Transactions of the Materials Research Society of Japan 32[2] 329-332 (2007)

Preparation of Carbon Nanofiber Emitters for Field Emission Display using Organic Thin Films

Masato Yoshikuni*, Shinji Ide, Nobuyuki Iwata and Hiroshi Yamamoto
College of Science & Technology, Nihon University
Funabashi-shi, Chiba 274-8501, Japan
Fax: 81-47-469-5457, e-mail: 2005_yoshikuni@yamanoya.ecs.cst.nihon-u.ac.jp

The purposes of this work are to prepare a low density carbon nanofiber (CNF) emitter by a spray spreading method and to investigate the performance of field emission. A sprayed paste was prepared with organic solution of tetrahydrofuran and also with binders of Au paste and Polycarbonate. The used CNF were massively synthesized by a thermal chemical vapor deposition and were burned to eliminate amorphous carbon and catalyst. The diameter of the CNF was about 0.1 μmϕ. Two types of CNF were studied with the length of *ca.* 10~20 μm (normal-CNF) and *ca.* 1.5 μm (cut-CNF). In the normal-CNF emitter the current density at 10 V/μm was about 1.4mA/cm^2 with an electric field enhancement factor β of about 1000, while 0.08mA/cm^2 with β of 4500 in the cut-CNF emitter. It was confirmed that the isolated CNF do play an important role as effective emitter sites.
Key words: carbon nanofiber (CNF), spray spreading, CNF emitter, field emission properties, Field Emission Display.

1. INTRODUCTION

We have been studying a novel low voltage Field Emission Displays (LV-FED) by using organic luminescence films as a phosphor. A stacking structure of Alq_3/α-NPD/CuPc on ITO substrate was irradiated by thermally activated electrons with the emission current density of *ca.* 1 mA/cm^2 [1,2]. Observed luminescence was, however, quenched quickly. It was found that the quench was caused by an accumulation of electrons at the interface of Alq_3/a-NPD due to insufficient electric field applied in the organic stacking layers. We have expected that the issue will be overcome by adopting carbon nanofiber (CNF) electron emitters to shorten the distance between the electrodes [3]. In this work we tried to prepare CNF emitters which achieve an emission current density of several mA/cm^2.

Recently screen-printing CNT emitter with accumulated many CNT layers have been vigorously developed for application to FED. The efficiency of emission is improved by adjusting a distance between isolated CNT. It was suggested that the optimum density of CNT to apply effectively the electric field is about 1.0×10^7 cm^{-2} in the case of 1 μm-long CNF which are dispersed in the distance of 3 μm [4]. Though a low density CNT emitter is desirable, it is difficult to prepare such an emitter by a conventional screen-printing method. The purpose of this study is to prepare a low density CNF emitter by a spray spreading method. Then the CNF emitter is also on investigated its field emission properties from a point of view of field enhancement factor β and a number of CNF as an emission site.

2. EXPERIMENTAL

We used multi-wall carbon nanofibers (MWCNF) which were massively produced by Showa Denko Co. Ltd. The CNF were typically synthesized from mixed solution of ferrocene, thiophene and benzene by thermal chemical vapor deposition at c.a.1000°C. The obtained CNF were burned out above 2500°C for 30 min to eliminate amorphous carbon and catalysts. The size of the CNF powders was typically about 0.1 μmϕ in a diameter and *ca.* 20 μm in a length (named as normal-CNF). On the other hand the CNF with short length of *ca.* 1.5 μm in a length (named as cut-CNF), which were prepared from

Table 1: The preparation conditions of CNF emitters.

Organic Solvent	THF
CNF powder (wt %.)	Cut or Normal-CNF (0.1)
Dissolution	Sonication for 24 h. Stirring for 30 min. at 70°C
Binder (wt %.)	Au-past (1.0)
Dispersion solvent (wt %)	PC (10)
Deposition by spray	0.1MPa.,400°C
Annealing	Baking at 400°C

the normal-CNF by a fragmentation process, were also used.

The preparation conditions of CNF emitters are summarized in Table 1. CNF were tetrahydrofuran (THF) and sonicated for 24 h. Au paste and polycarbonate (PC) were mixed and stirred for 30 min at 70°C. As binders Au paste was used to increase conductivity [5] and PC to improve distribution of CNF [6]. The CNF paste was loaded into a hand-spray gun and was sprayed with N_2 gas at 0.1 MPa on ITO substrates heated at 400°C. The size of the ITO substrate was 10×20 mm^2. The distance between the substrate and the spray-nozzle was 200 mm. The spray for one second was repeated taking care not to cool the substrate temperature at the set temperature. After spraying specimens were baked at 400℃ for 30 min to remove organic solution in the paste.

A surface morphology of the CNF emitter was observed by scanning electron microscopy (SEM). Measurement of emission current was carried out in a vacuum chamber in 3×10^{-6} Torr at room temperature. The distance between a copper plate (anode) and CNF (cathode) was *ca.* 50 μm. The measured emission area was 5×5 μm^2. The emission current-voltage (I-V) characteristics were analyzed by using the Fowler-Nordheim (F-N) equation for the field emission.

3. RESULTS AND DISCUSSION

Fig. 1 shows the SEM images of CNF films added the binder with two different types of CNF ((a), (b) normal-CNF: (c), (d) cut-CNF)). In Fig. 1(a) bundles of CNF with the size of 30-100 μmϕ were observed, where CNF bundles (i), a binder (ii) and surfaces of ITO substrate (iii) were confirmed. Many CNF bundles were separated by a distance of 40–150 μm, while isolated CNF were quite few. The most of surfaces of ITO substrate were covered by Au film. Figure 1(b) shows the shape of a CNF bundle, where bent CNF became tangled with one another each other and the density of CNF was very high. It is not expected that an electric field is effectively applied on each the tip of CNF, even though so many tips of CNF protruded from the bundle.

In Figs. 1(c) and (d) CNF bundles were not found on the substrate, where grains of the binder (i), surfaces of ITO substrate (ii), a binder (iii), were observed. The grains with size of 10-60 μmϕ were distributed randomly separated from one another. The surfaces of ITO substrate were covered by Au film and CNF were not included in the grain. In Fig. 1(d) straight CNF

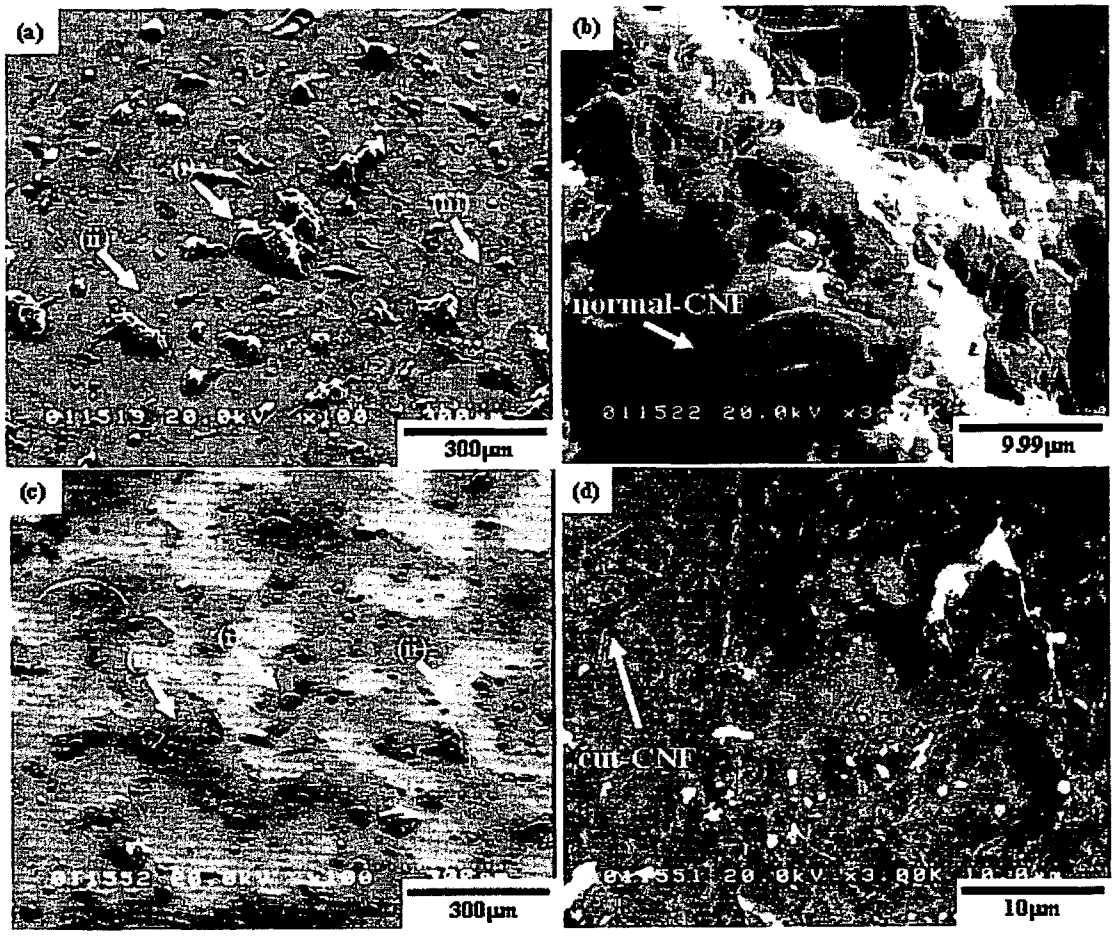

Fig. 1: The SEM images of the CNF films added binders of Au paste and PC with using two different CNF: normal-CNF (a), (c) and cut-CNF (b), (d).

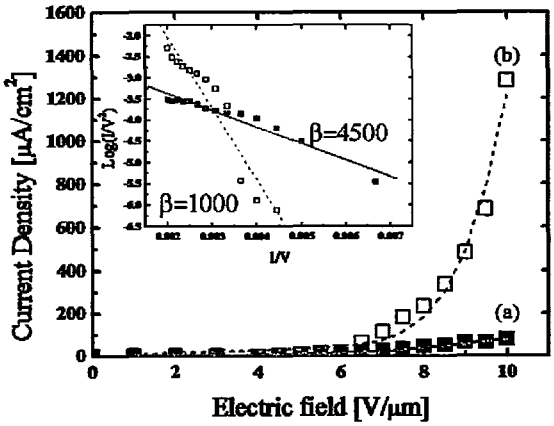

Fig. 2: Emission current versus applied voltage of CNF emitter with different two CNF (cut-CNF (a) and normal-CNF (b)). The inset shows the data plotted as log (I/V^2) versus 1/V, Fowler-Nordheim plot. The solid and dotted lines are fitting lines with the evaluated value of β.

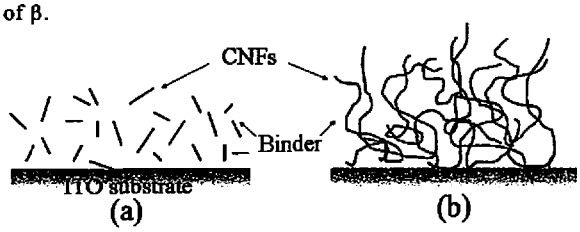

Fig. 3: Schematic cross sections of CNF films prepared with cut-CNF (a) and normal-CNF (b).

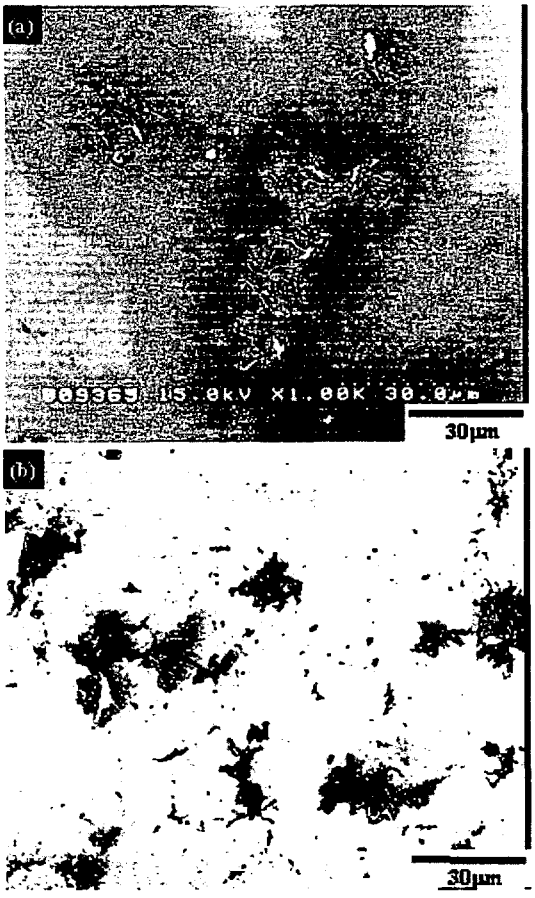

Fig. 4: SEM images of the CNF film with different numbers of isolated CNF. The densities of isolated CNF were 3.5×10^5 cm^{-2} (a) and 1.2×10^7 cm^{-2} (b).

were isolated and were buried in the Au film, and a few tips of CNF protruded from the surface.

Fig.2 shows the emission current versus applied voltage (I-V) characteristics of the CNF emitter prepared by cut-CNF (a) and normal-CNF (b), where Au paste and PC were added as binders. The inset is the data plotted as log (I/V^2) versus 1/V (Fowler-Nordheim plot). A turn-on electric field E_t was defined as the electric field at which the observed current attains to 1% of the value obtained at 10 V/μm. The E_t was about 6 V/μm in the both specimens and the current density at 10 V/μm in the specimen of cut-CNF and normal-CNF was 0.08 and 1.4 mA/cm^2, respectively. On the other hand, the field enhancement factor β in the F-N equation was estimated according to the equation (1). Since the current observed includes the both emission current and conduction current, we separated the term of emission current,

$$I = aJ + (1-a)I' = a\frac{A(\beta E)^2}{\phi}\exp\left(-\frac{B\phi^{3/2}}{\beta E}\right) + (1-a)\frac{V}{R} \quad . (1)$$

Where I is the current density obtained, J is emission current density in (F-N) equation [7], I' is conduction current obeying the Ohm's law, $A=1.56\times10^{-6}AeVV^{-2}$, $B=6.83\times10^7eV^{-3/2}Vcm^{-1}$, ϕ is work function of 4.85-5.05eV [8], a is a variable number ($0<a<1$), R is the resistance, and E is applied electric field. We assume that the work function of CNF was 5.0eV equal to that of graphite. From fitting the data, the value of β evaluated was 1000 and 4500 for the specimen of normal-CNF and cut-CNF, respectively. The rate of emission current was evaluated by a, of which the value was 95% in normal-CNF and 84% in cut-CNF.

Fig. 3 shows schematic diagrams of cross section of CNF films prepared with cut-CNF (a) and normal-CNF (b). Most of cut-CNF was buried in the binders. Since cut-CNF with short length hardly pass through binder surfaces, the number of emission sites was small and high emission current was not obtained. Normal-CNF with long length and bent shape protruded from binders. So, many tips of CNF worked as field emission sites and high current density was obtained. Cut-CNF isolated resulted in, however, the increase of the value of β because of effective electric field concentration caused from their shapes.

Since the two kinds of CNF (normal- and cut-CNF) were used, it was not clear from the result in Fig1 (a) ~ (d) whether isolated CNF did play an important role or not. The cut-CNF was studied because they were not so long and did not become bundles comparing with the normal-CNF. The number of isolated CNF was increased by using the cut-CNF. Then two types of CNF

emitters were prepared to make clear the role of isolated CNF by using same cut-CNF and/or changing only the number of isolated CNF.

The SEM images of CNF emitters with different number of isolated CNF are shown in Figs. 4(a), (b). The density of isolated CNF was *ca.* 3.1×10^5 cm^{-2} in Fig. 4(a) and *ca.* 1.2×10^7 cm^{-2} in Fig. 4(b), respectively. The number and the size of bundles were almost same in the both specimen. Fig. 5 shows I-V characteristics measured in the two CNF emitters in Fig.4 and the inset is the F-N plot. The current densities at 10 V/μm in (b) was larger than in (a). The value of β in (b) was 2500 and lager than in (a), 500. It was clear that the number of isolated CNF was larger in the CNF emitter with the high electronic emission performance. It was confirmed that isolated CNF play an important role as emitter sites [9] and/or the CNF emitter with high b was prepared in the structure with isolated CNF dispersed.

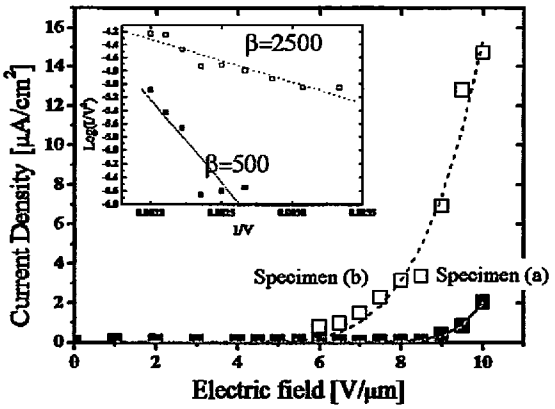

Fig.5: Emission current versus applied voltage in the different CNF film in fig.4 (a) and (b). The inset is the Fowler-Nordheim plot. The solid and dotted lines are fitted lines with the evaluated value of β.

4. CONCLUSION

A low density CNF emitter was prepared by a spray spreading method. The low density CNF emitter was investigated about its field emission properties from a point of view of β and the number of b and the number of field emission sites. From the normal-CNF emitter the current density of 1.4 mA/cm^2 @10V/μm was obtained. The cut-CNF emitter gave comparatively small current density, 80μA/cm^2 at 10V/μm and the β of 4500 was, however, much larger than that of the normal-CNF emitter, 1000. It was confirmed that the isolated CNF played an important role as effective emitter sites. Conclusively a current density of mA/cm^2 order was obtained from the CNF emitter prepared by a spray spreading method. We will apply the emitter to a novel luminescence device composed with organic light emitting diode films.

REFERENCES

[1] K. Onozuka, N. Iwata and H. Yamamoto, *Int. J. Mod. Phys.* **B16** (2002) 4445.
[2] Y. Hata, T. Ichinose, N. Iwata and H. Yamamoto, *Trans. Mate. Res. Soc. Jpn.* **30** (2005) 175.
[3] B. J. Chen, W. Y. Lai, Z. Q. Gao, C. S. Lee, S. T. Lee and W. A. Gambling, *Appl. Phys. Lett.* **75** (1999) 4010.
[4] J. Li, W. Lei, X. Zhang, and X. Zhou, *Apll. Surf. Sc.*, **220** (2003) 96.
[5] t. j. Vink, M. Gillies, J. C. Kriege, and H. W. J. J. van de Laar, *Appl. Phys. Lett.*, **83** (2003)3552.
[6] E. Sato, T. Takahashi, and K. Koyama, *TANSO*, **209** (2003) 159.
[7] R. H. Fowler, L. W. Nordheim, *Proc. R. Soc. Lond., Ser.*, **A 119** (1928) 173.
[8] M. Shiraishi, M. Ata, *Carbon*, **39** (2001) 2591.
[9] N. Iwata et al, *Materials Science and Engineering*, (2006). (In press)

(Received January 18, 2007;Accepted February 20, 2007)