Growth and fabrication with single-walled carbon nanotube probe microscopy tips

Chin Li Cheung, Jason H. Hafner, Teri W. Odom, Kyoungha Kim, and Charles M. Lieber[a)]

Harvard University, Cambridge, Massachusetts 02138

Single-walled carbon nanotube (SWNT) probe microscopy tips were grown by a surface growth chemical vapor deposition method. Tips consisting of individual SWNTs (1.5–4 nm in diameter) and SWNT bundles (4–12 nm in diameter) have been prepared by design through variations in the catalyst and growth conditions. In addition to high-resolution imaging, these tips have been used to fabricate SWNT nanostructures by spatially controlled deposition of specific length segments of the nanotube tips. © *2000 American Institute of Physics.* [S0003-6951(00)02821-7]

Carbon nanotubes are fascinating materials that exhibit exceptional electrical and mechanical properties.[1] These unique properties have been exploited for fundamental studies,[2,3] to make electronic devices,[3,4] and to create new nanoscale tools, such as probe microscopy tips,[5,6] and nanotweezers.[7] The use of carbon nanotubes for atomic force microscopy (AFM) and other scanned probe microscopy tips is especially exciting, since the small diameter, high aspect ratio, mechanical robustness, electrical conductivity, and selective chemical reactivity provide great advantages for imaging and manipulation compared to conventional silicon and silicon nitride tips.[5,6,8–10]

In the past, most nanotube probe tips have been made by mechanical attachment of multiwalled carbon nanotube (MWNT) and single-walled carbon nanotubes (SWNT) bundles to silicon tips in optical or electron microscopes.[5,6,8–10] Nanotube tips made this way have been used to demonstrate, for example, their potential for high-resolution and chemically sensitive imaging,[6,8] but have also highlighted limitations. Specifically, mechanical tip fabrication is a time consuming one-by-one process, and the resolution of these tips can vary widely due to their bundle structures. To overcome these and other limitations, we have been developing direct chemical vapor deposition (CVD) growth of SWNT and MWNT tips, and recently reported the first examples of nanotube tips prepared in this way.[11–13] Significantly, we showed that SWNT and MWNT tips with diameters of 2–8 and 6–12 nm, respectively, could be reproducibly grown by metal-catalyzed CVD. Herein, we report significant extensions of our initial discovery with the controlled growth of individual SWNT and SWNT bundle tips, and the manipulation and controlled deposition of tip segments to create nanotube nanostructures.

SWNT tips were grown using our reproducible and flexible metal-catalyzed CVD surface growth method.[12] Briefly, solutions of either alumina supported Fe–Mo or ferric nitrate were deposited on commercial Si tips, and then nanotube tips were grown at 800 °C in a flow of 0.5–2 sccm ethylene, 400 sccm H_2, and 600 sccm Ar in a CVD reactor. The structures of the nanotube tips were characterized by scanning electron microscopy [(SEM) LEO 982] and transmission electron microscopy [(TEM) Philips EM 420]. A Nanoscope III (Digital Instrument, Inc., Santa Barbara) was used for all AFM experiments as described previously.[11–13]

We have focused on the controlled growth of two general classes of SWNT tips—those composed of several SWNTs in a bundle and individual SWNTs—which are important for different types of imaging experiments. Bundle tips can be made relatively long while maintaining sufficient stiffness for high-resolution imaging of deep trenches or tall structures, and individual SWNT tips provide ultimate resolution for relatively short tips. We have selectively grown either type of tip through variation of the catalyst density: a high density of catalyst produces bundle tips by the surface growth mechanism, and a low density of catalyst yields individual tubes. Typical electron microscopy images of SWNT bundle and individual SWNT tips prepared in this way are shown in Fig. 1. Figure 1(a) shows a SEM image of a 5.8 μm long SWNT bundle tip. Nanotube tips can be controllably shortened by electrical etching to make them suitable for lithography and/or high-resolution imaging.[5,11–14] The TEM image [inset, Fig. 1(a)] shows a SWNT bundle tip shortened in this way for high-resolution imaging, with a length of 29 nm and diameter of 7.4 nm. Figure 1(b), which shows an individual 2.2 nm diameter, 10 nm long tube, dem-
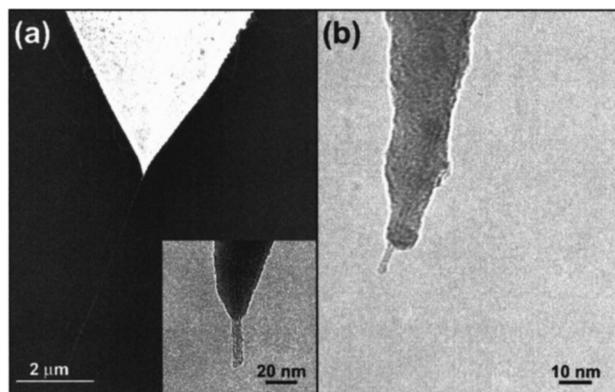

FIG. 1. Electron microscopy of CVD SWNT tips. (a) Field emission-SEM image of a SWNT bundle tip. The inset is a TEM image of a SWNT bundle tip shortened by electrical etching. (b) TEM image of an individual SWNT tip.
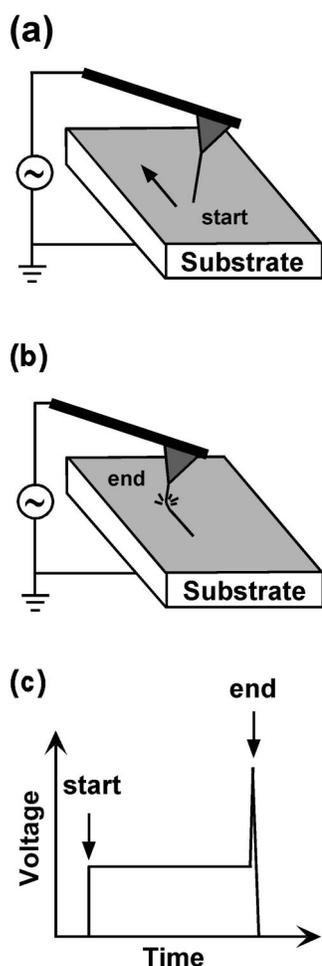
[a)]Electronic mail: cml@cmliris.harvard.edu

FIG. 2. Schematic illustrating the deposition of a segment of a SWNT tip onto a substrate. (a) The nanotube tip is positioned at the desired start point, and then (b) the tip is scanned in a predefined pattern. A voltage pulse separates the tip from deposited nanotube structure at the end of the scan. (c) Plot of the applied voltage during the course of the deposition process.
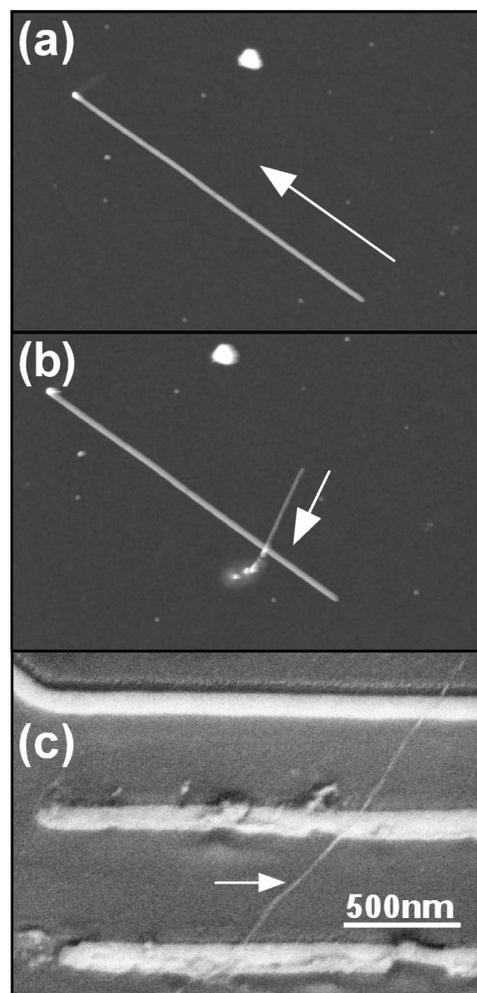

FIG. 3. (a) AFM image of a SWNT deposited along the direction of the arrow. (b) AFM image of a cross SWNT structure made by a second nanotube lithography step. The images in 3(a) and 3(b) are both 2 μm$\times$1.3 μm. (c) Field emission-SEM image of a SWNT deposited across three 40 nm high gold electrodes. The white arrow highlights the deposited nanotube.

onstrates that individual SWNT tips can also be prepared by our approach.[14]

These CVD SWNT tips can be grown with yields in excess of 75% for bundles and about 10% for individual SWNT, and thus may be suitable for large-scale commercial production. We believe that improvements in the yield of individual SWNT tips can be obtained through improvements in the catalyst activity. In addition, a limitation of the CVD method is that it is difficult to control precisely the nanotube length during growth. As discussed earlier, tip length can be optimized for imaging by electrical etching, which allows tips to be shortened with at least 2 nm control.[14]

Optimized tips are robust and can be used for high-resolution imaging of nanostructures and biological macromolecules,[13,14] although our focus here is the finding that these well-defined SWNT tips can be used to fabricate nanotube-based nanostructures by controlled deposition of segments of the tips in defined patterns. This approach is illustrated schematically in Fig. 2. To deposit a SWNT segment in a specific location, the tip is first biased at −6 to −12 V at the starting point, and then the tip is scanned along a set path. To complete the deposition, a voltage pulse is

used to disconnect the tip from the nanotube segment on the substrate.

Figure 3 illustrates several examples of this new nanofabrication approach. First, a 4.8 nm diameter SWNT bundle was deposited as a 1.5 μm long line across a silicon surface [Fig. 3(a)]. We note that this method can produce very straight structures, since we do not need to overcome tube-surface forces during deposition. In a second step, a thinner 2.1 nm SWNT was deposited over this small bundle at a near perfect 90° angle to create a SWNT crossed junction [Fig. 3(b)]. Last, we find that it is possible to deposit SWNT segments directly over prefabricated metal electrodes [Fig. 3(c)], which could facilitate the fabrication and testing of new nanotube devices. Related studies of MWNT bundle tips have shown that MWNTs can be "cleaved" from a bundle by the lateral shear force present during scanning.[9] However, it is difficult to control size by this method.

We believe that our approach offers some advantages compared to other methods that have been used to fabricate SWNT devices. For example, SWNTs have been deposited from solution onto electrodes,[2] or AFM has been used to push the nanotubes into a specific patterns.[15] These methods are limited in part by chance (of getting a suitable tube on or

near electrodes), potential tube damage caused by AFM manipulation, and a difficulty in knowing the SWNT electronic properties prior to making electrical connections. Another promising approach involves direct CVD growth of nanotube devices,[16] although it may be difficult to make crosses and more complex structures by this method. In addition, CVD cannot yet yield predictable metallic versus semiconducting tubes. With our nanotube tip deposition method, we can control the precise spatial location and size of deposited nanotubes, and to a large extent the electronic properties of the deposited tube. Specifically, current–voltage measurements made prior to deposition can be used to determine whether the SWNT is metallic or semiconducting, and thus tips having the required properties can be used selectively in the fabrication.

In conclusion, individual SWNT and SWNT bundle AFM tips have been grown in relatively high yield using CVD surface growth. These SWNT tips exhibit significant improvements in lateral AFM resolution compared with commercial silicon AFM tips. In addition, we developed an approach for constructing well-defined SWNT nanostructures on surfaces by using segments of the nanotubes tips as building blocks. The present study demonstrates that CVD SWNT nanotube tips have the potential to impact significantly imaging and the fabrication of SWNT nanostructures.

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