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Control of Carbon Nanotube Growth Directions via Electric Fields within a DC Plasma Sheath

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Accurate control of the growth direction of carbon nanotubes (CNTs) during chemical vapor deposition is demonstrated. The CNT growth in a dc plasma enhanced CVD process is guided by the directions of the electric field inside of the plasma sheath. By careful control of the cathode geometry utilizing movable conductor plates, the electric field directions can be controlled to allow the growth of CNTs over a large range of angles. Calculated electrostatic field diagrams predict electric field directions which correspond well with experimental growth results, showing that a predictable control over the CNT growth orientations is possible. Such control is an important step toward fabricating CNTs with desired configurations and utilizing them for various technical applications.

Keywords: carbon nanotube, carbon nanofiber, direction, morphology, dc plasma

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 some research work demonstrating CNTs' potential as nanointerconnections[6]. By virtue of their very small diameters, as small as about 1.2 nm, CNTs have a distinct advantage over current lithographically patterned circuit interconnections with practical feature size limitations of ~40 nm or larger.

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)[7-9]. 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)[10] and MWNTs[11]. Recently, we have demonstrated the ability to grow CNTs aligned at angles not perpendicular to a substrate, with abrupt and sharp bends or zigzag configurations. A radius of curvature less than 25 nm was obtained by manipulating the electric field directions in the CNT growth regions[12-13]. This adds great potential to CNTs as interconnections since using only straight CNTs would substantially limit device integration capability.

Although we have previously demonstrated that CNTs can be grown in various morphologies by manipulating the electric fields in their growth regions, the details of how the CNT growth directions were controlled were not presented. In this paper, we demonstrate the ability to explicitly control the growth directions of aligned CNTs by careful modification of the cathode geometry.

The growth of aligned arrays of CNTs was carried out using a direct current (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 the formation of the catalyst islands, the atmosphere was changed to NH_3 gas flowing at a rate of 150 sccm. 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 C_2H_2 gas was

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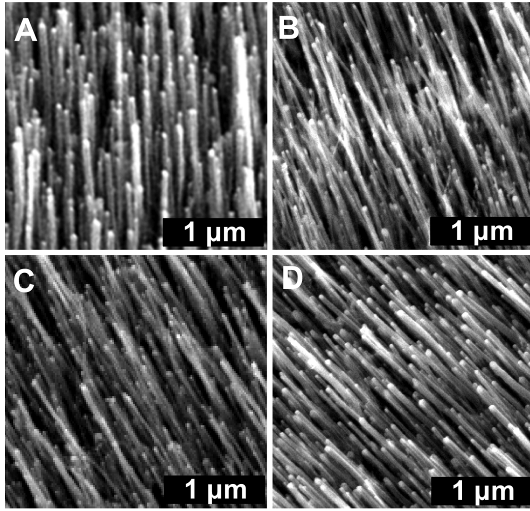

Fig. 1. SEM images of aligned CNTs grown along a range of growth directions that have CNT-substrate angles of A) 90°, B) 80°, C) 71°, and D) 51°. The images are taken with the flat substrates on the SEM stage tilted away by 45° so the angles as viewed in the images are not the real angle that the CNTs make with the substrate. The actual listed CNT angles were obtained from cross sectional images taken parallel to the substrate, which are presented later.

added to the chamber flowing at 30 sccm with the total NH_3 and C_2H_2 pressure held at 3 torr. For microstructural analysis, scanning electron microscopy (SEM) imaging was carried out in a Phillips field emission SEM operated at 30 keV.

Vertically aligned CNTs grown with a perpendicular electric field (90° with respect to the Si substrate) are shown in the SEM image in Figure 1A. The CNTs have a fairly narrow diameter distribution with the majority being between 30-40 nm, and have lengths of 1-2 µm. The sample is tilted 45° away from the viewer to allow better view of the growth morphology. Additional SEM images showing CNTs grown at angles of 80°, 71°, and 51° with respect to the substrate are shown in Figures 1B, 1C, and 1D, respectively. These four images were taken from four different samples, but the sample substrates were prepared identically and the images were taken from equivalent positions on each of the four samples. The only experimental difference between the four experiments was the cathode geometry. The sample in Figure 1A was grown on a flat molybdenum (Mo) cathode while the other three had a modified cathode geometry that had additional Mo pieces forming extensions of the cathode to a side of the sample in order to alter the electric field distribution.

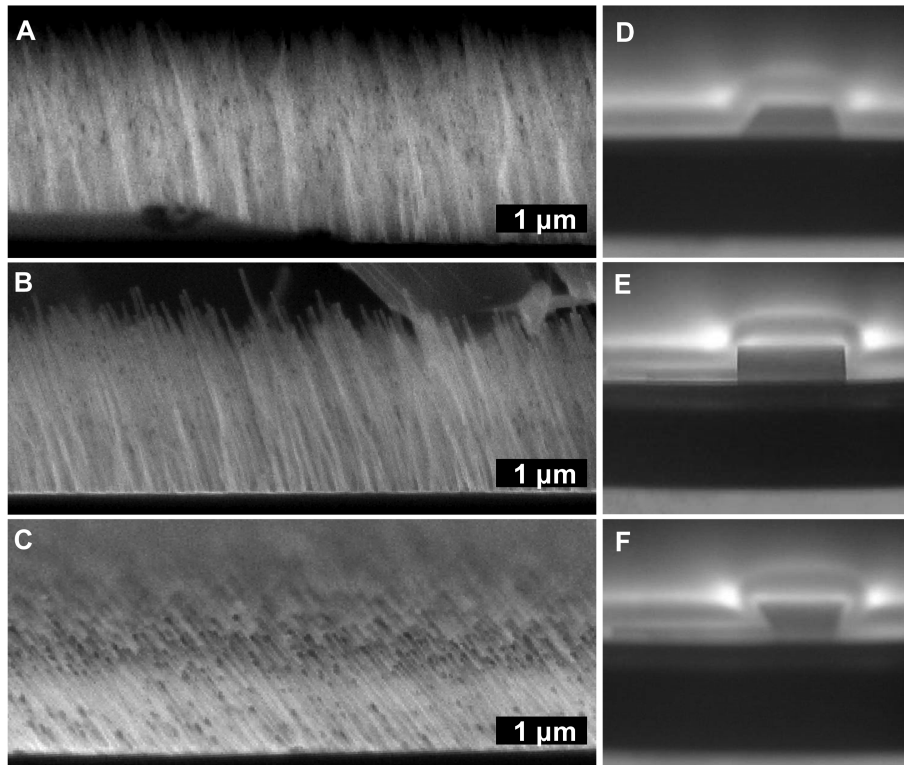

Fig. 2. Cross sectional SEM images taken parallel to the Si substrates are shown in A-C. The samples are the same as those shown in Figure 1B-D, and the CNTs were grown with tilt angles of 80°, 71°, and 51° with the substrate in A, B, and C, respectively. Photographic images showing the different cathode geometries and resulting dc plasma sheaths are shown in D-F with each image corresponding to the SEM image to its left. The Mo cathode extensions make three different angles with the main Mo stage, 55° away from the Si sample, 90°, and 55° towards the Si sample in D, E, and F, respectively. The CNTs were grown on identical substrates with identical growth conditions, and the images were obtained in the same manner and from equivalent positions on the samples 1 mm from the edge of the sample. The large change in the degree to which the CNT growth direction was displaced from the perpendicular orientation to the substrate is apparent, which clearly corresponds to the sequential changes in the cathode geometry.

Since the SEM images presented in Figure 1 were taken at an angle, it is difficult to see the true angle that the CNTs have with respect to the substrate, since most of their bases were obscured by other CNTs. In order to accurately represent the actual CNT angles, cross sectional SEM images taken along the plane of the substrate are shown in Figures 2A, 2B, and 2C, for the same samples that were presented in Figures 1B, 1C, and 1D, respectively. The three different angles that the CNTs make with the substrate is evident in the figures. We can also more easily see the distribution of heights in the CNTs. In Figures 2D, 2E, and 2F, photographic images of the three corresponding cathode geometries and resultant plasma sheath configurations used to obtain the CNT growth morphologies are presented. The images were taken through the growth chamber view port during the CVD growth processing. The presence of a dc plasma sheath above the cathode and Si sample is clearly shown. The three modified cathode geometries each contain an extension to the cathode stage by a 2.5 mm thick Mo piece that had been carefully shaped. In Figures 2D-2F, each Si sample is placed on the left side of the cathode extension and in contact with that extension. In the first cathode geometry, Figure 2D, the side wall of the Mo cathode extension plate that is next to the Si sample on the right makes an angle of 55° with respect to the horizontal cathode stage, and that slope is inclined away from the Si sample. In the next cathode geometry, Figure 2E, the Mo plate makes a 90° angle with the stage. In the final cathode geometry, Figure 2F, the Mo plate again makes a 55° angle with the stage, but this time it is inclined towards (or over) the Si sample. It can be seen that as the angle that he cathode extension plate makes with the stage changes, so does the resulting angle that the synthesized CNTs make with the Si substrate.

Our dc PECVD chamber uses a flat disk-shaped main Mo cathode stage 1 mm thick and 38 mm in diameter. Under normal plasma processing conditions, a dc plasma sheath forms above the surface of the cathode[14]. A schematic illustration of the voltage distribution for a dc glow discharge is show in Figure 3. At each electrode a plasma sheath forms.

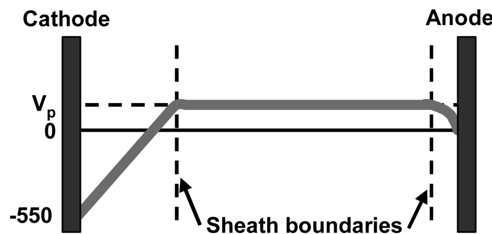

Fig. 3. Schematic plot of the voltage distribution in a dc glow discharge. The voltage in the plasma (V_p) is at a slight positive voltage of typically less than 10 V with respect to the grounded electrode (the anode as pictured). Since the cathode has a negative bias of -550 V the voltage drop across the cathode sheath is 550 V + V_p, which is approximately equal to the applied negative bias for small values of V_p.

The voltage within the bulk of the plasma is not at a potential between those of the two electrodes as one might expect, rather it takes on the slightly positive V_p which is typically less than 10 V and is actually the most positive body in the glow discharge. Since the cathode is negatively charged, there is an electron depleted region directly above the cathode. This electron depleted region decreases as the distance from the cathode increases, and this gradient of charges within the plasma sheath is referred to as the space charge density and results in an electric field within the dc plasma sheath. The fields within the electrode sheaths have a direction such that they repel electrons trying to reach either electrode. Poisson's equation relates the variation of potential difference V (between V_p and an electrode) with a distance x across regions of net space charge:

$$\frac{d^2V}{dx^2} = -\frac{\rho}{\varepsilon_0} \quad (1)$$

where ρ is the space charge density and å$_0$ is the permittivity of a vacuum[14]. Since the electric field intensity $E = -dV/dx$ and the space charge density $\rho = ne$, where n is the ion number density and e is the elementary charge, eq. (1) can also be expressed as

$$\frac{dE}{dx} = \frac{ne}{\varepsilon_0} \quad (2)$$

Model calculations for the electric fields within a dc plasma sheath using an expression like eq. (2) have been reported in literature[15].

The electric field strength in the cathode sheath has a function that can, to a first approximation, be taken as linear. Under such a linear approximation, the field can be expressed as

$$E = \frac{2V_b}{l}\left(1 - \frac{x}{l}\right) \quad (3)$$

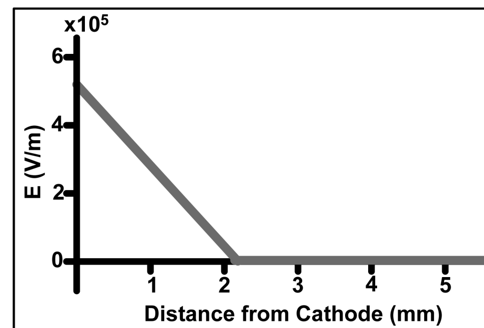

Fig. 4. The electric field strength near the cathode sheath region for a bias of -550 V. The voltage between the cathode and anode electrode sheaths is assumed to be constant at a slightly positive V_p, so there is no electric field present in that region. The field inside of the cathode sheath is assumed to be a linear function related to the applied bias and the ratio of the distance from the cathode to the total sheath thickness as shown in equation 3.

where V_b is the absolute value of the negative bias applied to the cathode(with respect to V_p), l is the thickness of the plasma sheath, and x is the distance from the cathode[16]. A plot of this for the portion of the glow discharge near the cathode in our system is shown in Figure 4. We estimate V_b as the difference between the cathode bias and the grounded anode, which assumes V_p is negligible, and we calculate l as 2.14 mm based on plasma probe measurements reported elsewhere for a similar dc PECVD system[17]. The electric field beyond the sheath thickness has a constant value of zero due to the constant potential V_p, however, within the plasma sheath, the field strength increases linearly to 5.14×10^5 V/m close to the cathode surface. Blazek et. al also calculated the force acting on the CNT tip due to a dc plasma sheath[15]. Based on these calculations, the electric field strength near the cathode that we calculated above would lead to a force that is roughly as much as four orders of magnitude higher than the weight of the catalyst particle, which is very similar to what Blazek *et al.* [15] reported.

The electric fields calculated in Figure 4 are one dimensional since we only consider the distance from a flat cathode of assumed large area. The cathode geometries that we used in this work to create various tilted CNT orientations are more complicated. 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[18]. The presence of the plasma environment creates a potential self-bias where the field lines are always perpendicular to the surface. Even when a substrate's surface is tilted at an 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 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 10V 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, since the sample substrate is located on the cathode, the resulting direction of the electric field due to the applied bias is towards the sample. The field lines will again be perpendicular to the local surface and will bend as they move away from the surface to connect the two electrodes of the applied bias. 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 resulting in vertically aligned CNTs like those shown in Figure 1A. 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[19]. 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 and are also expected to bend with those lines if they were to grow sufficiently long. These length scales strongly influenced by bending field directions are normally much longer than the lengths of nanotubes that we grow which are typically less than 10 μm.

The true net electric field is a combination of several components including the applied bias and the plasma induced self-bias. It has already been shown that the electric fields within a dc plasma sheath are of sufficient strength to sharply change the growth direction of a CNT[12], but the quantitative calculation of the field directions has yet to be reported. To estimate the directions of the electric fields, we start by making an assumption that their directions due to the applied bias and due to the formation of the dc plasma sheath will be similar. If this is the case, then modeling either case should give us a reasonable model. In Figure 5, we present plots generated using Maxwell 2D modeling software from Ansoft Corp. (Pittsburgh, PA) for the calculated electric fields due only to the applied bias under the assumption of a vacuum between the electrodes. The potential at the surface of a conductor is assumed to have the same potential as its interior and all metals are assumed to be perfect conductors, therefore no electric field will exist inside of one. The tangential component of the electric field at a surface is assumed to be zero, which forces the electric field E to be perpendicular to the boundary of a conductor. The chamber wall is assumed to be at infinite distance representing an electrically grounded system. The only difference among the Figures 5A-C is the geometry of the cathode extension plates, which are the same three geometries presented earlier. In Figures 5A-C, the Si sample is shown as an outlined rectangle to the left of the cathode plate, as was pictured in Figure 2. Figures 5D and 5E show progressively enlarged sections of 5B focusing on the area where the CNTs seen in Figures 1 and 2 would grow. In Figure 5E, a solid square marks a location 1 μm above the sample substrate. The calculated field direction for this case is 71.4°, which is remarkably close to what is observed experimentally.

A summery of the calculated angles and actual observed experimental angles is shown in Table 1. The results are very similar, which supports the assumption that the directions of the net electric field will coincide with the directions of the field due only to the applied bias. It is important to note that in the calculated fields in Figure 5, the Si substrate is not assumed to be a perfect conductor, so it is not an extension of the cathode itself. The fields were calculated both above and within the Si substrate. Had we used the same boundary conditions as we used for the metal electrodes, then the field directions within the CNT growth region would have been forced to be perpendicular. We believe that these electric

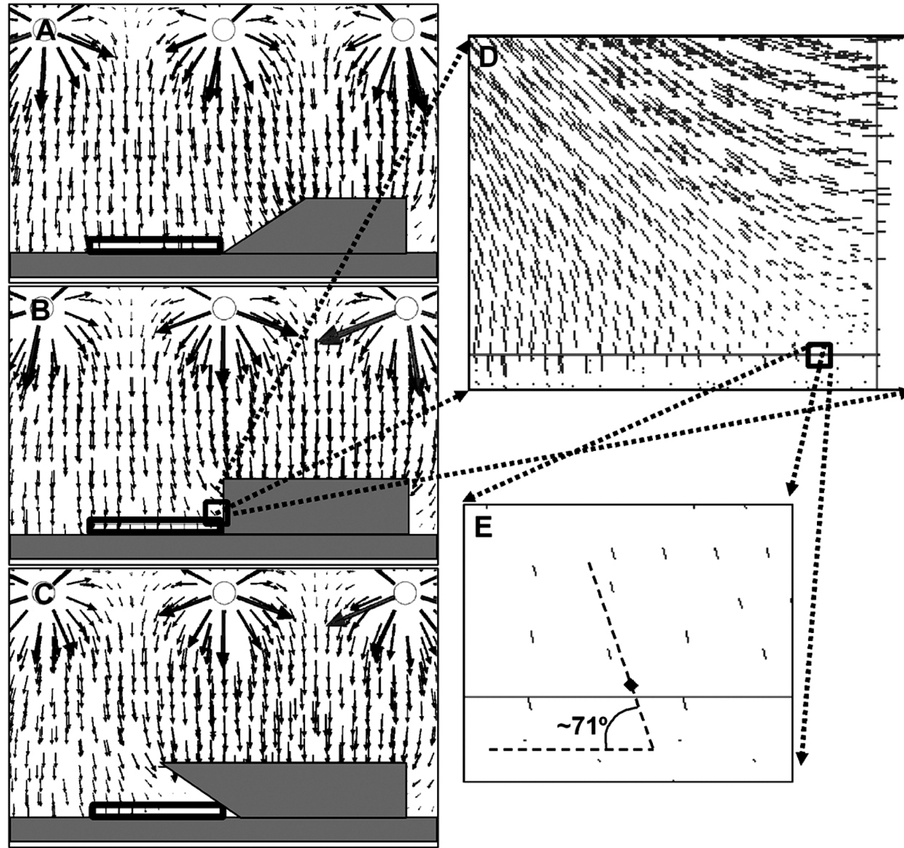

Fig. 5. Plots of the calculated electric fields between the anode and cathode with the assumption of a vacuum between the electrodes. The cathode is shown with grey shading, the Si sample is show as an outlined rectangle to the left of the upper cathode plate, and the three copper anode wires are shown as circles near the tops of the images. Without a gas present, no glow discharge would form and the plots are purely electrostatic. The three cathode geometries presented previously are shown in A-C while progressively enlarged areas of the CNT growth region in B are shown in D and E. The point in E is 1 μm above the substrate in the location where the CNTs pictured in Figure 2B would grow. These electrostatic plots predict very similar growth directions to those observed in experiment which supports the suggestion that the presence of the plasma does not significantly alter the directions of the electric fields in the CNT growth region.

Table 1. Comparative CNT orientation based on the electrostatic model prediction vs the experimental results for the three cathode geometries.

Cathode	Electrostatic	Experimental
Inclined away	80.6°	80°
Vertical	71.4°	71°
Inclined towards	52.7°	51°

fields within the Si sample could be part of the reason that our experimental results show a degree of bending greater than the present electrostatic prediction, but additional study is needed to confirm this. Further modeling is being done that takes into account the formation of a dc plasma sheath and these results will be reported in future, but initial findings appear to support the assumption that the dc plasma sheath only has a significant effect on the magnitude of the electric field in the growth region of the CNTs, not on the direction in which the field acts.

Understanding how to control the growth direction of CNTs is important for many applications. Control over growth direction can enable the creation of bent CNTs with specific bend angles and zigzag type configurations, which could be useful for circuit nano-interconnections[12]. For in-plane nano-interconnections between device components or contact pads, routing of circuit connections often require not just a straight but sharp-turn conductor circuit lines. Carefully engineered CNTs with specific bend angles could also be useful for such applications, especially if SWNTs or small diameter MWNTs can also be made to respond to electric field manipulations in a similar fashion. Also CNTs grown at various angles from a substrate or CNTs that are grown in bent configurations could be useful as improved AFM tips for probing side walls of channels or pores. For virtually all potential applications of CNTs, control over their growth morphology and the ability to produce them in large and uniform quantities will be of great importance, and the present

work helps take a step in achieving such control.

In summary, CNTs have been grown over a range of angles with respect to their substrates. By a simple change of the geometry of a single cathode plate, dramatic changes in the CNT growth orientations can be accomplished. The electric field within the plasma sheath was calculated and is of such strength that it would lead to a force which is orders of magnitude larger than the weight of the catalyst particles at the CNT tips. The electric fields due solely to the applied bias were calculated and the predicted field directions in the CNT growth regions agree well with the observed experimental results. This research provides a simple yet useful technique and understanding of how to adjust the growth direction of CNTs, and takes a step towards being able to control their growth morphology for significant technical applications.

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