J308 カーボンナノチューブのセンチメータースケール持続成長技術

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1. Introduction

Carbon nanotubes (CNTs) gather great attentions owing to their unique one-dimensional structure as well as excellent properties, such as mechanical strength, electrical and thermal conductivities, and chemical stability. Among their production methods, chemical vapor deposition (CVD) has advantages of the easiness of scale-up, low process temperature, and continuous operation, and is now widely used. Metal nanoparticles are generally used as catalysts, and when they are supported on substrates, CNTs can be grown continuously to longer lengths. Millimeter-length can now be realized by several methods [1-3], however, CNTs stop growing in the end. In this work, we demonstrate the continuous CNT growth to a centimeter-scale length on a selectively heated substrate by feeding a cold reactant gas with a trace of metalorganic vapor.

2. Method

A "cold-gas" CVD method [4] (Fig. 1), in which the substrate was selectively heated while the gas was kept at a low temperature, was used in this work. A ribbon-shaped carbon sheet was used as a substrate. Al_2O_3 (20 nm) as underlayer and either Fe (0.8 nm) or Co (2 nm) as catalyst were sequentially sputter-deposited on it. This substrate was set in a glass tube, and resistively heated to a target temperature of 780 ºC under a 26vol%H_2/ 50ppmv H_2O/ Ar flow at ambient pressure. After reducing the catalyst for 3 min, CVD was started by switching the gas to a mixture of 0.26vol%C_2H_2/ 50ppmv H_2O/ Ar. During these processes, a trace of ferrocene ($Fe(C_5H_5)_2$) was also supplied by flowing the gas over a ferrocene container at 50 ºC. The growing CNTs were observed in real-time by using a digital camera through the reactor tube. Microstructures of CNTs were characterized by Raman spectroscopy and scanning electron microscopy (SEM).

3. Results and Discussion

In case of the sputtered Fe layer, CNT growth continued for 12 h or more with a gradually decreasing growth rate, and about 2-cm-tall vertically aligned CNTs were synthesized (Fig. 2). Raman spectroscopy showed that these nanotubes were multi-walled. Both the sputtered Fe layer and the trace of ferrocene were essential for the centimeter-scale growth. SEM images showed a continuous increase in CNT diameters (Fig. 3), indicating that Fe particles continuously grew larger in the reaction with ferrocene. In contrast, in case of the sputtered Co layer, single-walled CNTs with a relatively good quality were synthesized. Though the CNT growth lasted only for 40 min and CNT height remained at a millimeter-scale, this result shows the possibility for the growth of ultra-long SWCNTs.

Next, we will discuss about the role of the ferrocene supply. Coarsening of catalyst particles are sometimes observed after the CNT growth termination, and Ostwald ripening is a possible cause for the coarsening [5]. Ferrocene may suppress the Ostwald ripening of the catalyst particles by keeping the surface Fe concentration on the substrate at a moderately high level. Actually, such effect has already been reported in the growth of InAs quantum dots [6]. Further research is now ongoing to clarify the role of ferrocene supply and to develop the growth method for even longer CNTs.

4. Conclusion

We developed a new method to elongate the CNT growth by coupling selective heating of a catalyst-supported substrate with feeding of a trace of ferrocene. CNT growth continued for 12 h and CNT height reached 2 cm. These achievements show the potential for further development of growth methods for ultra-long CNTs.

References

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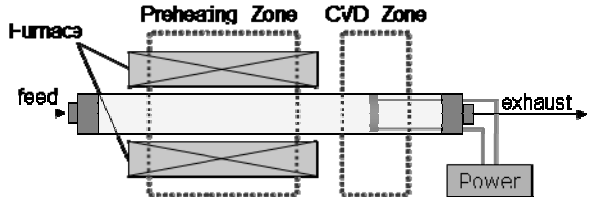

Fig. 1 A schematic of "cold-gas" CVD apparatus.

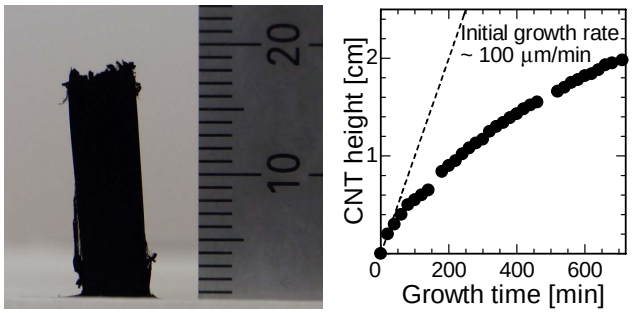

Fig. 2 A photograph of the 2-cm-tall CNTs grown in 12 h (left) and a time profile of the CNT height showing continuous CNT growth (right).

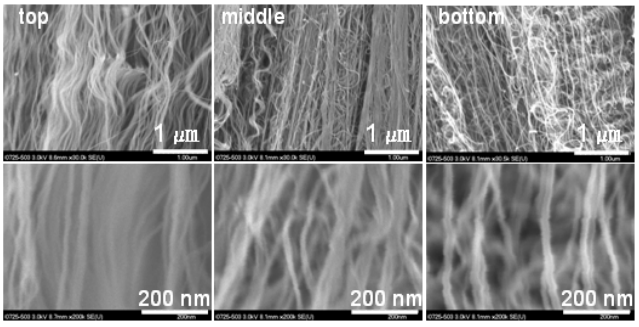

Fig. 3 SEM images of CNTs taken at different positions of the 2-cm-tall forest.

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