Field electron emission from single carbon nanorod fabricated by electron beam induced deposition

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Abstract. Individual carbon nanorod was fabricated on a tungsten needle tip by electron beam induced deposition. Precursor was phenanthrene (C4H10) and deposition experiment was done using a scanning electron microscope at room temperature. Tungsten needle tip together with the as-deposited nanorod was mounted inside a specially designed transmission electron microscope (TEM) specimen holder and its field electron emission properties were investigated in situ. Relationship between micro-structure and emission property of the nanorod was established. It was found that the surface structure at the top of nanorod, such as a small protrusion within only several nanometers scale, has significant influence on the field emission property. An emission current of several tens of nano-ampere flowing through this nanorod could induce resistance heating. In several minutes, this thermal energy could transform the original amorphous carbon into a graphite-like structure embedded with fullerenes. The turn-on voltage of the graphite-like nanorod was about 11 V less than that of the original amorphous case.

1. Introduction

Field electron emission from carbon nanotubes (CNTs) or other one-dimensional materials have been attracting much scientific and technological interest, because these one-dimensional nanomaterials are a type of promising field emission source. [1-8] The advantages of one-dimensional nanomaterials are their nanometer scale and high aspect ratio, so that they can be used as suitable field emitter or display device unit. Bonard et al. [2] reported the tuning of field emission properties of carbon nanotube film by controlling the density of nanotubes, inter-electrode distance, and tube radius. Their results indicated that low density film could generate high emission field and only small part of nanotubes contributes to the emitted current. Peng et al. [8] studied the field emission and structure damage of individual carbon nanotubes inside a transmission electron microscope (TEM). This structure damage is due to emission current heating through the outside graphite layers or strong electrostatic force. To control the shape and composition of the field emitter is an important issue. Electron beam induced deposition (EBID) is an excellent method to fabricate nanostructures with complicated geometries at desirable positions. The merits of EBID include fine fabrication resolution, flexibility in substrate
selectivity, and easily writing three-dimensional structures in a nanometer scale [9-10]. Recently, our group successfully fabricated nano-structures with desired shape by EBID technique [11-13].

In this investigation, EBID was applied to fabricate single free-standing nanorod at the apex of a tungsten needle along its axis direction. A specially designed TEM sample stage was used to measure the field emission property of the nanorod. Work function affects emission current of the nanorod, so that the precursor used for deposition could be selectively changed. In this experiment, phenanthrene was used to make carbon deposition. The field emission property of nanorod by other types of precursor will be addressed. [14] Our data shows that an emission current with only several tens of nano-ampere can effectively modify the structure of the original amorphous carbon nanorod and improve its field emission property. The maximum emission current was increased and the turn-on voltage was reduced.

2. Experimental procedure
In a typical deposition routine, one single nanorod was fabricated at the tip of a tungsten needle by EBID technique inside the chamber of a field-emission-gun scanning electron microscope (SEM, JSM-6700F) at room temperature. The working voltage of the JSM-6700F was 30 kV and the beam current used to make deposition was 0.8 nA. This microscope has a custom-made gas introduction system, which was composed of variable leak valves, a gas nozzle and a precursor reservoir. The partial pressure of precursor gas is about $1 \times 10^{-4}$ Pa for deposition. The precursor was heated to be 55 °C in this experiment to increase the gas flow rate. The nozzle end was located at a position about 1 mm away from the tungsten needle surface. After deposition, the structure and field emission property of the nanorod were investigated using a JEOL JEM-3000F field-emission-gun TEM operated at 300 kV.

3. Results and discussion

3.1.1. Fabrication of single nanorod at the tip of tungsten needle
Figure 1(a) is a SEM image showing a tungsten needle tip. Tungsten needle tip is conventionally used as a substrate to support emitter. The tungsten needle tip was etched by a standard electro-chemical process in NaOH aqueous solution. Deposition experiment was done at the apex of the tungsten needle. To make a self-standing nanorod, electron beam was scanned from the apex point of this tungsten needle and then moved away from the tip into vacuum space. Direction of beam scanning is parallel to the needle axis. A constant beam scanning speed (~6 nm/s) was maintained by a computer controlled scan generator. Energy of electron beam (30 kV) is enough to dissociate the molecule bonding of precursor gas, which was adsorbed at the surface of the tungsten needle. Gas molecules decomposed into volatile and nonvolatile parts. Therefore, nonvolatile component accumulates to form nanorod deposit, while the volatile component was pumped away. Detail of this deposition procedure can be found from Ref. [9-13]. Figure 1(b) is a low-magnification TEM image showing a carbon nanorod grown at the apex of a tungsten needle, as marked in this photo. This nanorod is around 300 nm in length and 25 nm in width. The aspect ratio is ~12, which is suitable to field emitter. The bottom part shown in Fig. 1(b) is an emission anode used to receive the emitted electron. This metallic anode was made of Mo plate and thinned by focused-ion-beam method. Both the tungsten needle and the Mo anode were mounted inside a specially made TEM sample holder for field emission measurement. Figure 1(c) shows the working principle of this holder. A tip stage was built inside the holder body. The alignment and movement of this tip were carried out via a stepping motor and a pizeo-driving device.

3.1.2. Field emission performance of carbon nanorod
Based on the experiments and equipments mentioned in the above section, field emission property of a single carbon nanorod was evaluated. The dependence of field emission characteristics on the structure of nanorod was correlated in detail.
Figure 2(a) is a TEM image showing a single carbon nanorod attached to a tungsten needle, which was moved to face a flat Mo electrode. The distance between the needle apex and the surface of Mo anode is about 420 nm. Thus, the strength of the mean electric field between electrodes can be approximately estimated via dividing the applied voltage by this distance value, which is between 0.12 ~ 0.19 V/nm (corresponding to an applied voltage of 50 ~ 80 V). Figure 2(b) is a high-resolution TEM image showing that the nanorod is actually a type of amorphous structure. A small protrusion was found on the tip. Both length and width of this protrusion are less than 10 nm. After a voltage was applied between the electrodes, this protrusion was destroyed and became smaller and finally disappeared, leaving a flat top surface at the outmost surface of this nanorod. Later we will show the significant influence of the existence of this small protrusion on the field emission performance.

*Figure 1.* (a) A scanning electron micrograph of a W needle tip. (b) An as-deposited nanorod attached with the W needle facing Mo anode. (c) Schematic drawing of the head part of a specially designed TEM sample holder.

*Figure 2.* (a) Low-magnification TEM image showing two electrodes. (b) High-resolution TEM image of the nanorod top. Four captured TEM images of the nanorod after different times of emission current flow: (c) 10, (d) 60, (e) 120, and (f) 660 s. Small protrusion was marked by the arrows.

Shown in Figs. 2(c)-2(f) are four captured images corresponding to the nanorod at different times of applying voltage: 10, 60, 120, and 660 s. The applied voltage means the voltage difference between the nanorod cathode and the Mo anode. In this experiment, values of the applied voltage are in the range from 0 V to 90 V. With the time increasing, the geometrical morphology of the nanorod changed evidently and the original amorphous carbon was transformed into graphite-like structure progressively, induced by the emission current. The most striking feature is the removal of the small
protrusion and a new flat top was left there. Moreover, many fullerenes were formed at the outside surface of the nanorod. The diameter of these fullerenes ranges from 0.5 nm to 2.5 nm, which possibly contribute to field emission. [17,18]

Figure 3(a) shows the dependence of emission current on the applied voltage (I-V relationships) measured from the nanorod. Three curves correspond to the nanorod at different times of applying voltage: 10, 60, 120 s and their structures correspond to Figs. 2(c), 2(d) and 2(e), respectively. Figure 3(b) shows the I-V curve of the nanorod at 660 s of applying voltage, at which time the structure already became a graphite-like nanorod embedded with some fullerenes. From Fig. 3(b), the nanorod can endure an emission current of around 1.5 µA, ~40 times larger than that of the nanorod shown in Fig. 3(a). It can be concluded that after a 600 s of current flow, the emission property of this nanorod was improved.

Figure 3. I-V curves for Fig. 2(c)-(f), corresponding to the three curves in (a) and (b).

To analyze the I-V data, Fowler-Nordheim (F-N) plots were drawn, as shown in Fig. 4. Considering image charge correction using the approximation by Spindt et al [15], F-N equation can be written as: $I = A(F^2 / \phi) \exp(9.84 / \sqrt{\phi}) \exp(-6.49 \times 10^9 \phi^{3/2} / F)$, where $A$ is a constant and $\phi$ is the work function. In the case of carbon nanorod, it is reasonable to assume $\phi$ is ~5 eV. $F$ is the local electric field strength, which is associated with applied voltage $V$ by $F=\beta V$. $\beta$ is defined as field enhancement factor. Approximately speaking, $\beta$ is a geometric factor relating the voltage to the local field at the emitting tip. F-N plots could be drawn as a relationship between $\ln(I/V^2)$ and $1/V$.

The $\beta$ values can be computed using the expression as $\beta=-6.49 \times 10^9 \phi^{3/2}/S$, where $S$ is the slope of F-N plot and $\phi$ is the work function of nanorod [7,14]. It was found from Fig. 4 that all the F-N plots can be basically fitted by straight lines, i.e., $\ln(I/V^2) = a - b(1/V))$. Therefore, the measured current really resulted from field emission and this electron emission follows F-N equations. It should be mentioned that after the removal of the small protrusion, the turn-on voltage of this nanorod decreases from about 62 V to 51 V. The maximum current the nanorod can endure was increased from $4 \times 10^{-8}$ to $1.5 \times 10^{-6}$ A, i.e., ~40 times more than before.

To compute the absolute values of $\beta$ is not quite physically meaningful in our case, because nanorod cannot obey well the assumptions required by Fowler-Nordheim formula. [16] Moreover, the detail shape of nanorod surface is not geometrically simple due to the small protrusion. In fact, it should be physically more meaningful to compare the field enhancement factor among the nanorods themselves.

It was calculated from Fig. 4 that, the slope values of the nanorod at 10, 60, 120, and 660 s of applying voltage were 567, 534, 498 and 390 respectively. Thus, if the field enhancement factor of the nanorod at 660 s of applying voltage was assumed to be $\beta_0$, the field enhancement factors of the other three cases were computed to be as $0.66\beta_0$, $0.70\beta_0$, and $0.78\beta_0$ respectively. In the measured range, with the time of the applied voltage increasing, the field enhancement factor becomes larger and larger.
The maximum value of $\beta$ happens at 660 s of applying voltage. The formation of fullerenes and the removal of small protrusion might be the reason of this improvement of field emission property.

![Figure 4](image-url). F-N plots calculated by the data shown in Fig. 3 (c)-(f).

4. Summary
To summarize, individual carbon nanorod was deposited at the apex of tungsten needle tip and the field emission property of this nanorod was investigated via a specially designed pizeo-driving TEM sample holder. After applying a voltage for several minutes, the original amorphous carbon could be transformed into graphite-like structure. At the same time, the geometrical shape of the top surface of this nanorod was changed to be a flat one, instead of with a small protrusion. After the transformation of the shape and micro-structure, the field emission property of the nanorod was improved.

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