

Low-Temperature Growth of Single-Walled Carbon Nanotubes by Water Plasma Chemical Vapor Deposition

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Due to unique one-dimensional structures with adjustable and ballistic electronic conductivity,^{1,2} single-walled carbon nanotubes (SWNTs) have been intensively investigated as an alternate material to replace the current silicon-based field effect transistors (FETs). To fabricate nanotube-based FETs, SWNTs must be grown without multi-walled carbon nanotubes (MWNTs) and carbonaceous impurities.^{2,3} However, the growth of SWNTs is generally accompanied by the undesired carbon materials, especially during the chemical vapor deposition (CVD) process, which is the preferred growth method of nanotubes for integrated electronic devices.

Different from other major preparation methods of SWNTs, which include arc-discharge, laser ablation, and high-pressure CO (HiPco) processes, CVD gives directly grown nanotubes on substrates, which have pre-patterned catalysts, such as Fe, Ni, and Co.^{1,2} This enables easier placement of nanotubes on proper positions, such as the region between source and drain.¹ However, the nanotubes by CVD cannot be purified before subsequent integration processes since current purification methods based on oxidative treatments may result in deformation of nanotubes.^{2,3} Although sulfidative purification of nanotubes was recently reported to selectively remove carbonaceous impurities from nanotubes integrated in devices,⁴ the undesired MWNTs would hinder reliable transistor performance. Therefore, preferential growth of SWNTs without both carbonaceous impurities and MWNTs is essential in CVD for device applications.

Another concern for the fabrication of nanotube-based devices is that SWNTs should be grown at the lowest possible temperature so that the growth can be compatible with other integration processes.⁵ Plasma-enhanced CVD (PECVD) is the most promising method to lower the growth temperature. However, growth of SWNTs by PECVD had not been successful as MWNTs or carbon fibers were reported despite much intensive efforts.⁵ Recently, the Dai group reported that SWNTs were grown at 600 °C by remote PECVD.⁶ Our group also demonstrated that the growth temperature of SWNTs could be lowered down to 450 °C with a weak argon plasma power by a remote PECVD.⁷ Nevertheless, the grown nanotubes were still a mixture of SWNTs and MWNTs.

Here, we report a low-temperature growth of SWNTs by water plasma CVD. Water plasma lowered the growth temperature down to 450 °C, and SWNTs were purely and densely grown without MWNTs. The grown SWNTs were characterized by micro-Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM), and electrical measurements of the grown nanotube networks.

Several groups have widely investigated the effect of water on purification and synthesis of carbon nanotubes. Tohji et al. reported that SWNTs could be purified with water by hydrothermal treatment.⁸ Yoshimura et al. demonstrated that MWNTs were synthesized in the absence of metal catalyst by hydrothermal treatment of amorphous carbon in pure water.⁹ Wang et al.

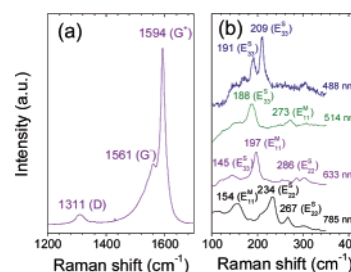


Figure 1. Raman spectra of the grown nanotubes. (a) G-band and D-band obtained from 633 nm laser excitation. (b) RBM peaks from 488, 514, 633, and 785 nm laser excitations. All spectra were measured on five different positions and averaged. Raman shifts were calibrated with a silicon peak at 521 cm^{-1} .

introduced a one-step water-assisted synthesis of MWNTs by dipping a hot graphite rod into cool water in the absence of catalyst.¹⁰ Hata et al. showed a thermal CVD synthesis of SWNTs, where the activity and lifetime of the catalysts were enhanced by water.¹¹ The most common finding is that all of the nanotubes prepared from the mentioned approaches are pure without carbonaceous impurities. Inspired by the water effect, we chose water plasma as both an oxidant for high purity of nanotubes and an energy source for low-temperature growth.

Iron catalyst nanoparticles were deposited on SiO_2 (400 nm)/Si substrates with a mixed solution of ferrocene and conventional photoresist, as described in the previous report.¹² A homemade radio frequency (13.56 MHz) remote PECVD system was used for nanotube growth.¹² Water was evaporated from a canister and carried to the quartz tube by the vacuum without any carrier gas. The amount of water vapor was regulated by a metering valve and monitored by pressure increase in the quartz tube (see Supporting Information for the detailed method).

SWNTs were grown on catalyst-deposited substrates at 450 °C with methane gas (60 sccm) and water plasma (15 W) in the remote PECVD system. Raman spectra from laser excitations of various wavelengths (488, 514, 633, and 785 nm) reveal that the grown nanotubes were single-walled. Parts a and b of Figure 1 show the typical Raman spectra of SWNTs, as characterized by the strong G-band (tangential stretch mode) and the presence of the sharp radial breathing mode (RBM).⁵ Most RBM peaks appear in the frequency region between 120 and 250 cm^{-1} , which roughly corresponds to the diameter range of 1–2 nm. It should be noted that the RBM peaks are much stronger than the peak at 303 cm^{-1} due to the substrate since SWNTs were densely grown by using water plasma (see Figures S1 and S2). According to the Kataura plot (transition energies as a function of nanotube diameter),¹³ the grown nanotubes are a mixture of metallic and semiconducting tubes, as designated in Figure 1b.⁵

To evaluate the quality of nanotubes from the amount of disordered and amorphous carbons, we monitored the Raman

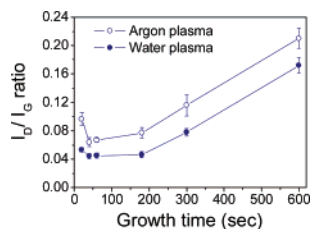


Figure 2. Variations of I_D/I_G ratios with growth time. Open and solid circles were plotted with the Raman intensity ratio (633 nm) of SWNTs grown by argon and water plasma, respectively.

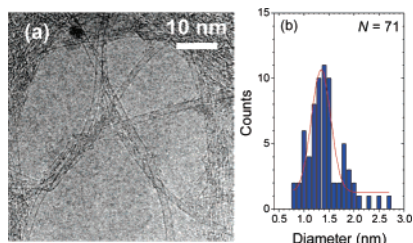


Figure 3. (a) HRTEM image of SWNTs grown at 450 °C with a water plasma power of 15 W. (b) The histogram of the diameter of SWNTs determined from HRTEM images.

intensity ratio (I_D/I_G) of D-band to G-band as growth time increased. The ratio of the nanotubes grown by water plasma is compared to that of the nanotube grown by argon plasma (15 W, methane 60 sccm), as shown in Figure 2. Since water plasma with a weak power (15 W) plays a role of oxidant which removes carbonaceous impurities and disordered carbons, SWNTs grown by water plasma show lower I_D/I_G ratios than argon plasma-grown tubes over all growth time. The I_D/I_G ratio decreases with the growth time in the initial stage of nanotube growth and then stays nearly constant during a period and subsequently increases, possibly due to deformation of nanotubes by active species, such as radicals or ions generated by plasma. It should be noted that growth and etch reactions of nanotubes compete more severely in plasma than in thermal CVD.

Figure 3a shows a HRTEM image of SWNTs, whose diameters are mainly in a range of 1–2 nm (Figure 3b), as expected in Raman spectra. The observed nanotubes were single-walled or bundled. MWNTs were rarely observed as the growth time is short. Among the nanotubes grown for 180 s, we could not find MWNTs in HRTEM images. Considering that MWNTs were rarely observed, in contrast to the frequent appearance of MWNTs from argon plasma CVD, the water plasma effect on the growth of pure SWNTs without MWNTs is evident.

To investigate the electrical nature of SWNTs grown by water plasma, we fabricated FETs with random networks of SWNTs as channels. The source–drain channel length was 5 μm , and the channel width was 40 μm . The number of SWNTs per unit area was $\sim 30/\mu\text{m}^2$ (see Supporting Information).

It is reported that, for SWNTs with densities exceeding a percolation threshold, FETs in the random network are electrically conducting.¹⁴ Above the percolation threshold, which is $0.3/\mu\text{m}^2$ for nanotubes with a length of 1–3 μm , the SWNTs will intersect with one another and form a continuous conduction path with metallic tubes. However, even though the nanotube density is much higher than the percolation threshold, the FET with the network of

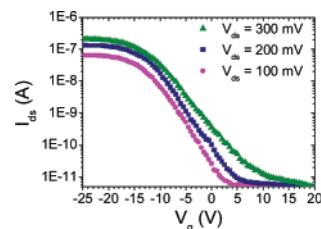


Figure 4. Drain–source current (I_{DS}) versus gate voltage (V_G) characteristics of a FET with a random network of SWNTs.

SWNTs grown by water plasma shows typical *p*-type semiconducting characteristics with an on/off ratio of $\sim 10^4$ (Figure 4). This can be explained by a higher portion of semiconducting nanotubes over metallic tubes than the 2:1 ratio expected for random chirality distribution. Dai et al. reported that nearly 90% of the grown nanotubes by remote PECVD are semiconducting due to a thermodynamic factor, while the HiPco and laser ablation nanotubes consist of 61 and 30% semiconductors, respectively.^{6,15}

The semiconducting nature of the network FETs also supports the preferential growth of SWNTs over MWNTs. Since MWNTs are generally metallic due to their large diameters, the network transistors should show metallic nature unless the preferential growth was used.

The water plasma CVD method for the low-temperature growth of pure SWNTs facilitates the fabrication of nanotube-based devices for fundamental characterizations and industrial applications.

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Supporting Information Available: SWNT growth and FET fabrication procedure, comparison of densities of SWNTs grown by Ar and water plasma CVD. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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