Carbon Nanotube Electron Source for Field Emission Scanning Electron Microscopy

Hitoshi Nakahara, Shunsuke Ichikawa, Tomoya Ochiai, Yoshikazu Kusano and Yahachi Saito
Department of Quantum Engineering, Nagoya University, Furo-cho, Nagoya 464-8603, JAPAN
nakahara@nagoya-u.jp

Abstract: A carbon nanotube (CNT) is one of the promising candidates for next generation field emission materials. We have been studied emission properties of CNTs and reported that even a thick ($\phi \sim 20$ nm) multi-walled nanotube (MWNT) have a small emission area of about 5×10^{-14} cm^2, which results in brightness enhancement by 1-2 orders as compared with conventional tungsten field emission electron source. In this study, a single MWNT emitter is mounted on a commercially available field emission scanning electron microscope (FE-SEM) in place of a single crystalline tungsten emitter. Focused ion beam nano-machinning and nano-manipulation methods are used to prepare MWNT emitters, and practicalities of these emitters for FE-SEM use (beam alignment, beam stability, life time, image quality etc.) are investigated. As a result, it is shown that a CNT emitter has better beam stability as compared with a tungsten emitter, however, difficulties in beam alignment is still a large problem.

1. Introduction

Because of its unique electric, physical and chemical properties such as ballistic electric conduction, high stiffness, small tip radius, chemical stability, etc., carbon nanotubes (CNTs) are expected to apply to many kinds of devices and materials. We have been studied on CNT applications to point electron sources, such as field emission (FE) electron guns. In the previous report[1], it has been found that even a thick ($\phi \sim 20$ nm) multi-walled nanotube (MWNT) have a small emission area of about 4.7×10^{-14} cm^2, which corresponds to a circular area with only 1.2 nm of radius. Considering that this area is a sum of 6 five-membered-ring emitting areas, one emission site only has a circular area with 0.5 nm of radius. Because of this small emission area, even a MWNT achieves a reduced brightness of 2.6×10^9 A/m^2 sr V, which is about 1-2 orders higher than conventional single crystalline tungsten (310) emitters. It is also important that mechanical strength and heat dissipation of thick MWNT is higher than thinner double-walled or single-walled CNTs. Therefor, a MWNT field emitter can be used as a high performance electron emitter for a point electron source application.

In this work, we applied a MWNT emitter to an electron source of commercial FE scanning electron microscope (FE-SEM) in place of a single crystalline tungsten emitter. Focused ion beam (FIB) nano-machinning and nano-manipulation methods are used to prepare MWNT emitters, and practicalities of these emitters for FE-SEM use (beam alignment, beam stability, life time, image quality etc.) were investigated.

2. Experimental

CNTs used for electron sources are MWNTs produced by catalyst free arc discharge method. With this method, we can obtain straight and few defect MWNTs with average diameter of 20 nm and length of 2-5 μm. The MWNTs were attached to a tip of a chemically etched polycrystalline tungsten needle. To compare shape effect of a tungsten needle on nanotube mounting, we prepare two kinds of tungsten needle, one is as etched, and another is machined by FIB to make a flat area as shown in Fig. 1. To mount a MWNT onto the needle, we used two nano manipulators (MM3A-EM; Kleindiek Nanotechnik) which are installed in an environmental SEM (Quanta 200 FEG; FEI Company). One manipulator holds a bundle of MWNT and the other holds a gas nozzle which provides $W(CO)_6$ gas for electron beam induced deposition (EBID). A tungsten needle, which is mounted on an emitter holder, is placed on the SEM specimen stage. A schematic figure and a SEM image during manipulation is shown in Fig. 2.

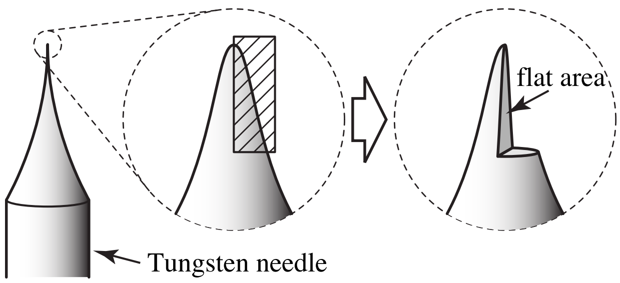

Figure 1: A schematic illustration of FIB nano-machinning of a tungsten needle. A half part of an etched tungsten tip (hatched area) is irradiated by an ion beam to make a flat area where a MWNT emitter is attached.

MWNT emitters prepared as explained above, were installed in a commercially available FE-SEM (S-800; Hitachi Ltd.) The electron gun of the FE-SEM, which is operated under cold FE condition, was used without any modification for CNT emitters. The control system was also used as is. Before starting electron emission, the emitter was heated by direct current at around 800 °C for several minutes to degas. Vacuum pressure of the emitter chamber was less than 10^{-7} Pa. An emission current target was setup to 5 μA and an extraction voltage was automatically applied for the target emission current. An acceleration voltage was selected as 20 kV for FE-SEM image measurements.

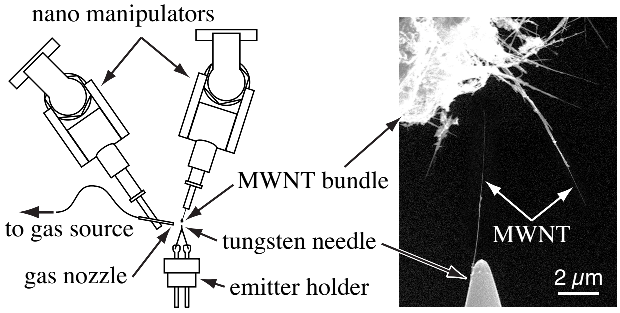

Figure 2: The left figure shows a schematic setup for nanotube manipulation in an environmental SEM. The right figure is a SEM image during manipulation.

Table 1: Mounting angles (θ), sticking out lengths of MWNT (ℓ), needle radii (r) and extraction voltages (V_e) to achieve a target emission current (5 μA) for respective emitters.

	#a1	#a2	#a3	#b1	#b2	#b3
θ [°]	45	20	10	10	3	10
ℓ [μm]	0.2	2.1	0.7	0.2	0.2	0.3
r [nm]	60	300	560	560	560	560
V_e [kV]	1.4	0.9	0.9	2.4	1.0	0.8

3. Results & Discussions

SEM images of MWNT emitters prepared by nano manipulation method are shown in Fig. 3. As etched tungsten needles were used for emitters #a1 to #a3, and FIB processed needles were used for #b1 to #b3. Mounting angles (θ), sticking out lengths of MWNT (ℓ) and needle radii (r) for respective emitters are summarized in Table 1. Definitions of θ, ℓ and r are shown in Fig. 3. Extraction voltages (V_e) to achieve the target emission current are also written in the table. A mounting angle was calculated from two orthogonal SEM measurements.

For mounting angles, it is apparent that MWNTs mounted on FIB processed needles have much smaller angles on average. This suggests that the FIB process is effective to mount a MWNT within a small tilt angle, which might be suitable for electron beam alignment. However, the very end of the flat area is slightly curved, which causes a small tilt angle as shown in the inset figure of #b1 (Fig. 3). Therefore optimized FIB conditions to make a sharp flat edge should be explored for more precise control of the angle.

V_e's in Table 1 were sufficiently lower than 3 kV, thus it can be said that these emissions were taken from MWNTs but not tungsten needles. As shown by Table 1, there is no strong relation between V_e and ℓ nor r. This means the extraction voltage slightly depends on macroscopic form factor but on microscopic diameter and apex structure of nanotubes. V_e values except for the emitter #b1 are almost 1 kV, while it is twice as high for the emitter #b1. It is well known that emission current strongly depends on adsorbate on a CNT tip. Although emitters were heated for cleaning before having an emission, it is considered that some kind of impurity substance remained on the tip surface of #b1 emitter, which caused increase in extraction voltage.

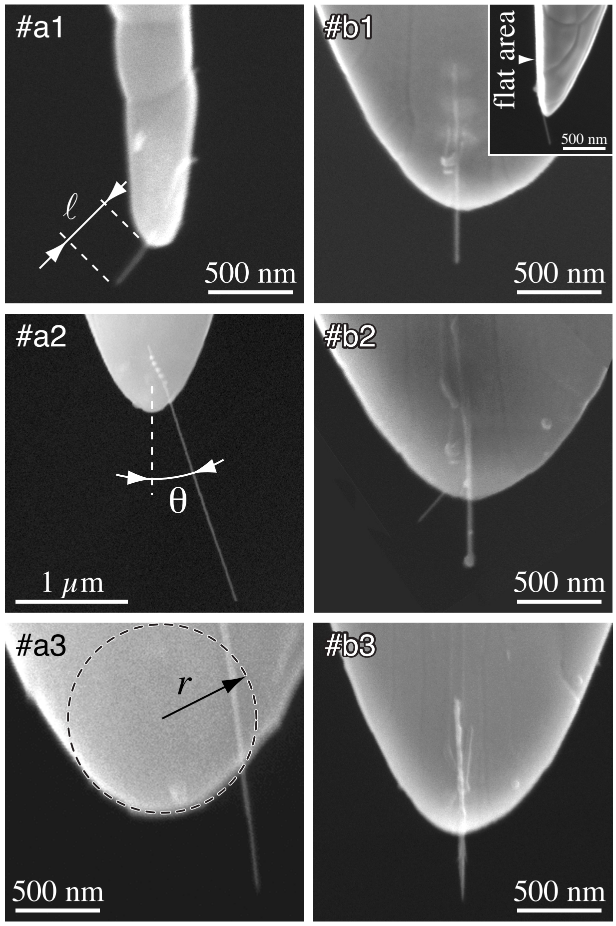

Figure 3: SEM images of MWNT emitters prepared by nano manipulation method. Emitters #a1 to #a3 use as etched tungsten needles, and emitters #b1 to #b3 use FIB processed needles. An inset figure in #b1 is a side view of the emitter.

Fig. 4 shows emission current stability of the emitter #a3. As shown in the figure, emission current has several step like fluctuations, but it keeps constant most of the time These step like change is due to adsorption/desorption of residual molecules, which is inevitable in a cold FE emitter. Emission stability (step fluctuations were excluded) was calculated as $< 1\%$ which is sufficiently stable for a SEM application. Usually, a normal tungsten cold emitter shows gradual decay in emission current. In case of a tungsten emitter, molecules adsorbed on the tip surface is hardly removed unless a flashing treatment is applied. This causes the decay in the current and periodical flashing (every several hours) is required. To prevent emission decay and frequent flashing procedure, recent FE-SEM uses thermal FE or Schottky emission

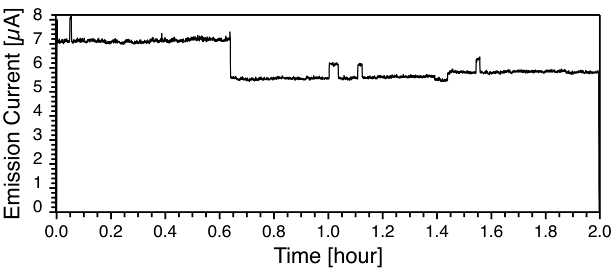

Figure 4: Emission current stability of emitter #a3 for two hours. The extraction voltage was kept constant during this measurement.

with tip heating at 800-1500 °C. In contrast, a MWNT emitter maintains its current without heating. It is reported that a CNT during field emission is heated by its emission current[2–4]. Purcell et al.[2] measured an apex temperature of a field emitting MWNT with a diameter of 30 nm and a length of 40 μm at emission current of 1 μA, and the result is that the temperature reaches almost 2000 K. Vincent et al.[3] reported that temperature raise ΔT for emission current of I_e can be written as:

$$\Delta T = \frac{\rho}{2\kappa}\frac{\ell^2 I_e^2}{\pi^2 (d/2)^4} \quad (1)$$

here ρ, κ and d are a resistivity, a thermal conductivity and a diameter of a MWNT. ℓ is as same as in Table 1. Using this equation to simulate our experiment ($\ell = 0.7$ μm, $d = 20$ nm and $I_e = 7$ μA for the emitter #a3), $\Delta T = 130$ °C. Therefore, it is considered that CNT heating effect is relatively small in our case. Another cause to enhance molecular desorption is small adhesive energy between molecules and a MWNT. In an ultra-high vacuum chamber, major residual gas molecules are hydrogen, carbon monoxide and water. It is known that a metal surface is rather active to these molecules than a graphite surface. Thus molecules adsorbed on the MWNT tip quickly re-evaporates, which results in constant emission.

As described above, emission currents from MWNTs have been successfully obtained. The next hurdle for electron gun application is beam alignment. An electron beam emitted from an emitter should be pass through several apertures. In our FE-SEM, two of them (an extractor electrode and an anode electrode) are fixed and other two (a beam monitor and an objective aperture) are adjustable. The emitter position relative to the extractor is also adjustable. Unfortunately, only the emitters #a2 and #a3 can obtain electron beam at the objective aperture, and others could not be aligned properly within adjustable range. Beam currents at the objective aperture were $\sim$10 nA and $\sim$1 nA for respective emitters of #a2 and #a3. The emitter #a3 works stably at least tens of hours, the emitter #a2 is under a life time test. As explained above, FIB processed emitter (#b1-#b3) has smaller mounting angle than etched ones (#a1-#a3), but it was not very helpful for beam alignment. At this moment this reason is unclear, however,

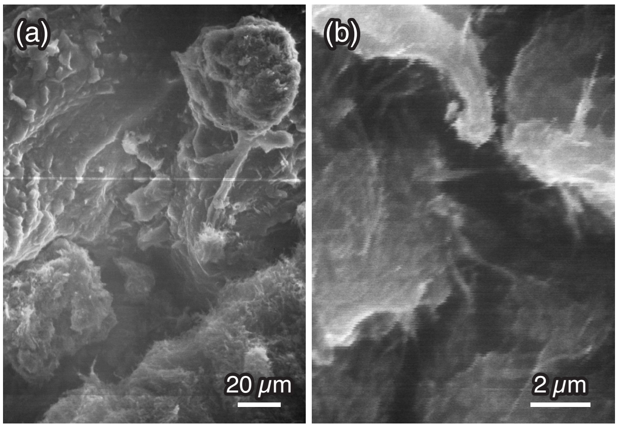

Figure 5: FE-SEM images taken by the emitter #a2. The specimen was a bundle of MWNTs. (a) and (b) were taken at different magnifications.

there are two possible causes. One is a disturbance in symmetry of electric field around an MWNT emitter caused by asymmetric shape of a tungsten tip. The other possibility is the cap structure of the MWNT. An apex of MWNT has 6 five-membered-ring structures but there are many kinds of configurations of those structures[5]. It is considered that a five-membered-ring should be placed on the CNT axis to obtain an electron beam on axis, thus cap structure control is also important as well as mounting angle control of MWNTs.

Fig. 5 shows FE-SEM images obtained by the emitter #a2. Although beam fluctuation cancellation is turned off, there are few noise lines in the obtained image, which proves the emitter stability is practical level. Although these images are very primitive results and not taken under optimized conditions, its image resolution is same order as that taken by a single crystalline tungsten emitter. In the magnified image (Fig. 5(b)), vibrating noise is rather prominent. It could be caused by a large MWNT length (2.1 μm), we need to compare with shorter emitters. Anyway, it is very important that a MWNT emitter works for FE-SEM electron source just by replacing a single crystalline tungsten emitter without any modification of the electron gun and the gun control system.

4. Summary

A MWNT emitter was mounted on a commercially available FE-SEM in place of a single crystalline tungsten emitter to investigate its practicalities for a point electron source. Emission current of the MWNT emitter is very stable and keeps constant, so that S/N ratio of images taken without noise reduction is excellent and sufficient for practical use. In contrast, beam alignment is very difficult even if FIB prepared needles are used for mounting base. However, it is proved that the MWNT emitter can be used as a replacement of a single crystalline tungsten emitter without any modification of an existing FE electron gun and its control system.

Acknowledgements

Authors wish to acknowledge financial supports from the Ministry of Education, Culture, Sports, Science and Technology Japan (Grants-in-Aids for Scientific Research on Priority Areas, 19054007).

References

[1] H. Nakahara, Y. Kusano, T. Kono and Y. Saito: Appl. Surf. Sci. **256** (2009) 1214.

[2] S. T. Purcell, P. Vincent, C. Journet and V. T. Binh: Phys. Rev. Lett. **88** (2002) 105502.

[3] P. Vincent, S. T. Purcell, C. Journet and V. T. Binh: Phys. Rev. B **66** (2002) 075406.

[4] W. Wei, Y. Liu, Y. Wei, K. Jiang, L.-M. Peng and S. Fan: Nano Lett. **7** (2007) 64.

[5] Y. Saito, K. Hata and T. Murata: Jpn. J. Appl. Phys. **39** (2000) L271.