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Focused-ion-beam assisted fabrication of individual multiwall carbon nanotube field emitter

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Abstract

We report the fabrication of an individual carbon nanotube (CNT) electron field emitter using a focused-ion-beam (FIB) technique. The monolithic multiwall CNT with a graphitic shield is synthesized using chemical vapor deposition technique. The FIB technique is applied to attach the monolithic multiwall CNT on an etched tungsten tip. Field emission measurements are carried out in a vacuum of 10^{-7} Torr. Threshold voltage as low as 120 V has been obtained.

Keywords: Carbon nanotubes; Focused-ion-beam; Field emission

1. Introduction

Since the pioneer work of Rinzler et al. [1] on the field emission from CNT there have been intense studies of the field emission properties of CNT. It is generally agreed that electron devices using carbon nanotube field emitter can be realized in the very near future. Several extensive reviews [2–6] of the subject have been published in the last few years. Among numerous field emission investigations of CNT reported so far, the majority have been the studies of thin film field emitters. Here, we would like to concentrate on the electron field emission from individual CNT. Among all the works on field emission from individual CNT, most works [7–13] were carried out inside a transmission (or scanning) electron microscope on a substrate that contains many CNTs. A microprobe is then used to selectively choose one particular CNT for field emission study. This method is useful for the study of field emission properties of an individual CNT but impractical for applications that only need one single CNT such as electron source for electron microscope. The few field emission measurements [1,2,14–16] carried out using a fabricated individual CNT emitter typically employed optical or electron microscope to attach CNT or CNT bundle to Au or W tip with conducting glue or with van der Waals force. It has been established that CNT is an ideal electron field emitter with the following advantages: (a) high brightness, (b) low energy spread, (c) emission current stability, and (d) long lifetime.

Recently there were several reports [11,13,17] indicating that damages and degradations to the CNT field emitters were either due to mechanical failure of the contact between the CNT and the metal support or due to heating of the contact resistance between the CNT and the metal support. In view of these repots, a better technique to attach the CNT to the metal support is needed to improve mechanical and electrical properties of the CNT–metal contact. Here, we report the focused-ion-beam fabrication of a CNT electron field emitter that

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possesses excellent mechanical and electrical properties of the CNT–metal contact.

2. Experimental techniques

We have reported a chemical vapor deposition synthesis of a monolithic open end multiwall CNT [18] with a graphitic shield in the past. The diameter of the CNT is about 48 nm. This unique structure of a CNT inside a carbon fiber is ideal for the fabrication of individual field emission tip because of its mechanical integrity, good electrical contact between the CNT and the carbon fiber, and ease of handling the carbon fiber. Details of the synthesis steps have been reported earlier [18] and will not be discussed here.

Once the CNT-containing fiber was produced, we employed FIB technique to attach the CNT-containing carbon fiber to a sharpened tungsten tip. The steps are as follows: we mounted a chemically etched tungsten tip and the CNT-containing substrate inside a FEI Vectra 200 FIB system. FIB was first employed to fabricate a two-micron slot at the end of the etched W tip and then we used the in situ micro-manipulator to pick up an ''intermediate'' carbon fiber as shown in Fig. 1(a). The pick up process involved first etching a slot on the tip of the micro-manipulator and then moving it to a carbon fiber such that the fiber is rested in the slot. Then platinum metal is deposited at the contact of the fiber and the tip of the micro-manipulator to form a rigid bond. The Ga ion beam energy and current are set at 30 keV and 30 pA, respectively during the deposition process. Then a 40 μm segment of the fiber is cutoff from the substrate. The beam energy and current settings are 30 keV and 300 pA, respectively, for the cutting procedure. Next we used this ''intermediate'' fiber to pick up a CNT-containing carbon fiber as shown in Fig. 1(b) and (c). Finally we put the CNT-containing fiber inside the slot fabricated at the tungsten tip with the help of the micro-manipulator as shown in Fig. 1(d). After depositing platinum metal to weld the fiber to the tungsten tip, the ''intermediate'' fiber is cutoff from the CNT-containing fiber as shown in Fig. 1(e). After FIB fabrication, an SEM image of the CNT-containing carbon fiber is shown in Fig. 2. An enlarged SEM image near the tip of carbon fiber is also shown as an inset in Fig. 2. It should be noted that the ion beam used for imaging, cutting, and depositing metal can affect the mechanical and electrical properties of the carbon nanotubes. At ion energy of 30 keV and beam current of 500 pA, the carbon nanotube can be easily damaged in a few seconds. To minimize any potential damage to the nanotube, we never image the carbon nanotube with Ga ion beam directly during the FIB process.

After the FIB fabrication, the CNT emitter is mounted on a home-made platform for field emission measurement. The platform is made of vacuum compatible insulator with the ends of two fine-thread stainless steel screws facing each other as counter electrodes. The end of one screw is polished to a mirror finish, while the other screw has a step at the end so the CNT emitter can be attached with silver paint. The CNT emitter is pointed at the center of the mirror finish end of the other screw perpendicularly. The distance between the two can be adjusted under optical microscope to within 2 μm. The typical distance between the CNT and the counter electrode is 50–200 μm.

3. Results and discussion

The platform is placed inside a stainless steel ultra-high vacuum chamber for the field emission measurement. The vacuum during measurement is kept at 1×10^{-7} Torr. The power supply we used is an ORTEC model 556 and Keithley multimeter and picoammeter are used for voltage and current measurements. In this measurement, we keep the distance between the CNT tip to the opposite electrode to be 150 μm. The I–V measurements are shown in Fig. 3. Similar to previous reports [7,11] we found that the CNT emitter went through a conditioning period initially. The conditioning effect is due to the apex contamination when the CNT emitter was first transferred into the vacuum. After the initial conditioning period, the emission characteristics become reproducible. We define the turn-on voltage as the voltage when the emission current reached 1 nA. In the current case, we obtained a $V_{\text{turn-on}}$ of 120 V.

In the Fowler–Nordheim relationship [19],

$$\mathrm{Ln}\left(\frac{I}{F^2}\right) = \frac{k \cdot \phi^{\frac{3}{2}}}{F} + \text{const}, \tag{1}$$

where F is the local electric field at the emitting area—the tip of the CNT and ϕ is the work function of CNT tip. Without the CNT tip, the local electric field due to the combination of the tungsten wire and the carbon fiber is F_0. We define the field enhancement factor of the CNT tip itself as $\beta = \frac{F}{F_0}$. Please note the unconventional notation we used here. It has been shown [20] that the electric field at the apex of the carbon fiber is approximately equal to that of a conducting sphere with the same radius. So the local field at the end of the carbon fiber neglecting the CNT tip can be estimated as $F_0 = \frac{V}{R}$, where V is applied voltage and $R = 0.7$ μm, is the radius of the carbon fiber. Thus the Fowler–Nordheim relationship can be written as

$$\mathrm{Ln}\left(\frac{I}{V^2}\right) = \frac{1000 \cdot \alpha \cdot \phi^{\frac{3}{2}} \cdot R}{V \cdot \beta} + \text{const} \tag{2}$$

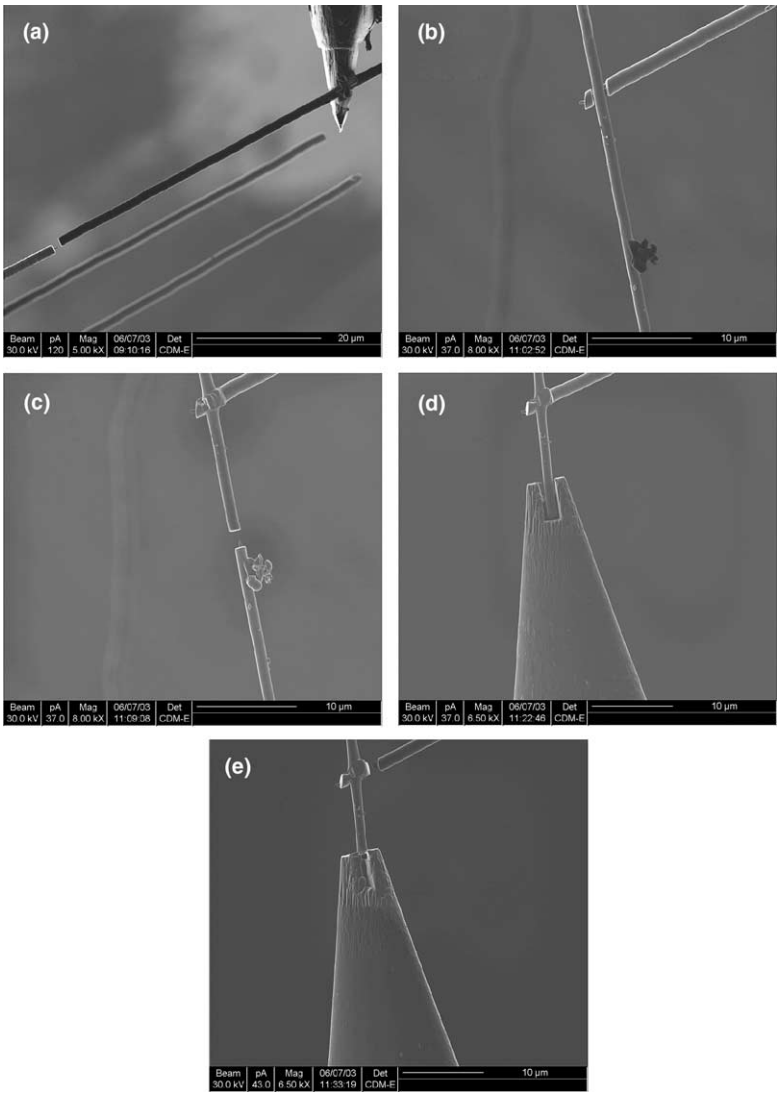

Fig. 1. (a) Secondary electron image showing the micro-manipulator with one ''intermediate'' fiber welded to it with the deposition of platinum metal. The fiber has been cut away from the underlying substrate. (b) Secondary electron image of a CNT-containing fiber to be welded to the ''intermediate'' fiber. (c) After the welding process, the CNT-containing fiber is cutoff from the substrate. (d) Secondary electron image of sliding the CNT-containing fiber into the slot fabricated at the end of the etched tungsten tip. (e) Platinum metal was deposited at the slot to weld the fiber with the W tip, and the CNT-containing fiber was then cut off from the ''intermediate'' fiber.

In the insert of Fig. 3, we plot $\mathrm{Ln}(I/V^2)$ vs. $1000/V$, the slope of the straight line is $\alpha\phi^{3/2}R/\beta$. Here the constant $\alpha = 6.82 \times 10^6$; ϕ is the work function of the carbon nanotube, a typical value is 5 eV; and β is the field emission enhancement factor due to the geometry of the CNT tip only. From the slope we obtained an enhancement factor, β of 21. From a theoretical prediction [21,22] of β for a planar anode and a shank of zero semiangle,

$$\beta = 1.2 \cdot \left(\frac{l}{r} + 2.15\right)^{0.9}, \tag{3}$$

where r is the curvature radius at the apex of the emitter and l is the length of the emitter. Even though our experimental set-up geometry is not planer, but if we use the above equation with $r = 24$ nm and $l = 3$ μm, we obtained a value of $\beta \sim 100$.

We also noticed that the degradation mode of our CNT emitter is different from previously reported [11,13,17]. In the previous cases, the degradation occurred at the contact between the CNT and metal support. This is understandable because those CNT tips were attached either by glue or by van der Waals force. In our case, the degradation starts at the end of CNT tip. We believe this is mainly due to our open-ended CNT and the relatively low vacuum (10^{-7} Torr) in our chamber. At high emission current, the CNT will act as heating resistance and burn the nanotube. At emission current of 10 μA for 5 min, our CNT burnt out totally. Yet the carbon fiber and the welding contact

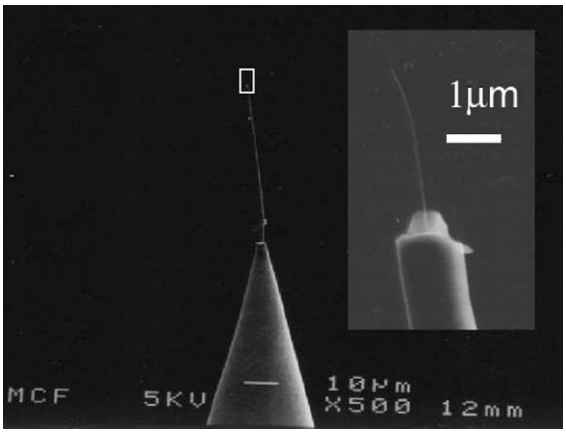

Fig. 2. An SEM image of the monolithic multiwall carbon nanotube field emitter. At 500× magnification, the cone-shaped etched tungsten tip and the carbon fiber are clearly shown. A close-up of the rectangular area at the tip of the carbon fiber is shown as an inset showing CNT at the end of carbon fiber.

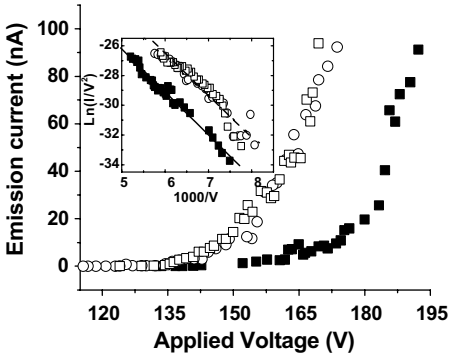

Fig. 3. Evolution of the current–voltage characteristics of our practical electron field emitter showing the conditioning process. The solid square (■) are data before conditioning, while the open (○) and (□) are data obtained after the conditioning process. The linear curve fit of (○) data is $\mathrm{Ln}\left(\frac{I}{V^2}\right) = -10.8 - 2.6\left(\frac{1000}{V}\right)$. The linear curve fit of (□) data is $\mathrm{Ln}\left(\frac{I}{V^2}\right) = -9.4 - 2.74\left(\frac{1000}{V}\right)$.

between fiber and tungsten support remained intact. After the CNT tip burned away, we measured the resistance of the whole set-up without the nanotube tip by reducing the inter-electrode distance to zero and made the carbon fiber in contact with the opposite electrode. The total resistance including the carbon fiber, the FIB welding junction and the contact resistance is only about 2000 Ω.

4. Conclusion

In conclusion, we report a method for fabricating individual multiwall CNT electron field emitters using a focused-ion-beam technique. This multiwall CNT electron field emitter is monolithic, with a graphitic outer layer. This CNT electron field emitter is monolithic with a graphite outer layer. It exhibits excellent structure integrity and excellent electric contacts between CNT and fiber, and between fiber and metal supports.

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References

[1] Rinzler AG, Hafner JH, Nikolaev P, Lou L, Kim SG, Tománek D, et al. Unraveling nanotubes—field-emission from an atomic wire. Science 1995;269:1550–3.
[2] Bonard JM, Salvetat JP, Stöckli T, Forró L, Châtelain A. Field emission from carbon nanotubes: Perspectives for applications and clues to the emission mechanism. Appl Phys A 1999;69:245–54.
[3] Bonard JM, Kind H, Stöckli T, Nilsson LO. Field emission from carbon nanotubes: The first five years. Solid-State Electron 2001;45:893–914.
[4] Bonard JM, Croci M, Klinke C, Kurt R, Noury O, Weiss N. Carbon nanotube films as electron field emitters. Carbon 2002;40:1715–28.
[5] Gröning O, Clergereaux R, Nilsson LO, Ruffieux P, Gröning P, Schlapbach P. Prospects and limitations of carbon nanotube field emission electron sources. Chimis 2002;56:553–61.
[6] Saito Y. Carbon nanotube field emitter. J Nanosci Nanotechnol 2003;3:39–50.
[7] Semet V, Binh VT, Vincent P, Guillot D, Teo KBK, Chhowalla M, et al. Field electron emission from individual carbon nanotubes of a vertically aligned array. Appl Phys Lett 2002;81:343–5.
[8] Purcell ST, Vincent P, Journet C, Binh VT. Hot nanotubes: Stable heating of individual multiwall carbon nanotubes to 2000 K induced by the field-emission current. Phys Rev Lett 2002;88:105502.
[9] Wang ZL, Gao RP, de Heer WA, Poncharal P. In situ imaging of field emission from individual carbon nanotubes and their structural damage. Appl Phys Lett 2002;80:856–8.
[10] Bonard JM, Dean KA, Coll BF, Klinke C. Field emission of individual carbon nanotubes in the scanning electron microscope. Phys Rev Lett 2002;89:197602.
[11] She JC, Xu NS, Deng SZ, Chen J, Bishop H, Huq SE, et al. Vacuum breakdown of carbon-nanotube field emitters on a silicon tip. Appl Phys Lett 2003;83:2671–3.
[12] Minh N, Tuyen LT, Ono T, Mimura H, Yokoo Y, Esashi M. Carbon nanotube on a Si tip for electron field emitter. Jpn J Appl Phys 2002;41:L1409–11.
[13] Kim DH, Yang HS, Kang HD, Lee HR. Novel emission degradation behavior of patterned carbon nanotubes by field emission. Chem Phys Lett 2003;368:439–44.
[14] de Jonge N, van Druten NJ. Field emission from individual multiwalled carbon nanotubes prepared in an electron microscope. Ultramicrosc 2003;95:85–91.
[15] de Jonge N, Lamy Y, Schoots K, Oosterkamp TH. High brightness electron beam from a multi-walled carbon nanotube nature 2002;420:393–5.

[16] Fransen MJ, van Rooy TL, Kruit P. Field emission energy distributions from individual multiwalled carbon nanotubes. Appl Surf Sci 1999;146:312–27.
[17] Bonard JM, Klinke C. Degradation and failure of carbon nanotube field emitters. Phy Rev B 2003;67:115406.
[18] Kleckley S, Chai GY, Zhou D, Vanfleet R, Chow L. Fabrication of multilayered nanotube probe tips. Carbon 2003;41:833–6.
[19] Fowler RH, Nordheim LW. Electron emission in intense electric fields. Proc R Soc London Ser A 1928;119:173–81.
[20] Vibrans GE. Vacuum voltage breakdown as a thermal instability of the emitting protrusion. J Appl Phys 1964;35:2855–7.
[21] Edgecombe CJ, Valdre U. Microscopy and computational modeling to elucidate the enhancement factor for field electron emitters. J Microsc 2001;203:188–94.
[22] Edgecombe CJ, Valdre U. Experimental and Computational study of field emission characteristics from amorphous carbon single nanotips grown by carbon contamination. Philos Mag B 2002;82:987–1007.