Alignment mechanism of carbon nanofibers produced by plasma-enhanced chemical-vapor deposition

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We report experimental evidence showing a direct correlation between the alignment of carbon nanofibers (CNFs) prepared by plasma-enhanced chemical-vapor deposition and the location of the catalyst particle during CNF growth. In particular, we find that CNFs that have a catalyst particle at the tip (i.e., growth proceeds from the tip) align along the electric-field lines, whereas CNFs with the particle at the base (i.e., growth proceeds from the base) grow in random orientations. We propose a model that explains the alignment process as a result of a feedback mechanism associated with a nonuniform stress (part tensile, part compressive) that is created across the interface of the catalyst particle with the CNF due to electrostatic forces. Furthermore, we propose that the alignment seen recently in some dense CNF films is due to a crowding effect and is not directly the result of electrostatic forces. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1415411]

Carbon nanostructures such as vertically aligned carbon nanofibers (VACNFs) (Refs. 1–3) and nanocones[4] produced by plasma-enhanced chemical-vapor deposition (PECVD) are nanoscale materials of great interest due to their potential applications in areas such as tips for scanning microscopy and field-emission devices, biological probes, and interconnects for nanoelectronics. The alignment of the nanofibers is essential for the realization of practical devices. To date, however, the alignment mechanism has not been well understood. While researchers agree that VACNFs are aligned due to the presence of the electric field in a PECVD process,[2,3,5] it is not clear whether the mechanism is simple electrostatic attraction of the fibers,[6] preferential etching, or some other effect. In the present work we provide experimental evidence and a corresponding model that explains the alignment and the conditions under which it occurs.

Experimental details on the synthesis of VACNFs can be found elsewhere.[2,4] Briefly, dc glow-discharge PECVD was utilized in a vacuum chamber evacuated to a base pressure of $\sim 1\times 10^{-5}$ Torr. A mixture of acetylene and ammonia, with flows of 40–50 and 200 sccm, respectively, was used as a gas source. The pressure during the growth was ~2 Torr, the growth temperature was ~700 °C, and the discharge voltage and current were ~550 V and 100 mA. Arrays of catalyst dots and lines (10 nm Ni/10 nm Ti/Si) of variable width were fabricated using electron-beam lithography to provide for the patterned growth of VACNFs. These structures were inspected using a Hitachi S4700 high-resolution scanning electron microscope (SEM).

The first step towards elucidating the alignment mechanism of carbon nanofibers (CNFs) in a glow discharge follows from Fig. 1(a), which depicts a forest of chaotically positioned VACNFs grown on a catalyst line. In this image, both vertically aligned and randomly oriented CNFs are seen. Furthermore, in Fig. 1(b) both aligned and nonaligned CNFs grow on the same catalyst dot array. These images demonstrate that in a single growth process, where all CNFs are subject to similar electrostatic conditions, both aligned and nonaligned CNFs can be formed. This would seem to indicate that something more than just the electrostatic forces plays a role in CNF alignment.

A careful examination of Figs. 1(a) and 1(b) revealed that all of the aligned CNFs that we imaged had the catalyst particles at the tips [Fig. 1(c)], whereas the nonaligned ones did not [Fig. 1(d)]. Apparently, at elevated temperatures some of the catalyst particles became attached to the substrate via interdiffusion of metals, and this attachment was sufficiently strong to prohibit the particle from moving during the CNF growth process. This resulted in the so-called ''base growth'' mode in which the catalytic particle is located at the base of the growing fiber. Figure 1(e) clearly shows base growth mode CNFs and illustrates that the CNFs are not aligned in this case.

The above observations require a reexamination of hypothesized alignment mechanisms. If alignment were due to preferential etching in the direction perpendicular to the electric-field lines the nonaligned nanofibers would have been etched. While we note that reduction or elimination of acetylene content does lead to etching of nonaligned CNFs, the alignment process itself cannot be governed by etching. A second hypothesis holds that simple electrostatic attraction of the nanofibers during the plasma growth process is responsible for alignment. The Debye length in our glow discharge should be at least of the order of 100 μm or higher,[7] and the nanofibers, whose length is of the order of a few μm, are located well within the high-field dark space of the discharge. Consequently, a significant electrostatic force is exerted on the fibers due to induced polarization. In the absence of shielding,[8] the field is highly enhanced at the tip of the nanofibers with an enhancement factor approximately equal to the ratio of the CNF length to the tip radius of curvature

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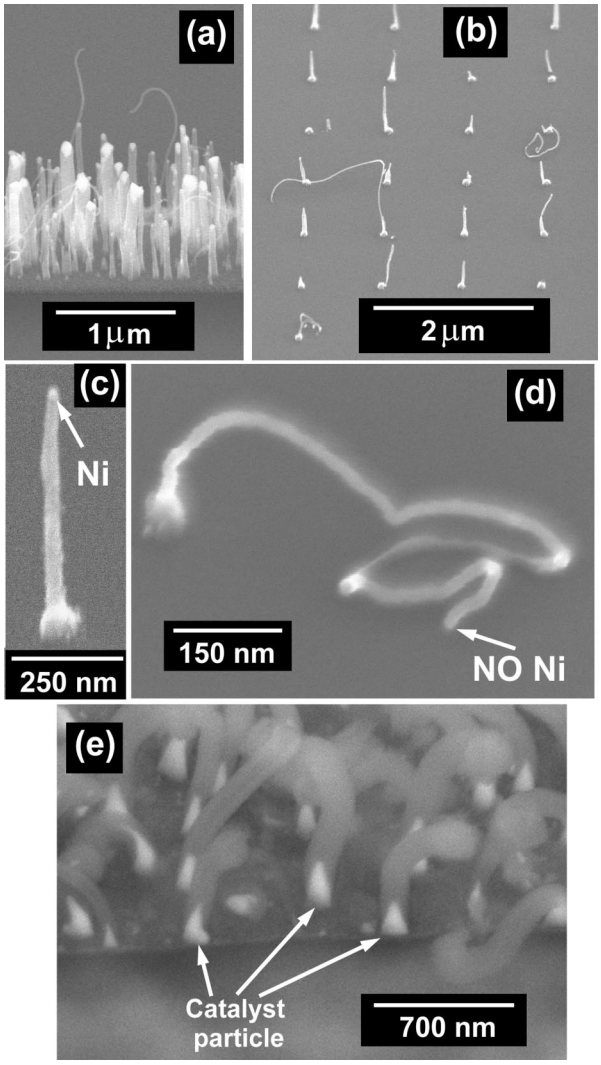

FIG. 1. SEM images of carbon nanofibers (CNFs) prepared by PECVD. Aligned and nonaligned CNFs can be produced in a single growth process on a patterned line of catalyst metal (a) or an array of catalyst dots (b). Aligned CNFs have the catalyst particle at the tip (c) while the nonaligned ones do not (d). The catalyst particle for nonaligned CNFs is located at the base (e). In case (e), a Si wafer covered with a 100-nm-thick Ti layer was used as a substrate, the acetylene flow was 55 sccm, and the discharge voltage during the growth was ~440 V. All images were taken at 10 kV and a 45° tilt angle.

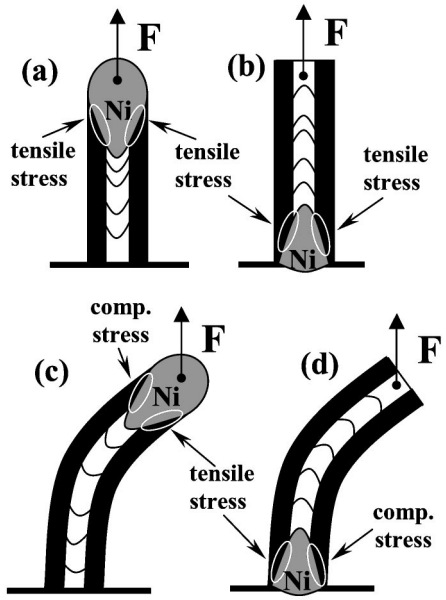

FIG. 2. Alignment mechanism of carbon nanofibers. If a CNF grows vertically (along the electric-field lines), electrostatic force F creates a uniform tensile stress across the entire catalyst particle/nanofiber interface, regardless of whether the particle is located at the tip (a) or at the base (b). If during the growth the CNF starts to bend due to spatial fluctuations in carbon precipitation at the particle/nanofiber interface, nonuniform stresses are created at the particle/nanofiber interface. For the nanoparticles at the tip (c) and at the base (d) the stresses are distributed in the opposite way, which leads to the nanofiber alignment in the first (c) but not in the second (d) case. White ellipses indicate the interface regions where the stresses occur.

(aspect ratio).[9] To a first approximation, we can assume that the force is applied just at the tips of the CNFs and is essentially directed perpendicular to the substrate. Since all the nanofibers are graphitic, and therefore conductive, two morphologically identical fibers will be subject to the same electrostatic force without regard for the position of the catalyst particle. Therefore, the images in Fig. 1 indicate that the magnitude of the electrostatic force on the CNFs is not alone a determining factor in fiber alignment.

Given this, we propose the following model to explain the vertical alignment of PECVD-grown CNFs. The growth of CNFs is believed to occur via decomposition of the carbonaceous gas molecules at the catalyst particle surface or in the glow discharge, diffusion of the carbon atoms through the particle, and subsequent precipitation at the particle/fiber interface.[10,11] The axis of a CNF growing perpendicular to the substrate coincides with the direction of the applied electrostatic force, resulting in a uniform tensile stress across the entire nanofiber/catalyst particle interface, as shown in Figs. 2(a) and 2(b). Consequently, carbon uniformly precipitates across the interface and the fiber continues to grow vertically (perpendicular to the substrate). However, if there were a spatial fluctuation in the C precipitation at the interface, CNF growth would deviate from vertical alignment, as shown in Figs. 2(c) and 2(d).

In the case of nanofibers growing from the tip (catalyst particle at the tip), the electrostatic force produces a compressive stress at the particle/nanofiber interface where the greater rate of growth is seen [Fig. 2(c)]. Likewise, a tensile stress is applied to the particle/nanofiber interface where the lesser rate of growth is seen. We propose that these opposing stresses favor subsequent C precipitation at the interface experiencing tensile stress and the lesser rate of growth. The net result is stable, negative feedback that acts to equalize the growth rate around the entire periphery of the particle/nanofiber interface, and vertically aligned CNFs are grown. The presence of the preferred direction of C precipitation can be caused by stress-induced diffusion (see, e.g., Ref. 12 and other refs. therein) due to the stress gradient in the catalyst particle and possibly by the variation in the stress-dependent sticking of diffusing C atoms to the C side of the Ni–C interface. In any case, the exact mechanism may be quite complex and detailed study of the stress-induced C diffusion and precipitation in the C–Ni system is needed.

The situation with the preferred direction of C precipitation is different, however, when the catalyst particle is located at the base of the CNF. Since the nanofiber base is attached to the substrate, the stress created at the particle/nanofiber interface with the greater growth rate is tensile

[Fig. 2(d)] and acts to continue the increased growth rate, thus causing the CNF to bend even further. This is essentially a positive feedback mechanism that is inherently unstable for the control of CNF orientation. We note, however, that near the base the nanofibers grow essentially perpendicular to the substrate [Fig. 1(e)]. Therefore, the applied stresses will be quite small and the direction of the nanofiber growth will be mostly governed by the fluctuations in the C precipitation across the particle/nanofiber interface.

To summarize, we find that the presence of the catalytic particle at the tip of the nanofibers is essential for their alignment during the PECVD growth. The interaction of the electrostatic force applied to the CNF tip with the catalyst particle located at the growing tip provides a stable negative feedback mechanism that assures vertically aligned growth. For the base-growth mode the situation is reversed, resulting in a positive feedback mechanism that further misaligns the growth. The inherent instability of positive feedback control systems leads to the wildly varying CNF orientation seen in Fig. 1. We note that, recently Bower and co-workers[5,13] reported the growth of aligned, closely spaced carbon nanofibers in which the catalyst particles were located at the base. We believe, however, that even though the presence of the electric field can be quite important for the initial stages of aligned CNF growth, the alignment of long, closely spaced nanofibers during these growth experiments was due to the crowding effect,[14,15] not the applied electrostatic force, and the growth of well-spaced (essentially isolated) VACNFs would be difficult in this case.

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