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Field Emission and Field Evaporation of Carbon Nanotubes

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Electrons are emitted from the tips of a carbon nanotube through the tunneling effect when a negative potential is applied to the nanotube. Cold electron emission from various types of nanofibers, viz., multiwall nanotubes (MWNTs), single-wall nanotubes (SWNTs), nanofibers (named "nanografibers") grown in hydrogen gas, and vapor grown carbon fibers (VGCFs), was investigated by field emission microscopy (FEM). As an application of nanotube field emitters, we manufactured cathode ray tube (CRT) lighting-elements and vacuum fluorescent display (VFD) panels equipped with carbon nanotube cathodes. Stable electron emission, high emission current at low electric field (~10 mA/cm^2 at 1.5 V/μm), and long life of the emitters were demonstrated. When a positive electric potential was applied to carbon nanotubes, on the other hand, carbon clusters are directly emitted from nanotubes through field evaporation. We found that C_{20}^+ were selectively emitted from both MWNTs and SWNTs under an extremely high field over 10V/nm.

Key words: carbon nanotube, field emission, field evaporation, display, clusters

1. INTRODUCTION

When a high electric field on the order of 10^7 V/cm is applied on a solid surface with negative electrical potential, electrons inside the solid are emitted into vacuum by the quantum mechanical tunneling effect. This phenomenon is called field emission of electrons. Such an extremely high field can be obtain on a sharp tip of a very thin needle, because electric fields concentrate at the sharp point. The carbon nanotubes possess the following properties favorable as field emitters: (1) needle-like shape with a sharp tip, (2) high chemical stability, (3) high mechanical strength, and (4) high thermal stability. In 1995, field emission (FE) from an isolated single MWNT was first reported by Rinzler et al. [1], and FE from a MWNT film was reported by de Heer et al. [2]. We have studied emission properties using field emission microscopy (FEM) [3-5], and then applied nanotubes as cold electron sources in display devices [6-8].

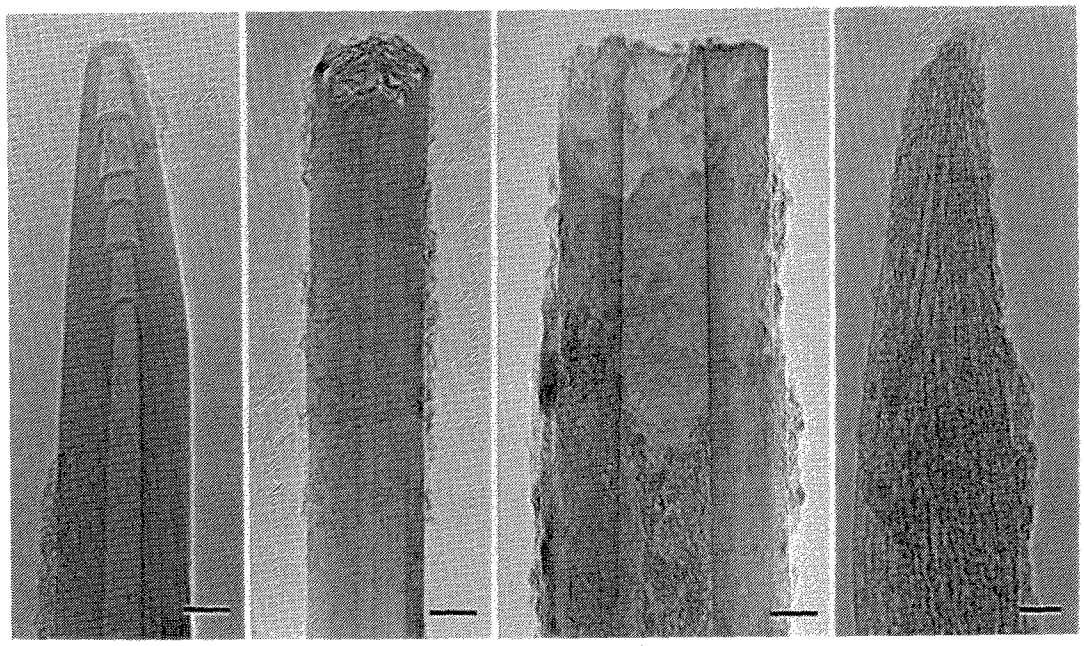
Contrary to the electron emission, carbon ions with positive charges can be emitted from a carbon nanotube by applying a positive high electric potential to it. An extremely high electric field on the order of 10^8 V/cm is required to extract atoms or clusters from solid surfaces. This phenomenon, ion emission under high electric field, is called field evaporation. Recently, we found that C_{20}^+ clusters were selectively emitted from nanotubes by field evaporation [9].

In this symposium, field emission of electrons from various types of nanofibers and its application as display devices are first presented, and then the field evaporation of magic C_{20}^+ clusters is discussed.

2. FEM STUDY OF NANOTUBES

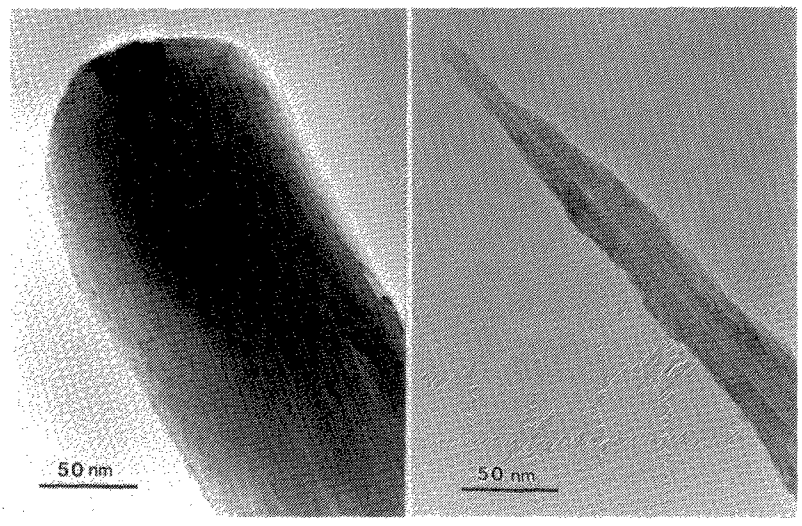
Six kinds of carbon nanofibers were employed as field emitters; (1) as-grown MWNTs prepared in the helium arc (hereafter, called "pristine MWNTs"), (2) as-grown MWNTs in hydrogen ("nanografibers [10] "), (3) purified MWNTs with open ends, (4) purified SWNTs, (5) vapor grown carbon nanofibers (VGCFs) purchased from Showa Denko Co. and (6) oxidized VGCFs [11]. Tips of the respective nanofibers are shown in Figs. 1 and 2. Tips of pristine MWNTs are capped by graphitic layers (Fig. 1 (a)) while purified MWNTs that were obtained after oxidation have open tips (Fig. 1 (c)). Nanografibers have an extremely narrow central channel. The smallest diameter of the innermost layer is about 1 nm or less. This is the reason why we call the nanotube-like material as "nanografibers" (the name coming from graphitic nanofibers) instead of multiwall nanotubes. A TEM image in Fig. 1 (b) shows another structural feature of nanografibers produced by hydrogen arc. The tip of a nanografiber is partially broken or etched. Purified SWNTs form bundles, each of which consists of roughly 100 nanotubes (Fig. 1 (d)).

VGCFs are graphitic fibers whose diameters are 100 to 500 nm as shown in Fig. 2 (a) and the



(a) (b) (c) (d)

Fig. 1. TEM images of tips of the four kinds of carbon nanotubes used for FEM study. (a) Pristine MWNT with a capped end, (b) pristine nanografiber formed in hydrogen arc, (c) MWNT with an open end, and (d) bundle of purified SWNTs. Scale bars; 5 nm.



(a) (b)

Fig. 2. TEM images of tips of VGCFs (vapor grown carbon fibers). (a) As-obtained VGCF, and (b) oxidized VGCF after a heat treatment (750°C) in air (mass reduction; 70-87%).

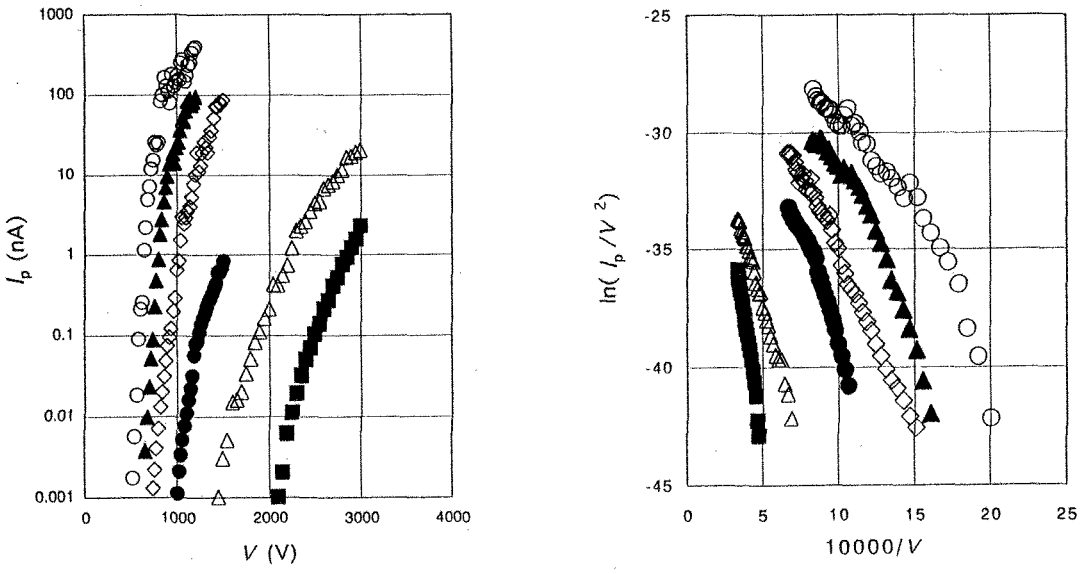
length exceeds 10 μm. Their structure and morphologies are similar to those of MWNTs grown by arc discharge though the diameter of VGCFs is about 5 times larger than that of the MWNTs. The thick diameter and dull tips of VGCFs are disadvantage as a field emitter. The morphology of VGCFs can be modified to have a sharp tip and a slender body by oxidizing them partially, as shown in Fig. 2 (b).

A bulk bundle of respective nanotubes for FEM study was fixed on the apex of a hairpin-shaped wire of tungsten (0.15 mm in diameter)

using conductive paste. The emitter tip of the nanotubes was positioned 60 mm in front of an anode screen with a 1-mm probe hole. Field emission patterns could be observed on the anode screen on which phosphor was spread. Behind the probe hole was a Faraday cup, and electron current emitted from a restricted region of an emitter could be measured. The acceptance half angle of the probe hole was 17 mrad. Details of the tip preparation and FEM apparatus were described in our previous publications [3-5, 11, 12].

All the nanofibers studied, except for purified MWNTs, gave emission patterns consisting of a number of bright solid spots that originated respectively from individual MWNTs and from bundles of SWNTs. On the other hand, emission patterns from open MWNTs showed "doughnut-like" annular bright rings. A black spot in the central region (i.e., the absence of electrons in the core of an electron beam) corresponds to a cavity of nanotube.

We can measure emission current from a single nanotube by using the probe hole on an anode screen. Emission current accepted by the probe hole, I_p, was measured as a function of voltage applied to the tip (V). The I_p-V characteristics for all the nanofibers are shown in Fig. 3.



(a) (b)

Fig. 3. (a) Current vs. voltage characteristics and (b) F-N plots for a pristine MWNT (●), a nanografiber (◇), an open MWNT (○), a bundle of SWNTs (▲), as-obtained VGCF (■), and oxidized VGCF (Δ). Current (I_p) was measured with the 1 mm probe hole.

Table I. Field emission properties of the four kinds of carbon nanotubes. Since emission current was measured by the 1-mm probe hole, the properties come from a single tube for MWNT and nanografiber, and from one bundle for SWNTs.

Carbon nanotubes	Threshold voltage* (V)	Maximum current density ($\times 10^6$A/cm^2)	β-factor ($\times 10^4$cm^{-1})
Capped MWNT	900-1000	0.1-1	2-4
Nanografiber	700-800	~1	4-7
Open MWNT	500-600	10-100	6-30
SWNTs	600-700	~10	5-10
As-obtained VGCF	~2000	~0.01	1.1-1.4
Oxidized VGCF	~1500	~0.1	3-4

* Threshold voltages represent tip voltages at which currents measured by the probe hole exceed 0.1 pA.

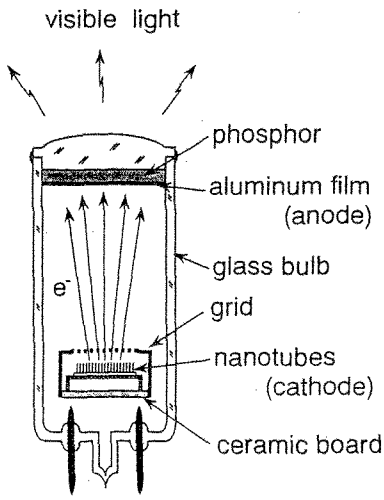


Fig. 4. Longitudinal cross section of a CRT fluorescent display with a field emission cathode made of carbon nanotubes [6]. The size of the element is 20 mm in diameter and 74 mm in length.

Threshold voltage and maximum current density are summarized in Table I. The open MWNTs begin to emit electrons at the lowest tip voltage and sustain the highest current density. Nanografibers grown in hydrogen give higher current than ordinary MWNTs (i.e., pristine MWNTs grown in helium). This is caused mainly by the cleanliness of nanografiber samples (i.e., less byproduct) and partially by the structural defects on nanografiber tips which have a lower work function. VGCFs showed poor emission properties, though some improvement was obtained by sharpening their tips.

3. NANOTUBE-BASED DISPLAY DEVICES

Developing the field emission study, we experimentally fabricated field emission display (FED) elements in collaboration with Ise Electronics Corp. FEDs that we employed for examining the performance of nanotube field emitters are CRT (cathode-ray tube)-type lighting bulbs and VFD panels.

Figure 4 shows a longitudinal cross section of a CRT lighting bulb with a nanotube cold cathode. Nanotubes we used were MWNTs produced by arc discharge. In our first trial fabrication, fibrous materials containing abundant MWNTs were directly glued onto a stainless steel plate by using conductive paste [6]. Subsequently, several methods were examined to fix nanotubes on the cathode surface, and the screen printing technique was found to be the most effective for industrial application [7].

The nanotube cathode is covered with a grid electrode; the spacing between the cathode and the grid ($d_{T\text{-}G}$) is 0.2-1.0 mm. The phosphor screen is printed on the inner surface of a front glass and backed by a thin aluminum film. After sealing the vacuum tube, getter material was flashed to attain high vacuum on the order of 10^{-6} Pa.

The cathode was grounded (0 V), and the grid was biased to a positive voltage. For $d_{T\text{-}G}$ = 0.2 mm, current density on the cathode was ca. 25 mA/cm^2 at an average field strength of 2 V/μm.

A high voltage (typically 10 kV) was applied to the anode to accelerate electrons, which excite the phosphor screen. Luminance of the phosphor screens was intense enough for practical use; e.g.,

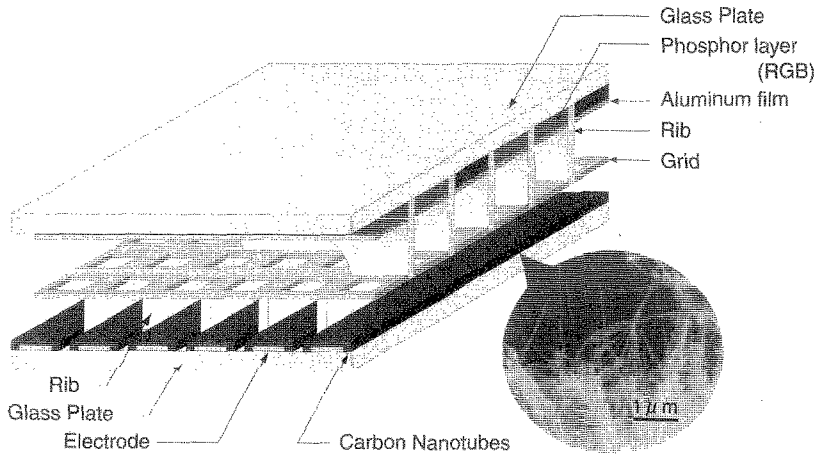


Fig. 5. Structure of a triode-type VFD-like flat panel display equipped with carbon nanotube cathodes.

6.3×10^4 cd/m^2 for green light (ZnS:Cu, Al for green phosphor) at an anode current of 200 μA, which is two times more intense than that of commercially available conventional thermionic CRT lighting elements which are operated at 100 μA. A lifetime test revealed that the nanotube cathode had a life of over 10,000 hours.

VFD (vacuum fluorescent display)-like flat panel displays were also experimentally fabricated. In Fig. 5 is shown the structure of a triode type panel display [8]. One set of anodes, operated at a high-positive potential, consists of lines of RGB (red, green, blue)-color-phosphor (1 mm width) with metal-back film. The phosphor screen is just like CRT-screen, besides the many ribs formed on black matrix area between each phosphor line. These ribs (ca. 0.15 mm width) prevent miss-addressing of color phosphor by stray electrons. The second electrode is one set of cold-cathodes, which consists of carbon nanotube layers printed on a glass substrate equipped with silver electrodes. The cathode is covered with a grid electrode, which is placed on cathode ribs and is parallel with a phosphor line. The grid controls emission of electrons from nanotubes. The distance between the anode and the grid is 2.0-4.0 mm, and the distance between the top of nanotube tips and the grid ($d_{T\text{-}G}$) is 0.3-0.6 mm. After evacuating and sealing the panel, getter material was flashed to attain high vacuum on the order of 10^{-5} Pa.

The screen size is 66×66 mm and a pixel size is 3 (RGB)×2.54 mm. Displayed colors depend on phosphors printed on the anode, viz., ZnS:Cu, Al for green, Y_2O_3:Eu for red, and ZnS:Ag for blue. A high voltage of typically 6 kV is applied to the anode. A luminance of the phosphor screens is ca.7×10^5 cd/m^2 for green, ca. 1.8×10^5 cd/m^2 for red, and ca. 1×10^5 cd/m^2 for blue under a dc-driving condition of 6 kV and ca. 1 mA/cm^2.

4. MAGIC CLUSTERS C_{20}^+ FIELD-EVAPORATED FROM CARBON NANOTUBES

Both MWNTs and SWNTs were used for the field evaporation experiment. A bundle of nanotubes was fixed to a hairpin wire using graphite cement. In front of the emitter tip, an extraction electrode with an aperture (2 mm in diameter) was placed at a distance of 1 mm from the tip. An electric potential of 1.5 or 3 kV was applied to the nanotube tip, and the potential of the extractor was varied from -1.0 to -6.5 kV. Carbon cluster ions produced by field evaporation

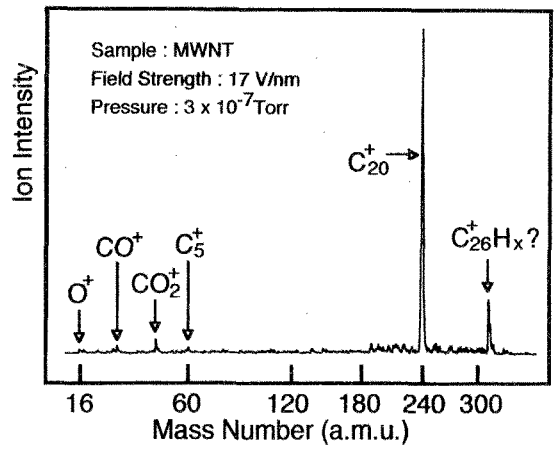


Fig. 6. Mass spectrum of field-evaporated carbon clusters from MWNTs. The mass peak at 240 u, corresponding to C_{20}^+, is prominently strong.

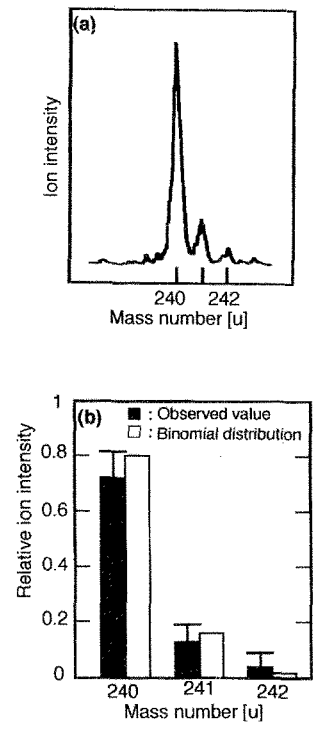


Fig. 7. (a) High resolution mass spectrum around 240 u. Relative intensities of resolved peaks at 240, 241 and 242 u are due to a binomial distribution of two kinds of carbon isotopes (^{12}C: 98.9%, ^{13}C: 1.1 %). (b) Comparison of experimental with theoretical values of relative intensities of 240, 241 and 242 u peaks.

were mass analyzed by a single-focusing magnetic mass spectrometer at various extraction voltages.

Figure 6 shows a mass spectrum obtained from MWNTs under the condition indicated in the inset. Singly charged carbon clusters, C_5^+ and C_{20}^+, are observed together with oxygen, hydrogen oxide and carbon oxide ions. The intensity of C_{20}^+ is prominently strong, indicating either the high stability or a preferred formation channel of C_{20}^+ ions. Around the C_{20}^+ peak observed are many weak peaks, the mass numbers of which are not integral multiple of twelve. Therefore, these peaks may be due to hydrocarbon ions, i.e., $C_mH_n^+$. Peaks with relatively high intensity are observed at 312, 314 and 316 u. We tentatively assign these peaks to $C_{26}H_x^+$(x ~ 0, 2 or 4). Similar mass spectra were observed from SWNTs. Figure 7 (a) shows a high-resolution mass spectrum in a region around 240 u corresponding to C_{20}^+ obtained from SWNTs. The resolved peaks at 240, 241 and 242 u are assigned combinations of carbon isotopes (^{12}C and ^{13}C) in C_{20}^+ clusters. In Fig. 7 (b), the relative intensities of these peaks are compared with a binomial distribution calculated from the natural abundance of carbon isotopes, 98.9% for ^{12}C and 1.1% for ^{13}C. A good agreement between the measured and calculated relative intensities shows that the prominent mass peak at 240 u is from pure carbon clusters, C_{20}^+.

If the C_{20} generated from nanotubes had ring or chain structures, then one could not explain why the cluster size was restricted to twenty.

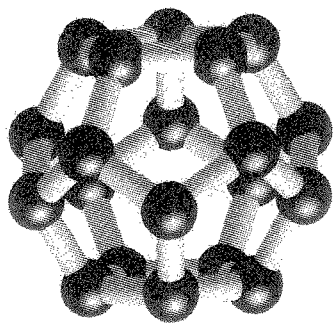


Fig. 8. Structure of a dodecahedron proposed for the C_{20}^+ ions.

From the magic nature of C_{20}, we expect that its structure is a dodecahedron, in which the number of corners is uniquely twenty (Fig. 8). The dodecahedron consists of twelve pentagons (only pentagons) and has the I_h symmetry. Therefore, all the carbon atoms placed on the corners are equivalent. This structure is the smallest cage among fullerenes that are formed by pentagons and hexagons.

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