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Vertical Array Growth of Small Diameter Single-Walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) have been intensively studied because of their many potential applications. Previous studies have shown that vertical arrays of SWNTs, SWNT carpets or forests, can be readily grown in the presence of hydrogen and various hydrocarbons at sub-atmospheric pressures (0.5−30 Torr), where the gas mixtures are activated with microwave or RF discharges.[1−5] Gas activation likely causes the formation of atomic hydrogen and free radical species containing carbon. Carbon nanotubes are formed when the activated gas is exposed to substrates on which particles of metal catalysts are present, where the metal is a catalyst that is known to catalyze the growth of carbon nanotubes.[6−10] It has also been previously shown that hot filament activation of gas mixtures of hydrogen and hydrocarbons activates the growth of multi-walled carbon nanotubes (MWNTs) in the presence of metal catalysts.[11]

In this study, substrates on which small islands of iron have been vacuum deposited are quickly heated in the presence of an activated gas. An activated gas is generated by rapidly flowing gas mixtures, typically 400 sccm H_2 and 40 sccm CH_4 at pressures of 15−25 Torr, over a hot filament (temperature greater than 2000 °C) to create activated gas mixtures of hydrogen and carbon-containing species. The substrate is supported in an open quartz boat which is mechanically inserted from the downstream side and placed ∼5 mm from the hot filament. The hot filament is located near the center of the furnace and the center of a 25 mm diameter quartz tube. The filament is ∼8 mm long and made from 10 mill tungsten wire. Typical filament operating voltages and currents are 4 V and 11 A, respectively. Filaments were brought up to the operating temperature over ∼10 min to allow for filament carburization. A small percentage of the methane is converted to acetylene and ethylene by the filament. A typical run involved generation of a ∼3% acetylene/methane ratio. The metal catalyst Fe was vacuum deposited as a 1 nm thin film on a 10 nm Al_2O_3 film previously vacuum deposited on an oxidized silicon wafer with a 3.5 μm layer of SiO_2. This process is similar to that used by other investigators.[1,4] The apparatus is better illustrated in the Supporting Information.

The combination of substrate heating in the presence of an activated gas is thought to be important because metal particle size strongly affects the diameter of a single-walled carbon nanotube that forms on a metal catalyst particle. When substrates are heated slowly to temperatures necessary for growing single-walled carbon nanotubes (temperatures typically greater than 600 °C) without the ability to nucleate and grow nanotubes, metal particles with diameters of 1−2 nm can readily move about on a substrate and aggregate into larger particles. This leads to growth of larger diameter and multi-walled nanotubes. Thus achieving the lowest possible temperature before surface particle diffusion occurs at which nucleation and initial growth of single-walled carbon nanotubes can occur is very important to growing SWNTs with the smallest possible diameters. The results of this study suggest that the simultaneous presence of atomic hydrogen and reactive hydrocarbon species, such as methyl radicals and acetylene, causes the nucleation and growth of single-walled carbon nanotubes at the lowest possible temperatures and in the shortest possible time when a substrate initially near room temperature is quickly heated to a steady state growth temperature (typically greater that 650 °C).

In our experiments, the substrate is placed in a quartz boat that is attached to a 10 in. quartz rod, which is attached to a small stir bar magnet that is encased in quartz. The boat is placed on the downstream side of the quartz tube and is always at room temperature until inserted into the furnace. After heating the furnace to 750 °C, the filament was heated to ∼2000 °C, which was measured with a PYRO micro-therm pyrometer. The flow of methane was then gradually increased to 40 mL/min over a 10 min time period. The filament undergoes carbonization and a change in resistance during this period. A final temperature adjustment of the filament is made such that a small amount of the methane is converted to acetylene and ethylene. Typical acetylene concentrations relative to methane are 1−3%, by increasing the hot filament power by ∼10%. After stabilization of the filament resistance, the substrate is quickly inserted into the furnace. After an allotted number of minutes for growth, the filament and methane flow are turned off. The substrate is removed from the furnace to the downstream cool zone. The furnace is then turned off and the system cooled to room temperature in a low flow of hydrogen. With the above conditions, it is observed that well-aligned vertical arrays of small diameter SWNTs are produced. If samples are first placed in the furnace in a flow of only H_2 and the furnace is heated to a typical growth temperature with or without the hot filament on, carpet growth is not observed. Also, if the substrate undergoes prior oxidation at evaluated temperatures or is exposed to an oxygen discharge, carpet growth has been found to produce much larger diameter nanotubes, which suggests that these treatments cause metal island aggregation.

The characterization of each sample was documented by SEM, TEM, fluorescence, and Raman spectroscopy. SEM pictures were taken with a JEOL 6500 SEM. Figure 1 shows carpet SWNTs grown with different times. We found that carpet thickness and presumably nanotube lengths have a linear relation to the growth time. The average growth rate was found to be ∼2.5 μm/min. Also, as shown in Figure 1d, holes of ∼1 μm are distributed about the surface of the carpet. It is unclear as to what causes the holes. It may be something as simple as surface particle contamination. TEM images were obtained with a JEOL 2010 TEM at 200 kV. As shown in Figure 2, all the observed nanotubes are SWNTs with diameters less than 2 nm, in agreement with fluorescence and Raman spectra,

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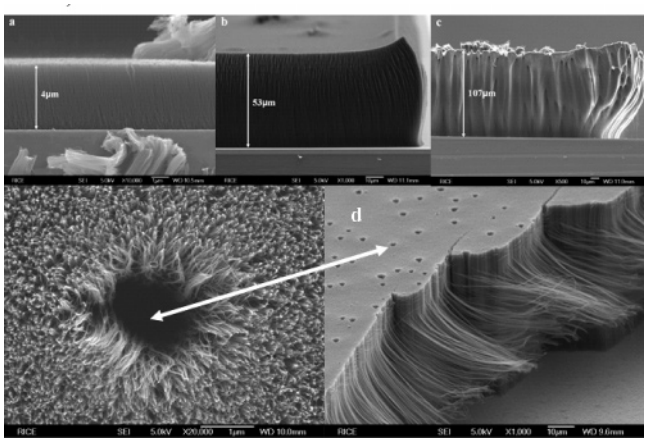

Figure 1. SEM pictures of carpet SWNTs grown with different time: (a) 1.3 min, scale bar = 1 μm; (b) 20 min, scale bar = 10 μm; (c) 40 min, scale bar = 10 μm; (d) inside view of the sample grown with 40 min, scale bar = 10 μm, inset image scale bar = 1 μm.

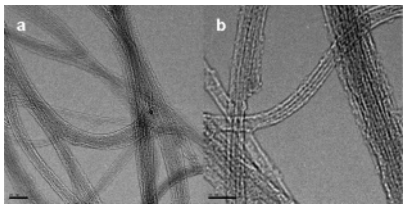

Figure 2. TEM images of carpet SWNTs: scale bar (a) 20 nm, (b) 10 nm.

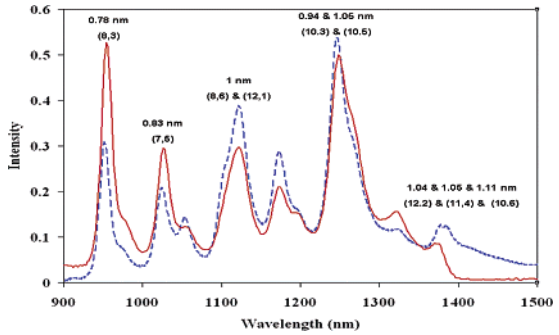

Figure 3. Fluorescence spectra of carpet SWNTs (red) and HiPco SWNTs (blue).

where a diameter distribution of SWNTs from 0.8 to 1.6 nm was found. Fluorescence spectroscopic measurements were taken with a J-Y Spex Fluorolog 3-211 equipped with an indium−gallium−arsenide near-infrared detector cooled by liquid nitrogen.[12] Emission intensity was measured as a function of emission wavelength (from 800 to 1570 nm), with excitation wavelength at 669 nm. The sample was dispersed in 1 wt % SDBS surfactant and sonicated for 10 min with a tip sonicator. Figure 3 compares the fluorescence spectra of carpet SWNTs and HiPco (high pressure CO) SWNTs. There are two intense peaks (950 and 1250 nm) in the fluorescence spectrum of carpet SWNTs. Surprisingly, the 950 nm peak is as intense as the 1250 nm peak. This is not the case for HiPco SWNTs, as seen in Figure 3. This indicates that the SWNT carpet as grown contains a higher percentage of small diameter SWNTs than HiPco. The observed diameters of SWNTs are in the range of 0.78 to 1.1 nm (the upper limit is set by a limitation of the fluorescence spectrometer). Raman spectra were collected with a Renishaw micro-Raman spectrometer equipped with 519, 633, and 780 nm lasers and are shown in the Supporting Information. Typical SWNT Raman features are observed for the tangential modes and radial breathing modes (RBMs) near 1591 and 200 cm^{-1}, respectively. From the RBMs, Raman spectra imply a SWNT diameter distribution between 0.8 and 1.6 nm.

In addition, during the growth process, the effluent gases were monitored with FT-IR spectroscopy. A typical FT-IR spectrum of the effluent gas during growth is shown in the Supporting Information. From the spectrum, we found that the methane is partially converted to ethylene and acetylene by the hot filament with more decomposition occurring at higher temperatures of the filament. In fact, reproducible growth conditions are obtained by heating the filament to a temperature that produces a specific ratio of acetylene to methane (1−3%). In addition to ethylene and acetylene, one expects the production of atomic hydrogen and methyl radicals. The importance of each of these species to the growth of small diameter SWNT carpets is currently under investigation.

In summary, we have developed a hot filament CVD method to produce vertical small diameter SWNT arrays, where SWNTs are less than 2 nm. It is thought that heating a substrate in the presence of an activated gas containing atomic hydrogen and hydrocarbons allows SWNT nucleation to occur as deposited iron metal islands without metal island aggregation due to rapid reduction of the island and nucleation of SWNTs at the lowest possible temperature.

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Supporting Information Available: A description of the hot filament CVD system; the Raman spectrum of carpet SWNTs by different excitation lasers and the FT-IR spectrum of the effluent gases during the carpet SWNT growth process. This material is available free of charge via the Internet at http://pubs.acs.org.

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