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Patterned growth of individual and multiple vertically aligned carbon nanofibers

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The results of studies of patterned growth of vertically aligned carbon nanofibers (VACNFs) prepared by plasma-enhanced chemical vapor deposition are reported. Nickel (Ni) dots of various diameters and Ni lines with variable widths and shapes were fabricated using electron beam lithography and evaporation, and served for catalytic growth of VACNFs whose structure was determined by high resolution transmission electron microscopy. It is found that upon plasma pre-etching and heating up to 600–700 °C, thin films of Ni break into droplets which initiate the growth of VACNFs. Above a critical dot size multiple droplets are formed, and consequently multiple VACNFs grow from a single evaporated dot. For dot sizes smaller than the critical size only one droplet is formed, resulting in a single VACNF. In the case of a patterned line, the growth mechanism is similar to that from a dot. VACNFs grow along the line, and above a critical linewidth multiple VACNFs are produced across the line. The mechanism of the formation of single and multiple catalyst droplets and subsequently of VACNFs is discussed. © *2000 American Institute of Physics.* [S0003-6951(00)00824-X]

Carbon nanotubes[1] (CNTs) are of great interest to the scientific and industrial communities due to their astounding properties[2] which include ballistic electron transport and high mechanical strength and flexibility. CNTs are much smaller than most of the vapor-grown carbon fibers (VGCFs) that have been studied for many years but the smallest VGCFs often closely resemble CNTs in their external morphology. CNTs and VGCFs also have been observed to grow concurrently.[3] However, CNTs are clearly distinguished from VGCFs by the fact that a perfect CNT is a single crystalline grain, and even a defective CNT is a single crystal in cross section, except where the defect occurs. In contrast, a VGCF has a grain size (or structural coherence length[4]) that is small compared with its circumference. This distinction is crucial because it is the single crystal nature of CNTs that is responsible for their one-dimensional quantum effects, and which permits the use of a Brillouin zone-folding approach to obtain their electron and phonon dispersion relations.[2]

In addition to their fundamental scientific importance, CNTs have numerous potential applications in nanoelectronics, nanoscale structural materials, hydrogen storage, and field-emission devices, among others. Unfortunately for electrical applications and integration with microelectronics, the structurally nearly perfect CNTs are prepared by a variety of methods including laser ablation,[5] arc discharge,[6] and chemical vapor deposition[7] (CVD), all of which involve high synthesis temperatures and produce randomly oriented CNTs that must be laboriously separated, purified, and cut to length before use. However, the CVD method has been used to produce ''carpets'' of vertically aligned (perpendicular to the substrate surface) multiwalled nanotubes and nonfibers,[8–11] although control of their placement was limited. Recently, patterned growth of individual, vertically aligned carbon fibers also was demonstrated by Ren *et al.* using a plasma-enhanced CVD (PECVD) method at a low substrate temperature estimated to be less than 660 °C.[12] In this case, arrays of nanoscale carbon fibers were grown from Ni dots, one fiber per dot. However, the resulting vertically aligned fibers are not single crystalline grains, so are more properly called vertically aligned carbon nanofibers (VACNFs), not CNTs. Their defective structure is due at least in part to the low growth temperature. Nevertheless, the PECVD growth of VACNFs is of particular interest for possible applications in field-emission arrays and scanning-probe microscopy.

There are several important issues about PECVD growth of VACNFs that remain to be addressed. First, the maximum size of a catalyst dot that produces only one VACNF has not been determined. (It is known that for a continuous Ni film a forest of VACNFs is formed.[8]) Second, growth of VACNFs on a continuous line of catalyst rather than a dot has not been explored. And, finally, the mechanism and conditions for the formation of single and multiple VACNFs on an evaporated catalyst dot or line have not been explained. In this work we studied various stages of VACNF growth on patterned Ni dots and lines in order to address all of these issues.

For VACNF preparation, *n*-type (001)-oriented Si wafers were used as substrates and Ni was employed as the catalyst. The catalyst patterns (dots and lines of various sizes) were fabricated by conventional electron beam lithography using a bilayer resist in conjunction with electron-gun metal evaporation. Following e-beam exposure and pattern development, a buffer layer consisting of 10 nm of Ti was deposited first to prevent the formation of Ni silicide at elevated temperatures and then a 15 nm thick Ni catalyst layer was deposited.

VACNFs were prepared by PECVD in a vacuum chamber evacuated by a mechanical pump to a base pressure $<5\times10^{-3}$ Torr. Acetylene (C_2H_2) and a mixture of 10%

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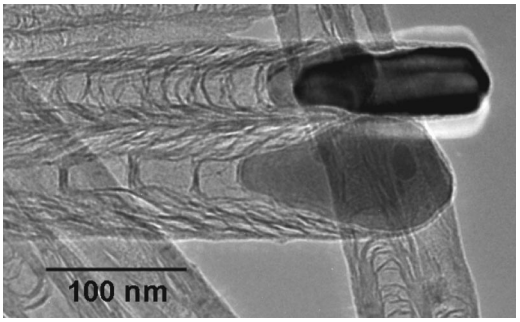

FIG. 1. High-resolution TEM image of VACNFs grown by PECVD at 700 °C. The VACNFs have a highly disordered ''bamboo'' structure (see Ref. 3). The Ni catalyst particles (dark) are seen at the nanotube tips.

ammonia (NH_3) and 90% helium (He), with gas flows of 15 and 200 sccm, respectively, were used as the gas source. NH_3 is needed to etch away graphitic C film that continuously forms during the growth from the plasma discharge and passives the Ni catalyst, thereby preventing the formation of nanofibers. Then Ni was pre-etched by the NH_3/He plasma for ~2 min to remove oxide, after which the acetylene flow was introduced. The total pressure during VACNF growth was ~6 Torr, the dc plasma discharge was operated at 50 mA and ~500 V, and the growth rate was ~150 nm/min. Changing the pressure by a factor of 2–3 did not significantly affect the growth. In contrast to hot filament PECVD,[8] the substrates were heated directly by placing them on a heater plate. This method has the advantage of enabling large-area deposition and excellent uniformity of VACNF films. The substrate temperature during growth was ~700 °C, as measured by a thermocouple. Growth at lower temperatures down to 600 °C was possible, although the growth rate in this case was substantially lower.

The formation of VACNFs was studied using a Philips XL30/FEG high resolution scanning electron microscope (HRSEM) with x-ray energy dispersive spectroscopy (EDS) capability. The structure of VACNFs was investigated using a Hitachi HF-2000 transmission electron microscope (TEM) equipped with a field emission gun. The VACNFs are quite disordered and have a bamboo-like structure, as shown in Fig. 1. This high degree of structural disorder is typical for PECVD growth at relatively low temperatures.[8]

Scanning electron microscopy (SEM) images presented in Fig. 2 demonstrate the combined effects of pre-etching and heating up to ~700 °C on the Ni/Ti dots deposited on Si. While the Ti layer continues to adhere to Si, the initially continuous Ni layer breaks into little droplets. This is consistent with the observations by Yudasaka *et al.*[13] For initially large dots, multiple droplets are formed [Fig. 2(a)]. As the size of the dots is reduced, the number of Ni droplets also decreases [Fig. 2(b)]. Finally, for a dot size less than ~350 nm only a single Ni droplet is formed [Fig. 2(c)]. These droplets are the necessary precursors for the catalytic growth of nanofibers. After the acetylene is introduced, the VACNF growth begins. The mechanism of the vertically oriented growth is not completely understood at this time. However, ''crowding'' of the nanofibers (suggested by others[9,11] as a mechanism for vertical alignment of nanotube ''forests'') clearly can be eliminated as an alignment mechanism in this case, since regular arrays of *single* VACNFs were grown at a

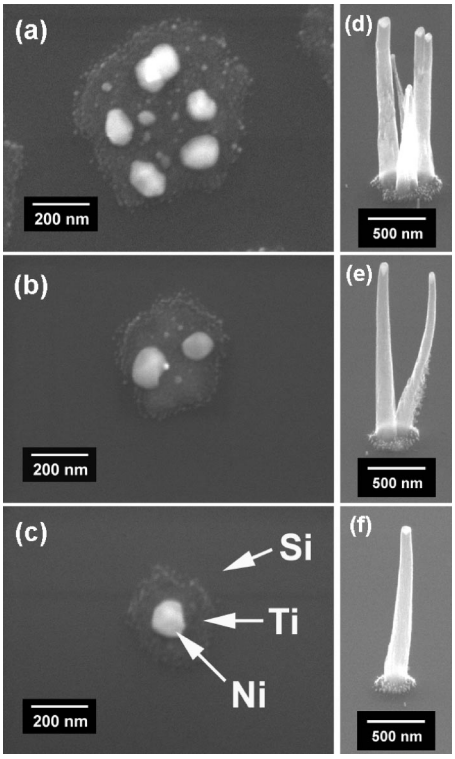

FIG. 2. Formation of multiple (a), (b) and single (c) Ni droplets on the patterned evaporated dots (15 nm Ni/10 nm Ti on Si) and subsequent growth of multiple (d), (e) and single (f) VACNFs. The Ni droplets were formed during NH_3/He plasma pre-etching and heating up to 600–700 °C. The SEM images were taken at 15 kV and 0° tilt (a)–(c) and at 50° tilt (d)–(f).

5 μm pitch. We believe instead that preferential plasma etching in the direction parallel to the substrate surface and perhaps the alignment of nanofiber growth along the plasma electric-field direction are responsible for the vertical orientation of CNFs.

Figures 2(d)–2(f) show VACNFs grown from the patterned Ni dots of various sizes. Once can see that for a large dot that produced multiple Ni droplets multiple VACNFs are grown [Fig. 2(d)], and the number of VACNFs decreases with decreasing dot size, corresponding to fewer Ni droplets [Fig. 2(e)]. Each Ni droplet initiates the growth of a single VACNF, and then resides on top of the nanofiber and provides for its continued catalytic growth.[14] For evaporated dots smaller than ~350 nm in diameter only a single Ni droplet is formed and only a single VACNF is grown [Fig. 2(f)]. Thus we estimate the critical dot size to be ~350 nm. Of course, it has to be realized that the critical size will depend upon several parameters, including the choice of the buffer layer, the substrate, and the type and thickness of the catalyst used (15 nm of Ni here). Nevertheless, the mechanism making possible the deterministic growth of a single VACNF from a single patterned Ni dot will remain the same.

When patterned lines are used instead of dots, the VACNFs grow along the lines, as illustrated in Fig. 3(a). There may be a single or multiple VACNFs across the line, depending upon the linewidth. The critical width is found to be ~200 nm under our preparation conditions. The VACNF formation mechanism is very similar to that in the case of evaporated dots. The patterned Ni line breaks into individual droplets, each of which catalyzes the growth of VACNFs. After the growth starts, the Ni particles reside on top of the

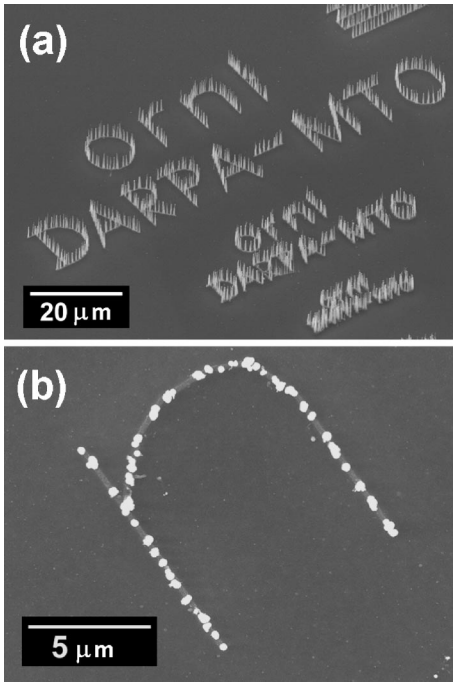

FIG. 3. SEM images taken at 50° tilt (a) and 0° tilt (b) showing VACNFs grown on Ni catalyst lines. (a) VACNF growth follows the catalyst line pattern. (b) The Ni film breaks into little droplets that initiate CNF formation and then reside on top of VACNFs that grow perpendicular to the substrate.

nanofibers, providing for their continued growth [Fig. 3(b)].

The formation of single or multiple catalyst droplets on a single patterned catalyst dot can be explained as follows. As-deposited Ni films have intrinsic tensile stress of $\sim 8 \times 10^9$ dynes/cm^2.[15] However, upon heating a compressive stress develops in the films[16] due to the different expansion coefficients for Ni (13×10^{-6}/°C) and Si (3×10^{-6}/°C). At 600–700 °C this thermal compressive stress is equal to $\sim 2 \times 10^{10}$ dynes/cm^2 and thus the net stress will be compressive. Furthermore, the compressively strained Ni film will develop propagating sinusoidal wrinkles to minimize the strain energy.[17] This will tend to break large-area films into smaller patches. However, the wrinkle formation and the subsequent film breakup increase the surface energy. Consequently, below a critical dot size the breakup does not occur because the increase in the surface energy would be larger than the reduction of the strain energy. Next, at elevated temperatures the metastable Ni film patches will tend to form clusters to further reduce the strain energy.[18] This results in the Stranski–Krastanov growth mode: Ni clusters are formed on top of one or a few monolayers of Ni attached to the substrate surface. The characteristic cluster size will be dictated by the minimum of the sum of the strain and surface energies. In the end, large-dot Ni films that break into multiple patches produce multiple Ni clusters, whereas Ni films on smaller dots below a critical size form only a single droplet. The Ti layer, on the other hand, does not form clusters due to its lower (8.5×10^{-6}/°C) expansion coefficient (lower strain energy) and higher melting point (lower mobility of the atoms at a given temperature).

In conclusion, the mechanism for PECVD growth of vertically aligned carbon nanofibers from catalyst dot and line patterns has been studied. Experiments reveal that the VACNFs are produced due to the formation of catalyst droplets and subsequent catalytic growth of one VACNF per droplet. For an initial 15 nm Ni/10 nm Ti dot on Si, the critical diameter below which only a single VACNF will grow is ~350 nm. Above this critical diameter multiple VACNFs are formed. VACNF growth along patterned catalyst lines also was demonstrated, and the growth mechanism is found to be similar, with a critical linewidth of ~200 nm for the same catalyst deposition. We also found that direct substrate heating during PECVD growth has a significant advantage in producing large-area growth of VACNFs with excellent uniformity.

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