Precise positioning of single-walled carbon nanotubes by ac dielectrophoresis

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The precise placement of single-walled carbon nanotubes (SWCNTs) in device architectures by ac dielectrophoresis involves the optimization of the electrode geometry, applied voltage and frequency, load resistance, and type of nanotube sample used. The authors have developed a toolkit to controllably integrate SWCNTs in device structures by the use of floating potential metal posts and appropriate electrode geometries, as designed using electric field simulations, and used it to fabricate structures such as crossed nanotube junctions. © *2006 American Vacuum Society.*
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I. INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) have attracted much attention because of their unique size-dependent electrical and mechanical properties.[1] Integration of these structures into electronic devices where they can act as either active elements or interconnects requires precise positioning and assembly into device architectures. Nanotubes have been assembled in device architectures by chemical modification of the substrate,[2] direct growth on patterned substrates by chemical vapor deposition,[3] and a mechanical transfer protocol that involves the stamping of nanotubes onto a substrate.[4] However, these techniques can be difficult to apply to more complex device structures, such as multiterminal transistors and branching interconnects. The ac dielectrophoresis of SWCNTs is a versatile way to build devices using prepatterned microelectrodes.[5,6] The availability of micelle-solubilized nanotubes has made it possible to obtain single SWCNTs in aqueous solution, which allows for much greater control over the dielectrophoretic assembly process.[7] Here, we have developed a toolkit to controllably integrate SWCNTs into device structures.

For a tube with a cylindrical shape, the dielectrophoresis force is

$$\vec{F}_{\mathrm{DEP}} = \frac{\pi d^2 l}{8} \varepsilon_l \,\mathrm{Re}\left(\frac{\varepsilon_t^* - \varepsilon_l^*}{\varepsilon_l^* + (\varepsilon_t^* - \varepsilon_l^*)L} \right) \nabla E_{\mathrm{rms}}^2, \tag{1}$$

$$\varepsilon_{t,l}^* = \varepsilon_{t,l} - i\frac{\sigma_{t,l}}{\omega}, \tag{2}$$

where ε_t^* and ε_l^* are the complex dielectric constants of the tube and the surrounding liquid, ε and σ are the corresponding real parts of the dielectric constants and conductivities, L is the depolarization factor, and d and l are the diameter and length of the tube.[8] The dielectric constant of metallic SWCNTs is expected to be very high due to the large number of mobile carriers.[9] Thus, nanotubes in aqueous solution should be drawn into and aligned across a gap when a voltage is applied across a pair of electrodes.

II. EXPERIMENTAL METHODS

High-pressure CO (HiPCO) SWCNTs made by the catalytic decomposition of CO (Carbon Nanotechnologies) and CoMo CAT nanotubes made by chemical vapor deposition over silica-supported Co and Mo catalysts (Southwest Nanotechnologies) were individualized by ultrasonication and dispersed in aqueous solution by wrapping with a surfactant, as described previously in the literature.[7] Sodium dodecylbenzene sulfonate (NaDDBS), sodium dodecyl sulfate, poly(maleic acid/octyl vinyl ether) (PMAOVE), and sodium bis-2-ethylhexyl-sulfosuccinate were used as the wrapping micelles. UV–visible–near infrared absorption and photoluminescence spectra showed that the tubes wrapped in micelles were mostly individual tubes.[10] (Bundles of tubes do not fluoresce because of quenching by metallic tubes.) The length and concentration of the tubes were controlled by the duration of the sonication process. We were successful in aligning SWCNTs wrapped in all the above micelles. Since most of the tubes in solution are single tubes, the aligned SWCNTs shown here are predominantly single tubes. However, the presence of small bundles of tubes cannot totally be ruled out. Most of the results presented here are for NaDDBS wrapped tubes.

Two or four microelectrodes were patterned on SiO_2 (500 nm)/Si substrates by e-beam lithography, followed by thermal or electron beam evaporation of Cr/Au electrodes (Fig. 1). Electrode heights ranged from 50 to 250 nm. The tubes were deposited by applying an ac voltage (specified by the peak-to-peak voltage) between opposite electrodes, with the other two electrodes floating when four electrodes were used. A 5 MHz field was found to be optimal for the alignment of SWCNTs. In a typical experiment, an 8 μl drop of

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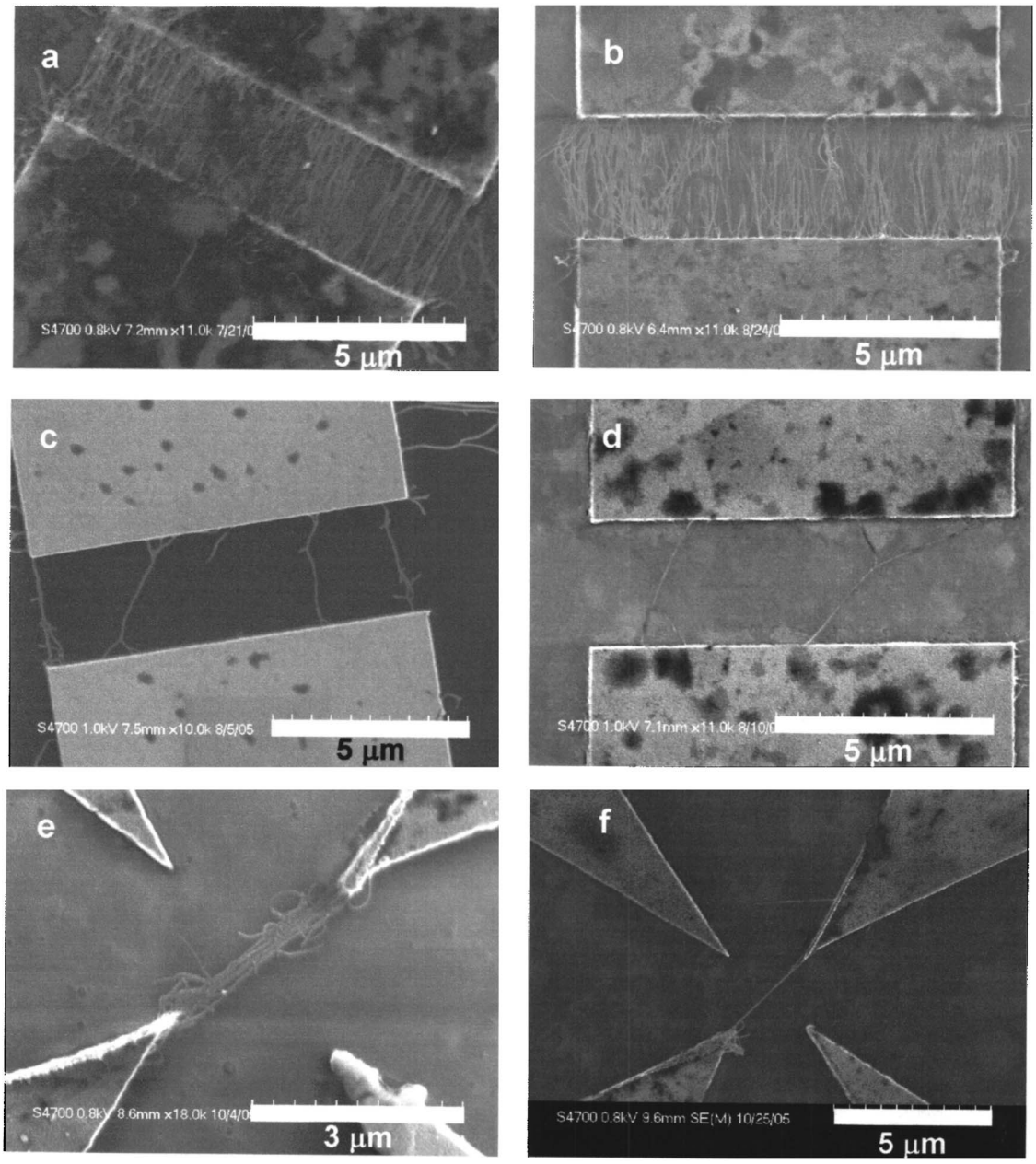

FIG. 1. [(a)–(d)] HiPCO SWCNTs aligned in a 3 μm gap between 10-μm-wide electrodes by applying an 8 V, 5 MHz ac voltage between the electrodes for 2 min. (a) NaDDBS-wrapped SWCNTs and (b) PMAOVE-wrapped HiPCO SWCNTs aligned in the gap. (c) Four NaDDBS-wrapped SWCNT bundles aligned in the gap under the same conditions as (a) but with a 44 MΩ limiting resistor in series with the circuit. (d) Two NaDDBS-wrapped HiPCO SWCNT bundles aligned in the gap under the conditions of (a) but with a 76 MΩ resistor in series with the circuit. (e) NaDDBS-wrapped HiPCO SWCNTs aligned between pointed electrodes separated by a 3 μm gap. A 6.5 V, 5 MHz ac voltage was applied between the electrodes for a period of 2 min. (f) A single nanotube aligned in the gap using the same conditions as (e), but with a 1 GΩ resistor in series with the circuit. Scanning electron microscopy (SEM) images were obtained using a Hitachi S4700 instrument operated at 0.8–1 kV with a working distance of 6–12 mm.

the aqueous nanotube dispersion was held in the gap for times ranging from 30 s to 5 min, followed by washing with 800 μl de-ionized H_2O, and drying with N_2.

The electric field profile was simulated by finite element analysis using MAXWELL 3D software from Ansoft Corporation (Pittsburgh, PA). *I-V* curves were obtained on an HP4145 semiconductor parameter analyzer.

III. RESISTANCE CONTROL

As shown in Figs. 1(a) and 1(b), several hundreds to thousands of SWCNTs were aligned across a 3 μm gap by applying an 8 V, 5 MHz voltage across an opposite pair of electrodes for 2 min. The tubes appeared to be quite straight and were aligned parallel to one another. Such nanotube network devices may be useful for certain applications, such as flexible electronics and sensors.[11] However, most applications require discrete devices based on single nanotubes,[12] and so it is important to control the number of nanotubes deposited in the gap. This can be achieved to some degree by controlling the time the ac voltage is applied, or more controllably, by placing a limiting resistor in series with the

circuit. Thus, when a single nanotube or nanotube bundle bridges the gap, the limiting resistor effectively shuts off the voltage, preventing any further dielectrophoretic trapping of SWCNTs. Figures 1(c) and 1(d) show examples of resistance control using different load resistors for the conditions of Figs. 1(a) and 1(b).

The contact resistance for our as-prepared SWCNT devices with sharp electrodes was approximately 1 GΩ. By using a 1 GΩ series load resistance, we have been able to control the number of nanotubes that bridge the 3 μm gap between pointed electrodes, as shown in Fig. 1(f) [and which should be compared to Fig. 1(e)]. A similar method has also been previously used to limit the number of multiwalled nanotubes trapped in a gap.[13]

IV. GUIDING NANOTUBES USING FLOATING POTENTIAL POSTS

When there are four symmetric electrodes and a voltage is applied across opposite electrodes, the tubes tend to span adjacent floating potential electrodes, as shown in Fig. 2(a). Patterning small metal posts or strips within the gap perturbs the electric field. As shown in Fig. 2(d), these posts lead to regions where the electric field is locally enhanced ("hotspots"), relative to the simulation with no posts [Fig. 2(b)]. This helps to guide nanotubes across a predictable path, in a zigzag pattern, along micropatterned posts, or along the edges of micropatterned strips.[14] Two common motifs are observed in this nanotube guiding: alignment with the tubes touching the posts and strips [Figs. 2(e) and 2(f)], sometimes touching the posts with zigzag alignment [Fig. 2(e)], and inline alignment of nanotubes between the posts [Fig. 2(c)]. Posts with diameters as small as 300 nm have been found to be effective in guiding the alignment of SWCNTs [Fig. 2(e)].

Control experiments indicated that there was no alignment of nanotubes without the application of a voltage. Moreover, when a voltage is applied across the electrodes labeled as floating in Fig. 2(e), while allowing the second pair of electrodes (with the line of posts between them) to float, the nanotubes are aligned across the first pair and they touch the central posts. No alignment is seen across the line of posts between the electrodes that are floating. This proves that the nanotubes are guided by the posts due to altered electric field patterns and not due to adhesion to the posts.

This guiding phenomenon provides remarkable control over the placement of nanotubes in device geometries and we expect to publish a more detailed discussion of this in the near future.[14] Such dielectrophoretically positioned metallic tubes may be especially useful for fabricating complex multiterminal interconnects.

V. CROSSED NANOTUBE JUNCTIONS

We have also used ac dielectrophoresis to build more complex geometries, such as crossed nanotube junctions, which could potentially be useful for applications such as nonvolatile random access memory.[15] The crossing between two semiconducting or two metallic tubes has been seen to behave as a tunnel junction, whereas junctions between a metallic and a semiconducting tube have shown Schottky diodelike behavior.[16,17] However, there are no known methods for controllably assembling crossed nanotube junctions within device architectures.

The major challenge to assembling crossed nanotube structures by ac dielectrophoresis is that, as shown in Fig. 2(a) and 3(a), the nanotubes tend to span to adjacent floating electrodes. One way to alleviate this problem is by using floating potential metal posts as discussed above. Another approach involves modifying the electrode geometry. As shown in Fig. 3(b), SWCNTs can be made to span opposite pairs of electrodes by using pointed electrodes. The sharp electrodes increase the distance between adjacent electrodes by virtue of their geometry [from 1.41 μm for the 1-μm-wide electrodes shown in Fig. 3(a) to 2.12 μm for the pointed electrodes shown in Fig. 3(b)], thus making it less likely that tubes will span to the floating electrodes.

The pointed electrode geometry by itself is not sufficient to prevent SWCNTs from aligning to a floating side electrode. When 8 V is applied across an opposite pair of electrodes, the field in the middle 1 μm of the 3 μm gap is in the range of $(1.08-1.25)\times 10^6$ V/m. This may still be enough for some nanotubes to be trapped across the adjacent floating and powered electrodes. However, at low enough voltage (6.5 V) the tubes align across the opposite powered electrodes and not between adjacent powered and floating electrodes. Thus, a combination of voltage control and pointed electrode geometries enables the reproducible and controllable fabrication of crossed nanotube junctions, as shown in Figs. 3(c) and 3(d). In Fig. 3(c), the nanotube deposited in the second step threads through the gap between the two tubes deposited in the first step.

By combining electrode design and voltage control (which control the location of tube placement) and the use of limiting series resistors, as discussed in Sec. III (which limits the number of tubes that are deposited), we were able to fabricate crossed nanotube structures with a single tube across each pair of opposite electrodes by sequential deposition across each pair [Fig. 3(e) and then Fig. 3(f)].

VI. DEVICE PROPERTIES

The as-prepared dielectrophoretically deposited devices had a relatively high contact resistance, ranging from 500 MΩ to 1 GΩ for NaDDBS wrapped samples. The *I-V* curves show pronounced gate dependence and occasionally exhibit significant asymmetry, as shown in Fig. 4. The gate dependence and asymmetry are likely due to the surfactant molecules forming a tunneling barrier at the contact.[14] The tethering of the tubes at the two electrodes can vary significantly depending on the surfactant coverage, presence of solvent at the contact, and the contact area. The contact resistance was greatly reduced (by up to three orders of magnitude) by annealing under a N_2 atmosphere at 350–400 °C for 10 min. The PMAOVE samples seem to have a much higher contact resistance, on the order of

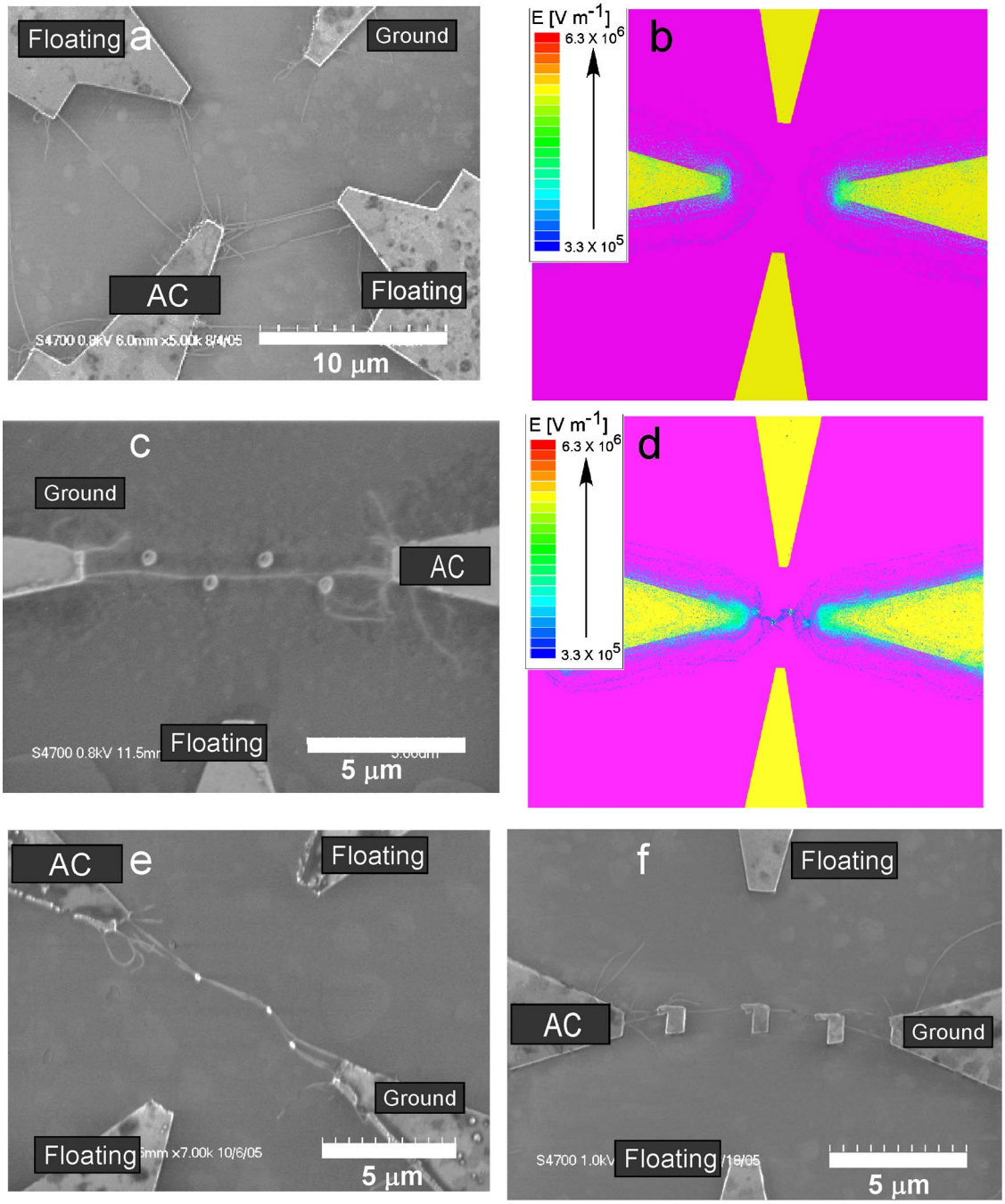

FIG. 2. (a) SWCNTs aligned across a 10 μm gap without any strips or posts in the gap. Some tubes were seen to bind to the floating electrodes. (b) Top view of the calculated electric field magnitude for 10 μm gap electrodes with the same geometry as shown in (a). The SiO_2 surface is shown in pink, while the gold electrodes are yellow (as per color code for the online version). The plotted electric field increases from a threshold of 3.3×10^5 to 6.3×10^6 V/m, linearly from the blue to the red color bars. The highest electric fields, near the electrodes, are denoted by red dots that are too small to be seen here in (b) and (d). (c) Tube alignment between 500 nm diameter posts, without necessarily touching all the posts, using an 8 V, 5 MHz ac voltage. The other pairs of opposing electrodes were floating. (d) Simulated electric field for the geometry used in (c). (e) The tubes are seen to zigzag between 300 nm diameter posts. (f) A single nanotube guided along the edge of 1-μm-wide strips (which is easier to see in the online version). An 8 V, 5 MHz voltage was applied in (e) and (f). All the electrodes shown here have a width of 1 μm. There was no load resistor in (a), (c), (e), and (f).

10–20 GΩ, which may be due to the better stacking and association of the polymer to the nanotube sidewalls.

The HiPCO samples ranged from 0.8 to 1.3 nm in diameter and had a wide distribution of chiralities, with about a third of the SWCNTs expected to be metallic, based on a random distribution of nanotube chiralities.[18] The CoMo CAT SWCNTs were enriched in (6,5) and (7,5) semiconducting nanotubes and there were 11 times as many semiconducting tubes as metallic tubes.[19] Nanotube devices were made from NaDDBS wrapped micelle solutions of both kinds of tubes. For the HiPCO samples, after annealing the gate dependence disappeared, indicating that the deposited tubes

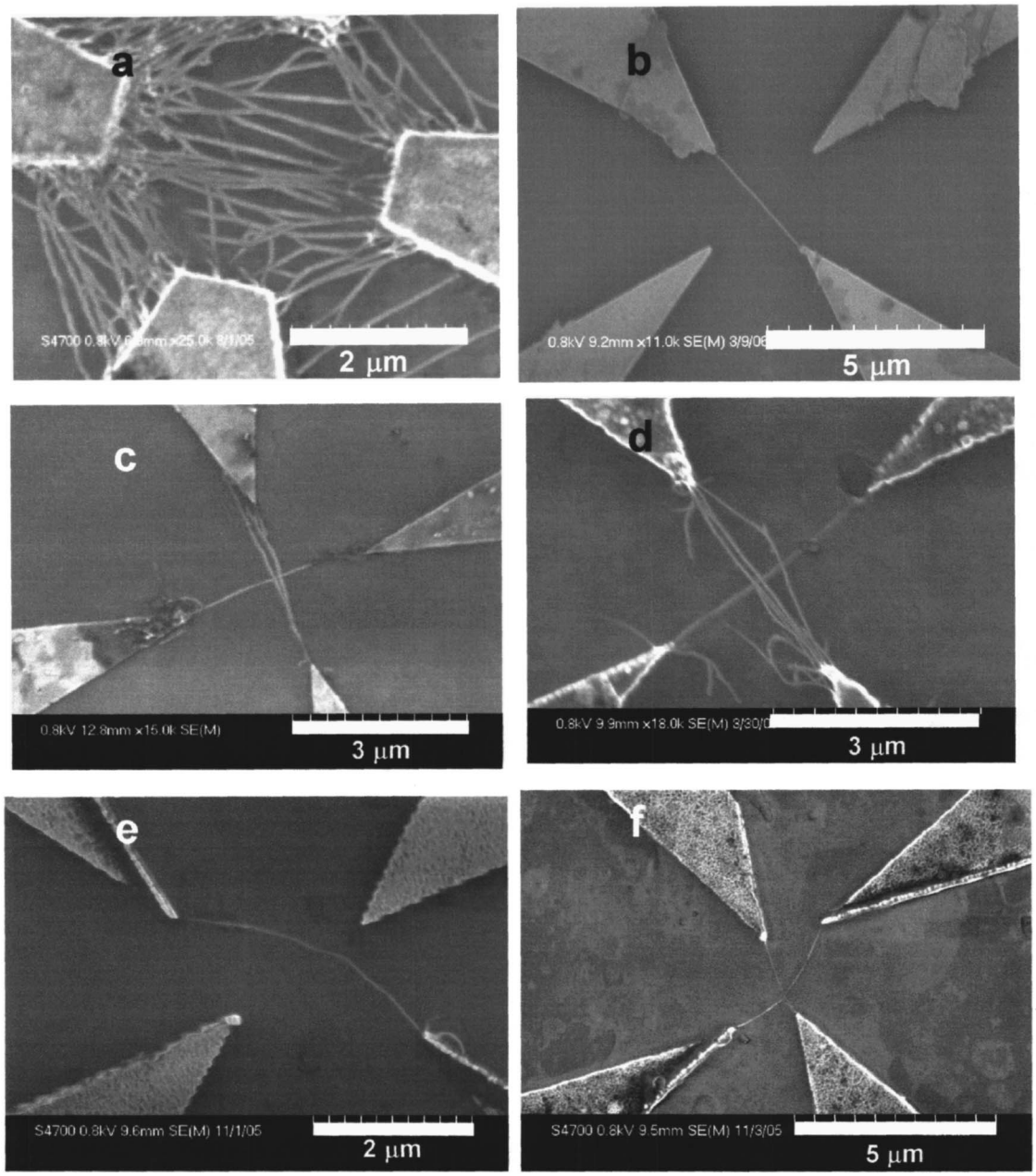

FIG. 3. NaDDBS-wrapped HiPCO SWCNTs dielectrophoretically aligned in (a) a 3 μm gap with 1-μm-wide electrodes using an 8 V, 5 MHz voltage and (b) a 3 μm gap with pointed electrodes using a 6.5 V, 5 MHz voltage. (c) A crossed nanotube junction obtained by sequentially applying a 6.5 V, 5 MHz voltage across opposite pairs of electrodes. This junction was made from NaDDBS-wrapped HiPCO tubes and illustrates the "threading" motif discussed in the text. (d) Crossed nanotube junction made from NaDDBS-wrapped CoMo CAT nanotubes by sequentially applying a 6.5 V voltage across opposite pairs of electrodes. The voltages were applied for 120 s. There was no load resistor in (a)–(d). [(e) and (f)] Crossed junction of two HiPCO nanotubes fabricated by applying a 6.5 V ac voltage across one opposite pair of electrodes in (e) with a 1 GΩ load series resistance and then across the other electrode pair in (f).

were mostly metallic [Fig. 4(a)]. This is consistent with the higher dielectric constants expected for metallic tubes.[5,9] In contrast, for CoMo CAT SWCNTs, a significant fraction of the tubes deposited dielectrophoretically are metallic. However, using these CoMo CAT samples, we have also been able to obtain semiconducting devices, which show a gate dependence even after annealing. Figure 4(b) shows ambipolar transport in such a semiconducting tube.

VII. CONCLUSIONS

We have obtained a considerable degree of control over the dielectrophoretic alignment of carbon nanotubes using prepatterned microelectrodes. We have used floating potential posts and strips to guide nanotubes across devices along predefined and predictable paths. We have also fabricated crossed nanotube architectures controllably with different nanotube preparations, by optimizing the electrode geometry, applied ac voltage, and load resistance. Future work will focus on improving the contact resistances of the devices and on the controllable fabrication of metal-semiconductor junctions, as well as more complex hierarchical nanotube circuits.

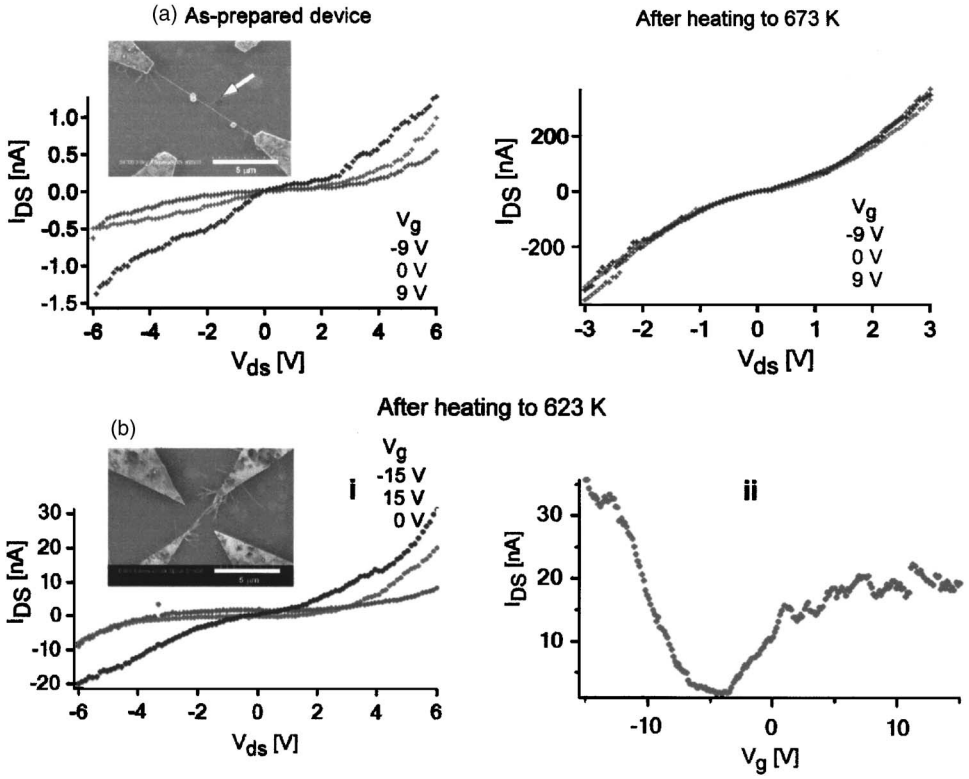

FIG. 4. (a) *I-V* characteristics of a HiPCO SWCNT device assembled using floating potential posts, without any load resistor, before and after heating under a nitrogen atmosphere at 400 °C for 10 min. After annealing, the contacts are seen to substantially improve and not much gate dependence is seen, indicating that the tube is metallic. The inset shows a SEM image of the device. (b) *I-V* characteristics of a CoMo CAT SWCNT device assembled across pointed electrodes without any load resistor. The device has been annealed under N_2 at 350 °C for 10 min. The inset shows a SEM image of the device. (i) shows drain-source curves measured at different gate voltages, whereas (ii) shows the gate curve measured at V_{ds}=6.0 V. The gate curve shows that the tube displays ambipolar transport, indicative of a semiconducting tube.

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