Correlation of field emission and surface microstructure of vertically aligned carbon nanotubes

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Two kinds of distinctive field emission behaviors were observed on vertically aligned multiwall carbon nanotube (CNT) films grown by hot filament dc-plasma enhanced chemical vapor deposition. Some samples have stable emission current for more than 60 h (type I), while others degrade substantially in the first 16 h (type II). During the field emission measurement, a brief exposure to air led an abrupt decrease of emission current of all samples. But subsequent reevacuation made type I samples recover the emission current fully, whereas type II samples were damaged permanently reflecting on the irrecoverable emission current. Microstructure studies by transmission electron microscope clearly showed that the stable emission is due to a surface passivation of CNTs by a thin layer of amorphous carbon that prevents CNTs from reacting with ambient gases, e.g., oxygen, during air exposure. © 2004 American Institute of Physics.

Field emission electron source to be used in field emission displays and microwave power amplifiers is probably one of the most promising applications of carbon nanotube (CNT) films because of the high field emission current. Much attention has been paid to the emission capability of CNT films (the emission of high current at low voltage) in order to obtain an efficient field emission electron source. In addition to the emission capability, the stability property of CNT films (the change of emission current over time) is also very important in order to obtain a long-time reliable field emission electron source. However, few results of stability property of CNT films have been reported, which were solely carried out on the randomly oriented CNT films.

Recently, vertically aligned multiwall CNTs have been successfully applied to gated field emission devices. Therefore, it is extremely important to investigate the stability property of vertically aligned multiwall CNT films in order to predict the lifetime of field emission electron source with such CNTs. Hot filament dc-plasma enhanced chemical vapor deposition (dc-PECVD) is one of the most efficient deposition methods to obtain vertically aligned multiwall CNT films. In this letter, two kinds of distinctive stability behaviors observed in field emission current of vertically aligned multiwall CNT films grown by hot filament dc-PECVD are reported.

Two samples of vertically aligned multiwall CNT films were grown on Cr-coated silicon substrate by hot filament dc-PECVD. Before the growth of CNTs, the catalyst Ni particles were deposited on the Cr-coated silicon substrate using pulse-current electrochemical deposition. The experimental details have been described before. Figure 1 shows the typical scanning electron microscope (SEM) micrographs of two samples. The average length and density of CNTs of sample A were ~8.5 μm and 1 × 10⁹/cm², respectively, and 12.5 μm and 6 × 10⁹/cm² for sample B. The diameter of the CNTs was in the range of 50–80 nm.

The stability property of field emission current was measured using planar diode configuration with Mo cylindrical disk anode. The diameters of the cathode and anode were 12 and 5 mm, respectively, and the gap between cathode and anode was 130 μm. After the initial field emission current-voltage characteristics were measured up to certain voltage corresponding to a current density of about 0.1 mA/cm², the applied voltage was maintained for an extended time and the time-dependent field emission current was measured. The vacuum level was between 1 × 10⁻⁶ and 1 × 10⁻⁷ Torr during measurement. After the time-dependent field emission current measurement, the vent valve of the measurement vacuum chamber was slightly opened while the voltage was still applied. The vacuum level immediately increased to (2–3) × 10⁻⁴ Torr and was maintained for 10 min. Finally, the vent valve was closed and the vacuum chamber was re-evacuated, and the field emission current was measured again.

Figure 2 shows the stability behavior of samples A and B. It can be seen that the field emission current of sample A was nearly constant during the entire time period of measurement, as shown in Fig. 2(a) (filled square). After a time period of 67 h with the voltage on, the vent valve was opened as described previously. When the CNT film of sample A was exposed to air, the emission current was dropped abruptly, but it was almost fully recovered to the initial current level after re-evacuation, as shown in Fig. 2(b) (filled square).

On the other hand, the stability behavior of sample B shown in Fig. 2(a) (open square) is completely different from that of sample A. It is clearly shown that the field emission current was quickly and substantially decreased during the...
initial 16 h and then stabilized. When the CNTs of sample B were exposed to air after a few more measurements during a time period of 90 h with the voltage on, the emission current was abruptly dropped and was not recovered after the subsequent reevacuation, as shown in Fig. 2(b) (open square).

Although the field emission capability can be affected by the apparent differences of the length and the density between the two CNT films shown in the SEM images, the stability property should be affected by other factors such as surface condition. In order to investigate the difference between the CNT films of the two samples, transmission electron microscope (TEM) observation was carried out, and Figs. 3(a) and 3(b) show the TEM image of samples A and B, respectively. It can be seen from Fig. 3(a) that the CNTs of sample A is covered with a thin layer of amorphous carbon that passivated the inner carbon nanotube. The thickness of the amorphous layer was in the range of 10–25 nm. On the contrary, Fig. 3(b) shows that the surface of CNTs of sample B is free of such amorphous carbon.

To further investigate the difference between two samples, the field emission current–voltage characteristics before and after the stability measurements, and after air exposure and reevacuation are compared, as shown in Fig. 4. Figure 4(a) shows that the field emission current–voltage curves of sample A can be approximated by two straight lines, which is similar to the field emission characteristics from adsorbate-covered CNTs, AlN-coated Mo emitters, and organic binder-covered CNT films. From this and the TEM image, it can be concluded that the field emission current of sample A comes out not from the clean CNT surface but from the passivation surface. This passivation is thought to be rather reinforced during measurements because the field emission current in the low current region is slightly increased. This passivation of CNT surface can explain why the initial field emission current is recovered after the exposure to air and the subsequent reevacuation. Since the field emission current from CNT films is decreased after being exposed to oxygen, the abrupt drop of field emission current after exposure to air can be attributed to the adsorption of oxygen in air. However, since the CNTs of sample A were passivated, no damage happened to CNTs during the adsorption of oxygen and, as a result, the initial current could be recovered after oxygen was desorbed by reevacuation.

On the contrary, Fig. 4(b) for sample B clearly shows that the decrease of field emission current after stability measurements is related to the saturation of field emission current in the high electric field region. Since the saturation of field emission current means that the CNTs have high resistance, the fact that the field emission current was more saturated during measurements means that the resistance of CNTs was increased. The resistance in series with CNTs can be estimated by using

\[ I = a(V - I - R)^2 \exp[-b(V - I - R)^2], \]

where \( I \) and \( V \) are the field emission current and applied voltage, respectively, and \( R \) is the resistance in series with carbon nanotubes. Assuming \( R = 0 \), \( a \) and \( b \) can be evaluated by fitting Eq. (1) to the low emission current part of the measured data. The resistances corresponding to before and after stability measurements, and after air exposure are estimated to be 1.29, 9.93, and 132.4 MΩ, respectively, as shown in Fig. 4(b). This increase of resistance can be caused by the structural damage of CNTs due to the resistive heating produced by emission current and reaction with ambient gas such as oxidation or reactive sputter etching of CNTs caused by oxygen and/or water molecules. The reaction of CNTs of sample B with ambient gas is supported by the fact that the resistance is dramatically increased after being exposed to air and by the fact that the surface of CNTs of sample B is not passivated.

![FIG. 1. SEM micrographs at grazing incidence of 45° to the substrate. (a) sample A and (b) sample B. The white scale bars represent 10 μm.](image1)

![FIG. 2. Stability of field emission current from sample A and sample B (open square): (a) field emission current stability dependence of time; (b) field emission current behavior after the air exposure and the subsequent reevacuation.](image2)
The reason why the surface of CNTs of sample A is passivated and that of sample B is clean can be found in the dual role of C₂H₂/NH₃ plasma during CNT growth. Since the amorphous carbon is deposited by C₂H₂ plasma and thermal decomposition of C₂H₂ and is etched by NH₃ plasma, it seems that the unbalance between the deposition and etching during turnoff of C₂H₂/NH₃ plasma resulted in such difference on the surface of the CNTs. It is obvious that the stability property of the vertically aligned multiwall CNT film can be improved by the thin layer of amorphous carbon, which can be in situ formed by adjusting the process parameters of hot filament dc-PECVD. The details of the effect of the amorphous carbon is deposited by C₂H₂ plasma and thermal decomposition of C₂H₂ and is etched by NH₃ plasma, 26 the unbalance between the deposition and etching during turnoff of C₂H₂/NH₃ plasma resulted in such difference on the surface of the CNTs. It is obvious that the stability property of the vertically aligned multiwall CNT film can be improved by the thin layer of amorphous carbon, which can be in situ formed by adjusting the process parameters of hot filament dc-PECVD. The details of the effect of passivation thickness on stability are being studied and will be reported.

In summary, two distinctive field emission stability behaviors were observed on vertically aligned multiwall CNT films grown by hot filament dc-PECVD using pulse-current electrochemically deposited catalyst Ni particles. The field emission current from CNTs with clean surface showed an unstable behavior due to reaction with ambient gas. On the contrary, it was shown that stable field emission current can be drawn during 67 h from CNTs with surface passivated by a thin layer of amorphous carbon. Our results show that in situ coating of CNTs with a thin amorphous carbon layer could be an effective method to obtain stable field emission current.

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