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Very Low-Field Emission from Aligned and Opened Carbon Nanotube Arrays

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A very low-field emission was achieved from aligned and opened carbon nanotube arrays. Field emission current densities of 10 microamperes per square centimeter were observed at applied fields of 0.6−1 V/μm, and current densities of 10 mA/cm^2 have been realized at applied fields as low as 2−2.7 V/μm. These fields are more than 2 times lower than those previously obtained for carbon nanotubes, and also represent the lowest field ever reported for any field emitting arrays at the same current densities, indicating that carbon nanotubes are superior field emitters.

1. Introduction

Carbon nanotubes possess various superior properties for use as field emitters, such as sharp tips with a nanometer-scale radius of curvature,[1,2] high mechanical stiffness,[3,4] high chemical stability,[5] and unique electrical properties.[6,7] Indeed, recent field emission measurements show that carbon nanotubes show promise as field emitters in applications such as flat panel displays.[8−19] The reported turn-on field (E_{to}) and threshold field (E_{thr}) for electron emission, defined as the macroscopic fields needed to produce a current density of 10 and 10 mA/cm^2, respectively, are in the range of 2−5 and 4−7 V/μm. These values should rank nanotubes among the best electron field emitter arrays that are now available; however, they are still much higher than those expected for this novel material. To obtain very low-field nanotube-based emitters, both aligned[9,10,16] and opened[12,13,16] nanotubes are desirable. Here, we report that specially prepared aligned and opened carbon nanotubes exhibit excellent field emission performances with E_{to} and E_{thr} in the range of 0.6−1 and 2−2.7 V/μm, respectively. These fields are more than two times lower than those previously obtained from carbon nanotubes,[9−15] and also represent the lowest fields ever reported for any field-emitting arrays.

2. Experimental Method

The aligned and opened carbon nanotubes were synthesized by pyrolysis of acetylene over film-like iron/silica substrates.[20,21] The characteristics of the nanotubes have been described in detail in refs 20 and 21. Briefly, scanning electron microscopy (SEM) studies show that the nanotubes with diameters of 10−40 nm and length of up to 2 mm grow outward separately and perpendicularly to the substrate, forming an aligned array of isolated tubes with spacing of about 100 nm between the tubes. The nanotube array can be readily removed from the substrate, without destroying the integrity of the array. Both ends of the nanotube array have the same surface areas, that are typically in the range of 1−10 mm^2. There exists a large quantity of catalyst nanoparticles on the top end (the end away from the substrate) of the nanotube array, while the bottom end (the end connected to the substrate) is composed of a high density ($\sim 10^9-10^{10}$/cm^2) of isolated nanotube tips (Figure 1a,b). Transmission electron microscopy (TEM) observation shows that these nanotube tips are all naturally opened (Figure 1c,d). The nanotubes are well graphitized and typically consist of 10−40 concentric shells of graphite sheets.

The field emission measurements were carried out in a vacuum chamber at a pressure of $\sim 5 \times 10^{-7}$ Torr at room temperature. Figure 2 shows the schematic diagram of the experimental setup. An aligned carbon nanotube array, which was used as the cathode, was attached to a stainless steel substrate by silver paste, with the bottom ends of the nanotubes facing upward. In this configuration, the nanotubes were placed with their long axes perpendicular to the substrates, and the bottom end of the nanotube array, which was composed of high density, well separated, highly aligned and opened nanotube tips, acted as the emitting surface. A copper plate with a diameter of 1 cm, mounted on a precision linear feedthrough, was used as the anode. A variable positive voltage up to 5 kV was applied to the anode and the emission current (I) was indirectly determined by measuring the voltage across a 500 kΩ resistor. The distance (d) between the emitting surface and the plate was determined by first lowers the plate to the sample until electrical contact was observed, then lifting the plate to a certain value. The macroscopic electric field (E) was estimated by dividing the applied voltage by the sample−anode separation (V/d). The

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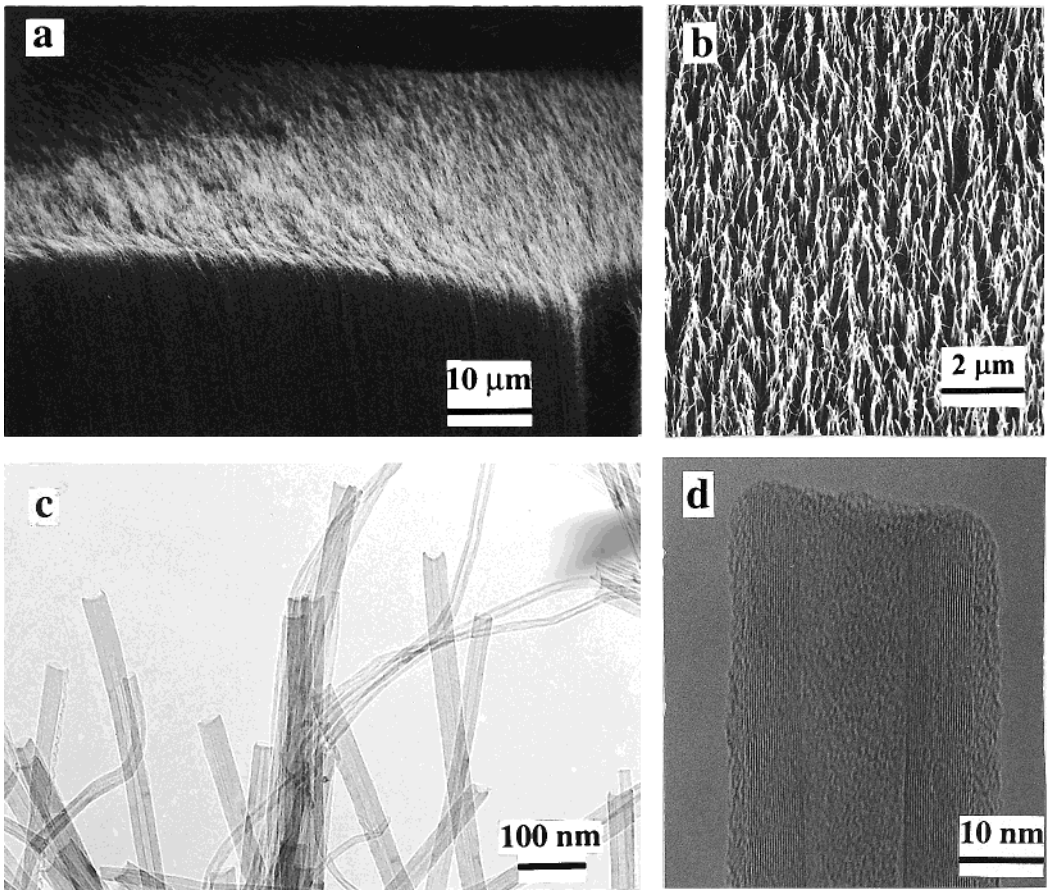

Figure 1. Scanning and transmission electron microscopy images of the aligned and opened carbon nanotube arrays. (a) Low-magnification SEM image of the bottom end of the nanotube array. (b) High-magnification SEM image of the bottom structure of the nanotube array showing high density, well-separated, and highly aligned nanotube tips. (c) Low-resolution TEM image of the bottom end of the nanotube array showing aligned and opened carbon nanotubes. (d) High-resolution TEM image of the bottom end of an opened nanotube.

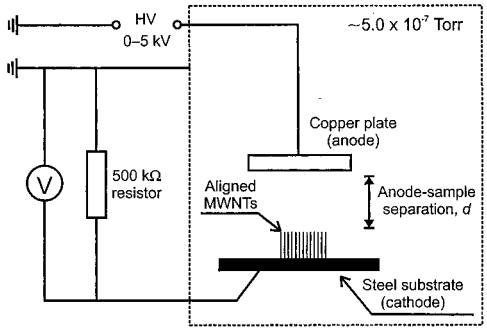

Figure 2. Schematic diagram of the experimental setup used to study the field emission performances of the aligned and opened carbon nanotube arrays.

emission current density (J) was calculated from the obtained emission current and the cathode surface area measured by SEM.

3. Results and Discussion

Four plots of emission current density versus electric field ($J-E$ plot) for a typical carbon nanotube array with an emitting surface area of ~4.62 mm^2 are displayed in Figure 3. These data were collected over four anode-sample distances, 600, 550, 500, and 450 μm. The voltage was raised from zero to 1500 V, then decreased to zero. After the anode was moved 50 μm closer to the emitting surface, the voltage cycle was repeated. It is clear from Figure 3 that the four cycles have almost the same $J-E$ characteristics, indicating a linear relation between the anode voltage and distance. The uniform $J-E$ characteristics

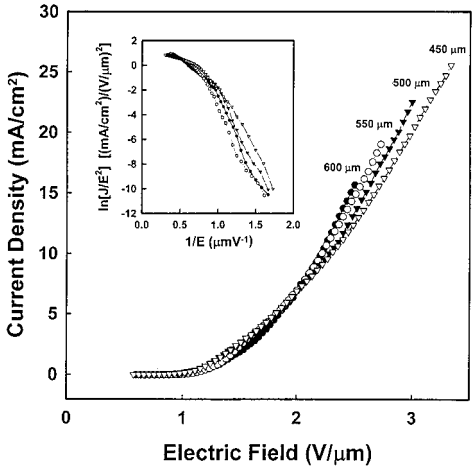

Figure 3. Emission $J-E$ curves from an aligned and opened carbon nanotube array (emitting surface area = 4.62 mm^2). The turn-on and threshold fields for this sample are 0.75−0.89 V/μm and 2.14−2.32 V/μm, respectively. (inset) The corresponding Fowler−Nordheim plots. Note that linear relationship is not observed in these $\ln(J/E^2)$ versus $1/E$ plots.

also justify the simple formula ($E = V/d$) used to estimate the macroscopic field strength between the anode and cathode. Electron emission is observed at an electric field as low as 0.5 V/μm. The electron emission turn-on field E_{to} and threshold field E_{thr} are in the range of 0.75−0.89 V/μm and 2.14−2.32 V/μm, respectively, for the four $J-E$ plots shown in Figure 3. Reproducibility tests from eight different nanotube arrays

TABLE 1: Average Turn-on (E_{to}) and Threshold (E_{thr}) Fields for Various Film Field Emitter

emitter	E_{to} (V/μm)	E_{thr} (V/μm)	ref
Values Obtained on Carbon Nanotubes by Other Groups and Our Devices			
arc SWNT film	2.8	5.2	12
	>1.7	6.5	15
arc MWNT film	4.0	6.5	9, 10
	2.6	4.6	13
catalytic MWNT film	4.8	6.5	14
catalytic MWNT array	>2	4.8	11
aligned and opened MWNT array	0.8	2.3	this work
Values Obtained on Various Diamond Emitters			
undoped defective diamond	>22	≫50	22
boron-doped diamond	>16	≫30	22
cesium-coated diamond	10	28	23
gold-coated diamond	3	>22	24
nitrogen-doped diamond	1.5	>12	25
nanostructured diamond	>1.5	4.9	26

consistently yield E_{to} and E_{thr} in the range of 0.6−1 V/μm and 2−2.7 V/μm, respectively, with average values of 0.8 and 2.3 V/μm.

The above values represent the lowest field emission ever reported for any type of emitter arrays. This is evident from a comparison of the emission results from the present aligned and opened nanotube samples with those previously obtained from carbon nanotube films, and from other efficient field emitters such as diamond. Useful parameters for such a comparison are the turn-on field E_{to} and the threshold field E_{thr}. These figures of merit correspond to the typical values encountered in panel display applications.[10,13] Table 1 lists the average values of E_{to} and E_{thr} for various types of carbon nanotubes obtained by other groups[9−15] and in the present work (the top part), as well as those for various diamond emitters[22−26] (the bottom part). Two conclusions are evident from this comparison: (1) our values for both E_{to} and E_{thr} are more than 2 times lower than those obtained for carbon nanotubes by other groups, and (2) our values are significantly lower than those for all diamond emitters and about an order of magnitude lower than most of them.

The $J-E$ data shown in Figure 3 were also analyzed by the Fowler−Nordheim theory[27] (see Figure 3 inset). A linear relation was not observed in the $\ln(J/E^2)$ versus $1/E$ characteristics, suggesting that the current limit is not dominated by the standard tunneling theory proposed by Fowler and Nordheim.[27] Deviations from the Fowler−Nordheim behavior for metal tips are usually attributed to the space-charge-limited current (SCLC) mechanism.[28] For our carbon nanotubes, although the total current density integrated over the entire anode area seems to be too low for the SCLC mechanism, the current could, nevertheless, be limited by the SCLC mechanism if a much higher local current density occurred at the cathode.[29]

The stability of the aligned and opened nanotube samples is remarkable. During 24 h of continuous operation at 5 mA/cm^2, the current fluctuation was as low as ±3% and the average current did not decrease over this period. No changes in the morphology after 24 h of continuous emission were observed by SEM.

The above results show that the aligned and opened carbon nanotube arrays possess excellent field emission performances, with the lowest values for turn-on and threshold fields. Such excellent field emission can be attributed to the characteristics of our nanotube samples. First, the nanotubes are highly aligned and well separated (see Figure 1a,b). Recent field emission measurement[13] of carbon nanotube films suggested that maximum efficiency can be reached only when the nanotube tips are well aligned and placed with their long axes perpendicular to the film substrate, and when the tips are well separated from one another. These conditions are all met in our nanotube arrays, when the bottom end of the nanotube array is used as the emitting surface. In such a configuration, as shown in Figure 1a,b, all nanotube tips are placed in the best position for electron emission, resulting in maximum emitting efficiency. In addition, the very high density ($\sim 10^9-10^{10}$/cm^2) and uniform distribution of the nanotube tips can further enhance the current and the uniformity of emission. Second, all of the nanotube tips are naturally opened (Figure 1c,d). It is well-known that good field emission performances of closed nanotubes are mainly derived from the small radius of curvature of the nanotube tips. Recently, Saito et al.[16,17] and Wang et al.[18] showed that the opened nanotubes began to emit electrons at a lower applied voltage than the closed ones. This is because the open-end nanotubes have circular sharp edges, which may have a smaller radius of curvature than the closed-end nanotubes. Thus, the open nanotubes may have a higher field amplification effect at the tube tips, resulting in electron emitting at a lower field. Finally, the present nanotube samples are of very high purity. It can be seen clearly from Figure 1a,b that no nanoparticles, which are always present in the samples prepared by the arc discharge method, are found at the bottom end of the nanotube array. It is important for efficient field emission that the samples have as few "foreign" materials as possible.

In conclusion, a very low-field emission was achieved from aligned and opened carbon nanotube arrays. The obtained electron emission turn-on field E_{to} and threshold field E_{thr} are in the range of 0.6−1 and 2−2.7 V/μm, respectively. Such extremely low turn-on and threshold fields for a remarkably stable electron emission in the aligned and opened carbon nanotube arrays offer excellent prospects for a low-field nanotube-based flat panel display. Once the procedure to prepare large area (>1 cm^2) nanotube arrays made of aligned and opened nanotubes is perfected and simplified, the present findings will greatly promote the application of carbon nanotubes as a field emitter.

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