No. 2 at $V>85$ V and curve Nos. 3–5). No current degradation was noticeable—indeed, each successive voltage sweep gave more stable emission current than the previous one. The last recorded curve (No. 5) demonstrated stable emission current up to at least 2.5 μA, which is close to the maximum stable FE current ($\sim 2\ \mu$A) observed for individual C NTs.[25] Surprisingly, each successively measured $I-V$ curve showed a slightly lower FE threshold voltage than the previous one. Since the rope length could not increase, the reduction of the threshold voltage must result solely from the decrease in the radius of the rope apex—sharpening. The positive effects of the sharpening of the NT ropes on FE characteristics have been recently reported for films of C NTs by Ito *et al.*:[26] when the NT soot was mechanically ground prior to formation of a FE film, the fraction of sharp tubes in the material increased and, subsequently, the FE performance improved. In our experiment, sharpening is likely to be directly induced by the applied electrical field. This removed the outermost NTs which had been weakly attached to the rope.

When plotted in Fowler–Nordheim coordinates[24] [inset to Fig. 3(d)] curve No. 5 lies on a line at low voltages proving that a conventional FE process is taking place. At high emission currents, a marginal deviation from linear behavior is seen. Such a deviation (or saturation) has been demonstrated by many researchers for FE on C NT films and individual NTs.[6,25] This saturation was shown to be caused by adsorbants on the emission surface and did not exist for clean NTs. The onset of saturation occurred at 0.1–0.3 μA for individual C NTs. For the B–C–N NT in our experiment, the onset occurred at substantially higher current ($\sim 0.5\ \mu$A) and the deviation from linear behavior was smaller that that for C NTs, demonstrating better environmental stability of B–C–N NTs.

In conclusion, B–C–N NT rope is a suitable field emitter with emission characteristics comparable to those of C NTs. While its ability to produce high FE currents is similar to that of C NTs, B–C–N NT rope exhibits better enviromental stability for FE. Before reaching the best emission conditions, the rope undergoes a ''training'' emission cycle, during which the rope is first substantially shortened and then sharpened under an applied electric field.

[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] W. A. de Heer, A. Chatelain, and D. Ugarte, Science **270**, 1179 (1995).
[3] A. 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).
[4] L. A. Chernozatonskii, Y. V. Gulyaev, Z. Y. Kosakovskaya, N. I. Sinitsyn, G. V. Torgashov, Y. F. Zakharchenko, E. A. Fedorov, and V. P. Val'chuk, Chem. Phys. Lett. **233**, 63 (1995).
[5] P. G. Collins and A. Zettl, Appl. Phys. Lett. **69**, 1969 (1996).
[6] J.-M. Bonard, H. Kind, T. Stockli, and L.-O. Nilsson, Solid-State Electron. **45**, 893 (2001).
[7] J-M. Bonard, F. Maier, T. Stockli, A. Chatelain, W. A. de Heer, J. P. Salvetat, and L. Forro, Ultramicroscopy **73**, 7 (1998).
[8] Y. Saito, K. Hamaguchi, K. Hata, K. Tohji, A. Kasuya, Y. Nishina, K. Uchida, Y. Tasaka, F. Ikazaki, and M. Yumura, Ultramicroscopy **73**, 1 (1998).
[9] O. Stéphan, P. M. Ajayan, C. Colliex, Ph. Redlich, J. M. Lambert, P. Bernier, and P. Lefin, Science **266**, 1683 (1994).
[10] N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, Science **269**, 966 (1995).
[11] D. Golberg, Y. Bando, K. Kurashima, and T. Sato, Scr. Mater. **44**, 1561 (2001).
[12] X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, Europhys. Lett. **28**, 335 (1994).
[13] J. W. G. Wildöer, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, Nature (London) **391**, 59 (1998).
[14] J.-M. Bonard, J.-P. Salvetat, T. Stockli, W. A. de Heer, L. Forro, and A. Chatelain, Appl. Phys. Lett. **73**, 918 (1998).
[15] K. A. Dean and B. R. Chalamala, Appl. Phys. Lett. **75**, 3017 (1999).
[16] J. Cumings and A. Zettl, *Electronic Properties of Molecular Nanostructures*, edited by H. Kuzmany *et al.* (AIP, Melville, New York), p. 577.
[17] X. D. Bai, J. D. Guo, Jie Yu, E. G Wang, J. Yuan, and W. Zhou, Appl. Phys. Lett. **76**, 2624 (2000).
[18] D. Golberg, Y. Bando, K. Kurashima, and T. Sato, Solid State Commun. **116**, 1 (2000).
[19] D. Golberg, Y. Bando, K. Kurashima, and T. Sato, Appl. Phys. Lett. **77**, 1979 (2000).
[20] D. Golberg and Y. Bando, Appl. Phys. Lett. **79**, 415 (2001).
[21] V. T. Binh and V. Semet, Ultramicroscopy **73**, 107 (1998).
[22] H. Schmid and H.-W. Fink, Appl. Phys. Lett. **70**, 2679 (1997).
[23] P. Dorozhkin, H. Nejoh, and D. Fujita, J. Vac. Sci. Technol. B **20**, 1044 (2002).
[24] R. Gomer: in *Field Emission and Field Ionization* (Harvard University Press, Cambridge, 1961) Chaps. 1 and 2.
[25] K. A. Dean and B. R. Chalamala, Appl. Phys. Lett. **76**, 375 (2000).
[26] F. Ito, K. Konuma, and A. Okamoto, J. Appl. Phys. **89**, 8141 (2001).