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Multiple Sharp Bendings of Carbon Nanotubes during Growth to Produce Zigzag Morphology

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ABSTRACT

Carbon nanotubes have been grown with a sharply defined zigzag structure by introducing changes in the direction of applied electric field during dc plasma enhanced chemical vapor deposition (PECVD). The nanotubes maintain the same diameter before and after each bend while preserving the catalyst particle at the tip of growing nanotubes. The bends have very sharp radii of curvature of only ∼25 nm. As a simple inclined field direction cannot produce such a zigzag growth due to the tendency of field lines intersecting perpendicular to the local surface, the bending has been introduced primarily by dramatically manipulating the electric field lines through controlled movement of field-concentrating conductor plates.

Since their discovery,[1] carbon nanotubes (CNTs) have been studied for many different applications because of their exceptional electrical and mechanical properties.[2,3] Carbon nanotubes have already been shown to be useful for a variety of applications such as field emission devices,[4−6] nanoscale electromechanical actuators,[7,8] field-effect transistors (FETs),[9] CNT-based random access memory (RAM),[10] and atomic force microscope (AFM) probes.[11] There has also been much work demonstrating CNTs potential as nanointerconnects[12] including no obvious degradation after 350 h in the current carrying capacities of multiwalled CNTs (MWNTs) at a very high current densities of 10^{10} A/cm^2,[13] the manufacture of deterministic CNT wiring networks,[14] and using an electron beam to form mechanical connections between two nanotubes.[15]

To utilize CNTs as interconnects and other device components, the ability to control their growth morphology is desired. The growth of vertically aligned MWNTs has been demonstrated by several groups using plasma enhanced chemical vapor deposition (PECVD).[16−19] These results all had CNTs aligned perpendicular to a substrate surface due to the applied field or electrical self-bias field created by the plasma environment. The aligned growth of CNTs by electric field in other directions, such as in-plane directions, has been demonstrated both for single walled carbon nanotubes (SWNTs)[20] and MWNTs.[21−23]

Although alignment of individual CNTs and CNT arrays has been demonstrated, there has been very little work done toward more complicated morphologies. Merkulov et al. showed a fabrication of bent CNTs consisting of one section perpendicular to a substrate and a second section aligned ∼45° off of the substrate normal with radii of curvature on the order of 1 μm.[22] The off-normal growth was achieved by positioning the sample near the edge of the sample holder where bending of the electric field lines occurs. In this work, we show the ability to grow CNTs with sharp bends that maintain a constant tube diameter before and after a bend and the ability to grow structures with multiple bends resulting in a zigzag morphology. Zigzag structured or singly bent CNTs could be used for many applications, e.g., related to mechanical nanosprings, or complicated circuit nanointerconnections.

Arrays of CNTs with zigzag morphology were grown using a DC plasma enhanced chemical vapor deposition (PECVD) process using Ni catalyst particles with a tip-growth mechanism and a mixed gas of ammonia (NH_3) and acetylene (C_2H_2). The arrays had a density of $\sim 2 \times 10^9$ CNTs/cm^2. They were fabricated by first sputter depositing a 50 Å Ni film over the surface of an n-type Si (100) substrate. The substrates were then transferred (in air) to the CVD chamber. Upon heating to ∼780 °C, the Ni film breaks up into islands with average diameters of 30∼40 nm. A DC bias of 550 V was applied between an anode above the sample and a cathode just below the sample. Under the applied voltage, plasma formed and acetylene (C_2H_2) was added to the chamber flowing at 30 sccm with the total NH_3 and C_2H_2 pressure held at 3 Torr.

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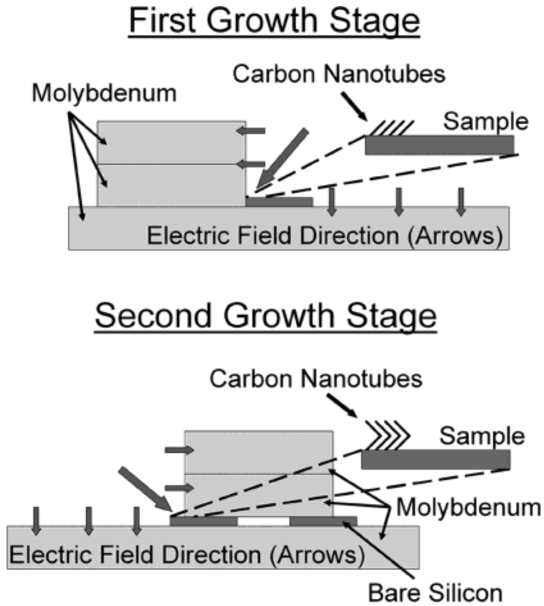

Figure 1. Schematic illustration of the two experimental geometries used to control the growth direction of the CNTs. By alternating between the two geometries, CNTs with zigzag morphologies were achieved as shown in locally expanded diagrams (marked by dashed-lines).

Electric-field-concentrating metal plates (molybdenum slabs) 1 mm thick (the same stock as the cathode stage) were placed in electrical contact with the cathode in the vicinity of the Si substrate in two different geometries (Figure 1). After the first growth stage was carried out resulting in CNTs grown at an inclined angle (aligned away from the sample edge) in the area 100−200 μm from that sample edge, the location of the Mo slabs was changed and the above process was repeated to result in the second growth stage where the nanotubes continued to grow but aligned in a direction toward the edge of the sample. The switching between the two growth stage setups was carried out by stopping the CVD growth process, cooling the sample under 60 Torr H_2 flowing at 150 sccm, and manualy repositioning the objects involved. These two growth stages were repeated to result in CNTs containing multiple segments joined by multiple sharp bends.

For microstructural analysis, field emission scanning electron microscopy (SEM) was performed using a Phillips ESEM operated at 30 kV.

In the absence of an applied DC bias, CNT growth in a microwave plasma environment has been shown to produce CNTs aligned perpendicular to the substrate.[17] The plasma environment creates a potential self-bias where the field lines are always perpendicular to the surface.[24] Even when a substrate's surface is tilted at any angle, the field lines will bend and, within a narrow region (less than 10 μm above substrate surface where CNT growth occurs), the field lines will be always be straight and perpendicular to the surface. Bower et al. estimated for a microwave plasma environment with no applied DC field that the self-bias potential is on the order of 10 V and the electric field has a magnitude on the order of 0.1 V/μm in the vicinity of the surface.

The application of a standard DC potential bias results in a different electric field around the sample. For our system, the sample substrate is located on the cathode, which results in the direction of the applied bias being toward the sample. The field lines will always be perpendicular to the local surface and will bend as they move away from the surface to connect the two poles of the applied field. As was the case before, within the region close to the sample surface where CNT growth occurs, the field lines will be straight and perpendicular to the surface and so will result in vertically aligned CNTs such as those shown in Figure 2. The alignment mechanism for CNTs in a DC field like this has been reportedly due to stresses created at the interface of the catalyst particle and CNT by the electric field.[25] This mechanism provides one possible reason why tubes that grow with the catalyst particle at the top of the tube (tip-growth) are aligned, although this does not apply to the case of nanotube alignment with the bottom-growth seen by Bower et al. The CNTs are expected to grow along the field line directions, so are expected to bend with those lines if they were to grow sufficiently long. These length scales are normally much longer than the typical length of nanotubes that we grow, e.g., less than ∼10 micrometers. For this work, the electric field in the growth region of the CNTs appears to be primarily controlled by the applied bias. The true net electric field is a combination of several parts including the applied bias and the plasma-induced self-bias. Further research and simulation of electric field distribution is under way and will be reported in the future.

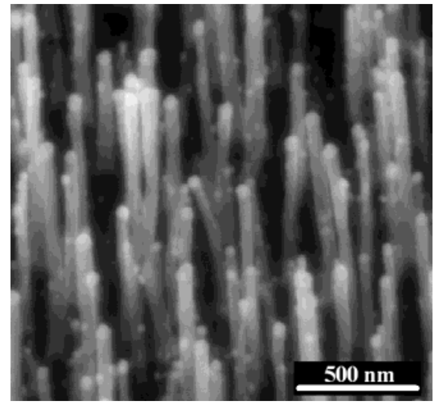

Figure 2. Vertically aligned MWNTs grown by DC plasma CVD growth.

To cause bending in the CNTs, we need to manipulate the electric field such that the field lines in the growth region of the CNTs are bent. Growth along field lines at angles not perpendicular to the substrate surface has previously been achieved by positioning the sample near the sharp cornered edge of the sample stage where the field lines are bent toward that sharp corner direction even at distances within the growth region.[22]

In this work, we used a different geometry that allowed for the presence of electric-field-concentrating metal plates to cause very large and dramatic changes in the direction of the electric field lines in the CNT growth region. The metal plates were made of the same material as the cathode stage and were given the same potential. The resulting electric field lines were bent dramatically, and even for distances ∼10

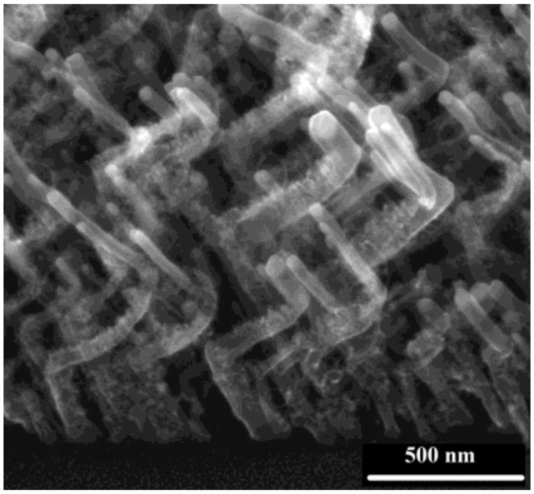

Figure 3. Array of CNTs grown with zigzag morphology using a three-stage growth process. Sample tilted 45° for SEM analysis.

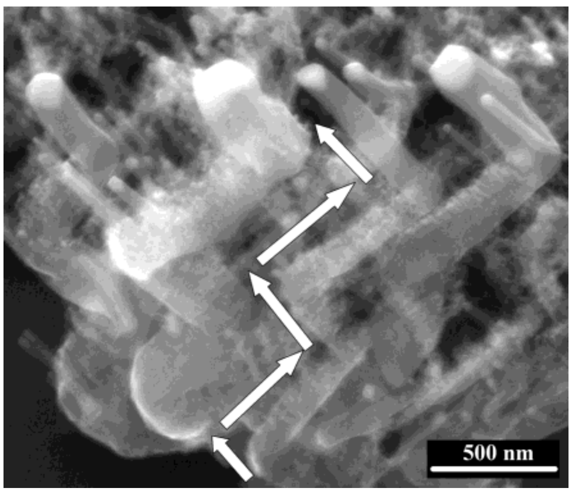

Figure 4. Multiple-bent CNTs grown with five growth stages.

nm above the surface the resulting CNTs were grown aligned at angles greatly tilted from perpendicular direction (to the surface). By moving the metal plates, we were able to again dramatically alter the direction of the electric field lines, which is how such sharp bends were obtained.

An SEM image of three-step zigzag CNTs obtained by using the conductor plate arrangement of Figure 1 is presented in Figure 3. The image shows that arrays of carbon nanotubes with an average diameter of ~30 nm were grown aligned at an angle ~57° from normal, then bent ~90° and continued to grow as an aligned array until they were again bent ~90° and grown along the original growth direction. Each growth stage had a duration of 8 min, and each straight segment in the bent nanotubes is on the order of ~500 nm in length. The two opposing ~90° bends are in-plane. The sample was grown two additional steps to produce five-step zigzag tubes with four alternating opposing in-plane bends shown in Figure 4. Such a multiple, sharp bend structure of carbon nanotubes has previously not been reported.

The bends present between two growth stages have small radii of curvature of only ~25 nm. These nanoscale bend angles obtained using a recessed corner of metal blocks in contact, Figure 1, are much sharper than the micrometer scale bends previously demonstrated in the literature using an open (convex) corner of a metal plate.[22] While the nanotubes have a variation of diameter determined by the initial size of the catalyst particle formed upon heating,[17] each individual tube shows essentially the same diameter for all growth stages. It is anticipated that such a sharp bend in a nanotube is likely to contain many defects, which will be an interesting subject of future study.

The surface of the CNTs appears clean on the last growth stage, while the earlier growth stages appear to have some fuzzy surfaces with additional, tiny CNTs and amorphous carbon present. This deposition is clearly most prevalent along the sides of the CNT segments that are orientated in the direction of the subsequent growth stages. A possibility of some sputtering of original Ni catalyst particles on CNT tips followed by redeposition as smaller catalyst particles for renucleation and growth of nanotubes may be speculated. The extra small nanotubes (as small as ~5 nm in diameter) generally appear to be growing along the direction of the electric field and perpendicular to the length of the segments previously grown. It is not clear whether this observed phenomenon can be further optimized/utilized for creation of much smaller diameter nanotubes (e.g., 1−5 nm regime) from coarse MWNTs (e.g., 20−100 nm regime). On a freshly growing segment in which the field direction coincides with the segment length, such a growth of tiny nanotubes is not observed. The exact cause for this additional material deposition is not clearly understood at the moment, and further study is needed to determine the nature of such additional deposition. Further optimization and modification of CVD processing conditions are being pursued to minimize such small features and grow cleaner nanotubes.

Our CNTs are all grown through a tip-growth process, and the catalyst particles are still clearly visible at the tips of the structures shown. The limited presence of carbon capping (for example, amorphous carbon coating that may poison the catalyst surface and prevent further CNT growth) implies that these shape-engineered carbon nanotubes can be grown further producing additional zigzag bends or other morphologies. The bends shown here are all in-plane bends (in a three-dimensional sense moving away from the substrate, not on the substrate plane). This was done to simplify the setup geometry and to make it easier for us to see the resulting structures. Using similar setups, we should be able to engineer out-of-plane bends and make more complicated three-dimensional structures such as nanocoils, segmental helixes, box-helixes, or horizontal−vertical 90 degree zigzag shapes, for example. Motorized rotational movement and stepper-motor movement of field-concentrating metal plates with respect to the substrate can be designed to continuously grow a variety of complex CNT shapes, and this work is presently underway.

Such a bent CNT can be utilized as a sharp probe tip that can be attached to an AFM tip with the bent portion (e.g., 60° bent) providing a sufficient contact length for enhanced bonding to the AFM pyramid sidewall, while the vertically straight, protruding portion serves as a high-resolution, nanotube scanning probe tip. A variety of bonding techniques may be used, e.g., electric arc, adhesives, solders, thin film metal deposition, or carbon-deposition by e-beam in SEM. Unlike the case of awkward CNT bonding at an angle to the inclined sidewall of Si pyramid tip, such a strongly bonded nanotube probe tip can provide better reliability and longer life.

Bent CNTs can also be useful for circuit nanointerconnections. Vertical nanointerconnections of electronic or optoelectronic components with substantially different coefficients of thermal expansion (CTE) can often result in undesirable stresses caused by thermal expansion mismatch, which can induce fatigue and fracture-related failures at connection joints. The zigzag shaped, spring-like nanotubes could conveniently be utilized to accommodate such CTE mismatch stresses. For in-plane nanointerconnections between device components or contact pads, routing of circuit connections often requires not just a straight but sharp-turn conductor circuit lines. Multiple, sharp bend zigzag nanotubes could also be useful for such applications, especially if SWNTs or small diameter MWNTs can also be made to respond to electric field manipulations and bend in a similar fashion. Future studies of electrical and mechanical properties of multiple-bent SWNTs (both n-type and p-type) or small-diameter MWNTs will be important for determining the usefulness of bent nanotubes for such nanointerconnection applications. Sharp bends, if introduced in SWNTs, will likely induce pentagon−heptagon or other types of defects and associated semiconductor heterojunctions[26] for potential nanoelectronics device applications.

In summary, the growth of CNTs with multiple bends was studied. Zigzag morphologies consisting of 2−4 very sharp and alternating ~90° bends were synthesized. The bending of the CNTs during growth was caused by changing the direction of the electric field lines in the growth region of the sample. The resulting structures have abrupt and nanoscale sharp bends, and maintain the same tube diameter throughout growth. The catalyst particles are still present at the tops of the zigzag structures, implying that many additional bent segments or other unique three-dimensional structures can be created. Such multiple bent nanotubes can be useful for a variety of applications including mechanical nanospring devices, high-resolution AFM tips, and nanocircuit interconnections.

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