Control of Carbon Capping for Regrowth of Aligned Carbon Nanotubes

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The regrowth of carbon nanotubes (CNTs) in a second growth stage after a first growth stage has been completely stopped has been found to be strongly related to the carbon capping present on their catalyst particles. It is shown that the undesirable carbon capping can be prevented from forming or removed and the nanotube growth can be rejuvenated by either control of plasma processing conditions during chemical vapor deposition or by inserting a room-temperature sputter etching process. The ability to cause sequential growth stages to take place in different directions makes it possible for us to clearly compare the occurrence and extent of CNT regrowth. Such a CNT regrowth process and understanding of controlling parameters can enable the creation of new nanowire configurations that could potentially be used for applications such as sharply bending nanointerconnections, nanosprings, bent AFM nanoprobes, or nanobarcodes.

I. Introduction

Carbon nanotubes (CNTs) have been studied for many different applications because of their exceptional electrical and mechanical properties.[1,2] Carbon nanotubes have already been shown to be useful for a variety of applications such as field emission devices,[3,4] nanoscale electromechanical actuators,[5] field-effect transistors (FETs), CNT based random access memory (RAM), and atomic force microscope (AFM) probes. There has also been work demonstrating CNTs potential as nanointerconnections[6] 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[2,7] the manufacture of deterministic CNT wiring networks, and using an electron beam to form mechanical connections between two nanotubes. By virtue of their very small diameters, as small as 1.1 nm, CNTs have a distinct advantage over current lithographic integrated circuit interconnections which are of larger size.

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).[8−10] 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)[11] and MWNTs.[12] Recently, we have demonstrated the ability to grow CNTs aligned at angles not perpendicular to a substrate containing sharp bends with radii of curvature less than 25 nm by manipulating the electric field directions in the CNT growth regions.[13] This adds great potential to CNTs as interconnections because using only straight CNTs would limit device geometries considerably. These nanobent structures were created using a multiple growth stage process where CNTs were grown one segment at a time with each subsequent growth segment taking place after the previous growth stage had been stopped completely.

The growth of CNTs by a catalytic growth mechanism has been studied by many groups. These groups essentially adopt the concepts established for CVD growth of carbon fibers developed in the 1970s.[14] The believed mechanism is that CNTs grow as carbon precipitates from a supersaturated metal catalyst particle. It was also noticed early on that the activation energies for carbon filament growth from several types of metal catalysts closely resembled activations energies for carbon diffusion through the bulk of those metals.[15] This suggests that the growth rate of a CNT will be limited by the rate of carbon diffusion through its catalyst particle. The growth rate of CNTs has also been suggested to be limited by the supply of carbon from the gas phase.[16] Depending on the situation, one of these mechanisms appears to have a more dominant effect than the other. Under thermal CVD conditions, the CNT growth rate does appear to be diffusion limited, whereas more PECVD processes appear to be supply limited.

It was previously reported that the metal catalyst particle becomes capped with a film of carbon during CNT growth.[9] Chhowalla et al. reported that the carbon capping was graphitic in nature when deposited under high-temperature conditions, and resembled disordered carbon at lower deposition temperatures. It has also been reported that the carbon film on the catalyst particle forms at a faster rate with a higher carbonaceous gas content. It has been proposed that under the right conditions the carbon film may form in patches that are not continuous across the catalyst surface.[16] In this model, the growth rate of a CNT is faster when there is a greater area of catalyst particle not coated by carbon and the areas of carbon coating and clean

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catalyst surface would dynamically change as carbon film islands emerge and disappear. This would lead to carbon supply limited growth for the CNTs as a greater exposed catalyst surface area would lead to a greater amount of decomposed carbon species.

In this letter, we investigated the controlling parameters and processes for nanotube regrowth in relation to the synthesis of sharply bent carbon nanotubes. We use the terms "regrowth" and "continued growth" to describe a second growth stage that occurs after a first growth stage has been completely stopped. The ability to stop and regrow nanotubes, especially along a different direction can be useful for a variety of nanotech applications. The use of sharply bent nanotubes also allows one to study the occurrence and extent of CNT regrowth. Continued growth or regrowth of CNTs after one stage of growth had been completely stopped has been reported for CNTs growth in both thermal[17] and plasma enhanced[13,18] CVD systems. These regrowth results were simply accomplished by loading the samples back into the growth chamber and exposing them to plasma with the standard parameters used for the initial growth stage. However, aligned forests of CNTs grown from catalyst particles that were initially a continuous thin film on a silicon substrate exhibit a considerable size distribution in both diameter and height (this can be avoided by using patterned catalyst islands such as electron-beam lithography). When an uneven "forest" of straight-growing CNTs such as this or even a patterned and uniform CNT arrays is regrown, the starting location and length of the second growth stage along the linear length of nanotubes is practically impossible to identify and hence it is difficult to study and understand the regrowth phenomena. The very clearly defined sharp bends we introduce by changing the growth direction solve this problem.

II. Experimental Section

Growth of aligned arrays of CNTs was done using a dc plasma enhanced chemical vapor deposition (PECVD) process using Ni catalyst particles with a tip-growth mechanism. A mixed gas of ammonia (NH_3) and acetylene (C_2H_2) was used for the CVD growth. The arrays had a density of $\sim 2 \times 10^9$ CNTs/cm^2. They were fabricated by first sputter depositing a 50 Å thick 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 ~ 700 °C in a low-pressure hydrogen atmosphere, the Ni film breaks up into islands with average diameters of 30 to 40 nm. After catalyst island formation, the atmosphere was changed to NH_3 flowing at 150 sccm. A dc bias of 450−600 V was applied between an anode above the sample and a cathode just below the sample. Under the applied voltage, plasma formed and C_2H_2 was added to the chamber flowing at 30−50 sccm with the total NH_3 and C_2H_2 pressure held at 3 Torr.

Sputter etching was performed at room temperature in the same dc plasma CVD system as the CNTs were grown in after the growth was completed and the chamber was cooled to room temperature. Samples were placed under H_2 flowing at 35 sccm and held at 0.5 Torr within the chamber. A bias of 500 V was applied and plasma formed with a current of 2 mA. A sputter etching time of 5−10 min was used to remove the carbon deposition on the catalyst particles of the CNTs. Scanning electron microscopy (SEM) imaging was done in a Phillips field emission SEM operated at 15−30 keV. Transmission electron microscopy (TEM) images were obtained using a JEOL 3010 operated at 300 kV and a JEOL 200CX operated at 200 kV.
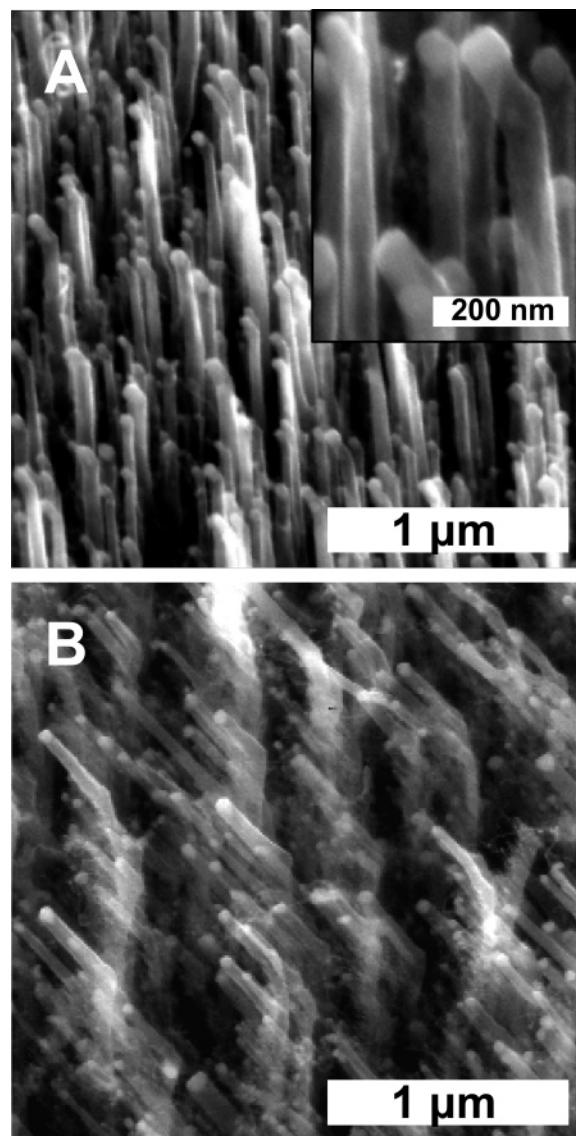

Figure 1. Two arrays of CNTs with growth continued at 45° displaced from perpendicular. Both samples have the same CNT diameters and heights during the first growth stage (before the bend). (A) CNTs that had a thick carbon film over the surface of their catalyst particles after their first growth stage show very little regrowth in their second growth stage (after the bend). (B) CNTs with a much thinner carbon film on their catalyst particles showing significantly longer regrowth in their second growth stage. The samples had identical growth times of 15 min for each growth stage.

III. Results and Discussion

Two samples showing very different extents of regrowth are presented in Figure 1. We first grew arrays of CNTs aligned perpendicular to the substrate surface under different conditions, one that resulted in a thick carbon coating forming over the CNTs' catalyst particles, and another that resulted in a much thinner carbon film being formed by adjusting multiple processing conditions as will be described below. The samples were then placed back in the chamber and both grown under identical conditions at an approximate 45° angle away from perpendicular. It can be seen from the scanning electron microscope (SEM) images in Figure 1 that some regrown CNTs (Figure 1A) showed a small amount of continued growth, less than 100 nm in length, in contrast to other CNTs with the same second growth stage conditions (Figure 1B), which grew 500 nm on average. The CNTs have the same average heights and diameters during

the first growth stage, it is the second growth stage that we are considering when discussing the CNT regrowth. The extent of regrowth is made clear by the sharp change in growth direction, which allows us to identify the start of the second growth stage; otherwise, the two images would appear quite similar. The samples had identical growth times of 15 min for both their first and second growth stages. TEM images of the bends show that the CNTs continue growing by precipitating new graphene planes along the bottom surfaces of the catalyst particles. There are many graphene plane stacking defects at the bends, but they are arranged such that the second growth stage is a true extension of the first growth stages with hollow cores at the bends. The difference in the extent of regrowth is due to the different degrees of carbon capping present on the catalyst particles and will be discussed in more detail below.

In our work, because the arrays of aligned CNT samples were grown through a dc-PECVD process using Ni catalyst particles, the catalyst particles were always present at the top ends of the CNTs, making this a "tip-growth" mechanism. In general, CNTs grown by dc plasma CVD have their graphene layer walls inclined at some angle rather than parallel to the growth direction of each CNT. Structures such as this have many sections where their cores have graphene projections bridging them and are sometimes referred to as carbon nanofibers in the literature. In contrast, the CNTs grown by microwave plasma or thermal CVD tend to have walls parallel to the main growth axis. These nanotubes with inclined walls are still denoted as CNTs in this paper in a broad sense, as they still have mostly hollow cores. The inclined walls in our CNTs will give them electrical transport properties different from CNTs with walls parallel to their tube axes, so they are not as favorable for applications such as circuit interconnections; however, the subject of this letter, regrowth of CNTs by control of catalyst carbon capping, is relevant for other nanostructures grown by a catalyst particle tip-growth mechanism, including CNTs with walls parallel to their tube axes.

Our growth conditions appear to be similar to those reported by Merkulov et al.[16] where the growth of the CNTs is limited by the supply of carbon at the exposed catalyst surface. However, for this to be true, there needs to be another process taking place at the end of the growth processing because it is reported that, following growth, most catalyst particles are completely coated in a carbon film of some sort. We believe a possible explanation for this could be that a carbon shell forms around the catalyst particles during the period after the plasma is turned off at the end of the growth processing. When the catalyst particle cools off, it should precipitate carbon at its surface as the solubility of carbon decreases with temperature for all potential catalyst metals. We have also seen indication that right after the plasma is extinguished in the growth chamber and the substrate heater is turned off, the sample is still under conditions to allow thermal CVD growth for a brief time. We see evidence of slight growth that we think occurs after the plasma processing in the form of some small random CNTs of 5−10 nm in diameter that form unaligned near the tops and on some of the side surfaces of our main array of aligned CNTs. We believe that these could be formed by small catalyst particles that had broken off from the main particle during growth or were possibly sputtered off of one of the main catalyst particles and deposited on the sides of a nearby CNT.

Along with the small unaligned CNTs, there also appears to be additional amorphous carbon deposited during the brief time the sample is under thermal CVD conditions. While under plasma growth conditions, the NH_3 present has an etching effect

and removes much of this disordered carbon deposition; however, it is not able to do so once the plasma has been stopped. We attempt to limit this terminal thermal CVD time by evacuating the CVD chamber and then purging with flowing hydrogen immediately after stopping the plasma processing. The amount of the carbon capping present on a catalyst particle following all growth processing and cooling can be controlled by several factors including carbonaceous gas content in the growth chamber, growth temperature, plasma power, and chamber purging during cooling. We generally observe a thicker carbon coating under conditions with a higher carbon containing gas content (higher acetylene-to-ammonia ratio in our case), higher temperature, higher plasma power, and slower chamber purging following the plasma processing. Although we can make samples with thicker or thinner carbon films on their catalyst particles by adjusting the above variables, it is still difficult to determine at what point and how the carbon deposition occurs without being able to look at the sample while growing it, i.e., in situ transmission electron microscopy (TEM). One might think another possible way to limit the formation of a carbon cap at the end of growth processing could be to gradually decrease the concentration of the carbon containing species in the reactor to zero before turning off the plasma. This would not solve the problem of carbon precipitating from the catalyst particle as it is cooled, and is also quite difficult to achieve considering the relatively high pressure in the chamber during plasma processing. The time required to remove the carbon containing species would require the CNTs to be subjected to equal time of destructive NH_3 plasma etching because the etching effect increases as the concentration of carbon containing species is decreased.[9]

Although we have an understanding of how many of the processing conditions affect the formation of a carbon capping layer and we can endeavor to avoid its formation, to ensure clean catalyst surface with no or minimal carbon capping, we devised a room-temperature hydrogen sputter etching process to remove the carbon capping layer once it has been formed. This process has been found effective as shown in Figure 2. Briefly, the mechanism of the sputter etching process involves incident positive ions in the plasma, such as hydrogen, colliding with the nanotube material and preferentially eroding the nanotube walls underneath the catalyst metal particles. If this is carried out in an extensive way, it is found that the process can eventually lead to the catalyst particles being completely etched and removed leaving an aligned array of open ended CNTs.[19] Using this same process under weaker and carefully controlled plasma conditions, we have been able to remove the carbon coating that had formed on the catalyst particles of an aligned CNT sample. A schematic illustration of a CNT end is shown in Figure 2A with the locations of the carbon capping layer, Ni catalyst particle, and CNT labeled. A similar schematic is shown in Figure 2B for a CNT end with no carbon capping layer. Figure 2C shows an SEM image of the tops of CNTs. The thick carbon film can be seen covering each of the catalyst particles. After sputter etching with hydrogen plasma, the image in Figure 2D shows the carbon coating has been completely removed. Because the sample shown in Figure 2 had processing done after the initial SEM images were taken, it was not possible to show the exact same CNT, but the results presented are typical of what was seen from all of the CNTs we examined on the sample. Figure 2E shows a TEM image of a catalyst particle clearly exhibiting complete carbon encapsulation. This encapsulation contained both graphitic and amorphous carbon. In Figure 2F, another TEM image shows a different catalyst particle
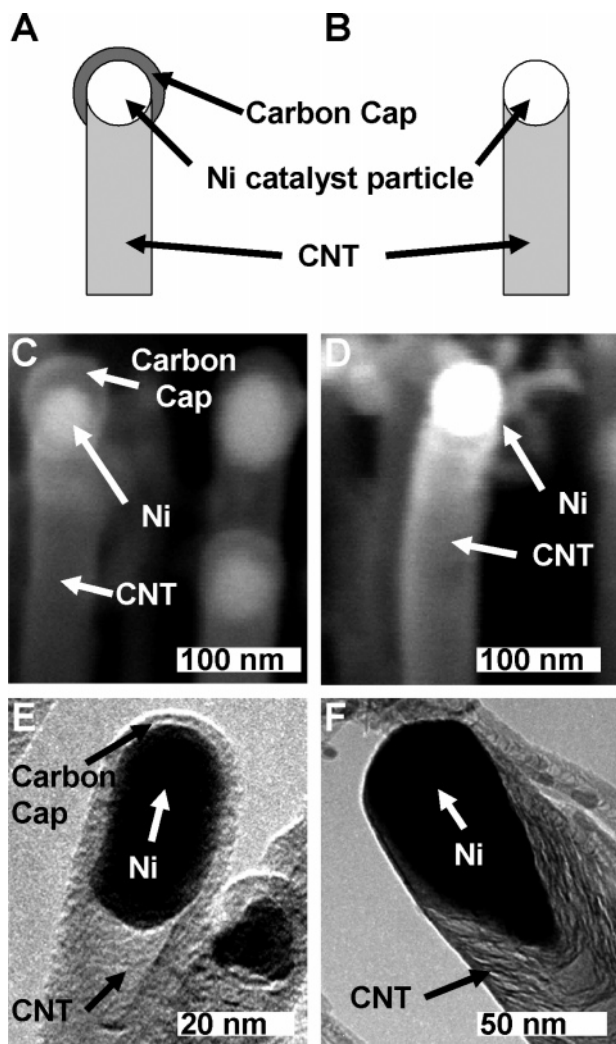
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Figure 2. (A) Schematic drawing illustrating the locations of the CNT, Ni catalyst particle, and the catalyst particle's carbon capping layer. (B) Similar schematic with the carbon capping layer removed. (C) SEM image of CNTs showing a thick carbon coating surrounding their catalyst particles. (D) After sputter etching, the carbon coating on the CNTs was removed leaving a clean Ni catalyst particle. (E) TEM image of Ni catalyst particle showing encapsulation by a carbon capping layer and (F) another catalyst particle with almost no carbon capping on its end.

that has almost no carbon capping on its end. The variation in carbon capping between Figure 2E,F was due to processing conditions (higher plasma power for the sample in Figure 2E in this case).

Using two samples of vertically aligned CNTs that had thick carbon coatings on their catalyst particles following growth, we attempted to see if our process for removal of the carbon coating improved the ability for continued CNT growth. One of the vertically aligned CNT arrays was sputter etched to remove the catalyst carbon capping as shown in Figure 2D; then the two samples were placed back into the CVD chamber and grown under conditions that should produce a second growth stage with a different growth direction as described before. The results were similar to those presented in Figure 1, where the CNTs that had had their carbon films sputter etched grew significantly longer than the un-etched sample.

Revived growth of CNTs can lead to many new nanostructures; Figure 3 shows a few of the example structures we have been able to obtain. These nanoscale bent structures were obtained by controlled CVD using the electric field near the
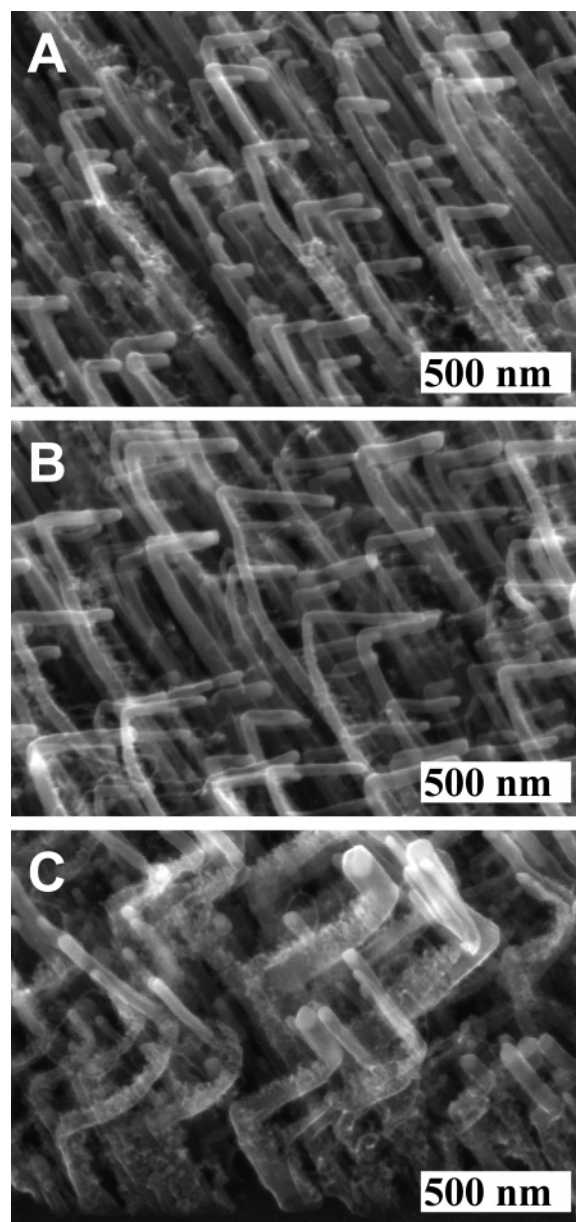

Figure 3. Structures obtained utilizing continued growth of CNTs: (A) CNTs with over 90° bends; (B) longer structures with second growth stage parallel to substrate surface' (C) multiple bends to produce a zigzag structure.

recessed intersection of conducting plates.[13] Despite all of the great potential CNTs have shown as interconnections, simple straight nanotubes are not particularly useful for circuit connections as many of the conductors in modern, nanoelectronic circuits need to bend for routing and other device design or packaging reasons. Bent nanotubes can serve a useful purpose in this regards. Sharply bent structures containing bend angles over 90° with a short second growth stage (Figure 3A) resemble nanohooks. Such nanohook CNTs could be potentially used as arms for a nanomanipulation device or for AFM or other probe tips where a bent tip could be useful for nanoscale metrology- or conductivity-probing of sidewalls inside vertical pores or channels. One can envision placing two such bent probes side by side for local conductivity measurements. Split electrodes, such as used by Lieber et al.,[5] may be employed for such configurations. For nanotweezer applications,[5] a pair of end-bent CNTs could allow easier grasping of a nanosized object than a pair of straight CNTs. Bent structures with longer second

growth stages that are grown horizontally (Figure 3B) could be potentially used as in-plane nanointerconnections. Vertically grown zigzag nanotube structures (Figure 3C) could be used as thermally compliant vertical interconnections for applications requiring connecting two materials with a large difference in coefficients of thermal expansion. The potential of these structures as interconnections would be even higher if they can be reproduced with CNTs containing walls parallel to their tube axes and for SWNTs in particular.

Bent or zigzag CNTs could also function as nanosprings or a forest of them could be a tunable energy absorption coating. Nanotube tips cleared of undesirable carbon capping can enable a continuous growth of nanosolenoids using rotating electric field during CVD growth, which can be useful for a variety of electromagnetic and electromechanical devices. Other novel CNT composite structures are also possible with the availability of regrowth, for example, segment-by-segment decoration of certain length portions of nanotubes with different types of functional nanoparticles, biomolecules, quantum dots, etc. could lead to nanobarcode structures.

IV. Conclusion

Regrowth of CNTs has been found to be strongly related to the carbon capping present on the catalyst particle. It is shown that such undesirable carbon capping can be controlled and the nanotube growth can be rejuvenated by either control of growth processing conditions including carbonaceous gas compositions, temperature, plasma power, and chamber purging timing or by inserting a room-temperature sputter etching process. The ability to cause sequential regrowth steps to take place in different directions makes it possible to clearly compare the occurrence and extent of CNT regrowth. Such a CNT regrowth process allows a design and creation of new nanostructures such as sharply bent 90° structures, zigzag structures, and nanocoils potentially useful for nanointerconnections, nanosprings, and conductance AFM nanoprobes.

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