Field emission of carbon nanotubes grown on carbon cloth

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Field emission from carbon nanotubes grown on carbon cloth has been studied. An extremely low electric field of less than 0.4 V/μm is required to reach an emission current density of 1 mA/cm². This ultralow operating electric field of carbon nanotubes grown on carbon cloth is mainly due to a very high field enhancement factor of 1.882 × 10⁴, which is the result of geometrical configuration of the carbon nanotubes and the substrate. In addition to the field enhancement, the highly disordered microstructure of carbon nanotubes grown on carbon cloth plays an important role to field emission. This unexpected result indicates that the roughness of the substrates on which carbon nanotubes grow is very important. This result also brings us significantly closer to practical applications such as highly efficient lamps, field emission displays, micro vacuum electron sources, etc. © 2004 American Institute of Physics. [DOI: 10.1063/1.1776330]

The extraction of an appreciable field emission current at low applied electric field is technologically important to the vacuum microelectronic devices such as field emission displays. Although planar electron sources with large emission area typically have been fabricated from arrays of metal such as molybdenum or semiconductors such as silicon microtips, recently carbon-based materials such as carbon nanotubes, diamond, diamond-like carbon, etc., have been actively investigated as less expensive and simpler alternatives. Electron emissions at low electric fields have been observed from these carbon-based films, but an emission current density of 1 mA/cm² still requires an electric field of 1 V/μm.

Carbon fiber is one of the carbon-based materials investigated for a long period of time, and has shown good field emission properties. The simplest way to make a large area field emission cathode is to form a very large bundle of individual carbon fibers. However, the field emission from the end of such bundle is not as good as expected due to the mutual screening and the nonuniformity in length. Carbon cloth is a woven sheet of carbon fiber bundles, as shown in Fig. 1. Even though carbon cloth is mechanically unstable, a large area field emission cathode can easily be made of the carbon cloth if the carbon cloth has good field emission properties.

Herein we report excellent field emission current density of 1 mA/cm² at a field of less than 0.4 V/μm from carbon nanotubes grown on carbon cloth. This result is of great interest to technological applications such as field emission displays, micro vacuum electron sources, etc., since the operating voltage can be significantly reduced.

We used commercially available carbon cloth as a starting material. Before the carbon nanotube growth, a 30-nm-thick stainless steel (type 304) film was deposited as catalyst on the carbon cloth by dc magnetron sputtering. Carbon nanotubes growth was carried out in a tube furnace by a thermal chemical vapor deposition technique. The catalyst layer was first heat-treated at 660 °C in 50 Torr of flowing mixture of H₂ (10 sccm, 99.999% purity) and N₂ (100 sccm, 99.998% purity) for 1.5 h to form the required catalyst particles and to enhance the catalyst activity, then the pressure was adjusted to 0.9 Torr by controlling the exhaust valve, and the hydrogen was replaced with C₂H₂ (10 sccm, 99.96% purity) for carbon nanotube growth for 1 h. Some carbon clothes were coated with chromium (Cr) before the stainless steel film deposition. Graphite foil was also substituted as a substrate on which to grow the carbon nanotubes in order to investigate the effect of the surface roughness of substrate on field emission properties.

Scanning electron microscopy (SEM) was employed to examine the carbon cloth, the carbon nanotubes grown on carbon cloth, the carbon nanotubes grown on Cr-coated carbon cloth, and the carbon nanotubes grown on graphite foil. In Fig. 2 are shown the low and high magnification images. Although the overall surface of each carbon fiber in carbon cloth is quite smooth in low magnification [Fig. 2(a)], several irregularities appear in high magnification [Fig. 2(b)]. These are thought to be the potential emitting centers. The overall surfaces of other samples are rough [Figs. 2(c), 2(e), and

![Fig. 1. SEM micrograph showing overall morphology of carbon cloth. The white scale bar represents 100 μm.](image-url)
The Fowler–Nordheim (FN) plots for the various samples are shown in Fig. 5. The average intercepts of FN plots, which are indicative of the emitting area, and the average field enhancement factors for the various samples are listed in Table I. The field enhancement factor can be calculated from the slope of FN plot since \( \log(J/F^2) = -\log(A \gamma^2 / \phi) - B \gamma^{3/2} / \gamma F \), where \( A = 1.54 \times 10^{-6} \) A eV V\(^{-2}\), \( B = 6.83 \times 10^9 \) eV\(^{-3/2}\) V m\(^{-1}\), \( \gamma \) is the field enhancement factor, and \( \phi \) is the work function. \(^{14}\) It was assumed \( \phi = 5 \) eV as for graphite. \(^{15}\) It is very surprising to see that the carbon cloth itself is a very good planar field emitter, comparable with the result reported for carbon nanotubes. \(^{3-7}\) In fact, it is too high to be explained from the geometry of the carbon fibers with diameters of \( \sim 10 \) \( \mu \)m. It is even surprising that the carbon nanotubes grown on the carbon cloth showed much lower operating electric field of less than 0.4 V/\( \mu \)m as shown in Fig. 3. This field emission is obviously due to the presence of carbon nanotubes that caused the increase of the number and the sharpness of the emission sites. This is based on the increase of average intercept \(-0.9945 \rightarrow 8.5445\) of FN plots and the increase of average field enhancement factor \((0.857 \times 10^4 \rightarrow 1.882 \times 10^4)\). This is clearly confirmed by the SEM image of the carbon nanotubes grown on carbon cloth [Figs. 2(c) and 2(d)]. The field enhancement factor of the carbon nanotubes grown on carbon cloth is much higher than those of the single-wall and multiwall carbon nanotube films \((\sim 1.1 \times 10^4)\) \(^{15,16}\) and is also a little higher than that of single tungsten wire field emitter \((\sim 1.8 \times 10^4)\). \(^{17}\)

The field emission properties cannot be explained solely by the field enhancement of the carbon nanotube itself. This is because the field enhancement factor calculated from the slope of the FN plot for the carbon nanotube grown on smooth graphite foil is only \(0.407 \times 10^3\), even though the average diameter of carbon nanotubes grown on graphite foil \([\sim 25 \) nm, Figs. 6(e) and 6(f)] is smaller than that on carbon cloth \([\sim 50 \) nm, Figs. 6(a) and 6(b)]. Smaller diameter normally means higher field enhancement factor. This means that the overall field enhancement is dependent not only on the carbon nanotube itself but also on the morphology of the vacuum chamber \(<3 \times 10^{-7}\) Torr) using the simple diode configuration with a 5-mm-diam cylindrical anode and a gap of 0.26, 1, 2, and 3 mm depending on samples. The field emission current density dependencies of electric field \((J-F)\) measured from various samples are shown in Fig. 3. From Fig. 3(a), the average operating electric fields for the carbon cloth, the carbon nanotubes grown on carbon cloth, the carbon nanotubes grown on Cr-coated carbon cloth, and the carbon nanotubes grown on graphite foil are determined to be 1.48, 0.34, 0.65, and 3.62 V/\( \mu \)m, respectively. In Fig. 3(b), we show the emission current density dependencies of electric field in the low current density region, which indicates the turn-on electric field—less than 0.2 V/\( \mu \)m.

In order to justify the accuracy of calculation of turn-on electric field, the applied voltage corresponding to 10 nA/cm\(^2\) is measured at different cathode-to-anode gap (2948, 3918, 4904 \( \mu \)m). The result is shown in Fig. 4, and it can be seen that the measured data fit well to a line passing through zero, which means that the possible error in the estimation of gap is negligible.

The Fowler–Nordheim (FN) plots for the various samples are shown in Fig. 5. The average intercepts of FN plots, which are indicative of the emitting area, and the average field enhancement factors for the various samples are listed in Table I. The field enhancement factor can be calculated from the slope of FN plot since \( \log(J/F^2) = -\log(A \gamma^2 / \phi) - B \gamma^{3/2} / \gamma F \), where \( A = 1.54 \times 10^{-6} \) A eV V\(^{-2}\), \( B = 6.83 \times 10^9 \) eV\(^{-3/2}\) V m\(^{-1}\), \( \gamma \) is the field enhancement factor, and \( \phi \) is the work function. \(^{14}\) It was assumed \( \phi = 5 \) eV as for graphite. \(^{15}\) It is very surprising to see that the carbon cloth itself is a very good planar field emitter, comparable with the result reported for carbon nanotubes. \(^{3-7}\) In fact, it is too high to be explained from the geometry of the carbon fibers with diameters of \( \sim 10 \) \( \mu \)m. It is even surprising that the carbon nanotubes grown on the carbon cloth showed much lower operating electric field of less than 0.4 V/\( \mu \)m as shown in Fig. 3. This field emission is obviously due to the presence of carbon nanotubes that caused the increase of the number and the sharpness of the emission sites. This is based on the increase of average intercept \(-0.9945 \rightarrow 8.5445\) of FN plots and the increase of average field enhancement factor \((0.857 \times 10^4 \rightarrow 1.882 \times 10^4)\). This is clearly confirmed by the SEM image of the carbon nanotubes grown on carbon cloth [Figs. 2(c) and 2(d)]. The field enhancement factor of the carbon nanotubes grown on carbon cloth is much higher than those of the single-wall and multiwall carbon nanotube films \((\sim 1.1 \times 10^4)\) \(^{15,16}\) and is also a little higher than that of single tungsten wire field emitter \((\sim 1.8 \times 10^4)\). \(^{17}\)

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substrate on which carbon nanotubes grow. Therefore the field emission properties of the carbon nanotubes grown on carbon cloth are a combined result of the field enhancement from carbon nanotubes and carbon cloth.

From careful examination of the microstructure of the carbon nanotubes grown on different substrates using transmission electron microscope (TEM), we also found that carbon nanotubes qualities such as crystallinity, graphitization, and defects also play an important role in field emission. Very surprisingly, the carbon nanotubes grown on carbon cloth that showed the best field emission property have very poor crystallinity, high density of bamboo structure, and amorphous phases [Figs. 6(a) and 6(b)] compared to those grown on Cr-coated carbon cloth [Figs. 6(c) and 6(d)]. The graphite layers in Fig. 6(b) are not continuous and inclined to the tube axis, which are detrimental to the electron transport and therefore should yield worse field emission property according to the conventional knowledge. Based on this, we have to conclude that high defects density shown in Fig. 6(b) is very favorable to field emission. This is further illustrated by the carbon nanotubes grown on graphite foil that showed much worse field emission property but much better graphitization, and clear parallel graphite layers in the tube walls [Fig. 6(f)]. It has been reported that field emission of carbon nanotubes can originate from the defects on the outer wall such as open ends of graphite layers.\(^1\) Our results clearly show that the defects density plays a crucial role in field emission properties in addition to geometrical configuration that is the main source for field enhancement factor.

In conclusion, we reported on field emission from the carbon nanotubes grown on the carbon cloth. The emission current of 1 mA/cm\(^2\) was observed at a field of 0.34 V/\(\mu\)m. This field emission properties result from the combined effect of the field enhancement from carbon nanotubes and carbon cloth. In addition, the field emission properties are partly due to the highly defective structure of carbon nanotubes grown on the carbon cloth.

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\(^1\) Brodie and P. R. Schweebel, Proc. IEEE 82, 1006 (1994).
\(^10\) 1 mA/cm\(^2\) is the minimum current density required to obtain the brightness of 300 cd/m\(^2\) from VGA field emission display having a typical high-voltage phosphor screen with the efficiency of 9 lm/W.
\(^12\) E. P. Sheshin, Ultramicroscopy 79, 101 (1999).