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Emission Enhancement by Excimer Laser Irradiation over a Weblike Carbon Nanotube Layer

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A surface treatment of a carbon-nanotube (CNT) layer by excimer-laser irradiation was investigated to obtain a uniform emission at a low driving voltage. A CNT layer was grown by thermal-chemical vapor deposition (CVD), and CNTs in the layer formed a weblike networked structure. The tips of the CNTs were found throughout the small-mesh networklike structure in the as-grown CNT layer. After laser irradiation, the number of CNT tips increased and the CNT tips created by laser irradiation had sharp edges and clean surfaces. As a result, the emission was greatly enhanced by laser irradiation at an energy density of 50–60 mJ/cm^2. [DOI: 10.1143/JJAP.43.L1459]

KEYWORDS: carbon nanotubes, uniform emission, low driving voltage, excimer-laser, thermal-chemical vapor deposition

Carbon nanotubes (CNTs) have been attracting considerable attention as field emitters because of their excellent properties such as high aspect ratio, high mechanical strength and high chemical stability.[1–3] Experimental studies about CNT emitters for field emission displays (FEDs) have been reported since 1998.[4–8] In 1998, we manufactured the first experimental devices with screen-printed CNT emitters.[4] The surface of screen-printed films, after being dried and sintered, had to be abraded to expose CNTs buried in the films. One of the effective methods of removing surface binder materials was laser ablation, by which numerous CNT tips were exposed from the sintered layer.[9] After that, some surface treatment technologies over the screen-printed CNT layer have been reported.[10,11] The screen printing method was suitable for fabricating a large-area cathode, but we considered that it was not suitable for fabricating a uniform emitter. For image-displays, a more uniform emission at a low applied voltage is required.

In this letter, we propose another method of surface treatment by excimer-laser irradiation on a networked CNT -layer grown by a thermal-chemical vapor deposition (CVD) technology. The CNT layer does not contain a binder material, and the surface morphology is an entangled network configuration. The new surface treatment improves the number density of CNT tips by cutting the nanotubes, forming the surface CNT network. We found that the new surface treatment technology is effective in improving the emission site density due to the increased number of CNT tips, and that a uniform emission is achieved by increasing the emission site density.

To be able to use CNTs as field emitters in display devices, it is necessary to realize a uniform emission of electrons at a low applied voltage. As a first trial of fabricating a uniform CNT cathode by the CVD technique, we prepared an aligned CNT -layer on a metal substrate by plasma-enhanced CVD.[7] Even though the CNTs thus prepared were vertically aligned, electron-emission density and uniformity were unsatisfactory. This may be caused by the nonuniform concentration of the electric field over individual CNTs. A more uniform electric field over the cathode surface will be formed when the surface of the CNT layer is smooth and round around the electrode edges and the surface resistivity is uniform. In 2000, we succeeded in obtaining a surface morphology favorable for the CNT field emitter fabricated by the newly developed thermal-CVD.[8] The CNTs grown on metal-electrode frames by the new method formed a weblike networked structure, and the tips of the CNTs were found throughout the small-mesh networklike structure. The spatial distribution of the electron emission from the new CNT emitter was moderately uniform, indicating that a uniform electric field is formed over the CNT electrode. The networked CNT layer in this letter was deposited by the technology mentioned above. The technology is also applicable to a large area by arranging many metal frames on a glass substrate.

The CNT layer was prepared using a thermal-CVD equipment, CVD-GN-300 (ULVAC), on a patterned plate of 426-alloy (Fe -42wt%Ni -6wt%Cr).[8] Metal catalysts necessary for CNT growth are included in the alloy. The alloy has a special thermal property, i.e., its thermal expansion coefficient coincides with that of glass which is used as a material of vacuum vessels. The metal electrode made of this alloy was 11.8 mm in diameter and 0.1 mm in thickness. A honeycomb pattern shown in Fig. 1(a) was realized by chemical etching. The side of a hexagon hole was 200 μm and the width of the metal stripe that remained after the etching was 100 μm.

The metal electrode was placed in the CVD chamber evacuated below 1 Pa, and 30% CO in hydrogen gas was introduced into the chamber up to a working pressure of 1 atm. The total flow rate of CO and hydrogen was 1500 sccm. The metal electrode was then heated to approximately 700°C and kept at this temperature for 30 min. Figures 1(a) and 1(b) show the SEM images of the electrode covered with a CNT layer, revealing that the cathode has round edges and smooth surfaces. The high-magnification image (Fig. 1(b)) shows that the CNTs form a networked structure. The thickness of the CNT layer was approximately 15 μm.

The surface treatment of the CNT cathode was carried out using a laser irradiation apparatus developed by The Japan Steel Works. A KrF excimer-laser (248 nm, LAMBDA PHYSIK) was used in the present experiment. The laser spot area with a uniform intensity was expanded to 8 mm × 8 mm using a special optics. The repetition frequency of laser irradiation was 20 Hz with a pulse width of 20 ns (full-width

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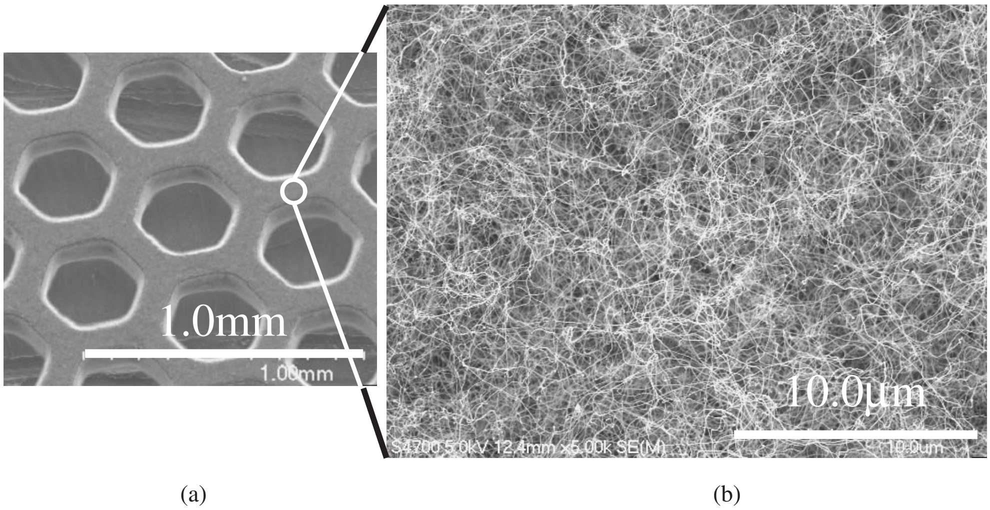

Fig. 1. CNT layer deposited on metal electrode. (a) Portion of patterned CNT emitter and (b) surface morphology of CNT layer.

at half-maximum). Laser energy densities were adjusted from 30 mJ/cm^2 to 110 mJ/cm^2. Laser irradiation was performed at the center of the specimen with 3 shots in air.

The surface of the CNT layer after the irradiation was examined by SEM to count the number of CNT tips. Field emission current versus voltage and electron-emission distribution over the CNT cathode were measured using a cathode emission profiler (Tokyo Cathode Laboratory).[12] The profiling instrument, based on an anode-hole scanning method, works under a pressure of less than 1×10^{-7} Pa. Emission characteristics were measured using a fixed anode that collected the emission current from the entire surface of the cathode. Emission profiles (two-dimensional distributions of electron emission) were obtained by scanning the anode hole (20 μm -diameter) over the emitter surface.

The specimen was attached to the cathode stage, which was covered with a thin metal foil with a 4 mm-diameter hole in order to measure the central area of the irradiated surface (8×8 mm^2). The thickness of the metal cover was 0.1 mm and the spacing between the cover and the anode was 0.2 mm, therefore the spacing between the anode and the surface of the CNT emitter was 0.3 mm.

Figure 2 shows the TEM image of the CNT tip created by laser irradiation at 50 mJ/cm^2. It is open-ended and has a cup-stacked structure. Most of the CNT tips before laser irradiation were capped including catalyst particles, while the created CNT tips exhibited sharp edges like a point of a hypodermic needle as revealed in Fig. 2.

Figures 3(a)–3(c) show the SEM images of the surfaces of the CNT emitters before and after laser irradiations at 50 mJ/cm^2 and 90 mJ/cm^2. The observed CNT tips increased in number according to the increase in laser energy density. In the case of laser irradiation at 50 mJ/cm^2, the tips of the CNTs were observed to be randomly distributed throughout the networked CNT structure as shown in Fig. 3(b). On the other hand, in the case of 90 mJ/cm^2, the networked CNT structure was severely damaged and the tips of the CNTs were observed to be gathered together as shown in Fig. 3(c).

The CNT emitters were irradiated in a range from 30 mJ/cm^2 to 110 mJ/cm^2 to determine the optimum laser energy density for realizing a uniform electron emission at the

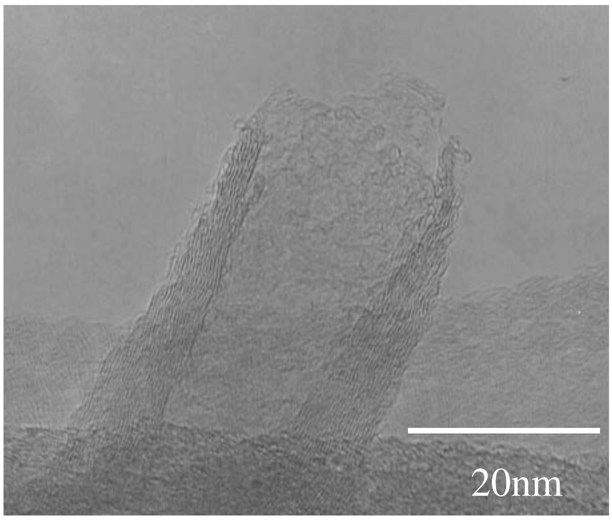

Fig. 2. TEM image of CNT tip created by laser irradiation at 50 mJ/cm^2.

lowest applied voltage. Figure 4(a) shows the emission current under a constant applied voltage of 660 V as a function of laser energy density. The emission current increased rapidly after laser irradiation up to 50 mJ/cm^2, while it decreased after laser irradiation over 60 mJ/cm^2. The spatial distribution of the electron emission was also measured over the CNT emitters before and after laser irradiation under a constant applied voltage of 700 V. Figures 5(a)–5(c) show emission distribution areas from the CNT layer deposited on the patterned electrode before and after laser irradiations of 45 mJ/cm^2 and 90 mJ/cm^2. The emission area giving a current density over 1 mA/cm^2 is displayed in the figures. In Fig. 5(b), the honeycomb pattern is clearly observed over the entire area, indicating that the emitting area is increased several times by laser irradiation compared with that before irradiation (Fig. 5(a)). However, it decreases at 90 mJ/cm^2 as shown in Fig. 5(c).

The number of CNT tips increased monotonically with the increase in laser energy density up to the highest energy as shown in Fig. 4(b). However, the emission current decreased at a high energy density over 60 mJ/cm^2 as shown in

(a)
(b)
(c)

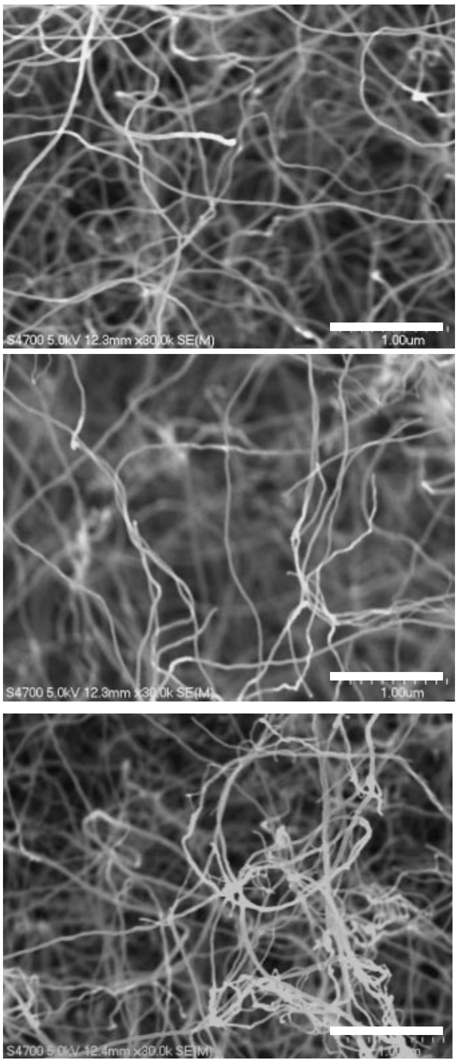

Fig. 3. SEM images of surfaces of CNT layer. (a) Intact CNT layer and (b) irradiated layers with energy densities of 50 mJ/cm^2 and (c) 90 mJ/cm^2. Scale bars show 1.0 µm.

(a)
(b)
(c)

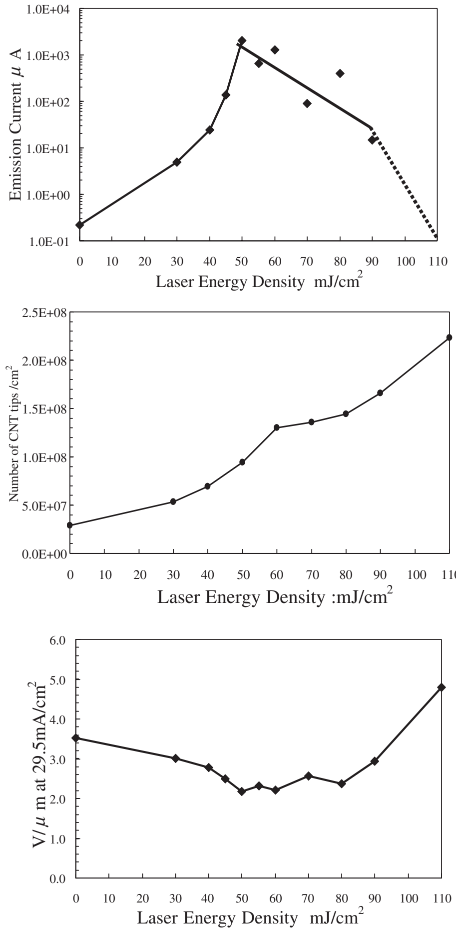

Fig. 4. (a) Emission current as a function of laser energy density under constant voltage. The applied voltage is 660 V. (b) Density of CNT tips as a function of laser energy density, and (c) electric field required to obtain constant emission current density (29.5 mA/cm^2) as a function of laser energy density. The emission measurement was performed with an anode-emitter spacing of 0.3 mm.

Fig. 4(a). We will consider the reason below. When the CNT emitters were irradiated up to 60 mJ/cm^2, the number of CNT tips approximately increased by one order of magnitude and they were randomly distributed throughout the networked surface. Moreover, the CNT tips created by laser irradiation had sharp edges and clean surfaces, which would facilitate electron emission. Simultaneously, the emitting area increased up to several times that of the initial emitting area (see Figs. 5(a) and 5(b)), indicating an increase in the number of emission sites. The observed increase in emission site density suggests that the CNT networked structure maintains a uniform electric field over the cathode surface even in a partially broken network, and the number of effective emission sites is greatly increased by the CNT tips created by laser irradiation.

Although the number of CNT tips increased continuously with the increase in laser energy density, the emitting area decreased at a laser energy over 60 mJ/cm^2. This would be due to the coarsening of the networked structure at a large laser energy. In the case of 90 mJ/cm^2, the surface of the CNT networked structure was rough (Fig. 3(c)) and the emission area decreased to less than one-half as shown in Fig. 5(c). It is thought that the electric field would be localized at a few protruding CNTs for the too-much-irradiated CNT layer. The mesh size of the CNT networked structure would become too large to keep the surface electric field uniform. In addition, a large number of tips gathered together, as shown in Fig. 3(c). The coalesced islandlike CNT tips resulted in electric field localization, and the electric field uniformity decreased. As a result, the number of emission sites decreased. These results suggest that an appropriate mesh size of the CNT networked structure and the number density of CNT tips are important for obtaining uniform emissions of electrons at lower voltages.

One of the most important technical issues for manufacturing CNT-FEDs is to realize the surface morphology of CNT layers that enables a uniform electron emission at a lower applied voltage. Figure 4(c) shows the electric field required to obtain a certain emission current density (29.5 mA/cm^2) as a function of laser energy density. The required electric field decreased to the minimum value of 2.2 V/µm at 50–60 mJ/cm^2, where the emission uniformity was also most improved.

The CNT-FED is a prospective large-size flat-panel display with a high luminance, a low-power consumption and a high-speed response. Field-emission cathodes, which

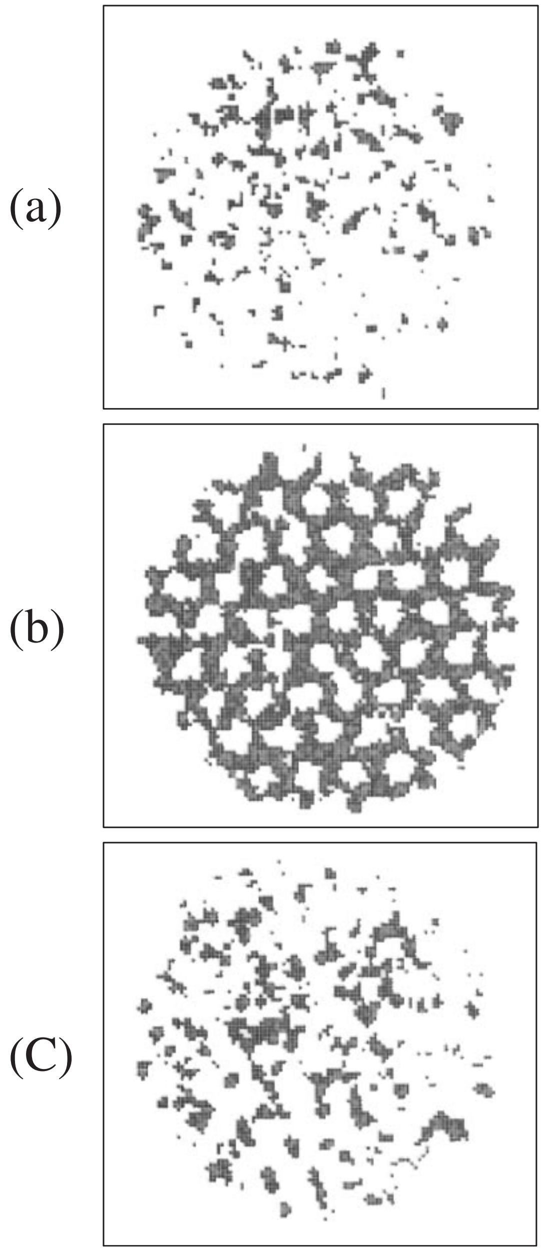

Fig. 5. Areal distribution of electron emission from patterned CNT electrode. The emission area giving current density over $1\,mA/cm^2$ is displayed. Emission measurement was performed using a pulsed anode voltage of 700 V and an anode-emitter spacing of 0.3 mm through an anode hole of $20\,\mu m\phi$ for a scanning area of $4\,mm^2$. (a) Before laser irradiation, the emitting area was approximately $1.7\,mm^2$. (b) After laser irradiation with an energy density of $45\,mJ/cm^2$, the emitting area was approximately $6.1\,mm^2$, and after laser irradiation (c) with an energy density of $90\,mJ/cm^2$, the emitting area was approximately $2.5\,mm^2$.

can emit electrons uniformly from the surface at a lower applied voltage, are required to realize CNT-FEDs for TV display application. We carried out the surface treatment of the CNT emitter grown by thermal-CVD. KrF excimer-laser light was irradiated over the CNT layer. The CNT tips created by laser irradiation had sharp edges and clean surfaces. Simultaneously, the active emission area increased up to several times that of the initial emission area, resulting from the increase in the number of emission sites. The laser irradiation resulted in the improvements in the emission characteristics and the emission uniformity.

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