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

Keywords: carbon nanofiber (CNF); electron emitter; field emission display; spray spreading method

INTRODUCTION

We have been studying a novel low voltage acceleration field emission display (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,

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quenched quickly. It was found that the quench was caused by an accumulation of electrons at the interface of Alq_3/α-NPD due to insufficient electric field applied in the organic stacking layer. We have expected that the issue will be overcome by adopting carbon nanofibers (CNFs) electron emitters to shorten the distance between the electrodes [3]. In this work we tried to prepare CNFs emitters which achieve an emission current density of several mA/cm^2.

Recently screen-printed carbon nanotubes (CNTs) emitters 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 CNTs. It was suggested that the optimum density of CNTs to apply effectively the electric field is about $1.0 \times 10^7\,cm^{-2}$ in the case of 1 μm-long CNTs which are dispersed in the distance of 3 μm [4]. Though a low density CNTs emitter is desirable, it is difficult to prepare such the 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 investigated its field emission properties from a point of view of field enhancement factor β and a number of CNFs as an emission site.

EXPERIMENTAL

We used multi-wall carbon nanofibers (MWCNFs) which were massively produced by Showa Denko Co. Ltd. The CNFs were typically synthesized from mixed solution of ferrocene, thiophene and benzene by thermal chemical vapor deposition at *ca*. 1300°C. The obtained CNFs were burned out above 2800°C for 30 min to eliminate amorphous carbon and/or catalyst. The size of the CNFs 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 CNFs with short length of *ca*. 1.5 μm (named as cut-CNF), which were prepared from the normal-CNFs by a fragmentation process, were also used.

The preparation conditions of CNF emitters are summarized in Table 1. CNFs were suspended with organic soulution of 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 CNFs [6]. The CNFs 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 $10 \times 20\,mm^2$. 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

TABLE 1 The Preparation Conditions of CNFs Emitters

Organic solution	THF
CNF powder (wt%.)	Cut or Normal-CNFs (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	0.1 MPa., 400°C
Annealing	Baking at 400°C

temperature at the set temperature. After spraying specimens were baked at 400°C for 30 min to remove organic solution in the paste.

A surface morphology of the CNFs 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 CNFs (cathode) was *ca*. 50 μm. The measured emission area was $5 \times 5\,\text{mm}^2$. The emission current-voltage (I-V) characteristics were analyzed by using the Fowler–Nordheim (F–N) equation for the field emission.

RESULTS AND DISCUSSION

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

In Figures 1(c) and (d) CNFs 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 $10 \sim 60\,\mu\text{m}\phi$ was distributed randomly separately. The surfaces of ITO substrates were covered by a binder and CNFs were not included in the grain. In Figure 1(d) straight CNFs were isolated and were buried into the binder, and a few tips of CNFs protruded from the surface.

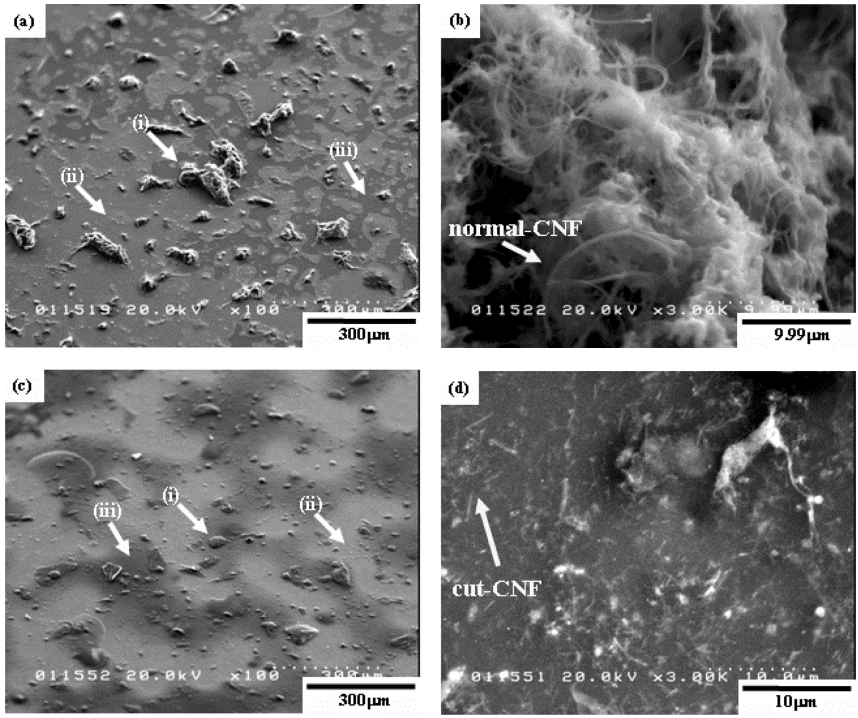

FIGURE 1 The SEM images of the CNFs films added binders of Au paste and PC with using two different CNFs: normal-CNF (a), (c) and cut-CNF (b), (d).

Figure 2 shows the emission current versus applied voltage (I-V) characteristics of the CNFs 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 $10\,V/\mu m$. The E_t was about $6\,V/\mu m$ in the both specimens and the current density at $10\,V/\mu m$ in the specimen of cut-CNF and normal-CNF was 0.08 and $1.4\,mA/cm^2$, respectably. On the other hand, the field enhancement factor β in the Fowler–Nordheim equation was estimated according to the Eq. (1). Since the current observed includes the both emission current and conduction current, we separated the term of emission current,

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

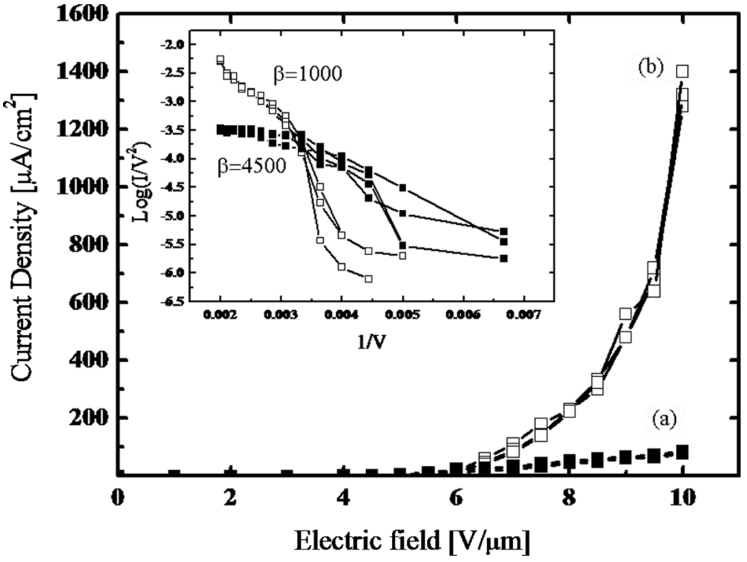

FIGURE 2 Emission current versus applied voltage of CNFs emitter with different two CNFs (normal- and cut-CNF). The inset shows the data plotted as log (I/V^2) versus 1/V, Fowler–Nordheim plot.

Where I is the current density obtained, J emission current density in Fowler-Nordheim (F-N) equation [7], I' conduction current, $A = 1.56 \times 10^{-6}$ AeVV^{-2}, $B = 6.83 \times 10^7$ eV$^{-3/2}$Vcm^{-1}, ϕ work function of 4.85 $\sim$ 5.05 eV [8], a a variable number ($0 < a < 1$), R the resistance, and E applied electric field. We assumed that the work function of CNFs was 5.0 eV equal to that of graphite. From fitting the data, the value of β evaluated was 1000 and 4500 for the specimen of normal-CNF

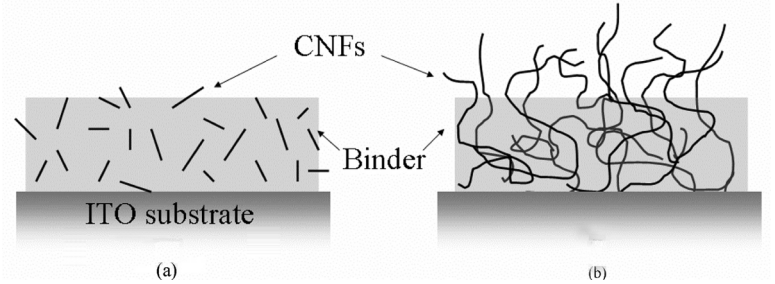

FIGURE 3 Schematic cross sections of CNFs films prepared with cut-CNF (a) and normal-CNF (b).

and cut-CNF, respectively. The rate of emission current was measured by α, of which the value was 95% in normal-CNF and 84% in cut-CNF.

Figure 3 shows schematic diagrams of cross section of CNFs film prepared with cut-CNF (a) and normal-CNF (b). Most of cut-CNFs were buried in binders. Since cut-CNFs with short length hardly pass through binder surfaces, the number of emission sites was small and high emission current was not obtained. The normal-CNFs with long length and bent shape protruded from binders. So many tips of CNFs worked as field emission sites and high current density was obtained. The cut-CNFs isolated resulted in, however, the increase

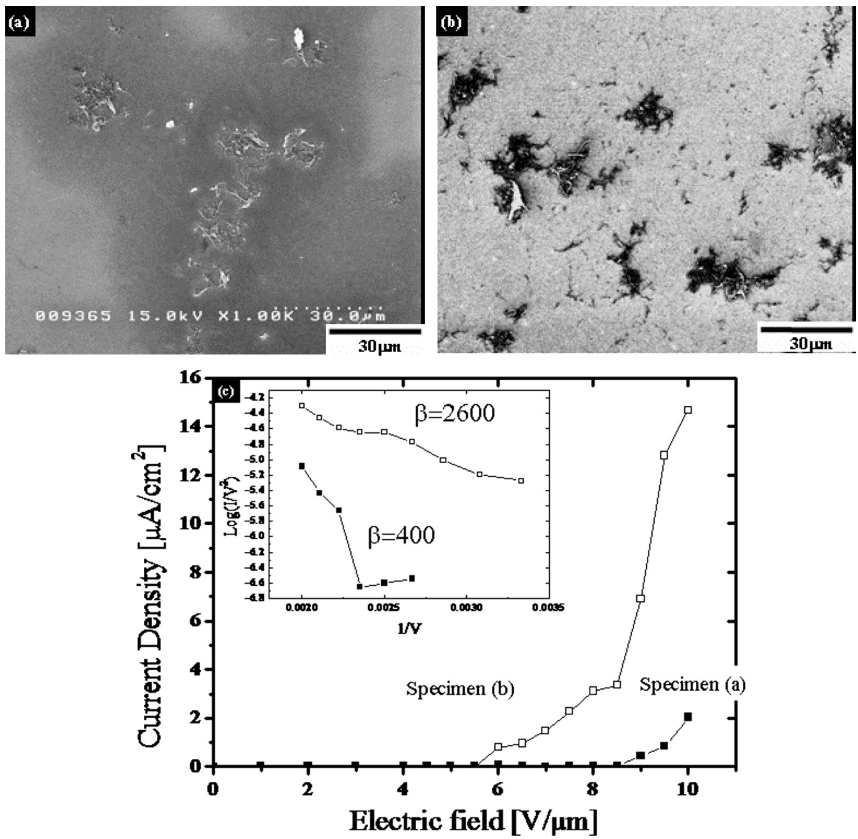

FIGURE 4 SEM images of the CNFs film with different number of isolated CNFs. The densities of isolated CNFs was $3.5^{*}10^{5}\,cm^{-2}$ (a) and $1.2^{*}10^{7}\,cm^{-2}$ (b). Figure (c) shows emission current versus applied voltage in the different CNF film (a) and (b). The inset is the Fowler–Nordheim plot.

of the value of β because of effective electric field concentration caused from their shapes.

Since the two kinds of CNFs (normal- and cut-CNFs) were used, it was not clear from the results in Figures 1 (a) $\sim$ (d) whether isolated CNFs did play an important role or not. The cut-CNFs were studied because they were not so long and did not become bundles comparing with the normal-CNFs. The number of isolated CNFs was increased by using the cut-CNFs. Then two types of CNF emitters were prepared to make clear the role of isolated CNFs by using same cut-CNFs and/or changing only the number of isolated CNFs.

The SEM images of CNFs emitters with different number of isolated CNFs are shown in Figures 4(a), (b). The density of isolated CNFs was *ca*. $3.1 \times 10^5\,\mathrm{cm}^{-2}$ in Figure 4(a) and *ca*. $1.2 \times 10^7\,\mathrm{cm}^{-2}$ in Figure 4(b), respectively. The number and the size of bundle were almost same in the both specimen. Figure 4(c) shows I-V characteristics measured in the two CNFs emitters and the inset is the Fowler-Nordheim plot. The current densities at $10\,\mathrm{V}/\mu\mathrm{m}$ in (b) was larger than that in (a). The value of β in (b) was 2600 and larger than that in (a), 400. It was clear that the number of isolated CNFs was large in the CNFs emitter with the high electronic emission performance. It was confirmed that isolated CNFs play an important role as emitter sites [9] and/or the CNFs emitter with high β was prepared in the structure with isolated CNFs dispersed.

CONCLUSION

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

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