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Low Temperature Growth of Single-walled Carbon Nanotube Forest

Il Ha Lee, Jiwoon Im,[†] Un Jeong Kim,[‡] Eun Ju Bae,[‡] Kyoung-Kook Kim,[#] Eun Hong Lee,[‡] Young Hee Lee, Seunghun Hong,[†] and Yo-Sep Min[§,*]

Department of Energy Science, BK21 Physics Division, Sungkyunkwan Advanced Institute of Nanotechnology, Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, Suwon 440-746, Korea
[†]School of Physics & Astronomy, Seoul National University, Seoul 151-747, Korea
[‡]Samsung Advanced Institute of Technology, Yong-In, Kyeongki-Do 449-712, Korea
[#]Department of Nano-Optical Engineering, Korea Polytechnic University, Siheung 429-793, Korea
[§]Department of Chemical Engineering, Konkuk University, Seoul 143-701, Korea. [*]E-mail: ysmin@konkuk.ac.kr
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Forest of single-walled carbon nanotubes (SWNTs) was grown at 450 °C by water-plasma chemical vapor deposition using ultrathin iron on alumina supporting film. The growth rate of the SWNT forest is ~ 0.9 μm/min, and the diameters of nanotubes are mainly in a range of 3.0 ~ 3.5 nm. The low intensity ratio of D- to G-band (I_D/I_G ~ 0.098) in Raman spectra indicates that our SWNT forest grown at 450 °C is fairly pure and crystalline. This low temperature growth of SWNT forest may enable variable applications requiring the vertically-aligned nanotubes to obtain large surface area.

Key Words: Single-walled carbon nanotube, Low temperature, Vertical growth, Forest

Introduction

Since the discovery of single-walled carbon nanotube (SW NT), the one-dimensional allotrope of carbon has been studied for various applications such as field emitters, channel of transistors, interconnecting material in integrated circuit chips, sensors, transparent conducting films and so on.[1] SWNTs have been mainly synthesized by arc-discharge, laser ablation, high pressure CO (HiPCO) or chemical vapor deposition (CVD).[1]

For mass production of SWNTs by CVD, SWNTs should be grown in a form of forest which means vertically-grown and highly dense SWNTs on substrate. It was recently reported that the SWNT forest was grown at 750 °C with a high growth rate of 250 μm/min by water-assisted thermal CVD method, so called super growth.[2,3] Dai *et al.* also demonstrated that the SWNT forest was grown at 720 °C by oxygen-assisted remote plasma CVD.[4] However, the growth temperature of SWNT forest should be lowered to integrate the vertically-grown nanotubes into a device. Although Cantoro *et al.* reported that SWNTs could be thermally grown even at 350 °C by CVD,[5] the reported lowest growth temperature of pure SWNT forest is 600 °C by using point-arc microwave plasma CVD.[6]

Recently we reported that random networks of highly pure SWNT were grown on silicon and glass substrates at 450 and 550 °C, respectively, by water plasma CVD using methane and water vapor wherein the catalyst nanoparticles of iron were formed by burning a photoresist film containing a catalyst precursor of ferrocene.[7-10] Here, we demonstrate the SWNT forest grown at 450 °C by water plasma CVD using ultrathin iron on alumina supporting film. The catalyst for SWNT forest and the role of water are discussed.

Experimental Section

Aluminum thin films (10 ~ 20 nm) were deposited on SiO_2 (200 nm)/Si wafer by radio frequency magnetron sputtering or thermal evaporation, and then oxidized at 600 ~ 700 °C in air in order to form the alumina supporting film. Ultrathin iron films were e-beam evaporated on the alumina specimens and subsequently thermally oxidized at 600 °C for 10 min in air. The thicknesses of catalyst film after the e-beam evaporation were measured to be ~ 0.5 nm by a thickness monitor using quartz crystal microbalance and 0.7 ~ 0.8 nm by spectroscopic ellipsometer.

A homemade radio frequency (13.56 MHz) remote-plasma CVD system using water vapor, of which the schematic diagram was previously reported, was used for the growth of SWNT forest.[7,8] The growth condition for the nanotube forest was the same as for the nanotube network except the catalyst substrate. The catalyst-formed substrates were placed on a quartz holder and then heated up to 450 °C for 300 sec in water atmosphere which resulted in an increase of ~5 mTorr in the base pressure. After an interval for the stabilization of substrate temperature, methane (60 sccm) was introduced into the quartz tube reactor and the subsequent plasma (15 W) was ignited to grow nanotubes. During the forest growth (3 ~ 30 min), the working pressure was maintained at ~ 0.48 torr.

Results and Discussion

Figure 1a shows a cross-sectional image of a 10 min-grown specimen by optical microscope (Nikon Optophot 200). Due to the long length of nanotubes, the height of nanotube forest is easily observed and measured with optical microscope. Scanning electron microscopic (SEM, Hitachi 5500) images (Figure 1b) of the specimen grown for 20 min clearly reveal that the nanotubes were grown with a vertical orientation to the substrate. Some of nanotubes were peeled off and thrown down from the adjacent tubes in the forest when the specimen had been divided for the cross-sectional observation. Figure 1c

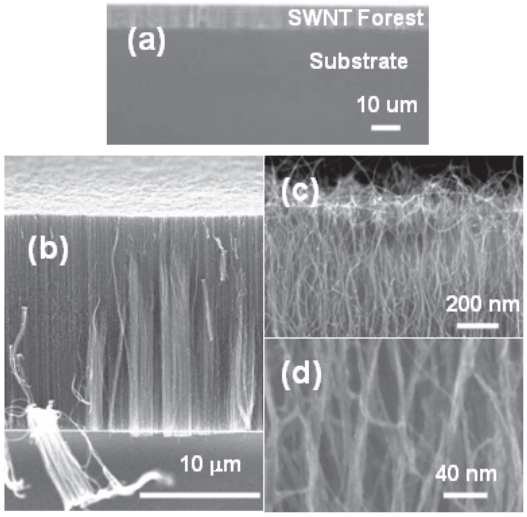

Figure 1. Images of SWNT Forests grown at 450 °C. (a) Optical microscopic image of a 10 min-grown forest. (b) SEM image of a 20 min-grown forest. (c and d) SEM images of the top and middle regions of a 30 min-grown forest, respectively.

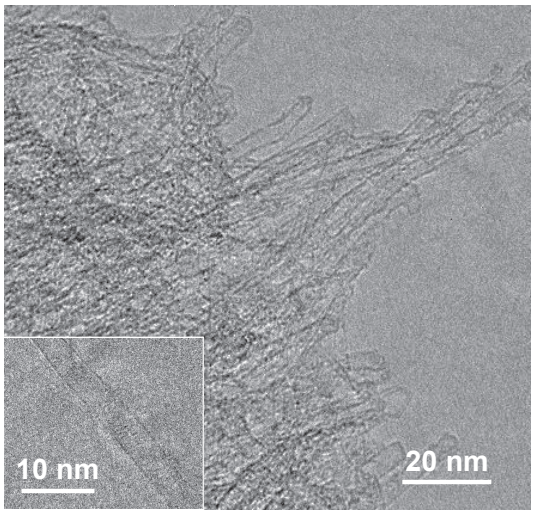

Figure 2. HRTEM images of SWNTs obtained from the 10 min-grown forest.

and 1d show magnified images in the top and middle regions of a 30 min-grown forest, respectively. Most of straightly-standing nanotubes have a diameter of 5 ~ 7 nm, and they seems to be bundled. Some nanotubes, in Fig. 1d, have smaller diameters, and they are less vertically aligned than bundles. We believe that they are individually- separated tubes, peeled off from a neighboring bundle, or bundles with a few number of tubes.

Figure 2 shows HRTEM images of our grown nanotubes. Most of nanotubes were single-walled with a large diameter of 3.0 ~ 3.5 nm as shown in the inset. Double- or multi-walled tubes were rarely observed in TEM analysis. Raman spectra in Figure 3 also show the grown forest was single-walled as characterized by the strong G-band (tangential mode, 1590 cm^{-1}) and the presence of the sharp radial breathing mode (RBM).[1]

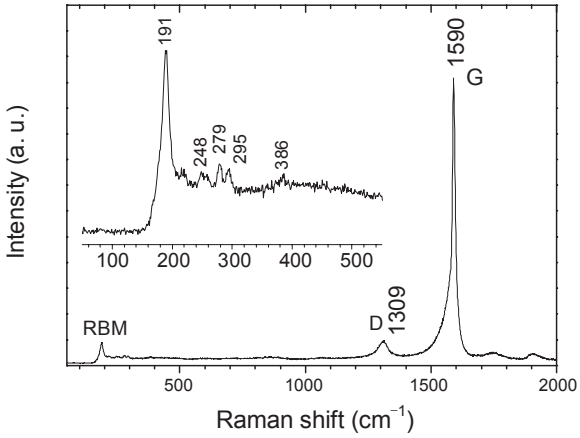

Figure 3. Raman spectrum of SWNT forest from 633 nm laser excitation. The inset shows magnified RBM modes.

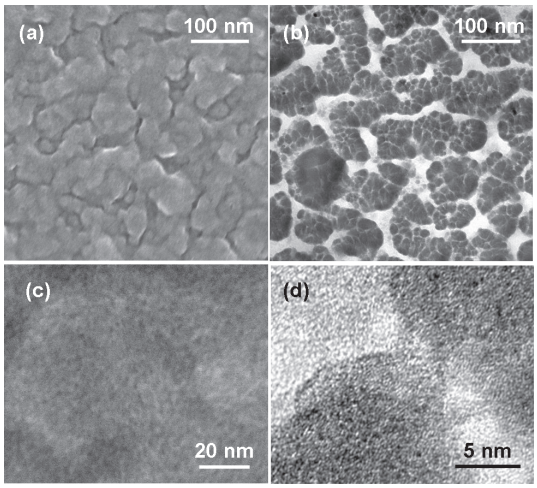

Figure 4. SEM (a, c) and TEM (b, d) images of the catalyst-formed surface before SWNT forest growth.

However, the RBM peaks from large diameter tubes (3.0 ~ 3.5 nm), mainly observed in TEM analysis, were not detected in the Raman spectra, due to the cut-off of our notch filter. A broad D-band centered at 1309 cm^{-1} is observed, which represents the degree of defects or amorphous carbon. The low intensity ratio of D- to G-band (I_D/I_G ~ 0.098) indicates that our SWNT forest grown at 450 °C was still fairly pure and crystalline.

Generally the diameter of SWNT depends on the size of catalyst particles.[1] SWNT nucleation requires nanometer-sized catalyst islands. Lager catalyst clusters can catalyze multi-walled tubes. However, on the catalyst substrate we could not find the catalyst particles with nanometer-sized diameters, which are comparable to the diameters (3.0 ~ 3.5 nm) of our SWNTs, but rather much smaller catalyst clusters were found as shown in Figure 4. Low resolution SEM (Fig. 4a) image shows a granular rough surface of the catalyst substrate prior to the SWNT growth, which is possibly due to the oxidation of Al film with grains. In the granular structure of alumina there were subgrains as shown in TEM image (Fig. 4b). Even in the magnified SEM (Fig. 4c) image of the subgrains, any nanoparticle with a diameter over 1 nm was not observed but catalyst clusters with a

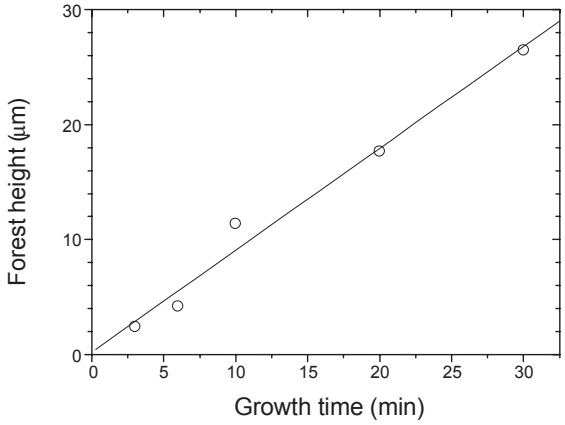

Figure 5. SWNT forest height as a function of growth time.

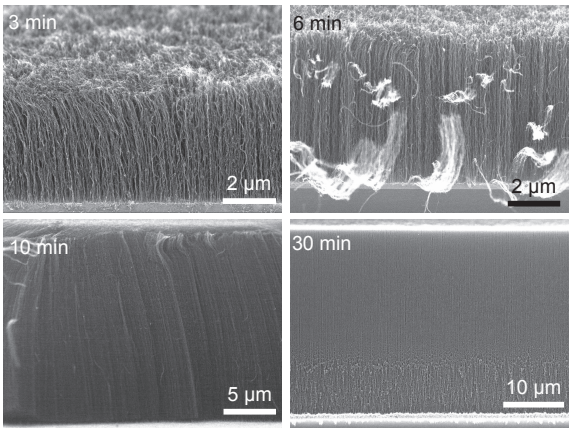

Figure 6. SEM images of SWNT forests grown at 450 °C. The growth times were denoted in the images.

much smaller diameter than 1 nm were resolved with a different contrast to the alumina subgrain in the HRTEM image (Fig. 4d). In terms of growth mechanism, our SWNT growth is via root-growth mechanism, as proved by the second growth of SWNT forest on the same catalyst substrate after the removal of the forest by ultrasonication (data not shown). Recently Cantoro, *et al*. reported that nanotube growth is governed by the catalyst surface without the necessity of catalyst liquefaction in low temperature CVD.[5] They proposed that the smaller the catalyst cluster, the more dominant its surface, thus SWNT growth could be fed by fast carbon diffusion on the catalyst surface. Different from the vapor-liquid-solid (VLS) model based on catalyst liquefaction, no supersaturation and segregation process of carbon is necessary in their model. Although it is unclear what is melting in the ultra-small catalyst cluster, since the size of clusters is not directly matched to the tube diameter in our SWNT forest, our forest growth supports the catalyst surface-governing mechanism without liquefaction. In addition it is believed that the water plasma plays a role to increase the surface mobility of carbon adsorbed on the catalyst surface (see the following sections).

Figure 5 shows the forest height variation as a function of the growth time. Within our experimental range of growth time, the forest height linearly increased with a growth rate of 0.9 μm/min. The forest heights were determined from SEM images in Fig. 6 (3, 6, 10, and 30 min-grown forests) and Fig. 1b (20 min-grown forest). This growth rate was lower than ~3.3 μm/min at 600 °C by point-arc microwave plasma CVD possibly due to our lower growth temperature (450 °C). However it should be noted that the amount of water used in our method was much higher than that (100 ~ 150 ppm) of the super-growth.[2,3] Assuming that water vapor and methane behaved like an ideal gas in our CVD set- up, the pressure increase of ~5 mTorr by supplying water from a base pressure of ~7 mTorr is roughly estimated to be ~1% (~10000 ppm) considering a working pressure of ~48 mTorr. Actually, when we monitored the amount of water with a water sensor (Alpha Moisture System, DS1000), of which the upper sensing limit is 1000 ppm, the water level is monitored to be over-ranged. It is believed that the large amount of water, which can play a role of mild etchant for carbon, resulted in the low growth rate of SWNTs.

Water enhances and preserves catalyst activity by removing carbonaceous impurities on the catalyst surface which may deteriorate or poison the catalytic activity.[2,3] Water also gets rid of carbonaceous impurities on the wall of nanotube to give pure nanotubes. Water also reacts with the wall of nanotubes even though the wall is more impervious to oxidation than carbonaceous impurities.[11] Plasma generally activates carbon source molecules so that not only the nanotube growth but also the deposition of carbonaceous impurities occurs at lower temperature in plasma CVD than in thermal CVD. Therefore, the larger amount of water in our plasma CVD is necessary to enhance and preserve catalyst activity by removing larger amount of carbonaceous impurities on the catalyst surface.

Conclusion

SWNT forests were grown at 450 °C by water plasma CVD using methane and water vapor. This low temperature growth of SWNT forest may enable nanotube-based interconnection in integrated circuit chips, hydrogen storage devices, sensors and supercapacitors requiring the vertically-aligned nanotubes to obtain large surface area.

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