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Electron emission from the side wall of an individual multiwall carbon nanotube

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Abstract

Electron emission from the sidewall of a bent individual multiwall carbon nanotube (CNT) is reported. The CNT was synthesized using a catalytic chemical vapor deposition method and the focused-ion beam technique was used to fabricate the CNT-based electron emitter. With controlled ion bombardment, individual carbon nanotubes can be bent into loops with different radii. An external electric field can be used to straighten the bent CNT. The electron field emission from the sidewall of CNT was measured, and compared with that from the tip of the CNT. The turn-on voltage from the sidewall of CNT is significantly lower than that from the tip. An enhancement factor β as large as 400,000 has been obtained for the electron emission from the side wall.

1. Introduction

Since the discovery [1] of carbon nanotubes (CNTs), there is a general consensus that a CNT could be an ideal electron field emitter due to its unique geometry and physical properties. Numerous papers on the filed emission properties of CNTs can be found in several extensive reviews [2–6]. Almost all electron field-emission measurements [7–10] on individual CNTs so far have been carried out with the electron emission occurring at the tip. There have been two reports that involve the electron emission from the body of CNT. Chen et al. [11] studied the electron field emission from CNTs with different orientation relative to the surface of the substrate. They used a plasma-assisted hot filament method to deposit aligned CNTs with different orientations, namely, perpendicular to the substrate; at 45° to the substrate; and parallel to the substrate. They found that the threshold voltage for the field emission is the lowest when the CNTs are parallel to the substrate. This result is counter-intuitive because from the geometry of the CNT, one would expect that electron emission from the sharp tip would have a lower threshold voltage. The authors argued that defects near the surface of the sidewalls might contribute to the low threshold voltage that they observed.

Recently Konishi et al. [12] has compared the electron field emission both from the tip and from the sidewall of an individual CNT. They employed a manipulator inside a scanning electron microscope to attach a multiwall CNT onto a tungsten tip. They found that some of the CNTs formed loops when attached to the tungsten tip. They further deposited amorphous carbon at the overlap portion of the multiwall CNT and the tungsten tip by electron induced deposition to strengthen the contact between the CNT and the tungsten tip. They found that the turn-on voltage of the sidewall emission is 3.8 times larger than that of the emission from the tip of a CNT. This result clearly contradicts the observation made by Chen et al. [11]. In this paper, we report our measurements of the electron field emission from the sidewall of individual CNTs and compare the results with our previous emission measurements from the tip of individual CNTs [13].

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2. Experimental

We have reported a chemical vapor deposition synthesis of a monolithic multiwall carbon nanotube [14] with a graphitic shield recently. This unique coaxial cable-like structure of a CNT inside a carbon fiber is ideal for the field-emission tip application due to its mechanical integrity, ease of handling, and good electrical contact between the CNT and the surrounding carbon fiber. Individual multiwall carbon nanotube field emitters based on this unique configuration have been developed and the field-emission properties have been reported [13].

During the focused-ion beam (FIB) assisted CNT tip pick up process, the CNT tip can be bent by a controlled exposure to the Ga ion beam. Individual carbon nanotubes can be bent with a beam current of 500 pA in a few seconds. When the beam current is reduced to several pA, by adjusting the exposure time, CNT loops with different radii can be produced. The bent individual CNT loop is then mounted into a vacuum chamber for the field-emission measurement.

A scanning electron microscope (SEM) image of a bent CNT loop is shown in Fig. 1(a). The diameter of the CNT is about 40 nm and the length of the CNT is about 10 μm. The CNT loop radius estimated from the SEM micrograph is about 300 nm. The details of experimental procedures have been reported elsewhere [13,15]. A schematic diagram of the experimental configuration is shown in Fig. 2. For all measurements reported here, the inter-electrode distance D is kept at $D = 5$ mm and the CNT to anode distance d is kept at 150 ± 2 μm.

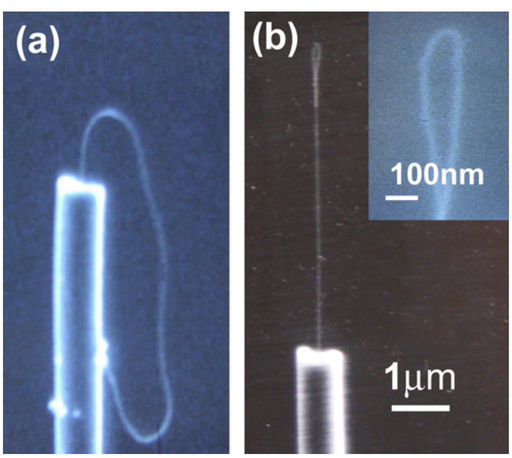

Fig. 1. (a) The SEM image of the CNT loop emitter before the high emitting current treatment. (b) The SEM image of the CNT loop emitter after the high emitting current treatment.

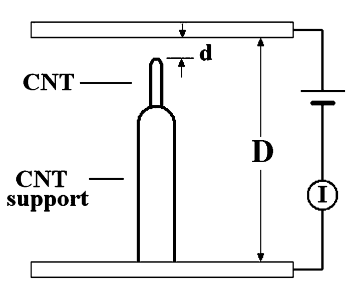

Fig. 2. Schematic diagram of the experimental configuration for the field-emission measurement.

3. Results and discussion

The field-emission results obtained from this bent CNT loop are shown in Fig. 3. In order to avoid damage to the CNT emitter, the field emission current is restricted to a range of 1–100 nA. For a pristine CNT emitter, the conditioning effect [16,17] is observed initially which is shown as curve A in Fig. 3(a). After the conditioning effect, the I–V characteristic curve becomes reproducible and is shown as curve B in Fig. 3(a). From Fig. 3(b), we can see that the I–V characteristic satisfies the Fowler–Nordheim (FN) relationship [18] quite well. In our experiment, very low turn-on voltages ($V_{\text{turn-on}} = 50$ volts) were measured. To obtain an emission current of 100 nA, the applied voltage is only about 70 V. The $V_{\text{turn-on}}$ and the $V(I = 100\text{ nA})$ are significantly lower than that of the individual CNT tip field emitter we reported earlier [13].

After several measurement cycles, the applied voltage is increased until an emitting current of 5 μA is achieved. The curved CNT field emitter is kept under this condition for about 2 min and then the applied voltage is reduced so that the emission current is decreased back to 1–100 nA range. Interestingly, we find that the field emission I–V characteristic changed significantly after our CNT loop goes through the high current emission treatment. This new I–V characteristic is reproducible and is shown as curve C in Fig. 3(a). The SEM image (Fig. 1(b)) taken after the measurement shows the detailed geometry of the CNT loop emitter after

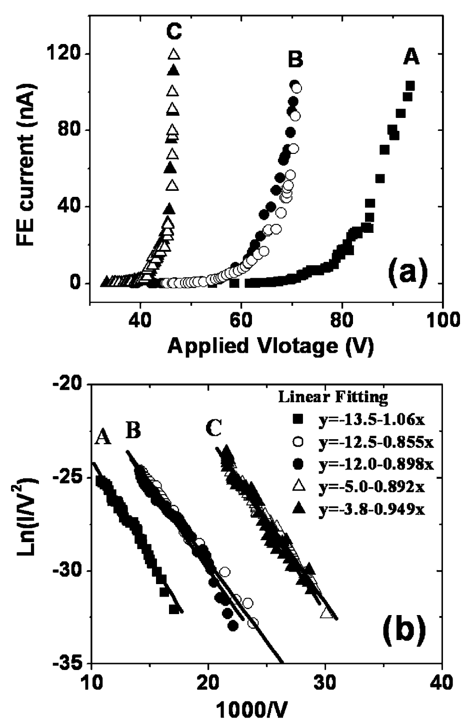

Fig. 3. (a) A is data due to conditioning effect; B is obtained after the cleaning effect and before the high emitting current treatment; C is obtained after the high emitting current treatment. (b) The semi-logarithmic plot shows the field emitting I–V characteristics of the CNT loop emitters satisfy FN relationship.

the high emitting current treatment. The CNT loop is partly vaporized and the length is reduced to 6.5 μm. In the meanwhile, it is straightened by the local electric field applied during the high emission current. We noticed that the straightened CNT has formed a smaller loop at the tip with a radius $R \sim 40$ nm. The field emission behavior of this smaller CNT loop is shown in Fig. 3(a), curve C.

The I–V characteristics obtained from the smaller CNT loop are similar compared to those of the larger CNT loop. The field enhancement factor of the CNT loops which is defined as $\beta = E_{\text{local}}/E_{\text{ave}}$ can be calculated by the linear curve fitting to the slopes of data in Fig. 3(b)

$$\ln\left(\frac{I}{V^2}\right) = \frac{\alpha \cdot \phi^{\frac{3}{2}} \cdot D}{1000 \cdot \beta} \cdot \frac{1000}{V} + \text{const} \tag{1}$$

$$\beta_{\text{experimental}} = \frac{\alpha \cdot \phi^{\frac{3}{2}} \cdot D}{1000 \cdot \text{slope}} \tag{2}$$

Here $D = 5$ mm is the inter-electrode distance and we assume $E_{\text{ave}} = V/D$. The constant α is equal to 6.82×10^9 and ϕ, the work function of the carbon nanotube, a typical value of 5.0 eV is used. For the large and small CNT loops, our results show that the field enhancement factors are 400,000 and 380,000 respectively.

Our results indicate that the field enhancement factors for CNT loops with different loop radii are almost identical. This can be understood as follow: the field enhancement factor is mainly determined by the geometry of the emitters; in the case of CNT loops, the diameter of the CNT and the loop radius. Since the CNT diameter is smaller than the loop radius by at least a factor of two, it is the dominant factor. For the CNTs with same diameter but different loop radius, the geometric field enhancement factor will be very similar.

We summarize our results in Table 1. (The field enhancement factor of the CNT tip is recalculated based on a new definition $\beta = E_{\text{local}}/E_{\text{ave}}$, instead of $\beta = F/F_0$ used in [13].) Here we can see that the turn on voltage for CNT loop emitters are much lower than that of the CNT tip, while the enhancement factor β of the loop emitters are higher than that of the CNT tip emitter. These results are counter-intuitive and could not be explained solely by the geometrical factor alone. During the FIB assisted CNT loop formation process, the incident Ga ion beam will inevitably introduce defects to the sidewall of the CNT. It is believed that the defects will contribute to the improvement of the field emission properties. Another factor that may also contribute to the improvement is the work function which is directly related to the energy band gap of the bent sidewall of the CNT. There have been a few theoretical studies of mechanical bending on the electronic properties of single-wall carbon nanotubes [19–23]. These studies showed that the energy band gap of a single-wall CNT can be modified by the mechanical strains applied to the carbon nanotube. Even though theses results can not be applied directly to our multiwall CNT measurements, we believe that our results imply that the effect of bending strains on a multiwall CNT could be similar to that of a single-wall CNT.

Table 1
Geometry and field-emission properties comparison of individual CNT tip and CNT loops

	CNT radius (nm)	Loop radius (nm)	Turn on voltage (V)	Enhancement factor β^*
CNT tip	24	N/A	120	150,000
Large CNT loop	20	300	50	400,000
Small CNT loop	20	40	35	380,000

* The β here is defined as $E_{\text{local}}/E_{\text{ave}}$, where E_{ave} is assumed to be V/D. In Ref. [13], the β is defined as F/F_0.

4. Conclusion

In conclusion, we demonstrated that (a) multiwall CNT can be bent by exposing it to a few pA of Ga ion beam current, (b) the bent multiwall CNT can be straighten by an external applied electric field, (c) the turn-on voltage for the electron field emission from a loop CNT emitter is a factor of 2–3 lower than that of the field emission from a CNT tip, and (d) the field enhancement factor, β of a loop emitter is about a factor of 2.6 larger than β of a CNT tip emitter.

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