Controlled alignment of carbon nanofibers in a large-scale synthesis process

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Controlled alignment of catalytically grown carbon nanofibers (CNFs) at a variable angle to the substrate during a plasma-enhanced chemical vapor deposition process is achieved. The CNF alignment is controlled by the direction of the electric field lines during the synthesis process. Off normal CNF orientations are achieved by positioning the sample in the vicinity of geometrical features of the sample holder, where bending of the electric field lines occurs. The controlled growth of kinked CNFs that consist of two parts aligned at different angles to the substrate normal also is demonstrated. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1487920]

Fabrication of commercially valuable devices based upon nanoscale components requires large-scale processes that allow massive production of these components with very well specified properties, (e.g., shape, structure, chemical composition, etc.), secure placement of these components in the right orientation that is determined by a device functionality, and fabrication of robust input and output (IO) connections. Several research groups have recently demonstrated fabrication of devices based upon carbon nanotubes (CNTs) (see, e.g., Refs. 1–4 and references therein), which is a material with superior electronic and mechanical properties.[5] Despite the vast advances in this field, the ability to (i) synthesize large quantities of CNTs with predetermined properties, (ii) place them in the required configuration, and (iii) create IO, all in the context of a *fast large-scale* fabrication process, is still too limited for commercial production.

Recently, our group has demonstrated the suitability of vertically aligned carbon nanofibers (VACNFs),[6–9] also often referred to in literature as vertically aligned carbon nanotubes, for nanoscale device fabrication.[10,11] VACNFs can be deterministically synthesized on predetermined locations using the standard large-scale fabrication processes: lithography and plasma-enhanced chemical vapor deposition (PECVD). Deterministic VACNF growth achieved in these studies included the control of the location, length, tip diameter, shape, and chemical composition of VACNFs.[7,12–14] (Hereafter, the term VACNFs includes conically shaped VACNFs, also referred to as vertically aligned carbon nanocones in some of our previous work.[13]) The control of the VACNF orientation was limited to the direction perpendicular to the substrate. We note that there was a report in literature demonstrating PECVD growth of carbon nanofibers (CNFs) aligned at ~45° to the substrate.[15] However, it is not clear how it was achieved and whether the CNF orientation could be controlled.

The control of the orientation of a nanoscale object is a very important technological and scientific aspect and can be highly beneficial for production of various nanoscale devices. Recently, Zhang *et al.* successfully demonstrated the ability to align CNTs by applying an electric field.[16] However, the CNT alignment in this work was limited only to the in-plane geometry, whereas out-of-plane alignment is required for some applications. For instance, fabrication of probes for scanning microscopy in which a cantilever tip is oriented at a relatively large angle to the normal of the cantilever surface could allow inspection of the sidewalls of vertical trenches. The ability to do such an inspection can be quite valuable for applications in various technological fields, in particular for the semiconductor industry. In the present work, we describe a method for synthesis of aligned CNFs, in which the CNF orientation is not fixed to the direction perpendicular to the substrate, but can be controlled over a wide range of angles. Moreover, our method for the alignment control is not limited to CNFs or CNTs, but can be applied to any other structures whose growth process is similar to the catalytic growth of CNFs/ CNTs.[13,17]

In order to initiate growth of CNFs, formation of catalyst nanoparticles is required.[7] In this work, nickel (Ni) and nickel–iron alloy (Ni:Fe ratio ~50:50) were used as the catalyst and ~1 cm×1 cm pieces of *n*-type (100)-oriented Si wafers were employed as the substrates. To form ''forests'' of chaotically placed CNFs, 10 nm thick catalyst thin films atop of a 100 nm thick W–Ti buffer layer were used. For synthesis of individual CNFs, 10 nm thick catalyst dots which were 100 nm in diameter with a 10 nm thick Ti buffer layer were produced using electron-beam lithography and

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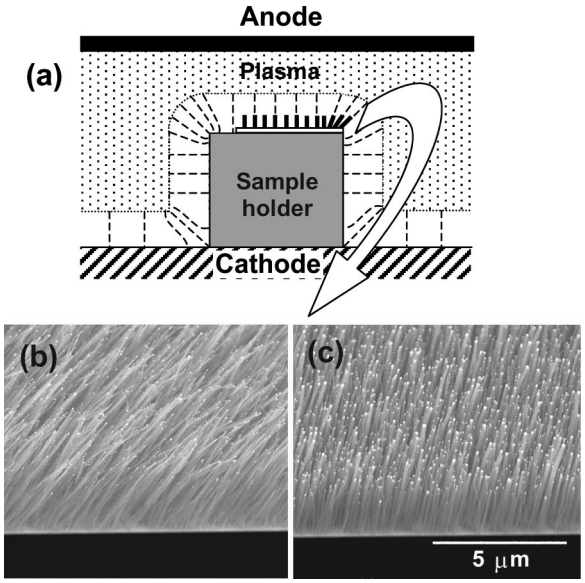

FIG. 1. (a) A schematic representation of the experimental setup during the PECVD process, in which the substrate is located close to the sample holder edge, and scanning electron microscopy images showing the resultant CNF forests located at (b) 100 μm and (c) 1000 μm away from the edge and aligned at $\sim$38° and 12° angles to the substrate normal, respectively.

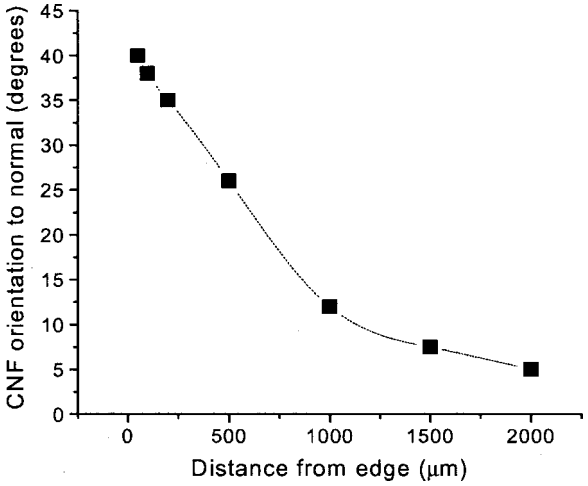

FIG. 2. Plot showing the CNF alignment angle to the substrate normal as a function of the distance away from the sample holder edge. It can be clearly seen that CNFs become more vertically aligned with increasing distance from the edge.

metal evaporation. The actual nanoparticles where CNF growth is initiated were formed by dc plasma pre-etching of the catalyst thin films with ammonia and annealing them at the elevated temperatures (up to $\sim$700 °C) in a vacuum chamber. dc PECVD was used to produce VACNFs. The plasma current was 100 mA for VACNF forests and 120 mA for individual VACNFs and the discharge voltage was $\sim$550–570 V. The dark space had the width of a few mm. If no geometrical enhancement is present, this yields an electric field of the order of 0.1 V/μm at the substrate surface. A mixture of a carbonaceous gas (acetylene, C_2H_2) and an etchant (ammonia, NH_3) was used during the growth, and the total pressure was $\sim$3 Torr. The substrates were heated directly by placing them on a heater plate (the cathode of the plasma discharge) and the growth temperature was $\sim$700 °C.

Recently, we have proposed that orientation of CNFs synthesized by PECVD occurs due to negative feedback that requires the presence of both the catalytic nanoparticle at the CNF tip and the electric field during the growth process, which is nominally directed perpendicular to the substrate surface.[18] The direction of the electric field lines determines the orientation of CNFs. Therefore, in order to control the CNF orientation, the direction of the electric field lines must be controlled. In a PECVD process, a plasma is present between the two electrodes, as shown in Fig. 1 (a). The plasma surrounds all faces of the sample holder (nominally the cathode). Consequently, the entire sample holder surface, except for the regions around the edges, is surrounded by the electric field lines that are essentially straight and oriented perpendicular to the surface. As a result, CNFs located far enough from the edges are aligned perpendicular to the substrate surface, regardless of whether the growth occurs on the top face or the sidewalls of the sample holder.

The direction and shape of the field lines is different, however, around the cathode corners. Significant bending of the electric field lines occurs in that region. The closer to the edge, the greater the bending. At the very edge, the bending is the largest. As the distance away from the edge increases, the field line bending decreases until the lines become completely straight [see Fig. 1(a)]. Thus, it is possible to position the substrate such that the CNFs grow aligned at angles other than substrate normal.

Figure 1(a) shows an experimental setup in which the substrate edge is aligned with that of the sample holder. In this case, the CNF alignment will deviate the most from substrate normal at the substrate/ sample holder edge. As the distance from the edge increases, the alignment becomes closer to the normal until vertical (perpendicular to the substrate) CNFs (VACNFs) are obtained. As shown in Figs. 1(b) and 1(c), indeed CNFs with variable alignment angle can be synthesized this way, and the alignment angle depends on the distance between the CNF location and the substrate/sample holder edge. The alignment angle of the VACNF forest as a function of the distance from the edge is shown in Fig. 2, which shows that the angle relative to substrate normal decreases with the distance away from the edge and approaches zero at large distances.

Synthesis of *isolated* CNFs aligned at a variable angle to the substrate normal also is possible. To grow individual CNFs, patterned catalyst dots were used. A sample was positioned on the cathode sample holder so that the catalyst dots were located close to the edge, similar to the arrangement in Fig. 1 (a). The resultant CNFs, located close to the edge of the substrate/sample holder, were aligned at a relatively large angle to substrate normal as shown in Fig. 3. Just as in the case of the CNF forests, the alignment angle of individual CNFs is a function of the distance from the substrate/ sample holder edge, and decreases as the distances increases.

To better understand and control the CNF alignment, calculations were done simulating a plasma and a plasma sheath adjacent to a finite dielectric ($\varepsilon\sim12$) Si substrate in turn attached to a metal (cathode) support. Preliminary results indicate that the direction of the nanofiber growth may mostly be governed by the electric field *inside,* not outside,

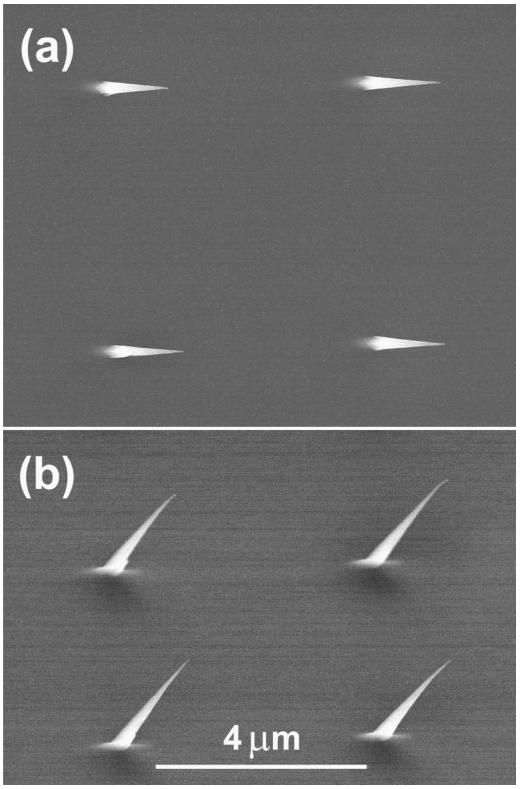

FIG. 3. SEM images, taken at (a) 0° and (b) 45° tilt angles, of an array of individual CNFs grown in the vicinity ($\sim 10\,\mu$m) of the substrate/the sample holder edge.

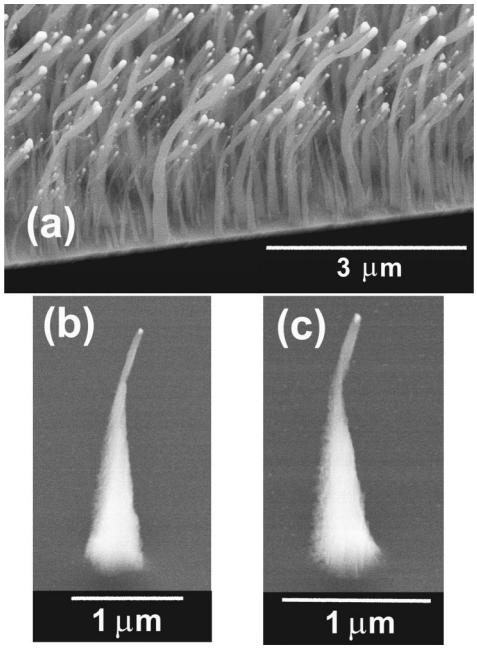

FIG. 4. SEM images of (a) a forest of and (b) individual kinked CNFs (KCNFs). KCNFs consist of two sections: the vertical base and the tip oriented at a nonzero angle to the substrate normal. KCNFs are grown in a two step process: (i) catalyst located far from the sample holder edge (vertical growth direction), and (ii) catalyst located close to the sample holder edge (off vertical growth direction).

the silicon. This latter conclusion has many implications in the tailoring of nanofiber growth directions. More calculations are underway and will be discussed elsewhere.

The ability to control the CNF alignment allows for the synthesis of kinked nanostructures. These structures consist of a section aligned perpendicular to the substrate and a section aligned off of the substrate normal. The first section can be synthesized by positioning the catalyst dots at a large distance from the sample holder edge. In this case, the electric field lines are straight and perpendicular to the substrate surface and vertically aligned CNFs are formed. Following this, the substrate is repositioned such that the catalyst is located near the sample holder edge. In this case, bending of the electric field lines occurs at the CNF location and CNFs start to grow off normal. As a result, kinked CNFs (Fig. 4) are formed. By repositioning the substrate several times, multiple-section nanostructures can be obtained.

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