Electric-field-directed growth of carbon nanotubes in two dimensions

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The interplay between mechanical and electronic properties in carbon nanotubes leads to interesting characteristics in devices such as a nanotube cross structure. The fabrication of nanotube devices has often been based on random growth or deposition of nanotubes and subsequently searching for those in desired locations with proper orientations. Obviously we want to be able to make such devices controllably. We present data on extending the technique of one-dimensional alignment of nanotubes using electric field to two dimensions in order to make more complicated structures such as nanotube crosses. It appears that nanotubes assemble in the regions of the most intense electric field. Also, they tend to follow the local field lines, even in nonuniform fields. Furthermore, they tend to grow away from negative toward positive polarities. © *2004 American Vacuum Society.*
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I. INTRODUCTION

Carbon nanotubes (CNTs) can be either metallic or semiconducting, with various band gaps based on their geometrical structure. Therefore, nanoscale heterojunctions can be made by making different types of nanotubes cross each other.[1] Also, the induced local mechanical deformation in the tubes at the intersection point of a nanotube cross structure can cause a local modulation of the electronic structure and create a nanoscale quantum device.[2] Making such structures requires well-controlled fabrication processes. Traditionally, the majority of CNT devices has been made based on the random growth of tubes and subsequently finding the useful devices using microscopy. Recently, valuable attempts have been made in increasing the degree of control in the fabrication process using the gas flow direction during growth[3] or an external electric field[4–6] to align the nanotubes in one direction. Here, we present results on extending the technique of alignment using electric field to two dimensions to make more elaborate structures such as crosses. This study provides information about the nanotube–field interaction during the growth process that could not be obtained from the one-dimensional case.

In making a certain nanotube device using electric-field-assisted growth, the key is to find out what distribution of the electric field in space is needed and then make a set of electrodes that can generate that field distribution during the growth. The designs presented here are based on our interest in making nanotube cross junctions.

II. SIMULATIONS

We have used the program MEDICI to simulate the electrostatic field distribution in several two-dimensional structures. Previously, it has been shown that nanotubes align themselves to the direction of an applied electric field during their growth or deposition from solution.[4–6] Thus, one might think that a field distribution like the one shown in Fig. 1 would yield a cross. However, the regions between nearest-neighbor electrodes of opposite polarity in such a design have the strongest electric field, since the electric field is equal to potential difference divided by distance. As a result, such a voltage configuration will yield nanotubes bridging nearest-neighbor electrodes rather than growing between opposing electrodes and yielding crosses. In order to overcome this, we included a fifth electrode in the middle of the structure. Since this electrode is an equipotential surface, all the potential difference between opposing electrodes falls in the gap regions and so the field there becomes much stronger [Fig. 2(a)]. This fifth electrode also makes a voltage configuration possible where all the outer electrodes are set at the same potential [Fig. 2(b)], thus completely eliminating the field between adjacent electrodes. The fifth electrode, however, should not occupy the region that is going to be used for the device itself; the problem can be avoided by burying the middle electrode just underneath the surface.

Note that the field distributions in Fig. 2 are the results of two-dimensional simulations, whereas the real problem is three-dimensional. However, since the middle buried elec-

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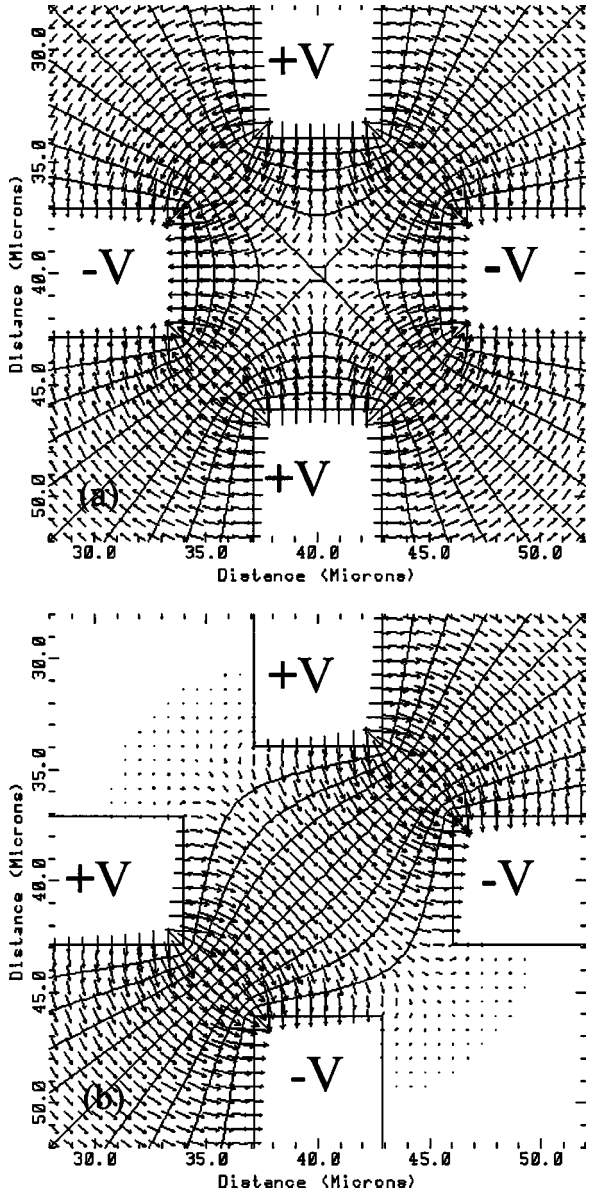

FIG. 1. Electric field distributions (arrows) and equipotential lines (continuous lines) in a four-electrode structure [(a) and (b) represent different voltage configurations]. The magnitude of V is arbitrary since the field intensity scales with the magnitude of V, but its relative distribution is independent of V.

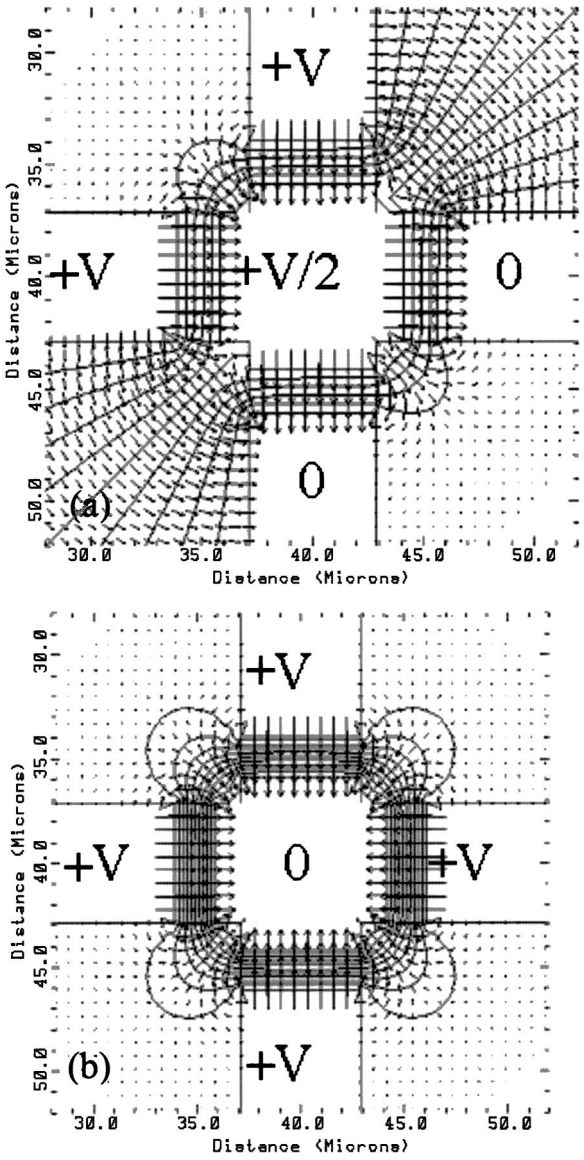

FIG. 2. Electric field distributions (arrows) and equipotential lines (continuous lines) in the presence of a middle electrode in the structure [(a) and (b) represent different voltage configurations]. The magnitude of V is arbitrary since the field intensity scales with the magnitude of V, but its relative distribution is independent of V.

trode is located very close to the surface (20–100 nm below the surface), and the thickness of the surrounding electrodes in our experiments is very small (~50 nm) compared to the lateral dimensions (microns), it is a very good approximation to represent the top view of the electric field distribution close to the surface with a two-dimensional simulation.

III. FABRICATION

Optical lithography and subsequent anisotropic dry etching were used to carve the middle electrode out of the highly doped silicon substrate [Fig. 3(a)]. Two microns of low-temperature oxide was then deposited [Fig. 3(b)]. The oxide was subsequently polished down to a level of only a few tens of nanometers above the raised middle electrodes using chemical mechanical polishing [Fig. 3(c)]. Lithography, metal deposition, and lift-off were then used to pattern the surrounding molybdenum electrodes [Fig. 3(d)]. Catalyst islands (mixture of iron and molybdenum nanoparticles and alumina) were then deposited using a final lithography and lift-off [Fig. 3(e)].[7] Single-walled nanotubes were grown using chemical vapor deposition (CVD) at 800–900 °C in the presence of a flow of hydrogen (500 sccm), methane (1000 sccm), and ethylene (10–20 sccm), while appropriate voltages were applied to all five electrodes to create the desired electric field distribution in space. Voltages of a few volts were used in various experiments, and a voltage that yielded a maximum field intensity of about 1 V/μm was usually found to be enough for alignment. The maximum

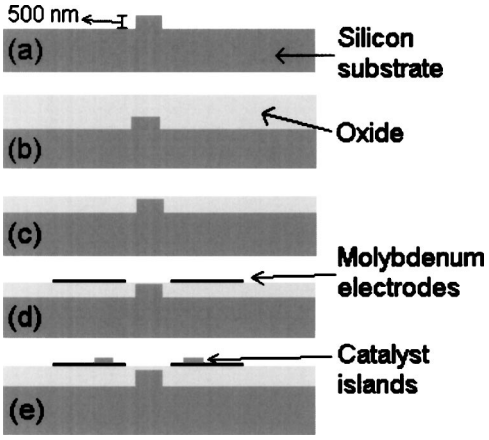

FIG. 3. Fabrication steps: (a) lithography and etching of silicon; (b) low-temperature oxide deposition; (c) chemical mechanical polishing of oxide; (d) lithography, metal deposition, and lift-off to pattern electrodes; (e) lithography, deposition from solution, and lift-off to pattern catalyst islands.

field intensity is the amount of voltage divided by the shortest distance between nearest-neighbor electrodes. Based on sample geometry, this corresponded to voltage values in the 1–5 V range.

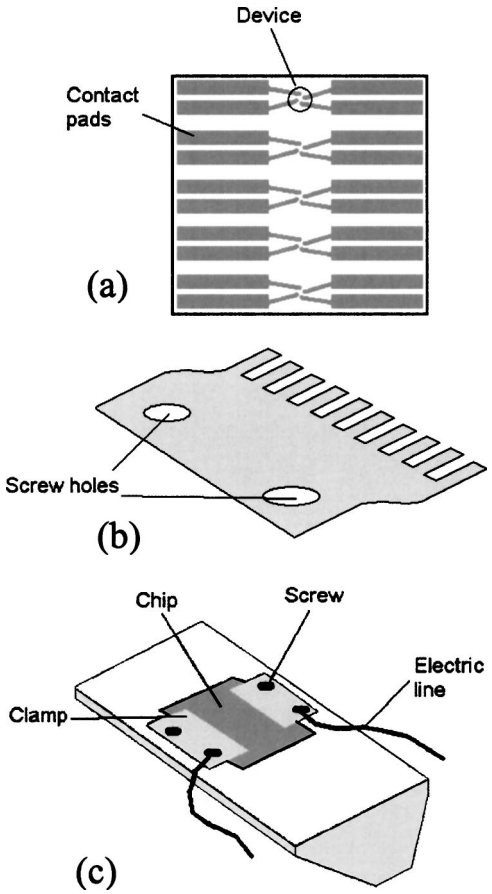

FIG. 4. Schematic of the (a) chip; (b) clamps that make contact to the electrodes on the chip; (c) sample holder that is used for the application of electric field during the high-temperature nanotube growth process.

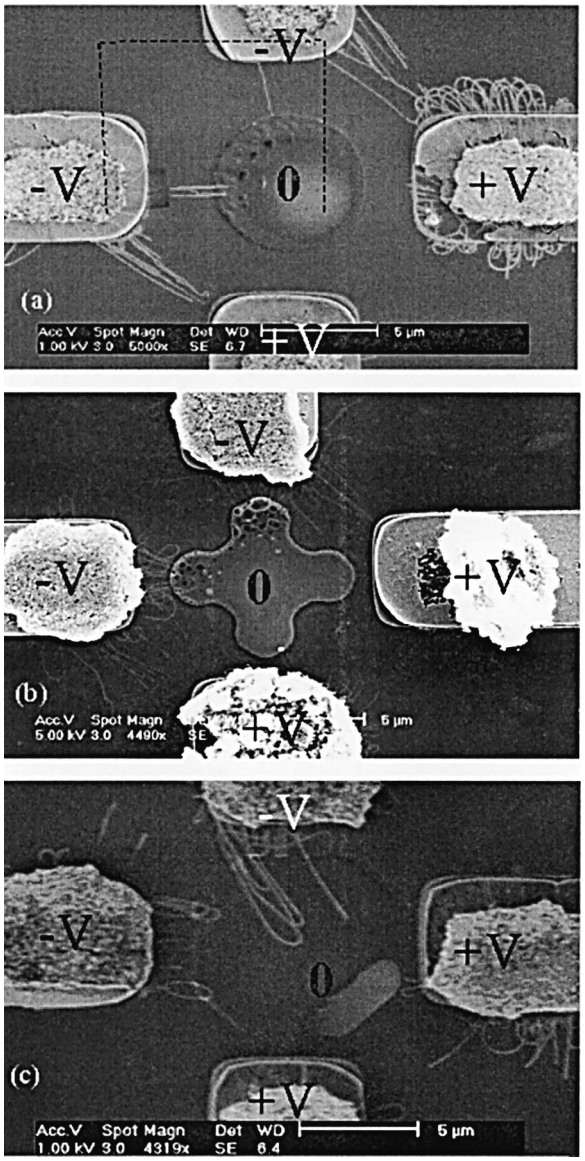

FIG. 5. Scanning electron micrograph of a device with (a) a circular middle electrode; (b) a long cross-shaped middle electrode; (c) a wide cross-shaped middle electrode. The voltage configuration of Fig. 2(a) was used during the growth with *V* approximately equal to 2 V. In (a), the area bordered by the dashed lines shows how nanotubes have been aligned to two perpendicular directions within a few microns of each other.

The application of voltage during the high-temperature growth could be challenging. In our devices, the electrodes were connected to large pads on the sides of the chip [Fig. 4(a)]. A custom-made sample holder with digitated stainless-steel clamps [Fig. 4(b)] was used to make external contact to these pads [Fig. 4(c)]. The stainless-steel electric lines were brought into the growth chamber using feed-throughs at the exhaust end and were screwed onto the clamps. The molybdenum device electrodes survived the high-temperature process easily.

IV. RESULTS AND DISCUSSION

The experiments described here show that nanotube positioning and alignment is a function of the electric field mag-

nitude, direction, and polarity. Figure 5(a) shows a scanning electron micrograph of a structure after nanotube growth. The voltage configuration corresponds to that of Fig. 2(a). As mentioned before, the nanotubes grown under these process conditions are predominantly single-walled—their diameters appear much larger than the actual values due to contrast mechanisms in scanning electron microscopy.[8] The middle electrode is revealed as a slightly raised area since the polishing was not able to flatten the oxide surface completely. The height of this raised area was measured to be about 20 nm using atomic force microscopy. Since this value is small compared to the lateral dimensions of the structure, it does not affect the electric field distribution significantly. Note that the distribution of the nanotubes on the structure very closely matches the electric field distribution: high field regions (shortest paths between electrodes of opposite polarity) have a high concentration of nanotubes, and in regions with no electric field (between adjacent electrodes with the same value of voltage), there is a lack of nanotube population. This is a clear indication that nanotubes respond not only to the direction of the electric field (as in the one-dimensional case[4–6]), but also to its magnitude [see also Fig. 5(b)]. Also, the nanotubes respond to rapid variations of the electric field direction within a small area: in the region inside the dashed line in Fig. 5(a), the electric field is changing its direction by 90 deg within a distance of about 5 microns, and nanotubes have been aligned in two perpendicular directions. The effect of polarity is also critical: note in Fig. 5 that nanotubes have grown from negatively biased toward positively biased electrodes. Nanotubes growing out of positively biased catalyst islands tend to curl back toward their home catalyst. This dependence on polarity suggests that nanotubes are negatively charged. Negative charge on nanotubes has previously been observed.[9] We suggest an explanation based on the so-called tribo-electricity for this negative charge: As a nanotube is growing in the hot, reactive environment of the furnace, it may acquire negative charge from the gas molecules as a result of friction. It is also possible that negative charge is first accumulated on the iron/molybdenum/alumina catalyst and subsequently transferred to the nanotubes. Nanotubes have higher electron affinities (4.8 eV for semiconducting nanotubes on average[10]) than iron and molybdenum (with work functions of 4.7 and 4.6 eV, respectively). Therefore, in the nanotube/iron or nanotube/molybdenum heterojunctions, negative charge could be transferred to the nanotubes. This negative charge could explain why nanotubes grow away from negative toward positive polarities.

Note, however, that the above argument does not suggest a preference for more growth from a certain catalyst island based on the polarity of the supporting electrode. The catalyst islands are microscopic clusters that contain nanoparticles, and the growth yield from a catalyst island depends on how many actual nanoparticles it contains, as well as the random nanoparticle arrangement in the cluster and how well they are exposed to the precursor gases. Therefore, even in a growth process with no electric field, there are many variations in nanotube yield from one catalyst island to another. The application of a bias has been reported to affect the growth yield in making vertical nanotubes in processes such as the hot-filament CVD.[11–13] However, in using a standard CVD to grow nanotubes on the surface, having repeated these experiments several times, we have not observed a direct relation between the number of nanotubes emanating from a particular catalyst island and the polarity of the supporting electrode.

Figure 5(c) presents a case where the middle electrode is large enough to create regions of strong uniform electric field on its sides. Again, a significant number of tubes have grown away from negatively biased electrodes and aligned with the electric field. These tubes can be divided into two categories: first the ones that have short lengths and are all terminated around the edge of the middle electrode. This is an indication that the obstruction created by the middle electrode has been the cause for the termination of their growth. This means that they have been very close to the oxide surface while growing, possibly even on the surface. The second group includes longer tubes with endings on the surface of the middle electrode. This suggests that these tubes have been far enough from the oxide surface during growth so they have been able to overcome the bump caused by the middle electrode. Therefore, we conclude that nanotubes can grow both on the surface and above it: the latter subsequently fall onto the substrate.

In another growth all the surrounding electrodes were kept at the same negative potential with respect to the middle [as in Fig. 2(b)]. Negative bias was used based on the previous observation that tubes grow from negative to positive polarities. Figure 6(a) shows a sample with the same shape of the middle electrode as in Fig. 5(a), but with the new voltage configuration. Due to nonuniformities in the oxide polishing from device to device across the wafer, in some areas [such as in Fig. 6(a)] there is more oxide left on the middle electrode, and hence the electrode cannot be seen on the image. There is obviously random nanotube growth on the sides of the outer electrodes due to the lack of electric field in those regions. However, a nanotube cross that is exactly along the electric field lines can be seen in the middle of the structure. Test samples were also prepared under the same process conditions, but with no electric field [Fig. 6(b)]. The comparison strongly suggests that the cross in Fig. 6(a) is not a random outcome of the process, but has been made because of the effect of the electric field. Note that other than the field distribution, parameters such as the starting point of a nanotube and its final length play an important role in the final device structure. Therefore, successful making of a cross also depends on the growth process conditions, and so far we have a poor yield of good devices. We are working on finding the optimal process parameters to improve the chances of making crosses.

For a given catalyst island, the growth yield of the nanotubes depends on the exact process conditions that include gas flow rates, as well as growth temperature and duration. In these experiments, the emphasis has been on affecting the arrangement of the tubes with electric field, and preference

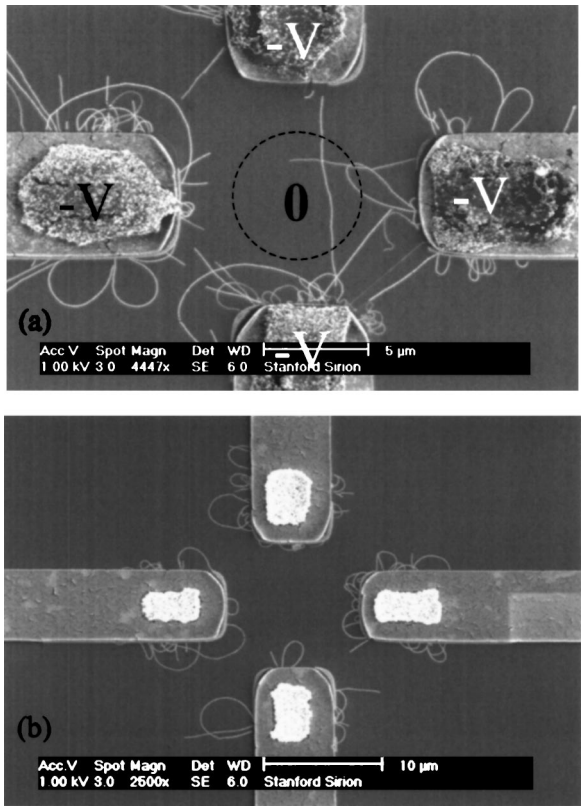

FIG. 6. (a) Scanning electron micrograph of a device with a circular middle electrode (not visible on the image—shown as a dashed circle). The voltage configuration of Fig. 2(b) was used during the growth. (b) Outcome of the growth on a device with no electric field.

was given to relatively low-yield conditions in order to have a lower nanotube density and observe the alignment effects on each nanotube more clearly. The tube density can be increased by using higher yield conditions (such as a higher flow rate of ethylene) for applications that require more nanotubes per surface area. However, if the nanotube density is so high that they form closely packed groups, other effects such as van der Waals interactions between neighboring nanotubes will also play an important role in their alignment.[14]

V. CONCLUSION

It appears that nanotubes assemble in the regions of the most intense electric field. Also, they tend to align along the direction of the field lines, even in nonuniform fields where the field direction changes by 90 deg over a distance of a few microns. They also grow away from negative toward positive polarities. Furthermore, it is possible for them to continue growing after falling on the oxide surface, at least in the presence of an electric field. There are still nanotubes that do not follow the above trend, so it is clear that there are other parameters that need to be identified and controlled before we can claim to be able to grow well-directed nanotubes. Current difficulties include the application of the electric field during the high-temperature growth in a consistent manner, as well as large interelectrode leakage currents during growth.

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