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Field emission and current-voltage properties of boron nitride nanotubes

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Abstract

We have measured electrical transport properties of boron nitride nanotubes using an in situ manipulation stage inside a transmission electron microscope. Stable currents were measured in a field emission geometry, but in contact the nanotubes are insulating at low bias. At high bias, the nanotubes show stable, reversible breakdown current.

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There is great interest recently in both the transport properties [1] and field emission properties [2] of wide bandgap semiconductors. The field emission characteristics are connected in part with a negative electron affinity (NEA) that is often present in wide bandgap semiconductors. It has recently been demonstrated that boron nitride surfaces can exhibit an NEA condition [3–5], and boron nitride films have been examined in several studies as a potentially beneficial material for field emission sources [6–9]. There is also considerable interest recently in the field emission properties of carbon nanotubes [10,11]. A number of studies also examine the field emission and transport properties of nanotubes composed of boron, carbon, and nitrogen [12–17].

In the present studies, we have performed field emission and contact current-voltage measurements on boron nitride (BN) nanotubes. Fig. 1 shows the setup for the measurements. The nanotubes were manipulated with a piezo-driven manipulation stage inside a transmission electron microscope (TEM). The BN nanotubes are double-wall nanotubes synthesized by arc discharge [18], and purified by ultrasonic assisted filtration [19]. The as-purified BN nanotube samples are electrically insulating in bulk, but for the TEM in situ measurements the nanotubes were mixed with a conductive epoxy (Epo-Tek H20E) in a volume ratio of approximately 1:1. The resulting composite was then cleaved before loading into the TEM (Philips CM-200 operated at 120 kV), and TEM imaging verified that clean nanotubes were protruding from the surface of the composite. The second electrode for the electrical measurements was a 50 μm gold wire. For field emission experiments, the tips of the protruding nanotubes were positioned 6 μm from the surface of the wire, and for contact IV measurements, the tips of individual nanotubes were gently brought into contact with the gold wire by the piezo manipulator. Control experiments were also performed to verify that the conductive epoxy itself does not field emit at the voltages applied in these experiments. The current was monitored in all cases with a high gain preamplifier (DL Instruments 1211).

Fig. 2 shows the results of field emission experiments. The turn-on voltages are approximately 150 V. Here, the turn-on voltage is defined to be the point where the measured current exceeds the systematic background

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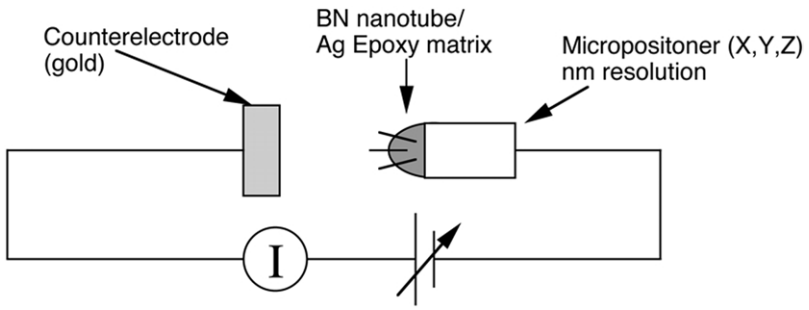

Fig. 1. The experimental setup for electrical measurements inside the TEM.

current of ~0.1 nA. The turn on voltages measured here are approximately twice those measured in control experiments we performed using carbon nanotube samples in similar geometries. The current densities, however, are similar in both cases. One notable difference between the field-emission behavior of BN and carbon nanotubes is the current-voltage characteristic. Generally, field emission is characterized using the theory of Fowler and Nordheim [20], which predicts a linear relationship between $\ln(I/V^2)$ and V^{-1}. For carbon nanotubes, however, the theory often breaks down, frequently with the current showing saturation at high fields, or two distinct Fowler–Nordheim slopes [21]. For the field emission for BN nanotubes we observed a single slope in the Fowler–Nordheim plot. Additionally, carbon nanotubes usually have a noisy, switching behavior most likely associated with gas molecules adsorbed to the tips of the nanotubes [22]. Boron nitride nanotubes, however, show stable field emission with less noise than for typical carbon nanotube samples. This may have implications for the use of BN nanotubes as stable field emission sources for lighting and flat panel displays.

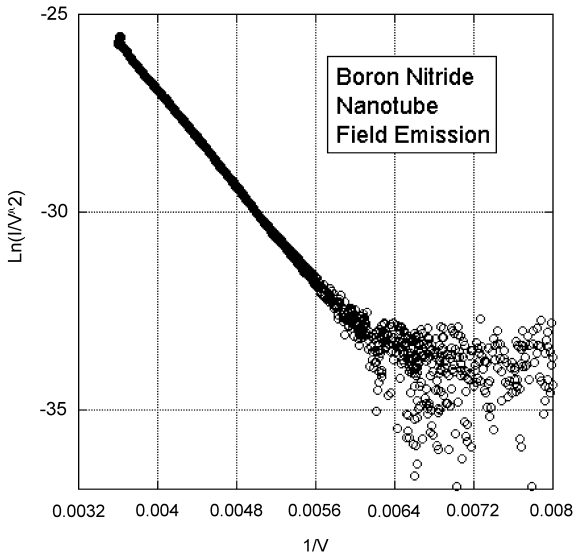

Fig. 2. Fowler–Nordheim plot of the current-voltage characteristic of field emitting BN nanotubes.

From the slope of the Fowler–Nordheim characteristic, it is possible to extract the work-function of the field emitting material. Following the analysis in Ref. [21], it is possible to model the field at the tip of the nanotube by modeling the nanotube tip as a hemisphere. In this model, the field at the tip of the nanotubes can be expressed as

$$E_{\mathrm{loc}} = V_{\mathrm{applied}}/(\alpha R_{\mathrm{tip}}); \tag{1}$$

where R_{tip} is the radius of the nanotube tip (in nm) and α is a parameter which captures the details of the geometry of the field emission environment. In this model, the work function (in eV) can then be extracted from the Fowler–Nordheim slope (S_{FN}) as

$$\Phi = [-S_{\mathrm{FN}}/(6.8\alpha R_{\mathrm{tip}})]^{2/3}. \tag{2}$$

As in Ref. [21], we take the enhancement factor, α, to be approximately 10. Over repeated field-emission experiments performed using BN nanotubes inside the TEM, the slope of the Fowler–Nordheim characteristic varies from −2600 to −3100. From independent TEM observations, the radius of the tips of the BN nanotubes has been measured to be approximately 1 nm. From these quantities, it is possible to make a rough estimate of the work function in the range of 11–13 eV. This large work function is obviously unphysical, and may indicate that field emission from BN nanotubes does not truly obey the Fowler–Nordheim theory. If instead we use the expected work function for hexagonal BN (approximately 6 eV), Eq. (2) can be used to calculate the radius of the tip of the field emitting nanotube. From this analysis, we calculate $R_{\mathrm{tip}} =$ 3 nm. This above analysis also assumes a traditional field emission mechanism from a metallic tip. The boron nitride nanotubes may not exclude internal electric field in the same way a standard conductor would, and in this case the strong field which leads to emission may not even occur at the tip of the nanotube. Such an effect has been observed with diamond field emitters, where the high field comes from a Schottky effect at a diamond-metal-vacuum triple junction and emission ensues along a diamond surface state [2]. Such a field emission mechanism might possibly be implicated in the field emission we observe here.

It is surprising that boron nitride nanotubes can pass any current at all, given that they are wide bandgap

semiconductors. Such a counter-intuitive observation deserves careful inspection. We should note that the nanotubes in these experiments were observed in the TEM where they are subjected to possible electron beam-induced damage. It may be possible that this beam damage affects the intrinsic properties of the nanotubes, leading to the conductivity. Control experiments, however, were performed outside the TEM in a vacuum field-emission setup. In this setup, the nanotubes exhibit field emission with characteristics similar to those observed in the TEM. Therefore, electron beam damage is not essential for field emission from boron nitride nanotubes. The nanotubes are also observed in the TEM to be partly covered with amorphous material from the non-conducting organic binder material of the conducting epoxy used in the preparation of the nanotube composites. It may be that this material plays some role in the field emission, and future studies using mixtures with different types of binder material, or little to no binder may help address this issue.

An additional useful future study would be to look carefully at the current noise during field emission from boron nitride nanotubes. Here, it was observed that BN nanotubes seem to have less noise during field emission, but it would be useful to put this observation on a more solid empirical footing. For instance, the noise frequency spectrum could be carefully measured [23] during field emission from both BN nanotubes and from carbon nanotubes (both SWNT and MWNT). Comparison of the noise spectra would show whether BN nanotubes are indeed less noisy than carbon nanotubes, and may even help elucidate the source of the noise.

The field emission properties of BN nanotubes are surprising given that they are predicted to be wide bandgap semiconductors [24,25], and therefore electrically insulating. To test whether or not individual nanotubes are in fact insulating, the nanotube tips were brought into contact with the gold counter-electrode. Contact was obtained by causing the nanotube to deflect a small amount using the gold surface. From previously reported measurements of the elastic properties of BN nanotubes [26], we estimate the contact force to be on the order of 0.1 nN. For all BN nanotubes observed, there was no conduction at low bias, that is the current does not rise above the experimental background current of $\sim$0.01 nA. It is known that often carbon nanotubes can have high contact resistance, but we can rule out contact resistance for the case of BN nanotubes, because the voltage can be increased through 10 V with no current or damage to the tube. When this is done with carbon nanotubes, the nanotubes generally fail or burn-out between 2 and 4 V, even in cases when there is initially high contact resistance at low bias. BN nanotubes, therefore, are a good dielectric material up to approximately 10 V. At higher bias voltages, however, some of the BN nanotubes observed pass current, but do so in a reversible, non-destructive manner. Fig. 3 shows a typical current-voltage relation for an individual BN nanotube. The breakdown generally occurs between 12 and 25 V, and has a characteristic reminiscent of gas-discharge tubes. In the lower plot of Fig. 3, a sharp, reversible turn-on can be seen at 22 V. Such behavior might be characteristic of an avalanche effect leading to breakdown conductivity.

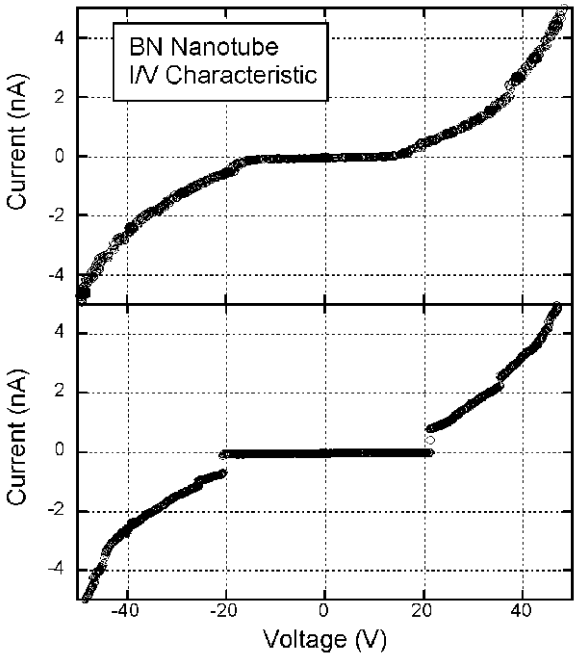

Fig. 3. The current-voltage characteristic of typical BN nanotubes under contact conditions. In both cases, the nanotubes protrude from the conducting matrix approximately 400 nm.

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References

[1] J. Isberg, J. Hammersberg, E. Johansson, T. Wilkstrom, D.J. Twitchen, A.J. Whitehead, S.E. Coe, G.A. Scarsbrook, Science 297 (2002) 1670–1672.
[2] M.W. Geis, N.N. Efremow, K.E. Krohn, J.C. Twichell, T.M. Lyszczarz, R. Kalish, J.A. Greer, M.D. Tabat, Nature 393 (1998) 431–435.
[3] K.P. Loh, Sakaguchi, M. Nishitani-Gamo, T. Taniguchi, T. Ando, Diam. Relat. Mater. 8 (1999) 781–784.
[4] M.J. Powers, M.C. Benjamin, L.M. Porter, R.J. Nemanich, R.F. Davis, J.J. Cuomo, G.L. Doll, S.J. Harris, Appl. Phys. Lett. 67 (1995) 3912–3914.

[5] R.Z. Wang, B. Wang, H. Wang, H. Zhou, A.P. Huang, M.K. Zhu, H. Yan, X.H. Yan, Appl. Phys. Lett. 81 (2002) 2782–2784.
[6] B.L. McCarson, R. Schlesser, M.T. McClure, Z. Sitar, Appl. Phys. Lett. 72 (1998) 2909–2911.
[7] Y. Yokota, S. Tagawa, T. Sugino, Appl. Surf. Sci. 146 (1999) 193–197.
[8] C. Kimura, T. Yamamoto, T. Sugino, J. Vac. Sci. Technol. B 19 (2001) 1051–1054.
[9] T. Sugino, C. Kimura, T. Yamamoto, Appl. Phys. Lett. 80 (2002) 3602–3604.
[10] W.A. de Heer, A. Chatelain, D. Ugarte, Science 270 (1995) 1179–1180.
[11] J.M. Bonard, H. Kind, T. Stockli, L.O. Nilsson, Solid State Electron. 45 (2001) 893–914.
[12] V. Meunier, C. Roland, J. Bernholc, M.B. Nardelli, Appl. Phys. Lett. 81 (2002) 46–48.
[13] D. Golberg, P. Dorozhkin, Y. Bando, M. Hasegawa, Z.C. Dong, Chem. Phys. Lett. 359 (2002) 220–228.
[14] P. Dorozhkin, D. Golberg, Y. Bando, Z.C. Dong, Appl. Phys. Lett. 81 (2002) 1083–1085.
[15] X. Wang, Y. Liu, D. Zhu, L. Zhang, H. Ma, N. Yao, B. Zhang, J. Phys. Chem. B 106 (2002) 2186–2190.
[16] J.B. Yoo, J.H. Han, S.H. Choi, T.Y. Lee, C.Y. Park, T.W. Jeong, L.J.H.S.G. Yu, G.S. Park, W.K. Yi, H.S. Kim, Y.J. Baik, J.M. Kim, Physica B 323 (2002) 180–181.
[17] T. Sugino, T. Yamamoto, C. Kimura, H. Murakami, M. Hirakawa, Appl. Phys. Lett. 80 (2002) 3808–3810.
[18] J. Cumings, A. Zettl, Chem. Phys. Lett. 316 (2000) 211–216.
[19] K.B. Shelimov, R.O. Esenaliev, A.G. Rinzler, C.B. Huffman, R.E. Smalley, Chem. Phys. Lett. 282 (1998) 429–434.
[20] R.H. Fowler, L. Nordheim, P. Roy, Soc. Lond. A Mat. 119 (1928) 173–181.
[21] P.G. Collins, A. Zettl, Phys. Rev. B 55 (1997) 9391–9399.
[22] K.A. Dean, B.R. Chalamala, Appl. Phys. Lett. 76 (2000) 375–377.
[23] P.G. Collins, M.S. Fuhrer, A. Zettl, Appl. Phys. Lett. 76 (2000) 894–896.
[24] A. Rubio, J.L. Corkill, M.L. Cohen, Phys. Rev. B 49 (1994) 5081–5084.
[25] X. Blase, A. Rubio, S.G. Louie, M.L. Cohen, Europhys. Lett. 28 (1994) 335–340.
[26] N.G. Chopra, A. Zettl, Solid State Commun. 105 (1998) 297.