Electric field-induced carbon nanotube junction formation

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We present experimental evidence of nanojunction structures explicitly observed after application of high electric fields on multiwall carbon nanotube arrays. The electric field as well as thermal effects result in carbon–carbon bond breaking and redeposition leading to nanojunction formation. The growth mechanism of the nanojunction is believed to be open-ended topological defect growth in which carbon atoms at two adjacent nanotube tips chemically react and fuse forming an array of nanojunctions. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1383279]

The prospect of carbon nanotubes (CNT) for many potential applications has triggered a rapidly growing research field. CNTs have been shown to be good field emitters due to its geometry, high aspect ratios, and small tip radius of curvature, as well as high chemical and mechanical stability.[1–3] Current nanoscale electronic devices include quantum dots functioning as single electron transistors[4] and CNTs used as field-effect transistors.[5] CNT-based devices can offer higher device density than conventional semiconductor technology.

In this letter, we report the observation of nanojunctions formed after the application of a high electric field on an array of well-aligned multiwall carbon nanotubes (MWNT). The fabrication of MWNTs is based on plasma enhanced chemical vapor deposition (PECVD) by decomposition of acetylene and ammonia gases on thin FeNiCo catalyst films deposited by radio frequency magnetron sputtering. The CNTs were grown at 1000 mTorr in a rf-PECVD chamber with the sample grounded and a rf power of 90 W applied. The synthesis temperature was ~650 °C. The CNTs were characterized using a JEOL JSM 6430F field emission scanning electron microscope (FESEM). Figure 1(a) shows an array of well-aligned CNTs grown on a FeNiCo catalyst film supported by a Si substrate. The CNTs were of high density and well distributed over a large area. A striking feature is that the as-grown nanotubes have a uniform diameter of about 5–15 nm and uniform length of 13 μm. The SEM image in Fig. 1(b) shows that the CNTs are relatively straight before the application of high electric fields. Secondary ion mass spectrometry (SIMS) depth profiles (not shown here) have also indicated that most of the catalyst particles are located at the base of the CNTs.

Field emission measurements were performed in a vacuum of $\sim 1\times 10^{-6}$ Torr. The CNT array was directly configured as the cathode, with a Fe film as the anode.[6] Measurements were obtained by applying a voltage of up to 2000 V across a fixed gap distance of 300 μm. Figure 2 shows the field emission I–V curve for the CNT film under different vacuum ambience over increasing time periods. The CNTs in the high vacuum environment (10^{-6} Torr) have a low turn-on electric field of ~0.5–1 V/μm at 10^{-5} μA/mm^2 and a low threshold field of ~4.0–4.5 V/μm at 100 μA/mm^2. The inset in Fig. 2 shows the corresponding Fowler–Nordheim plot that suggests a conventional field emission mechanism from a free electron gas. The field emission characteristics can be fitted using the Fowler–Nordheim formula $I \sim E_{\mathrm{loc}}^2 \exp(A\phi^{3/2}E_{\mathrm{loc}})$.[7] The local electric field is given by $E_{\mathrm{loc}}=\beta V/d$, where β is the enhancement field, i.e., ratio of height of the tip to the radius of curvature of the tip apex. Using a work function ϕ of ~4 eV and a constant A of 6.8×10^9, the field enhancement is calculated to be greater than 10 000. Local enhancement of the emission field at the individual tips is expected to be much greater than the geometrical measurement. This is because only the last atoms in the chain of carbon atoms at the end of an emitting CNT participate in electron field emission.[8] Under a controlled vacuum environment of $\sim 1\times 10^{-6}$ Torr, the CNT were able to display stable emission currents for >10 h with no degradation. No physical or geometrical changes in the tips were observed under SEM analysis.

Similar field emission measurements on the same sample were also carried out at a background pressure of $\sim 1\times 10^{-2}$ Torr under a constant bias of 2000 V. The resulting changes in the emission currents were observed over a period of 6 h and FESEM images were taken after every two hours. The field emission of the CNTs after different times is plotted in Fig. 2. There was a ~20% irreversible drop in current density after field emission for 2 h. No appreciable changes in morphology of the nanotubes were detected by SEM measurements. After 4 h, the maximum emission current density decreased by half. The irreversible degradation is attributed to microscopic physical changes to the tips as observed under SEM. The diameter of the CNTs was observed to have increased to ~15–100 nm and the length decreased to ~10 μm. The prolonged electric field effect may have caused evaporation of graphene layers from the tip and re-deposition around the CNT walls resulting in a shortening and thickening of the MWNTs. This increases the nanotube tip radius resulting in less effective electron emission when a voltage is applied. Furthermore, the electric field at the tip of nanotubes lowers when the protruded length is short. Further exposure to high electric fields (6 h) caused the maximum emission current density to drop by a further 93%. The turn-on voltage is increased to 3 V/μm. Figure 1(c) shows the SEM image of CNT after 6 h of operation. It is evident that the CNT geometry changes drastically with junction formation, exhibiting numerous ''V'' and ''L'' nanojunction structures. Each indi-

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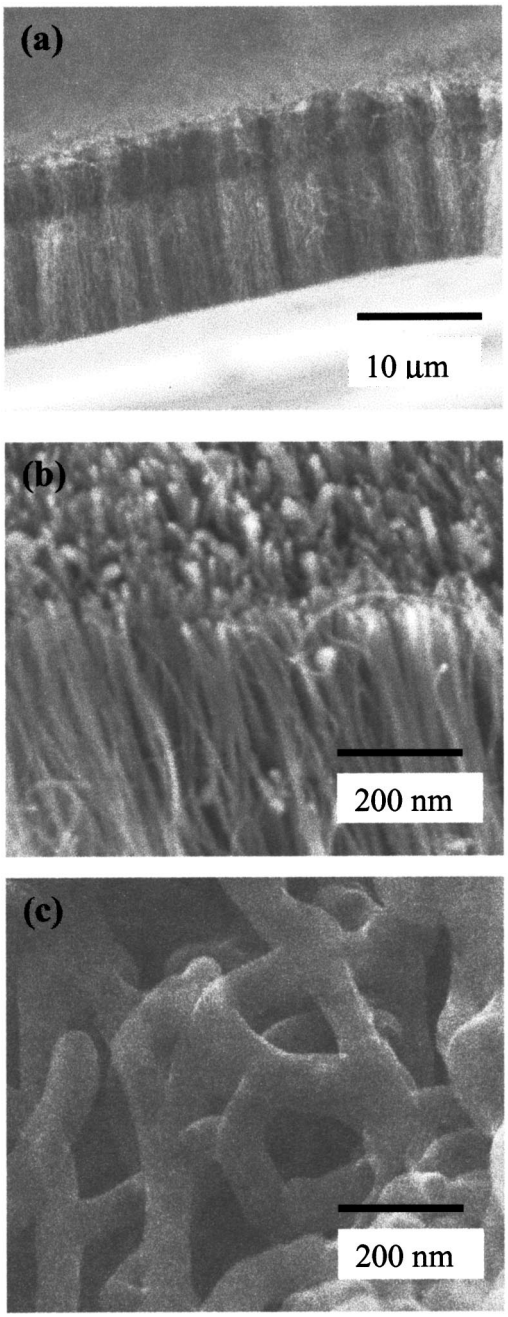

FIG. 1. (a) A SEM image of an array of well-defined CNTs grown on FeNiCo catalyst film supported by Si substrate. The two color contrast is due to deposition of carbonaceous particles on the nanotubes after the growth process (during the cooling down period), whereby the darker top represents parts of the CNT with deposited carbonaceous particles on the surfaces; (b) Higher magnification SEM image showing that the CNTs are relatively straight before the application of high electric-field; (c) CNTs after 6 h of exposure to high electric fields.

vidual CNT becomes shorter (~5–10 μm) with tube diameters of 15–100 nm. Colbert and Smalley have shown that applying a bias voltage of −75 V for about 30 s is sufficient to sublime some C atoms from the nanotube tips.[9] Thus it is deduced that the electric field at the nanotube tips is sufficiently large enough to break C–C bonds, causing C atom sublimation thereby shortening the nanotubes. The sublimated C atoms are likely to redeposit on the cooler tube walls leading to the growth of additional graphene layers that increase the tube diameter, and facilitate nanojunction formation.

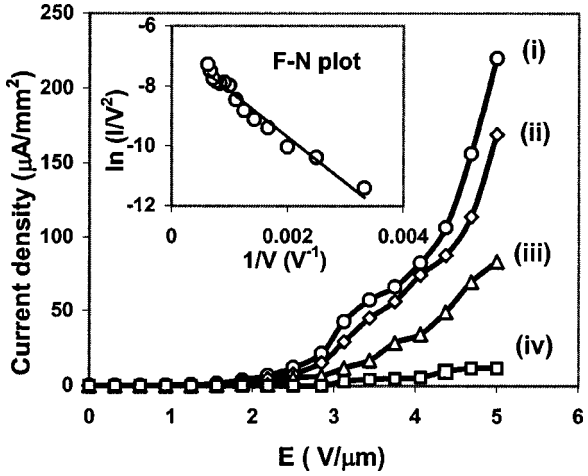

FIG. 2. Field emission I–V curve for the CNT film under different vacuum ambience over a period of time in (i) controlled vacuum 10^{-6} Torr, (ii) 2 h at 10^{-2} Torr, (iii) 4 h at 10^{-2} Torr, (iv) 6 h at 10^{-2} Torr. (inset) Fowler–Nordheim plot of CNT under controlled vacuum at 10^{-6} Torr.

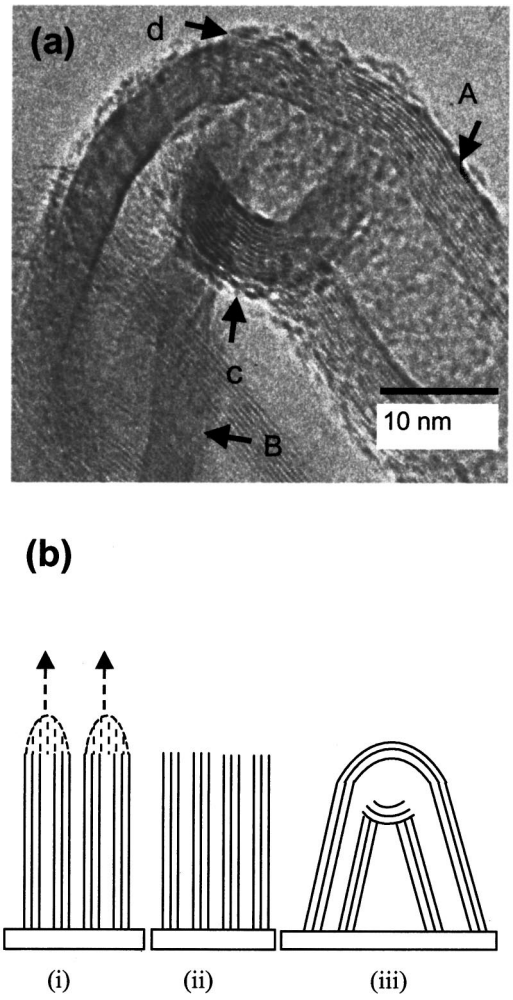

FIG. 3. (a) TEM image of a typical nanojunction formed by fusion of two adjacent tips under high electric field conditions. (b) Model illustrating formation of nanojunction structure in (a): (i) E field as well as thermal effects lead to C–C bond breaking; (ii) nanotubes are left with open tips and structural defects; (iii) fusion of adjacent CNTs to form a nanojunction. The outer walls form a fairly continuous junction as seen at region d in (a). For the inner walls at region c, discontinuous and defective joints appear to have formed so as to minimize the energy that would have been required to form a high curvature and high stress junction.

Atomic-scale structural information was obtained using a high resolution transmission electron microscope (HRTEM) Philips CM300 FEG at 300 kV. Figure 3(a) shows a TEM image of a typical nanojunction. Tube A and tube B with outer diameters of approximately 20 and 15 nm, respectively, are joined at regions c and d. Dislocation defects observed at region d due to the different wall thicknesses of tubes A and B suggest that this is the fusing interface. A model illustrating the nanojunction structure formation is shown in Fig. 3(b). (i) High electric fields at the nanotube tips cause C–C bond breaking. (ii) This results in open tip structures that fuse easily under high electric fields and temperatures. It was observed that densely packed and vertically aligned carbon nanotubes show preferential nanojunction formation as compared to sparse and randomly aligned carbon nanotubes due to the proximity of adjacent open tips. (iii) This important observation supports our proposed model of tip to tip fusion during the application of high electric fields. The outer walls form a fairly continuous junction as seen at region d in Fig. 3(a). For the inner walls at region c, discontinuous and defective joints appear to have formed so as to minimize the energy that would have been required to form a high curvature and high stress junction. The nanojunction structure at the joint is believed to be formed by pentagon–heptagon pairs which are related to topological defects.[10] Such a connection of two CNTs has already been theoretically predicted by the insertion of pentagon–heptagon pairs into the honeycomb lattice.[11]

It is believed that the dissociation of residual gases in the higher ambient pressure environment ($\sim 10^{-2}$ Torr) may have also contributed to nanotube wall growth under high field conditions. The high electric field is believed to cause local heating and ionization thereby inducing chemical reactions at the tip and bent regions. Ions and free radicals that are formed also play a role in modifying the surface morphology and tip geometry.

The application of an electric field under controlled gas pressures may provide an alternative way of synthesizing nanotube junctions for nanoelectronic devices. Nanoelectronic devices can be realized by joining two nanotubes to create different combinations of metal and semiconductor junctions depending on their helicity and diameter. On the other hand, under a low vacuum environment, CNTs are able to display stable emission currents for long durations with little degradation.

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