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Fabrication and characteristics of field emitter using carbon nanotubes directly grown by thermal chemical vapor deposition

Yoon-Taek Jang[a], Chang-Hoon Choi[a], Byeong-Kwon Ju[a], Jin-Ho Ahn[b], Yun-Hi Lee[c,]*

[a]*Microsystem Res. Ctr., Korea Institute of Science and Technology, Seoul, South Korea*
[b]*Department of Materials Science and Engineering, Hanyang University, Seoul, South Korea*
[c]*Department of Physics, Korea University, Seoul, South Korea*

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Abstract

We experimentally present the effects of vertical alignment and density of carbon nanotubes on the emission current level. For practical display application, we have fabricated the triode type emitter using directly grown nanotubes as emission tip, and characterized their basic field emission properties. The triode type emitter exhibited a turn-on voltage of 37 V and an anode current density of 1.7 μA with gate voltage at 47 V. The vertical alignment of nanotubes does not play a key role in improving the emission properties in triode type nanotubes emitter.

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Keywords: Carbon nanotube; Triode type emitter; Field emission; Vertical alignment

1. Introduction

Recently carbon nanotubes (CNTs) have attracted considerable interest because of their unique physical properties and many potential applications [1,2]. Especially, due to their extreme aspect ratios, CNTs emitter feature large local field enhancement and thus yield considerable field emission currents at relatively low applied voltages. One of key contributing factors to stability of CNTs as a field emitter is the lack of surface oxide formation. Surface oxide formation on metal emitter impedes electron transfer to the surface and is a cause for field emitter catastrophic destruction by trapping charge, which could lead to arcing. Therefore, CNTs have a strong potential to be applied to field emitters [3,4]. There are two streams of fabrication process for the CNTs field emitter so far. One is to the thick-film printing, and the other is to directly grow the CNTs into gated holes. The thick-film printing process is mainly used for large area displays because of being limited to reduce pixel size and device size. Then, the triode type emitter using CNTs directly grown into triode type holes is advantageous for small area electron source, such as microwave generator and micro display [5,6]. The biggest difficulties in demonstrating successful fabrication of triode type emitter using CNTs are the precisely controlled selective growth of CNTs within triode type holes and the vertically aligned growth of nanotubes [7–11].

In this paper, we present the fabrication and field emission properties of field emitter using multi-walled CNTs directly grown by thermal CVD, and also discuss the need for vertical aligning of CNTs in triode type emitter applications.

2. Experimental details

Fig. 1 shows the schematic diagram for fabrication of the triode CNTs-emitter. The details of our process are as follows. After sequentially growing 1 μm-thick thermal oxide and sputtered gate metal (Cr or Nb) on a highly doped silicon substrate, the gate aperture of 1–2

*Corresponding author. Tel.: +82-2-2290-3108.
E-mail addresses: yh-lee@korea.ac.kr (Y.-H. Lee), ytjang@kist.re.kr (Y.-T. Jang).

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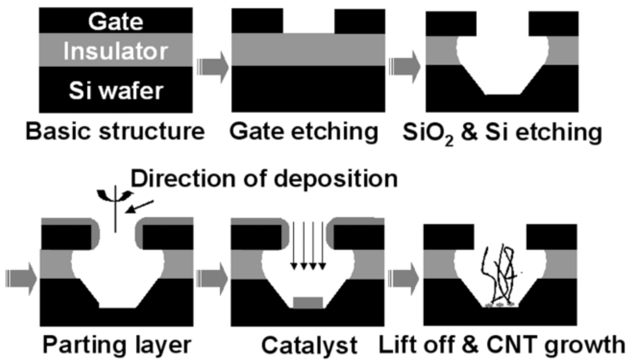

Fig. 1. Process flow of triode type emitter using directly grown CNTs as emitter tips.

μm in diameter is defined by photolithography. The gate metal was removed by reactive ion etching, followed by SiO_2 and silicon substrate etched by dipping in buffered oxide etchant and tetra methyl ammonium hydroxide. Then, Al sacrificial layer was deposited by electron beam evaporation during the deposition. The substrate was rotated and tilted about an axis perpendicular to the substrate surface. Thin layer of 10–20 nm-thick cobalt was evaporated as the catalyst metal into the holes. After the parting layer was removed, the specimens were placed into the quartz reactor for growing CNTs and were pumped down to less than $\sim 10^{-3}$ Torr using a mechanical pump. The substrate was then heated to a synthesis temperature while introducing Ar and H_2 with a flow rate of 70 and 80 sccm, respectively. The synthesis temperature and pressure were approximately 750 °C and 50 Torr, respectively. When temperature and pressure were stabilized, NH_3 gas instead of H_2 was introduced for 10 min. C_2H_2 gas was then introduced with a flow rate of 5 sccm. The samples were then cooled in Ar and H_2 flow ambient. To investigate CNTs and emitter structure, high resolution scanning electron microscopy (SEM) were used. The field emission characterization was carried out in a high vacuum chamber (base pressure 10^{-7} Torr) equipped with cathode, gate, and anode probes. A Keithley 237 source measure unit was used for sourcing the voltage and measuring the current.

3. Results and discussion

We observed the field emission properties of CNTs before fabricating the triode type emitter using CNTs. Fig. 2a and b show a typical SEM image of vertically aligned and non-aligned CNTs, respectively. The nanotubes are with outer diameter range from 20 to 30 nm. According to change the ambient gas in reaction chamber and pretreatment conditions of catalytic metal, the alignment of nanotubes was roughly controlled. For example, vertical alignment of nanotubes is affected by NH_3 pretreatment that prohibited the deactivation of the catalyst before the growth of nanotubes [12]. Fig. 2c shows emission current density vs. applied electric field characteristics for a typical diode structure corresponding to Fig. 2a and b. For I–V characteristics, an anode was placed directly above the CNTs using a 200 μm-thick spacer. The emission current density of non-aligned CNTs is lower than that of aligned CNTs, while maintaining a higher turn-on field. The field emission currents of 4.2 and 2.6 mA/cm^2 were obtained at a field of 3 V/μm, respectively. However these results can explain that randomly distributed CNTs still have impressive field emission capabilities. The insert of Fig. 2c shows Fowler–Nordheim (F–N) plots. We observed nearly straight lines to indicate F–N behavior: $I \propto aE^2 \exp(-b/E)$, where a and b are constant and E is the electrical field strength at emitting point. The slopes of F–N plots were out of all relation to alignment. From this fact we deduce that the local field conversion factors at the emitting surface are similar [13].

Fig. 3a shows the field emission properties of vertically aligned and non-aligned CNTs according to growth time. In general, the length of the CNTs increases but the density of CNTs is almost unchanged with the growth time. The emission current of aligned CNTs slightly increased but that of non-aligned CNTs dramatically increased with growth time. The rate of increase

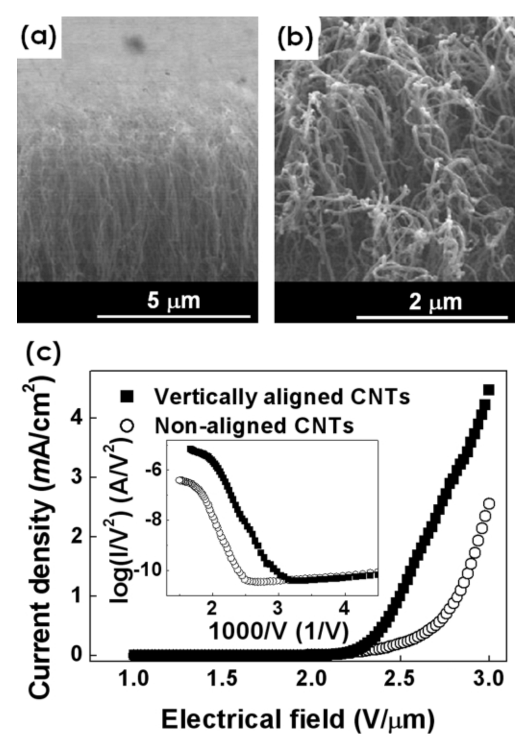

Fig. 2. SEM images of (a) vertically aligned nanotubes and (b) non-aligned nanotubes film grown on silicon substrate. (c) Field emission current density vs. electrical field according to alignment of nanotubes. The insert shows F–N plots for typical diode structure.

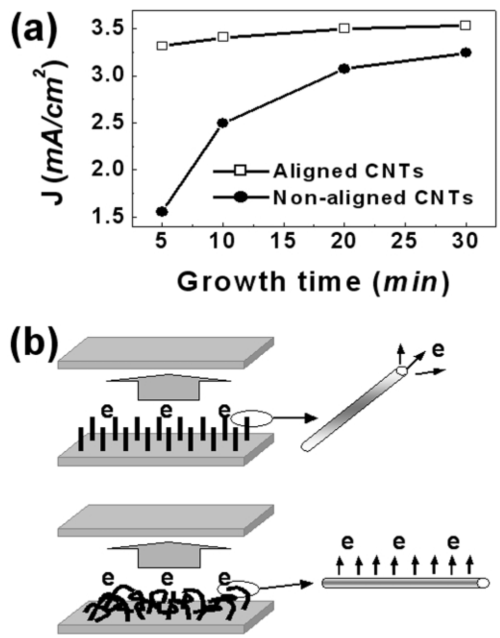

Fig. 3. (a) The emission current density of vertically aligned and non-aligned CNTs according to growth time. (b) The schematic diagram of the emission site according to the alignment of CNTs.

in emission current is decreased with the saturation of CNTs' length without regard to alignment of CNTs. The above experimental results indicate that dominant emission site varies with alignment of CNTs and that the length of CNTs is not important for emitter applications using vertically aligned CNTs. Fig. 3b shows the schematic diagram of the emission site according to the alignment of CNTs. In vertically aligned CNTs, the tip emission is dominant. Therefore the length of CNTs does not play a key role in improving the emission properties because number of emission site is not changed. On the other hand, in non-aligned CNTs, the body emission is dominant. The electron emission under DC field could come from the whole body of the CNTs behaving as a nanowire conductor. Therefore, the length of CNTs is concerned with emission properties due to increases of the emission site.

We synthesized CNTs with different densities for observing the effect of CNTs density on field emission properties in diode structure. Fig. 4a and b show a typical SEM image of vertically aligned nanotubes with higher density and lower density, respectively. The length of CNTs was approximately 5 μm catalytic metal should be generally prepared in the forms of nanocrystalline by heat treatments or chemical etchings before nanotubes growth. The density of CNTs was controlled by changing the distributions of catalyst nanodot. Fig. 4c shows typical emission properties according to density. The emission current density of the CNTs with lower density is higher than that of the dense nanotubes. The lower emission current density for the dense CNTs suggest probably that the efficient electron emission require balance between the field enhancement at the individual CNT and available electronic states and tube-to-tube interaction by the way of spacing between tubes. The typical example is the electric field screening effect of the surrounding conductive CNTs of different heights. Therefore, it is very important to control density and length of CNTs in order to minimize the local electrical field screening [14].

Fig. 5a–c are the SEM images of CNTs grown on Co microdot at 750 °C for 1 min under the mixture of C_2H_2, NH_3 and Ar. The corresponding thickness of the Co layer is 10, 15, 20 nm in images (a), (b) and (c), respectively. CNTs were laid down and non-aligned perpendicular to the substrate when we deposited 10 and 20 nm-thick catalytic metal. CNTs were too thin to vertically align when thickness of catalyst was below 10 nm in our experiments. In case of thickness of 15 nm, CNTs were freestanding without disturbing neighboring CNTs bundles at each patterned dot. There was difference between thin film and microdot in alignment of CNTs because the morphology of patterned dot was

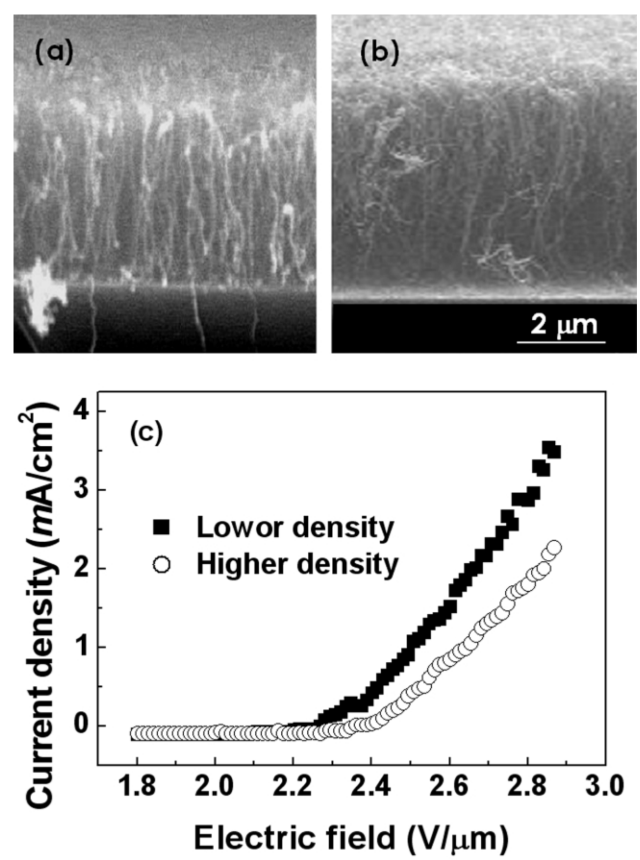

Fig. 4. Cross-sectional view of vertically aligned nanotubes with (a) high density and (b) low density. (c) Field emission current density vs. electrical field according to density. The insert shows F–N plots for typical diode structure.

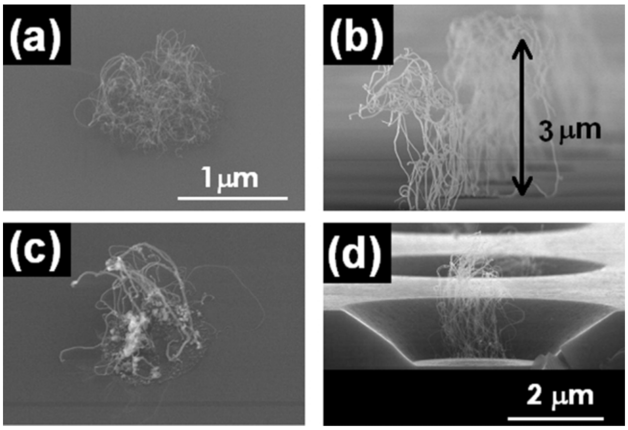

Fig. 5. The SEM images of CNTs directly grown on Co dot. Thickness of Co layer is (a) 10 nm; (b) 15 nm; (c) 20 nm; and (d) CNTs vertically grown in micro-hole.

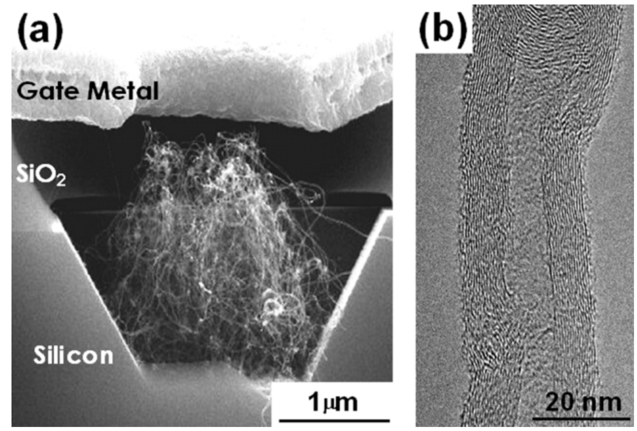

Fig. 6. (a) The cross-sectional view of fabricated triode emitter using CNTs directly grown on Co nanodots with original film thickness of 15 nm and (b) TEM image of vertically grown CNTs.

earlier changed than that of thin film. We have repeatedly tried trial and error process and then, successfully grown vertically aligned CNTs in the center of a hole without gate as shown in Fig. 5d. The end of CNTs was slightly bended because the CNT is freestanding without leaning against neighboring CNT bundles. We have not yet perfectly prevented the end of CNT from bending.

Fig. 6a shows the cross-sectional images of the emitter viewed from different angles. CNTs were well located at the center of holes. The gate aperture is 1.5 μm in diameter and the hole depth is approximately 2.5 μm. The CNTs are multi-wall CNTs with outer diameter range from 20 to 30 nm and consists of hollow compartments, looking like a bamboo, as shown in Fig. 6b. There is small hole-to-hole disparity in the density and length of CNTs but it is not a problem on only CNTs emitter. In case of metal tip emitter, we also observed the tip-to-tip disparity in the emission level. To overcome this problem, several techniques have been developed, such as the resistive layer, active-matrix field emitter, and MOSFET controlled emitter. Therefore, small hole-to-hole disparity is not a critical problem for achieving good operation of CNTs emitter if not creates short circuits between cathode and gate.

Fig. 7a shows the current–gate voltage characteristics of triode type CNTs emitter. The anode plate was placed approximately 1 mm from the gate metal and the anode voltage of 700 V was used. The triode type emitter exhibited a turn-on voltage of 37 V and an anode current density of 1.7 μA with gate voltage at 47 V. The emission current of emitter using vertically grown CNTs is similar to that of emitter using non-aligned CNTs as shown in our previous report [7]. The insert of Fig. 7a shows a F–N plot, whose linearity indicates that I–V characteristics are governed by a conventional field emission mechanism, $I \propto V^2 \exp(-6.53\times10^7 \phi^{3/2}/\beta V)$, where ϕ and β are the work function and field enhancement factors of CNT emitters, respectively. The field enhancement factor is calculated to be $\beta = 1.06\times10^6/$

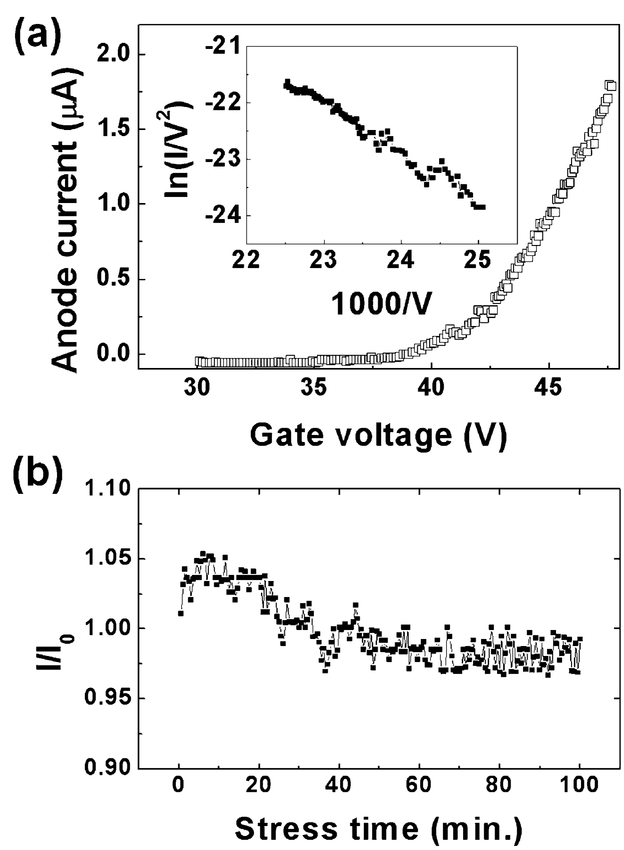

Fig. 7. (a) Field emission current vs. gate voltage, with anode was set at 700 V. The insert shows a Fowler–Nordheim plot of fabricated device; (b) The current fluctuation vs. stress time as the gate voltage is set at 50 V.

cm from the F–N slope of −688.5 under the assumption of a work function of 5 eV for CNTs. Fig. 7b reveals the stability of the emission current. There was little degradation of emission current and, however, no arcing was in the earlier stage. After the short-term aging, the fluctuation was approximately ±10% over 100 min when the gate voltage was set at 50 V.

The above experimental results indicate that the vertical alignment and density of CNTs do not play a key role in improving the emission properties in triode type CNTs emitter because only a few of CNTs per one square micrometer are required for applying directly grown CNTs to vacuum microelectronic devices. The important factors are to control the length of CNTs without overgrowing and modify the structure and materials.

4. Summary

The emission current density of non-aligned CNTs is lower than that of aligned CNTs, while maintaining a higher turn-on field, but both of value are plenty value in emitter applications. The emission current density of the CNTs with lower density is higher than that of the dense nanotubes due to the local electrical field screening. For triode type emitter using directly grown CNTs, the vertical alignment of CNTs does not play a key role in improving the emission properties. In order to realize better functions of the gated CNTs emitter, the modification of emitter structure, long-duration stability, effect of gas flow within holes, and nanotubes-substrate distributions should be investigated in future study.

Acknowledgments

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