Filament discharge enhances field emission properties by making twisted carbon nanofibers stand up

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Abstract. Twisted carbon nanofibers, named carbon nanotwists (CNTws), in a flocculated form were pasted, printed on the conductive silicon substrate, and then treated by dielectric barrier discharge using He and N_2 gases. Vertically upright nanofibers were clearly obtained by "filament discharge mode" in N_2 gas. As the treating time increased up to ~60 s, the height of the nanofiber tips became uniform. Consequently, the field emission property was greatly enhanced and showed a threshold electric field of 4.6 V/μm and maximum current of 0.433 mA/cm^2 at 8 V/μm.

PACS: 52.40.Hf, 81.05.Uw, 81.65.Cf, 85.45.Db

1. Introduction

Recent development of the synthesis of micro- or nanometer-sized carbon tubular and coiled structures has drawn much attention to the application of these materials in electronics [1–3]. Depending on the catalyst and process conditions, each of them can be formed from hydrocarbons in chemical vapor deposition (CVD) [4] and plasma-enhanced CVD [5–7]. We have focused on the formation of helical carbon nanofiber (HCNF) and its application to a field emitter device [8]. HCNF is categorized as either a spring-like helix form (carbon nanocoil, CNC) [9–13] or a twisted form (carbon nanotwist, CNTw) [14–16], depending on the internal diameter. These materials are applicable to field emission display owing to their high aspect ratio and electrical conductivity [12,13,16]. Some techniques for fabrication of field emitter devices, including direct growth [17], screen-printing [18], spraying [19] and electrophoresis [20] are well known. Table 1 shows the drawbacks and advantages of each of these four techniques. Screen-printing and spraying are inexpensive and simple processes with the advantage of large-area treatment. However, HCNF must be made to stand up in the emitter to obtain effective field emission properties.

So far, stand-up treatments including adhesive tape [21], heat treatment [22] and excimer laser irradiation [23] have been reported. Making HCNF stand by adhesive tape application is a simple method, but problems of surface contamination and exfoliation of HCNF from substrate arise. Laser irradiation is extremely expensive even if it is possible to treat a surface uniformly. In heat treatment, available substrates are limited due to high temperature (~400°C). A new way to stand up HCNF and thus overcome the problems and drawbacks previously reported is awaited.

We have synthesized a quantity of CNTw with 100% purity and developed their printed field emitter devices [16]. In this paper, we report a stand-up treatment for vertical nanofiber alignment using a dielectric barrier discharge.

2. Experimental setup

2.1 Fabrication of CNTw emitter

CNTw was synthesized by catalytic chemical vapor deposition (CVD) [15,16]. Briefly, Ni and Sn liquid catalysts (Kojundo Chemical Laboratory Co., Ltd.) were dropped on a graphite substrate and dried at 400°C for 10 min. The catalytic substrate was placed in a CVD chamber and the chamber temperature was raised to 650°C while N_2 gas was introduced at a flow rate of 1400 ml/min. After reaching the reaction temperature, C_2H_2 was introduced at a flow rate of 300 ml/min and CNTw was grown for 10 min. The CNTws grown were mixed with an organic binder composed of ethyl cellulose in a mortar for 30 min and the CNTw paste was made. The mixture ratio by weight of CNTw and binder was 7:93.

The CNTw paste was screen-printed on a Si substrate (n-type, 80 Ω/sq.) measuring 5 mm × 40 mm, and a dot pattern of CNTw film (dot size = 100 μm × 100 μm, spacing = 100 μm) was formed. The CNTw film was calcined in an electric furnace at 120°C for 2 hours or 400°C for 1 hour [22]. The film thickness after the calcination was 3 μm.

2.2 Stand-up treatment

The CNTw emitter was treated by a dielectric barrier discharge apparatus as shown in Fig. 1. A quartz plate was glued on both electrode surfaces and dielectric barrier discharge was generated between the plates [24]. In He gas, the glow discharge was uniformly generated ("glow mode"), whereas filamentary discharge was seen in N_2 ("filament mode"). In this study, both modes were applied to the CNTw emitter. The emitter was placed on the grounded electrode and treated by generating a discharge on the substrate surface (Fig. 2). On the surface treatment, the following conditions were commonly used: the gap distance (distance from the emitter surface to upper electrode) = 1 mm, discharge frequency = 30 kHz, pulse duration = 2.0 μs and gas flow rate = 2000 ml/min. For "glow mode," He gas was used, and an electric field of 4.4 kV/mm was applied for 30 s. On the other hand, N_2 gas was used and an electric field of 6.8 kV/mm was applied for "filament mode." The treatment time was varied from 0 to 180 s. The filaments between the electrodes move randomly while the discharge is sustained. Therefore, it is possible to treat the whole area of the substrate uniformly if the size of substrate is smaller than that of dielectric plate. The surface of the emitter after the treatment was analyzed with a scanning electron microscope (SEM, Hitachi, S-4500). To measure the field emission property, Zn:ZnO phosphor was used as an anode, and the anode area, gap distance and pressure were 0.1 cm^2 (ϕ3.6 mm), 100 mm and 10^{-4} Pa, respectively.

Table 1. Drawbacks and advantages of field emitter fabrication techniques.

Fabrication technique	Advantage	Drawback
Direct growth	Vertically aligned CNTs easily grown	Difficult for large-area treatment
Screen-printing	Good for low-cost large-area treatment	Stand-up treatment necessary
Spraying	Good for large-area treatment	Adhesion and stand-up treatment necessary
Electrophoresis	—	Difficult for large area treatment

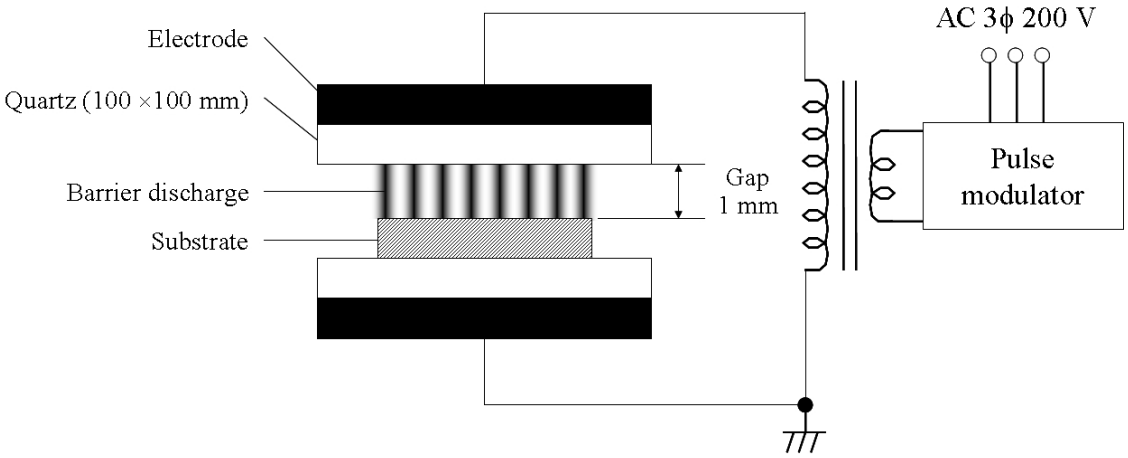

Figure 1. Schematic of dielectric barrier discharge apparatus.

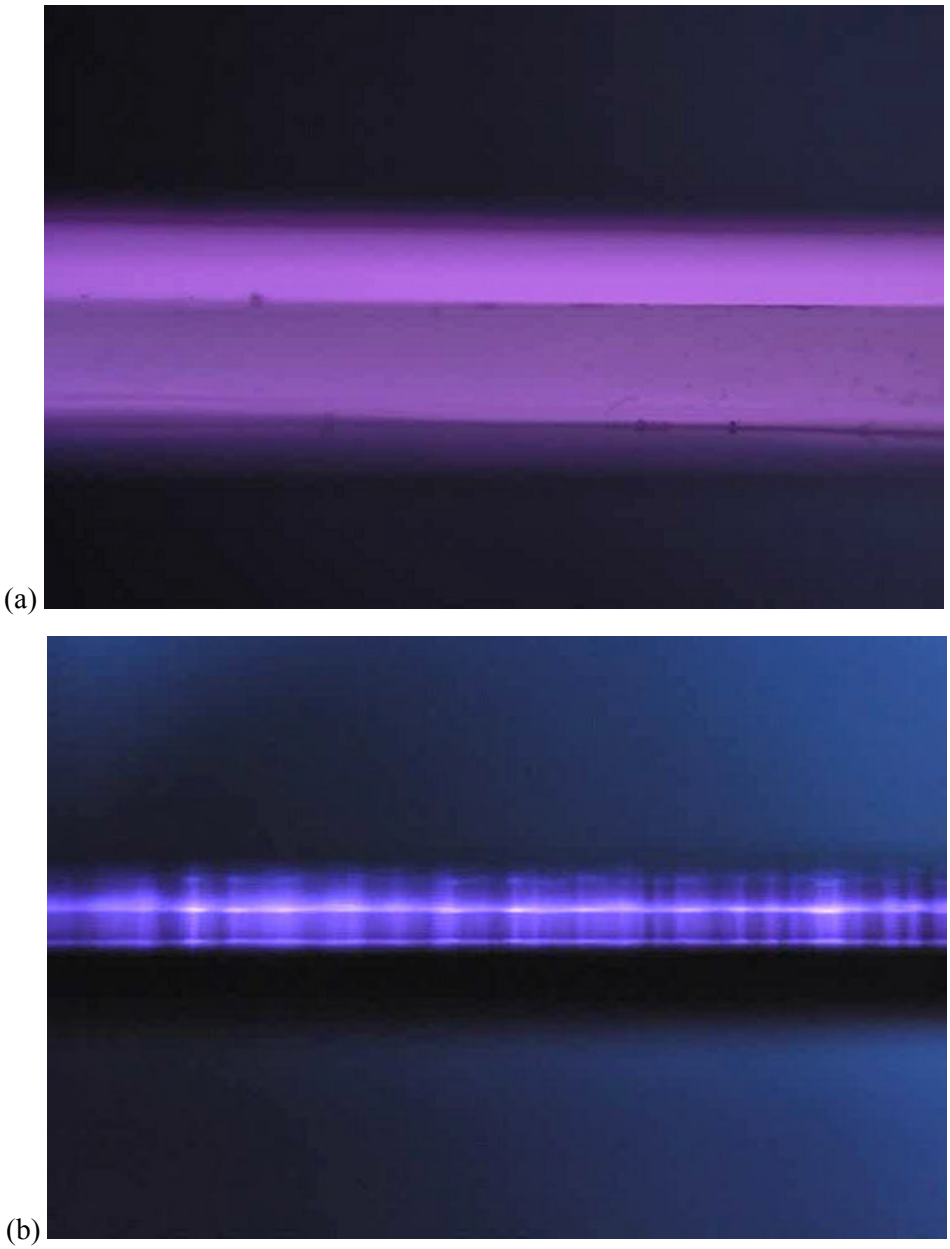

Figure 2. Photographs of stand-up treatment by: (a) “glow mode” and (b) “filament mode.”

3. Results and discussion

3.1 Making CNTws stand up

Fig. 3 shows an SEM micrograph of the emitter treated by "glow mode." The surface does not seem changed by "glow mode" treatment, and CNTws remain tangled and heaped on the substrate. On the other hand, by "filament mode" treatment, the CNTws were made to stand vertically from the substrate as shown in Fig. 4. For a treatment time ≥ 30 s, flocculated CNTws are not seen any more, and it is confirmed that 3 to 5 CNTws are upright at 5-micron intervals on the emitter treated for 30 and 60 s. Their length from the substrate surface became shorter due to etching as the treatment time increased. The great difference in the treatment result between the "glow" and "filament" modes is clearly shown in Figs. 3 and 4. To explain this, the orientation forces applied to CNTws in each mode are illustrated in Fig. 5. The electric field is almost uniform in the vertical direction from the substrate in the "glow mode" (Fig. 5(a)), and Coulomb force:

$$F = qE, \tag{1}$$

where q: electric charge on CNTw; E: electric field, only acts on CNTws. On the other hand, in the "filament mode," a non-uniform electric field is generated between the electrodes, and not only Coulomb force but also gradient force [25]

$$F = \frac{1}{2} grad\left(E^2 \rho_m \frac{\partial \varepsilon}{\partial \rho_m} \right), \tag{2}$$

where ε: permittivity of CNTw; ρ_m: density of CNTw, acts on CNTws in the direction in which the electric field strength is increasing. The gradient force in the "filament mode" is larger than the Coulomb force since the gradient force is proportional to the gradient of the product of permittivity and electric field squared. Consequently, CNTws could be raised by the gradient force in the "filament mode."

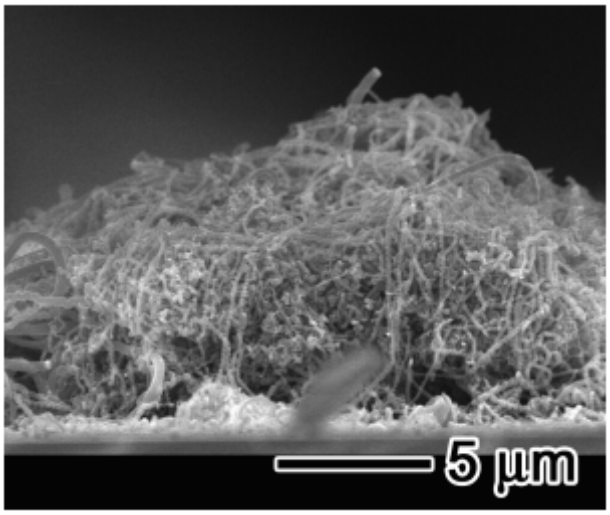

Figure 3. SEM micrographs of emitter treated by "glow mode."

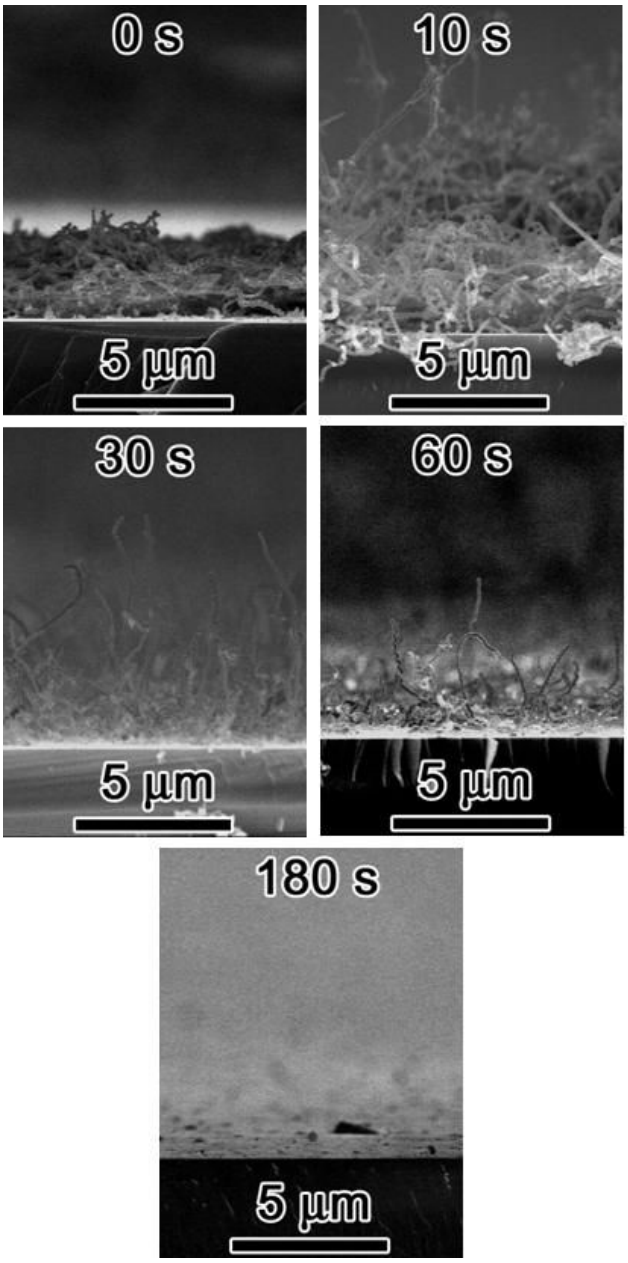

Figure 4. SEM micrographs of emitter treated by "filament mode" at different treatment times.

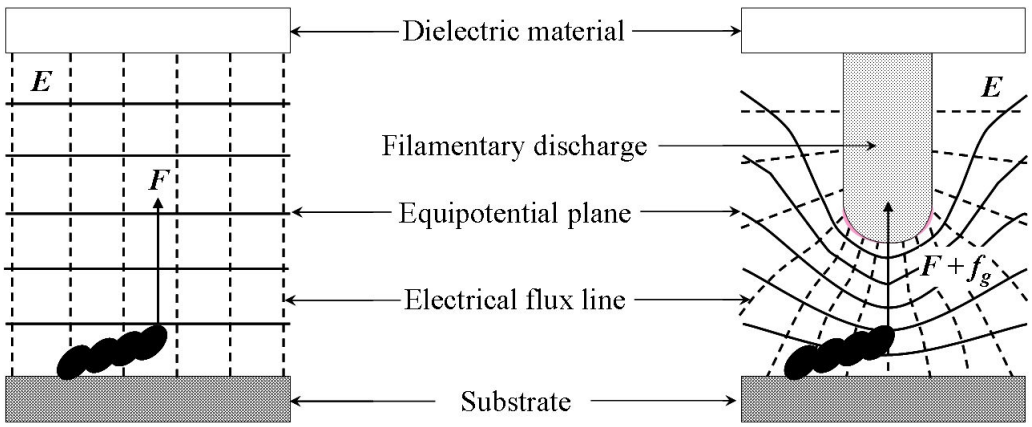

Figure 5. Schematic illustrations of orientation force on CNTw: (a) uniform electric field in "glow mode," (b) non-uniform electric field in "filament mode."

3.2 Field emission property

Fig. 6 shows the field emission properties of the CNTw emitter treated by the "filament mode" and emission pattern at a maximum current. Before the treatment, there were many flocculated CNTws in the emitter and a spark easily occurred at a low electric field. The treatment made the field emission current higher. The field emission properties of the emitter at different treatment times are listed in Table 2. With emitter treatment for 10 s, the emission site is not uniformly distributed as shown in Fig. 6. By the 30-s treatment, the emission is not concentrated but uniformly spread, and the field emission properties are greatly enhanced. The ratio of the emitting area of the sample treated for 30 s to the phosphor surface reached 57% though that of the untreated sample was 2% only. As shown in Table 2, the length of CNTws was also gradually decreased and the distribution of CNTw length was narrowed due to etching with an increase in treatment time. This indicates that the treatment by "filament mode" serves to flatten the emitter tips as well as make them stand up. However, the number of CNTws by the 60-s treatment was decreased and it made the field emission virtually impossible. Field emission did not occur from the 180-s treated emitter because mostly CNTws were removed. We conclude that the optimal treatment time for field emission is 30 s. In this study, the influences of discharge power and frequency on the treatment were not seen. Filament discharge did not occur at an electric field less than 6.8 kV/mm.

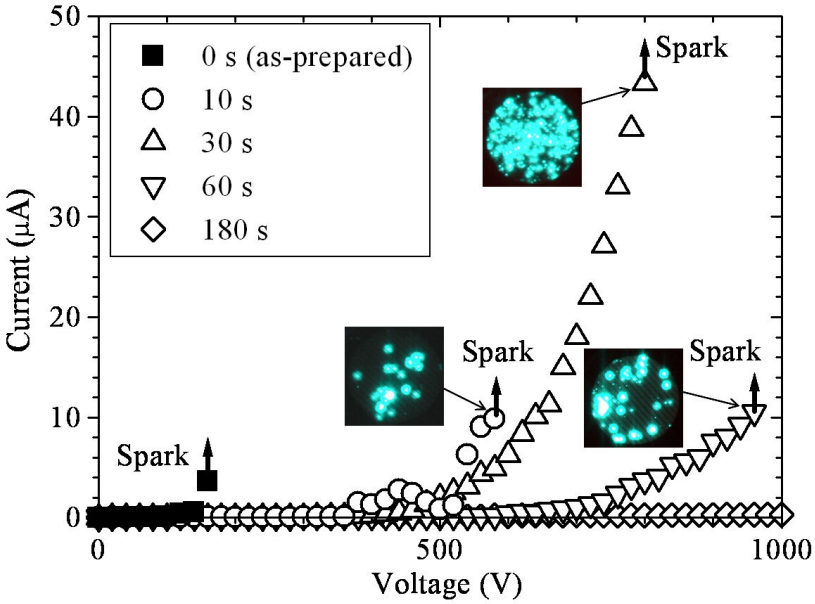

Figure 6. Field emission property of CNTw emitter treated by "filament mode" at different treatment times. Inset photos show the emission pattern from each CNTw emitter.

Table 2. Field emission property of CNTw emitter at different treatment times. As for the untreated CNTws, we measured the length of powdery carbon nanotwists before fabricating the emitter.

Treatment time (s)	Threshold electric field for field emission current = 1 μA (V/μm)	Maximum current density (mA/cm^2)	CNTws length (μm)
0	1.5	0.037 (at 160 V)	5–10
10	5.2	0.098 (at 580 V)	5–10
30	4.6	0.433 (at 800 V)	3.6–5.4
60	7.0	0.105 (at 960 V)	1–3
180	Not measured	0.003 (at 1000 V)	0

Also, we tried to treat the emitters composed of conductive/nonconductive whiskers and thin carbon nanotubes (CNTs) by the "filament mode" and confirmed that the conductive whiskers were made to stand up. The CNTs were easily removed just after the ignition of filament discharge. A possible explanation for this is that the diameter of CNTs used was much thinner (~10 nm) than that of CNTws. Therefore this stand-up treatment by filament discharge would be suitable for thick CNFs. In this filamentary discharge technique, any kinds of polymer may be applied since the binder made of ethylcellulose is almost removed by annealing at 400°C in air to fabricate the field emitter.

4. Conclusions

Dielectric barrier discharge is an inexpensive process capable of making CNFs stand up in a field emitter and flattening its tips. The technique does not produce any surface contamination, is able to treat uniformly in a large area, eliminates thermal deformation because of the room temperature process, and can treat any kind of conductive whisker, substrate and polymer at atmospheric pressure. Since dielectric barrier discharge is also able to process glass substrate, an electron source can be produced at lower cost.

Acknowledgements

This work has been partly supported by the Outstanding Research Project of the Research Center for Future Technology, Toyohashi University of Technology; the Research Project of the Research Center for Future Vehicle, Toyohashi University of Technology; the Research Project of the Venture Business Laboratory, Toyohashi University of Technology; the 21st Century COE Program "Intelligent Human Sensing" and Global COE Program "Frontiers of Intelligent Sensing" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT); The Japan Society for the Promotion of Science (JSPS), Core University Programs (JSPS-KOSEF program in the field of "R&D of Advanced Semiconductor" and JSPS-CAS program in the field of "Plasma and Nuclear Fusion"); and Grant-in-Aid for Young Scientists (B) from MEXT.

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