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Synthesis of Ultra-Long Super-Aligned Double-Walled Carbon Nanotube Forests

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The pre-treatment (catalyst reduction with H_2) time effect on the carbon nanotube (CNT) growth is reported. The total CNT height, the initial growth rate, the diameter, the number of walls, and the alignment in the CNT forests change with the catalyst reduction time. Densely packed, vertically super-aligned, double-walled CNT (DWCNT) forests with 9 mm height were synthesized in 10 hrs. We find that the density and the size of catalysts plays an important role in the alignment of the DWCNT forests, which is evidenced by atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy.

Keywords: Double-Walled Carbon Nanotubes, Super-Growth, Thermal Chemical Vapor Deposition, Vertically Aligned Growth.

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1. INTRODUCTION

Recently, vertically aligned double-walled carbon nanotubes (VA-DWCNTs) have been widely used for various applications due to their unique electrical, optical and mechanical properties.[1–3] One of the most prominent applications is an electronic emitter since it shows relatively low threshold voltage compared to single-walled carbon nanotubes (SWCNTs). In addition, it has long lifetime comparable to multi-walled carbon nanotubes (MWCNTs).[4] However, the vertical alignment of DWCNTs with ultra-long length has been hardly achieved so far since the synthesis process is very complicated. Recently, many research groups have noted the importance of catalyst size effect, source gases, and buffer layers in controlling the structure of CNTs.[5–13] Recently, Hata and coworkers[5] synthesized the forest composed of various CNTs with different sizes and number of walls by controlling the thickness of catalyst film. Thompson group[6] also reported the dependence of the diameter and the areal density of vertically-aligned CNTs on the pre-treatment of catalysts controlling time and duration of hydrogen exposure. Recently, we succeeded to synthesize CNTs forest using sandwich-like catalysts,[14, 15] and found that the thickness of catalysts needs to be more precisely controlled to enhance the quality of CNT growth. Here, we present the efficient synthesis of VA-DWCNT forest as tall as 9 mm by using chemical vapor deposition (CVD). We also investigate the defect degree and the purity of CNTs with respect to the position of the VA-DWCNT forest.

2. EXPERIMENTAL DETAILS

The experimental details were reported in our previous studies.[14, 15] A brief description of the process is as follows. Initially, Fe catalysts with 1 nm thickness were deposited onto Al_2O_3 (30 nm)/SiO_2 (300 nm)/Si (500 μm) substrates using an e-beam evaporator.[15] After the deposition, the substrates were divided into 5×5 mm^2 pieces using a dicing saw (DASCO: DAC552). The synthetic process is illustrated in Figure 1. Unlike our previous reports, here we used He (180 sccm) instead of Ar as a carrier gas.[14, 15] The CVD reactor was heated up to 750 °C in 13 min in He atmosphere. After reaching the growth temperature, H_2 (55 sccm) was purged into the reactor as a reducing agent. The reduction process was carried out with different time lengths (0, 5, 10 and 20 min) (see Fig. 1). The gas flow was then switched to C_2H_4 (25 sccm), He (180 sccm), and H_2 (55 sccm) for the CNT growth. After

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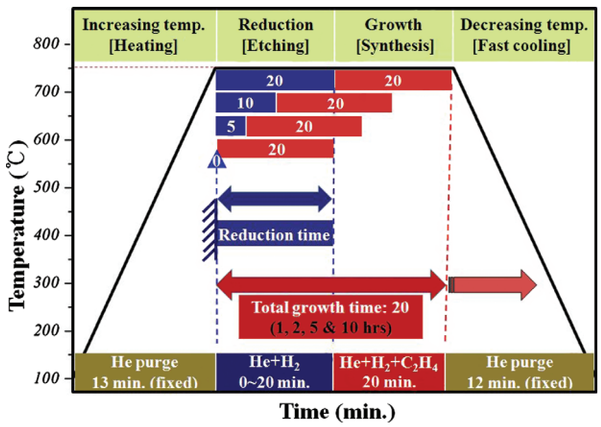

Fig. 1. A schematic showing the evolution of temperature with the CVD run time. The blue zone indicated the reduction environment and the red zone indicates the growth environment.

the growth, reactor was rapidly cooled (~2 °C/sec) to room temperature in He atmosphere.

Structural characterization of the VA-DWCNTs was performed using field emission scanning electron microscope (FESEM; JEOL, JSM7500F), high-resolution transmission electron microscope (HRTEM; JEOL, JEM2100F), and Raman spectroscopy (Kaiser, Optical) with 632.8 nm excitation wavelength. The size and the density of the catalyst were measured using atomic force microscopy (AFM; SPA-300 HV, SII Nanotechnology Inc.) and FESEM.

3. RESULTS AND DISCUSSION

The variation in the CNT height with the growth time is shown in Figure 2. It is clearly seen that the CNT growth behavior changes according to the reduction time. The sample treated for 5 min in reduction environment resulted in the maximum growth of CNT forests as tall as 9 mm in

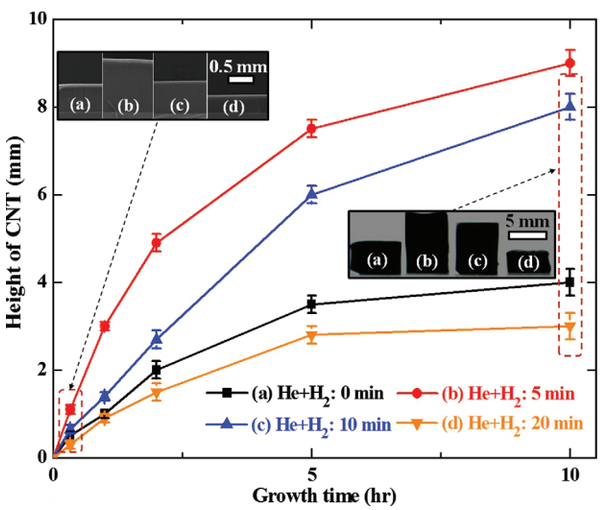

Fig. 2. CNT height as a function of growth time. The insets show FESEM (left side) and digital camera (right side) images of as-grown VA-DWCNT forests synthesized for 20 min and 10 hrs respectively.

10 hrs. On the other hand, the sample treated with 20 min reduction environment shows the minimum growth shorter than 2.5 mm in 10 hrs. The initial growth rate also changes with the reduction time, where the steep slope tends to saturate after 5 hrs as shown in Figure 2.

The CNT alignment in the bottom of the forest as well as the typical structural characteristics of CNTs are shown in Figure 3. Depending on the reduction time, the vertical alignment and the diameter of CNTs resulted in considerable differences. In case of Figures 3(b and c), the CNTs are well aligned, while the CNTs are misaligned in Figures 3(a and d). In this figure, the gap between neighboring CNT walls is around 0.34 nm and the average inner diameter is around 3.8 (± 0.5) nm. It gives evidence that reduction time doesn't have an influence on the inner diameter of CNTs. In addition, the formation of amorphous carbon on the surface of CNTs is similar regardless of reduction time, which is consistent with the previous reports.[14, 15]

The typical TEM images of CNTs grown with 5 min reduction time are shown in Figure 4. These images were taken from the bottom and the top of the 9 mm long CNT forests. The diameter and the number of walls remained same, while the amorphous carbon observed on the outer walls changed from top to bottom. The insets of Figure 4 show that the top CNTs are surrounded by a lot of amorphous carbon.

Raman spectroscopic analyses on the top and the bottom of 5 min-reduced sample are shown in Figure 5. The Raman spectra show D-, G-, 2D band, and radial breathing modes (RBM) peaks.[1, 5, 16–19] The graphite-induced G band (I_G) at 1586 cm^{-1} identifies in-plane vibration movement of carbon atoms in the CNTs, and the D band (I_D) at 1350 cm^{-1} indicates the degree of disorder in the graphite structure or the number of defects in the CNTs.[14, 16] As shown in Figure 5, it was observed that I_D/I_G area ratio[20–21] of as-grown DWCNTs depends on the position of the DWCNT forests.

The I_D/I_G area ratios of the bottom and the top of CNTs were calculated to be 0.31 and 0.55, respectively. The I_D/I_G area ratios increase with the growth time, indicating the increase of amorphous carbon as depicted in Figure 4. We suppose the temperature gradient in the CVD chamber causes the different quality of growth, resulting in the different defect degree. However, the position and the intensity of the RBM peaks remain unchanged with the growth time.[22]

The AFM and FESEM images of the catalysts on the substrate with different reduction time are shown in Figure 6. The changed surface morphology with the reduction time is clearly seen in the AFM images. The sample treated with 5 min reduction (Fig. 6(b)) shows the smallest grains optimized for high-quality growth. However, the reduction longer than 5 min dramatically increases the size of catalysts, leading to the degradation of structural properties.

Furthermore, the reduction time longer than 20 min induces the agglomeration of sandwich-like catalysts,

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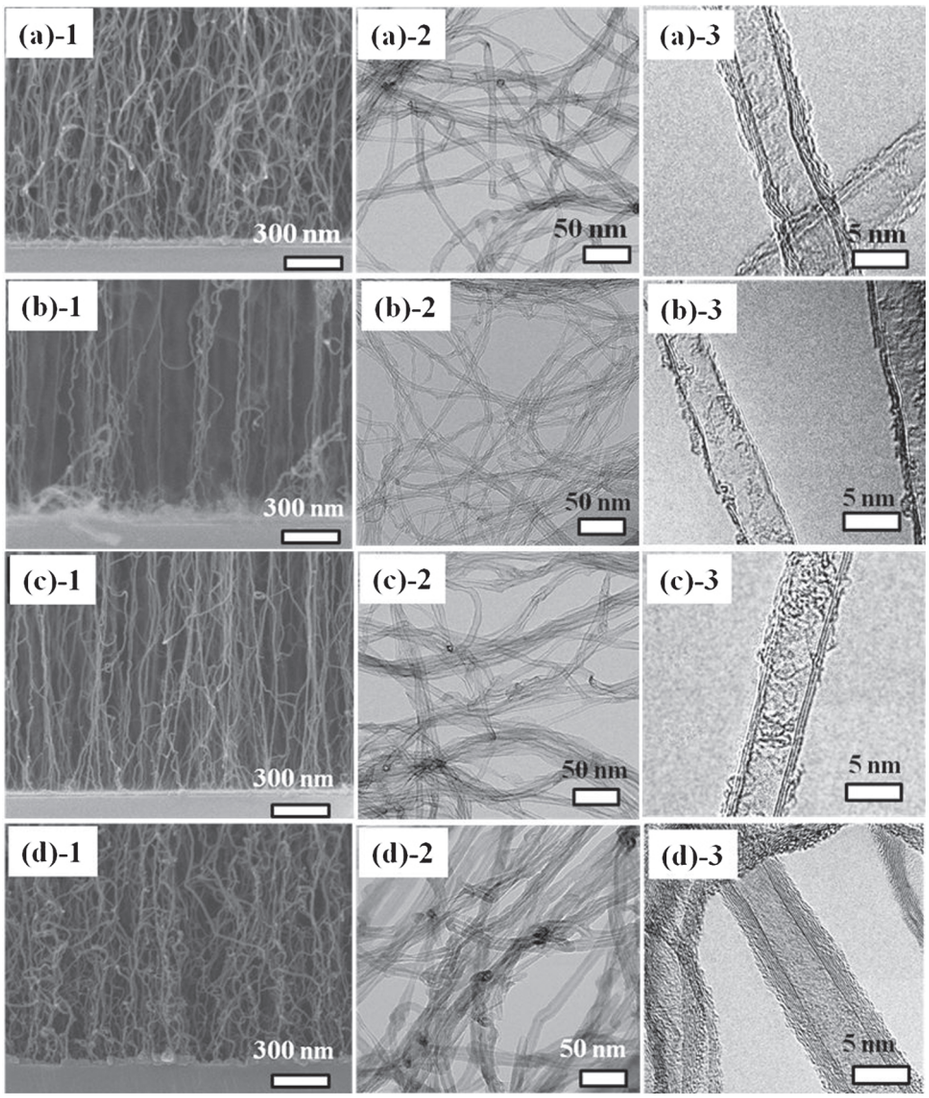

Fig. 3. FESEM and HRTEM images of CNT forest with different reduction time, (a) 0 min, (b) 5 min, (c) 10 min, and (d) 20 min.

resulting in ~5 times increase of surface roughness (Fig. 6(d)). The grain sizes of the catalysts are roughly matched with the outer diameters of CNTs. Thus, we conclude that the H_2 treatment played important role in the

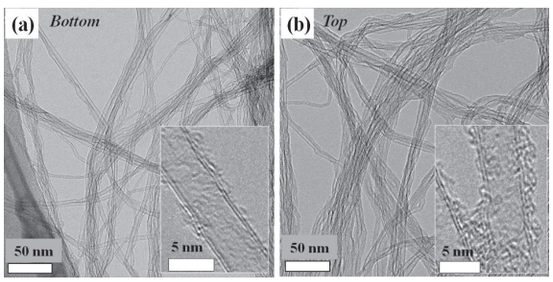

Fig. 4. Typical TEM images showing DWCNTs grown with 5 min reduction time. The images were taken from (a) the bottom and (b) the top of the 9 mm-long CNT forests. The inset HRTEM images show amorphous carbon surrounding the outer surface of wall.

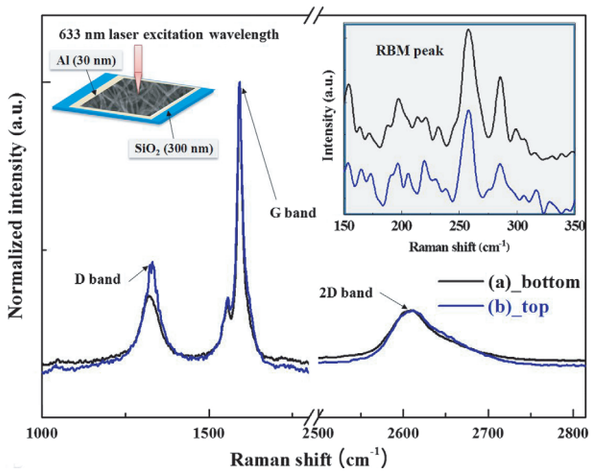

Fig. 5. Raman spectra of the samples shown in (a) and (b). The insets show the experimental conditions and the corresponding RBM peaks.

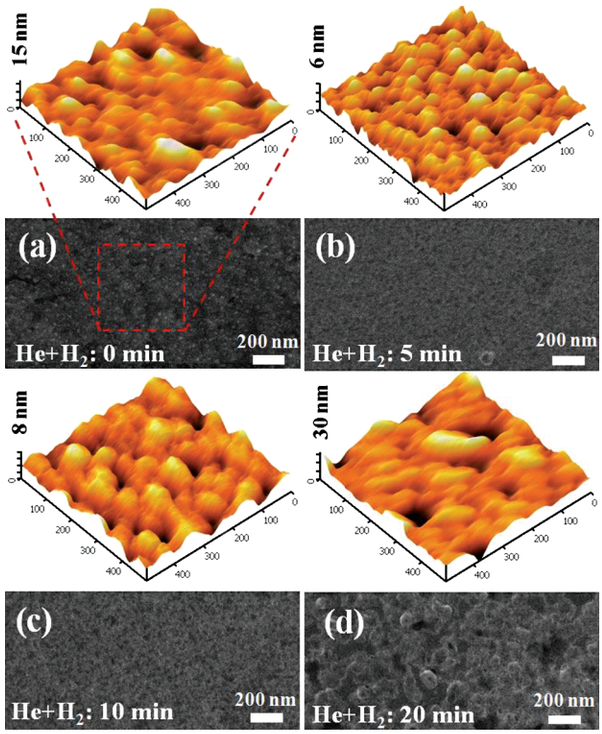

Fig. 6. AFM (tapping mode) and FESEM images showing the surface morphologies of catalysts with different reduction time, (a) 0, (b) 5, (c) 10, and (d) 20 min.

CNT growth and it changes the density and the size of catalysts. It ultimately affects the quality and alignment of CNT forests. We also found that the size of the catalysts is a critical factor in determining the number of walls in the CNT. The exact role of H_2 in the CNT growth process is still unknown and further studies in this area are underway.[23]

4. CONCLUSIONS

The pre-treatment and the catalyst reduction time effects on the CNT growth are investigated. The CNT growth parameters such as height, initial growth rate, number of walls, and vertical alignment are varying with the reduction time. The TEM and Raman studies reveal that the amount of amorphous carbon is larger around the top of CNT forests compared to the bottom, which is due to the vertical thermal gradient inside the reaction chamber. We found the 5 min reduction time and 10 hrs growth produce high-quality DWCNT forests as tall as 9 mm with the narrow distribution of diameters, 3.8 (±0.5) nm.

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