Growth of a single freestanding multiwall carbon nanotube on each nanonickel dot

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Patterned growth of freestanding carbon nanotube(s) on submicron nickel dot(s) on silicon has been achieved by plasma-enhanced-hot-filament-chemical-vapor deposition (PE-HF-CVD). A thin film nickel grid was fabricated on a silicon wafer by standard microlithographic techniques, and the PE-HF-CVD was done using acetylene (C_2H_2) gas as the carbon source and ammonia (NH_3) as a catalyst and dilution gas. Well separated, single carbon nanotubes were observed to grow on the grid. The structures had rounded base diameters of approximately 150 nm, heights ranging from 0.1 to 5 μm, and sharp pointed tips. Transmission electron microscopy cross-sectional image clearly showed that the structures are indeed hollow nanotubes. The diameter and height depend on the nickel dot size and growth time, respectively. This nanotube growth process is compatible with silicon integrated circuit processing. Using this method, devices requiring freestanding vertical carbon nanotube(s) such as scanning probe microscopy, field emission flat panel displays, etc. can be fabricated without difficulty. © *1999 American Institute of Physics.* [S0003-6951(99)03634-7]

Selective positioning and growth of carbon nanotube(s) is necessary for future integration with conventional microelectronics as well as the development of novel devices. Limited progress has been reported in the controlled placement of nanotubes[1–3] since the first observation of carbon nanotubes.[4] Specifically, vertical alignment has been an important goal due to its technological importance for applications such as scanning probe microscopy and field emission flat panel displays (FEDs). Attempts to manipulate nanotubes for these applications have been made by postgrowth methods such as cutting a polymer resin−nanotube composite,[5] or drawing a nanotube-ethanol suspension through a ceramic filter.[6] Because these techniques are difficult and labor intensive, *in situ* aligning of nanotubes during growth using means such as laser etched tracks[7] and the nanopores of porous alumina membranes[8] have been attempted. Aligned growths of carbon nanotubes have been produced by chemical vapor deposition (CVD) on mesoporous silica with imbedded iron particles.[9] The growth of large arrays of well aligned carbon nanotubes has been demonstrated on glass,[10] on nickel,[11] and on silicon.[12,13]

Here we report the growth of an array of individual multiwall carbon nanotubes onto a grid of patterned metal. Previously, researchers have investigated arrays of carbon nanotubes for applications such as cold-cathode flat panel FEDs[14,15] and vacuum microelectronic sources.[16–18] The growth process described here is selective and relevant for applications involving electron field emission since the structures are aligned atop the patterned film and terminate in sharp points. This process could also be extremely useful in the fabrication of scanning probe microscopy tips terminating in carbon nanotubes, since growth of the nanotubes directly on the tip would be preferable to manual placement.[1–3]

Thin film nickel (Ni) patterns were fabricated on a *p*-type boron doped 9.5 Ω cm (100) silicon substrate by electron beam lithography and metal evaporation. We used a bilayer e-beam resist (5% 100 MW (molecular weight) PMMA (polymethylmethacralate) capped by 2% 950 MW PMMA) that was patterned with a JEOL J6400 scanning electron microscope (SEM) converted for lithography. The resist was developed in a solution of methyl isobutyl ketone and isopropyl alcohol (3:1). Subsequently, 150 Å of Ni was deposited by electron beam evaporation. The final Ni pattern remained after resist/metal liftoff in acetone. The patterned substrate was loaded into a plasma-enhanced-hot-filament-(CVD) system described previously[10–12] with a base pressure below 10^{-6} Torr. Growth was performed at a pressure of 1–10 Torr with an acetylene ammonia mixture of 40:160 (standard cubic centimeter per minute, both acetylene and ammonia were highly purified with a minimum purity of 99.99%). The growth time was about 5 min, and the sample temperature during growth was below 660 °C.[10]

Figure 1(a) is a SEM micrograph of tubes grown on a large (~0.25 mm^2) Ni pad near the grid, and have a morphology similar to those previously observed.[10] The region shown in the picture is the edge of the Ni pad; the absence of growth in the foreground of the picture indicates selective growth on the Ni and not on the Si substrate. These tubular-

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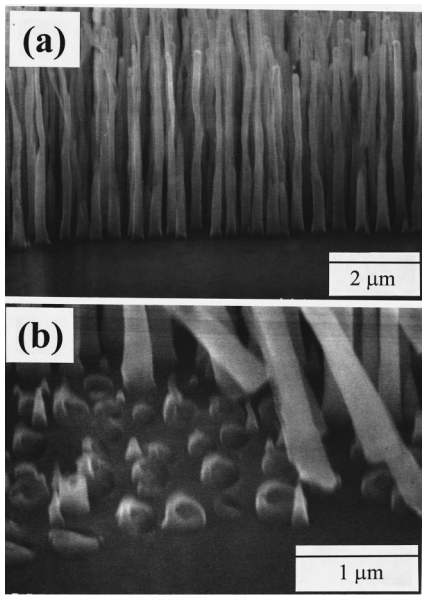

FIG. 1. (a) A SEM micrograph showing grown carbon nanotubes at the edge of a ~0.25 mm^2 Ni pad. (b) A SEM micrograph showing a region similar to (a) in which the nanotubes were mechanically broken.

like structures were mechanically broken using a tweezers [Fig. 1(b)]. It is observed that the tubes break somewhere along the tube and not at the interface between the nickel and silicon. This is different from previous observations of Ni-on-glass tube growth, where the tubes broke cleanly at the Ni–glass surface.[10]

We observed that growth on submicron Ni structures was distinct from that on large area structures. Figure 2 is a series of SEM micrographs showing the growth of single multiwall carbon nanotubes on each dot of an array of ~100 nm nickel dots. Figures 2(a), 2(c), 2(e), and 2(f) were taken at an inclined angle, and Figs. 2(b) and 2(d) are top views taken normal to the substrate. Figures 2(a) and 2(b) demonstrate selective growth of the carbon structures on the multiply repeated array patterns. The grown structures accurately reflect the spacing and periodicity of the lithographically patterned Ni dots. Figures 2(c) and 2(d) were taken at a higher magnification and show the repeated array pattern where the nanotubes are spaced either 2 μm apart (left) or 1 μm apart (right). The sharp, tapered tips observed in the higher magnification SEM micrograph of Fig. 2(e) have not been previously observed using this growth method.[10–12] Significant variation in the height (0.1–5 μm) of the grown bundles is observed (recent experiments showed that the variation in height is smaller than 20%), with no apparent relationship between height and spatial position. We note that even though the heights are different by more than a factor of 10, the base diameters are approximately uniform (~150 nm). Figure 2(f) shows the growth on a grid of Ni dots spaced 5 μm apart, indicating little dependence of growth on spacing (for spacings >1 μm). The factors that control growth, uniformity, and electrical characteristics are under investigation. In order to prove that the structures are indeed hollow nanotubes, not solid nanofibers, cross-sectional images were taken by transmission electron microscopy. Figure 3 shows part of the cross section of one of the structures. It clearly shows that the structure is indeed hollow at the center and layered on both sides with typical inside diameters of 16 nm in agreement with the value in the literature and outside di-

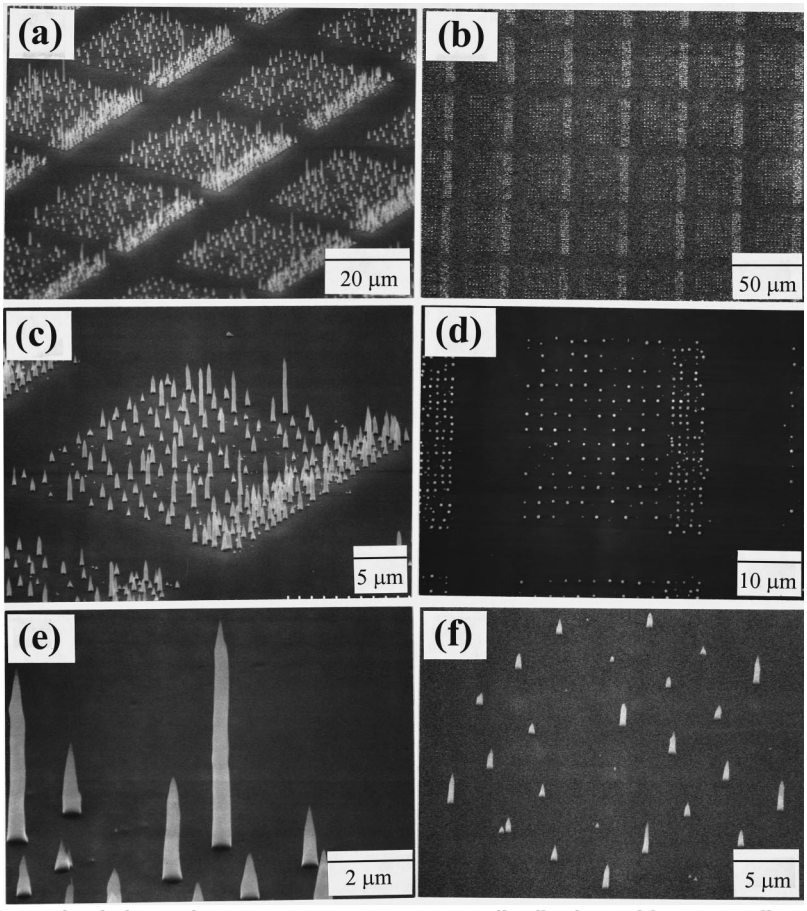

FIG. 2. A series of SEM micrographs from different viewing angles showing growth of carbon nanotube obelisks on an array of submicron nickel dots. (a) An inclined view of a repeated array pattern. (b) A top (normal) view of a repeated array pattern. (c) An inclined view of one array pattern. (d) A top (normal) view of one array pattern. The initial Ni dots (and subsequently the grown carbon structures) are spaced either 2 μm apart (left) or 1 μm apart (right). (e) A magnified view along the edge of one pattern. A sharp, tapered tip is evident. (f) An inclined view of carbon obelisks grown on nickel dots separated by 5 μm.

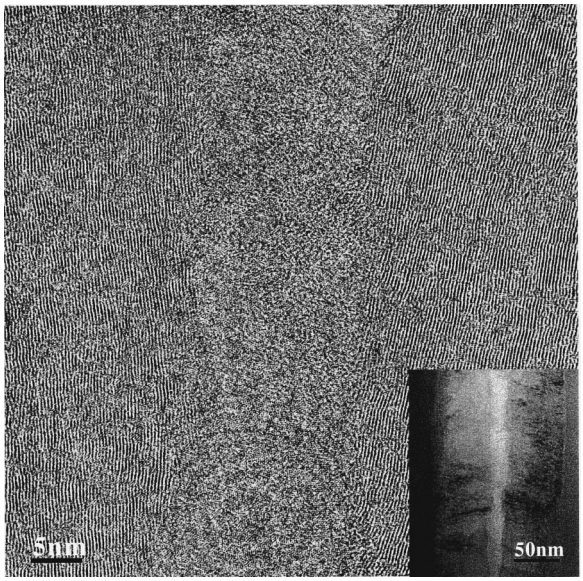

FIG. 3. Cross-sectional TEM image of part of one of the structures. The hollow center and layered sidewalls are clearly seen. The inset shows the outside diameter of one of the structures.

ameters (o.d.) of 150 nm shown in the inset. The large o.d. is due to the large size of the nickel dots (>100 nm). Further experiments using much smaller nickel dots (<50 nm) are under investigation. Due to the low growth temperature (<500 °C), there are defects along the growth direction. Further investigation using higher growth temperature (>650 °C) should result in well-graphitized continuous layers. The reason for such aligned growth of single carbon nanotubes in our system is probably due to the plasma, which is not used by others.

The demonstrated selective growth of multiwall carbon nanotube structures aligned to a lithographic pattern suggests numerous potential applications. Scanning probe microscope tips are one evident application, particularly if the tapered tip of the carbon nanotube bundle terminates with a single carbon nanotube. Determination of the electrical properties, and control of uniformity, will indicate if the bundles are useful for electronic applications such as flat panel FEDs, vacuum microelectronics, and three-dimensional electrode arrays.

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