Extended Abstracts of the 2004 International Conference on Solid State Devices and Materials, Tokyo, 2004, pp. 338-339

H-3-6

Growth of High-Quality Carbon Nanotubes by Grid-Inserted Plasma-Enhanced Chemical Vapor Deposition for Field Emitters.

Yoshihiro Kojima*, Shigeru Kishimoto, Yutaka Ohno, Takashi Mizutani
Department of Quantum Engineering, Nagoya University, Chikusa-ku, Nagoya, Aichi 464-8603, Japan

Tel: +81-52-789-5230, Fax: +81-52-789-5232, E-mail: yosihi_k@echo.nuee.nagoya-u.ac.jp

Carbon nanotubes (CNTs) have attracted considerable interest in application to electron emitters for field emission display. Among various growth techniques, plasma-enhanced CVD (PECVD) [1,2] seems to be promising because of an advantage of low-temperature growth. However it is very difficult to grow high-quality CNTs with small diameter because of the damages caused by the ion bombardment [3]. In this work, we grew CNTs by grid-inserted PECVD to suppress the ion bombardment damage.

Microwave (2.45 GHz) plasma was used for the nanotube growth. DC bias voltage of 200 V was applied between an anode and a cathode with a distance of 5 cm. A grid was inserted between the anode and the cathode to suppress the ion bombardment damage. The standard grid-cathode distance was 4 mm. CNTs were grown by using mixture of CH_4 and H_2 as a source gas.

Figure 1 shows scanning electron microscopy images of CNTs grown on invar (Ni and Co alloy) at various grid voltages. Even though no CNTs except carbon particles were grown when grid voltage was 0 V, as shown in Fig. 1(a). CNTs with diameters of 10-30 nm were grown at grid voltage of 5 V, as shown in Fig. 1(b). When the grid voltage was 50 V, diameter of CNTs became large as shown in Fig. 1(c). When grid voltage was larger than 50 V, similar SEM images as that of 50 V were obtained. When CNTs were grown without grid, CNT structure was almost same as that grown at grid voltages of 50 V or above as shown in Fig. 1(d). These results indicate that it is important to apply small grid voltage.

The grid voltage dependence of length and density of CNTs are shown in Fig. 2(a). Abrupt change in length and density of CNTs was observed when grid voltage was larger than 50 V. Figure 2(b) shows the distribution of the diameter of CNTs. When grid voltage was smaller than 10 V, most of CNTs have diameters smaller than 30 nm. The ratio of small-diameter CNTs decreased, however, when the grid voltage was larger than 50 V probably due to the etching effect of the ion bombardment. This indicates that damages, which might be introduced during CNT growth by PECVD, were suppressed when grid voltage was less than 50 V. When no grid was inserted, the situation was almost same as that at large grid voltage. Ion bombardment with a large energy occurred because of the electric field above substrate due to plasma sheath. It is notable that no nanotubes were grown at grid voltage of 0 V. Even though the grid is effective in suppressing the ion bombardment damage, a small amount of ion energy is necessary to grow CNTs.

We studied the effect of grid-cathode distance at grid-cathode voltage of 5 V. Optimum grid-cathode distance was 4 mm. When the distance was 1-2 mm, amorphous carbon grew and no CNTs were obtained. When the distance was longer than 6 mm, the diameter of the CNTs was similar to those grown without grid.

In order to study the effect of using thin catalyst, CNTs were grown on 1-nm-thick Co catalyst evaporated on SiO_2/p^+-Si substrate. Figure 3 shows TEM image of CNTs grown at grid voltage of 5 V. The diameter of the CNT was 3 nm having three graphene layers. This is among the smallest. Small-diameter CNTs were grown at grid voltages of 2-10 V, but were not grown when grid voltages was larger than 50 V. The reason why small diameter NTs were not grown at large grid voltages is probably due to that the nanotube caps with small diameter, which played an important role in the first stage of CNT growth, were etched away by ion bombardment.

Field emission characteristics of the CNTs grown on the Co catalyst are shown in Fig. 4. A very low ON voltage of 30 V was obtained. Moreover, two times higher current density was obtained than that grown by PECVD without grid. A dotted line is a calculated result assuming FN tunneling assuming work function of 4.8 eV and diameter of 10 nm of the CNTs. The experimental results are fitted well by the calculated result, indicating that the electron emission is dominated by the FN tunneling.

In summary, we have successfully grown high-quality CNTs with small diameter by PECVD by introducing grid. Field emission characteristics of the CNTs, with low ON voltage and high current density were explained well by the FN tunneling.

References

[1] W. K. Hong, H. C. Shih, S. H. Tsai, C. T. Shu, F. G. Tarntair and H. C. Cheng, Jpn. J. Appl. Phys. **39** (2000) L925.
[2] H. Murakami, M. Hirakawa, C. Tanaka and H. Yamakawa, Appl. Phys. Lett. **76** (2000) 1776.
[3] Yun-Sung Woo, In-Taek Han, Young-Jun Park, Ha-Jin Kim, Jae-Eun Jung, Nae-Sung Lee, Duk-Young Jeon and J. M. Kim, Jpn. J. Appl. Phys. **42** (2003) 1410.

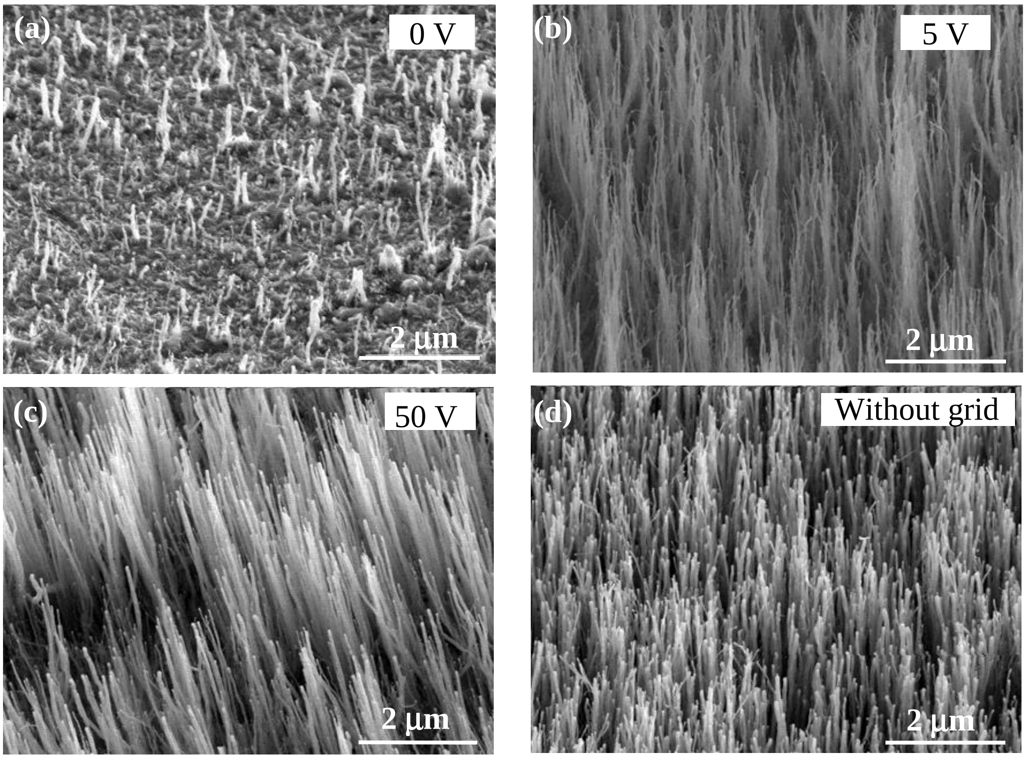

Fig.1. SEM images of CNTs grown by PECVD with various grid voltages; (a) 0 V, (b) 5 V, (c) 50 V, and (d) without grid.

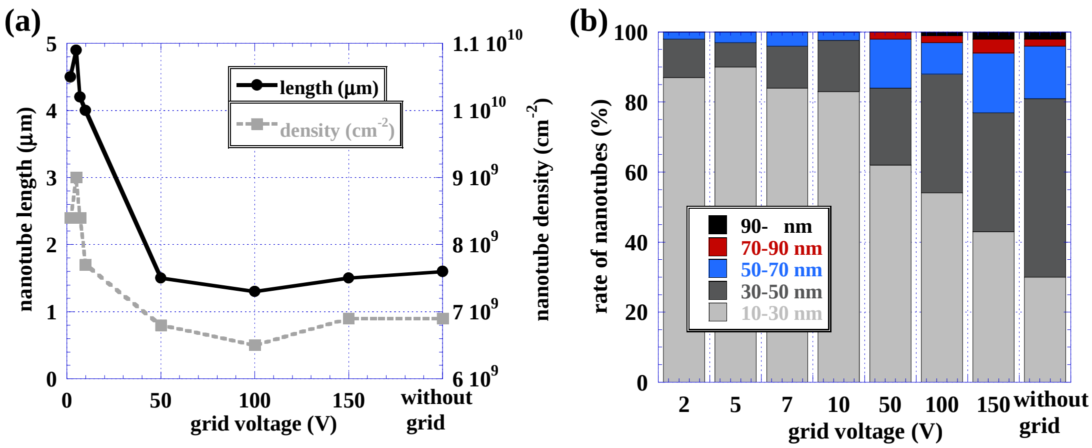

Fig.2. Grid voltage dependence of (a) length and density and (b) diameter distribution.

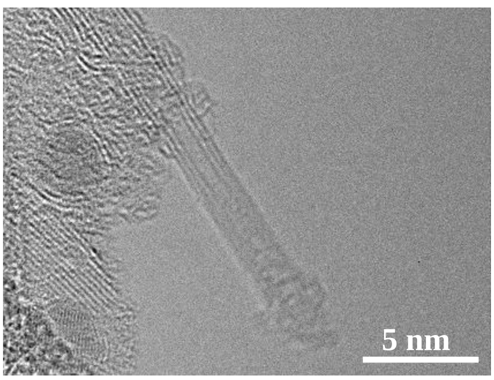

Fig.3. TEM image of CNTs grown on Co catalyst at grid voltage of 5 V.

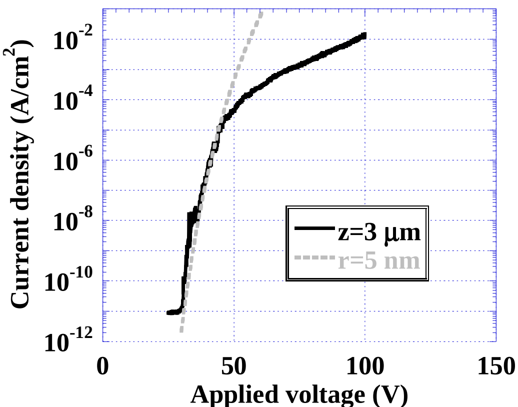

Fig.4. Field emission characteristics of the CNTs grown on the Co catalyst.