

Effect of Fe Catalyst on Growth of Carbon Nanotubes by thermal CVD

Seung-il Yoon*, Sung-Taek Heo, Sam-Soo Kim, Yang-Kyu Lee, and Dong-Gu Lee¹

Department of Information and Nano Materials Engineering,

Kumoh National Institute of Technology, Gumi 730-701, Gyungbuk, Korea

TEL: +82-54-478-7739, ¹e-mail: dglee@kumoh.ac.kr

Keywords : carbon nanotubes, Fe catalyst, chemical vapor deposition, ammonia gas, acetylene gas

Abstract

The properties of carbon nanotube obtained by thermal chemical vapor deposition (CVD) process were investigated as a function of ammonia (NH₃) gas in hydrocarbon gas, Fe catalyst thickness, and growth temperature. Fe catalyst was prepared by DC magnetron sputter and pre-treated with ammonia gas. CNTs were then grown with ammonia-acetylene gas mixture by thermal CVD. The diameter of these CNTs shows a strong correlation with the gas rate, the catalyst film thickness and temperature. From our results, it was found that the factors of grown CNTs positively acted to improve CNT quality.

1. Introduction

Owing to their nano-scale sharpness¹, high chemical stability², thermal conductivity³, and mechanical strength⁴, carbon nanotubes (CNTs) have been attracting a great deal of attention. There exist several techniques for fabricating CNTs such as arc discharge⁵, laser ablation⁶, and CVD⁷. Among these techniques, CVD is the most effective method for fabrication of CNTs with precise control parameters. To initiate the growth of nanotubes, two gases are fed into the reactor: a process gas (such as ammonia, argon, nitrogen, hydrogen, etc.) and a carbon-containing gas (such as acetylene, ethylene, ethanol, methane, etc.). In a typical CVD process for CNT growth, a metallic film or metal precursor deposited on a substrate is transformed into catalytic particles by pretreatment before CNTs are grown.⁸ CNTs grow only at catalytic particles in which carbon is soluble; carbon atoms in carbon-containing gas are solid-solutioned at the surface of the catalytic particle, and diffused to the edges of the particle, where it forms the nanotubes.^{9,10} The catalytic particles can stay at the tip of the growing nanotube during the growth process,¹¹

or remain at the nanotube base,¹² depending on the adhesion between the catalytic particle and the substrate.¹³ Since the size of the individual particle, which determines the diameter of CNTs, is not easily controlled during the pretreatment, it is difficult to obtain CNTs having uniform diameter. In order to obtain high-quality and uniform CNTs, a lot of controlling factors for the CNT growth should be understood in details. Here, as a fundamental study, several factors such as (1) growth time, (2) ammonia gas in hydrocarbon gas, (3) catalyst thickness and (4) growth temperature during CNT growth were investigated in thermal CVD process.

2. Experimental

Fe thin films with thickness of 5-40 nm were prepared on Si substrate using DC magnetron sputtering. Ar gas (200 sccm) was applied into a CVD quartz reactor in order to prevent the oxidation of the Fe catalytic film while increasing the temperature. Before growing CNTs, four Fe catalytic films were pretreated using NH₃ gas with a flow rate of 50 sccm for 10 minutes at 700, 800, and 900 °C, respectively. CNTs were then chemically vapor-deposited using the mixture C₂H₂ gas and NH₃ gas with a total flow ratio of 40 sccm for 10 minutes at the same pretreatment temperature. After the growth, the reactor was cooled down to room temperature. The morphology of Fe catalytic layer and CNTs was observed from scanning electron microscope (SEM, Jeol JSM-7000F) and transmission electron microscope (TEM, Hitachi H-7600, 120 kV), respectively. The crystallinity and impurities of CNTs were investigated by Raman spectroscopy (Renishaw, Invia system). Main peaks of CNTs in Raman spectra are D peak at 1350 cm⁻¹ and G peak at 1590 cm⁻¹. The D peak represents the presence of disordered carbons and the G peak

indicates the crystalline graphite. The ratio of the integrated intensity of G peak (I_G) to the integrated intensity of D peak (I_D) shows the degree of crystallinity of CNTs.¹⁴

3. Results and discussion

The effect of the NH_3 gas in C_2H_2 gas on CNT growth was studied. Total flow rate was doubled at the gas ratio of $\text{NH}_3/\text{C}_2\text{H}_2=1/3$. The length of grown CNTs was almost same each other (Fig. 1(a) and 1(c)), but the thickness of the amorphous carbon was much distinct (Fig. 1(b) and 1(d)). When the total flow rate increased, the significant amount of the amorphous carbon formed on the outer wall of CNTs. Faster flow rate of gas mixture might not give enough time to dissolve carbon atoms into Fe catalyst.

The gas ratio of NH_3 to C_2H_2 was changed at total flow rate of 40 sccm. The SEM images are shown in Fig. 2(a-f). As NH_3 gas increased, the length was increased while the diameter was decreased. The TEM images are shown in Fig. 2(g-i). In case of using only C_2H_2 gas, the wall of CNT was quite thick and amorphous carbon was significantly deposited on the outer wall of CNT as shown in Fig. 2(g). However with addition of NH_3 gas in C_2H_2 gas, the diameter of CNT walls was smaller and amorphous carbons disappeared (Fig. 2(h) and 2(i)). From Raman spectra result in Fig. 3, it can be seen that the crystallinity (I_G/I_D ratio) of CNTs is improved with addition of NH_3 . We noticed that NH_3 prevented the formation of amorphous carbon during the CNT growth, leading to high-quality CNT. Interestingly, the inner diameters of

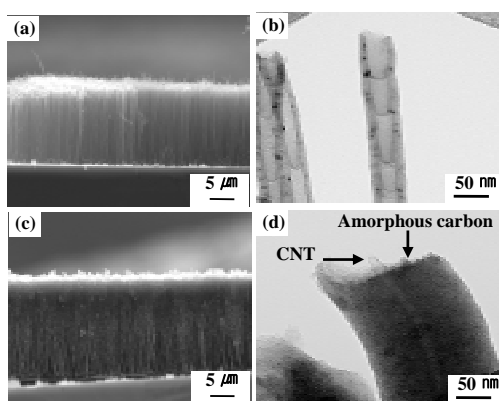


Fig. 1. Surface morphologies of the CNTs synthesized on 20 nm Fe catalyst film at 800 °C, according to the change of total flow in the constant gas ratio. (a), (b) $\text{NH}_3 : \text{C}_2\text{H}_2 = 10 : 30$ sccm and (c), (d) $\text{NH}_3 : \text{C}_2\text{H}_2 = 20 : 60$ sccm.

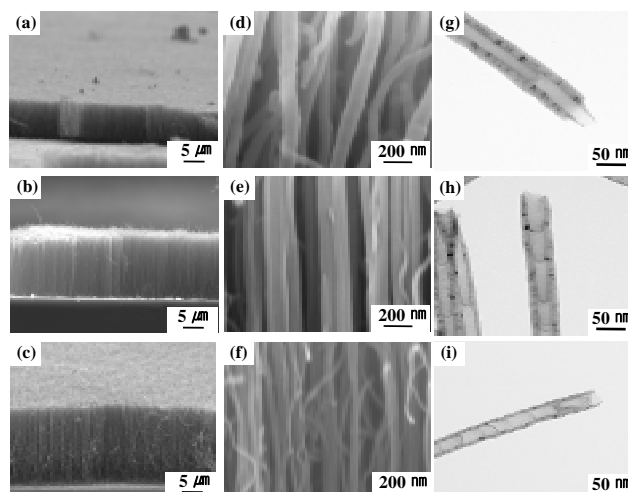


Fig. 2. SEM and TEM images of the grown CNTs on Fe catalyst as a function of gas ratio; (a)(d)(g) $\text{NH}_3 : \text{C}_2\text{H}_2=0:40$ sccm, (b)(e)(h) $\text{NH}_3:\text{C}_2\text{H}_2=10:30$ sccm, and (c)(f)(i) $\text{NH}_3:\text{C}_2\text{H}_2=20:20$ sccm.

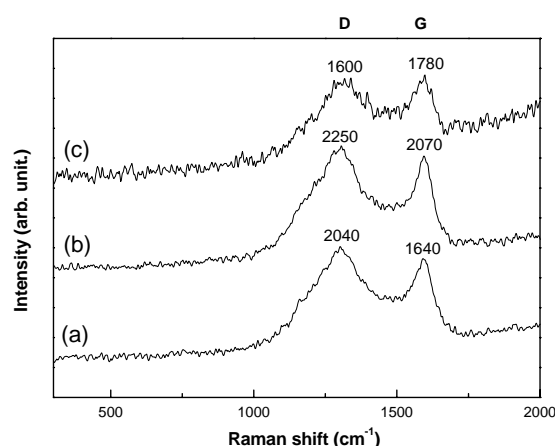


Fig. 3. Raman spectra of the grown CNTs according to the change of gas ratio; (a) $\text{NH}_3:\text{C}_2\text{H}_2=0:40$ sccm, (b) $\text{NH}_3:\text{C}_2\text{H}_2=10:30$ sccm, and (c) $\text{NH}_3:\text{C}_2\text{H}_2=20:20$ sccm.

CNTs were almost same irrespective of gas composition. That means that the inner diameter of CNTs depends on the size of Fe catalytic particles.

Fig. 4(a-d) shows the SEM images of Fe catalytic particles which were deposited on Si substrate with thickness from 5 to 40 nm and then pre-treated with NH_3 at 900 °C for 10 minute. The thinner is the sputtered Fe film, the smaller and denser the particles of pre-treated Fe catalyst. The diameter of the grown CNTs was affected by the size of Fe particles (Fig. 4(e-h)). The crystallinity of CNTs from Raman spectra (Fig. 5) was a little improved with increase in CNT

size, but almost negligible.

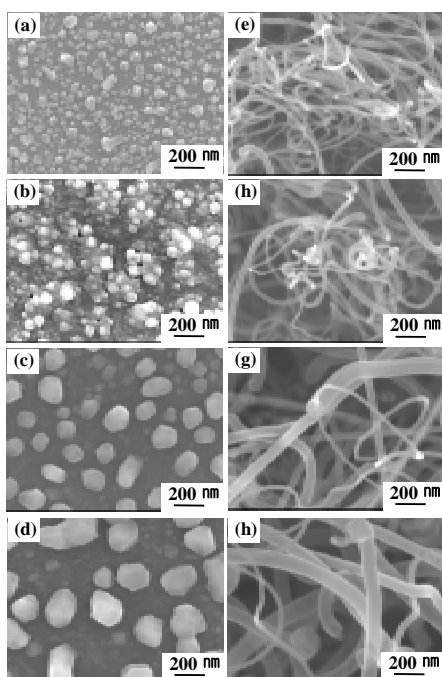


Fig. 4. SEM images of the pre-treated (900°C, 10min) Fe catalyst films having thickness of (a) 5, (b) 10, (c) 20, and (d) 40 nm and the corresponding CNTs images ((e)-(h)) grown at 900°C using each Fe catalyst film.

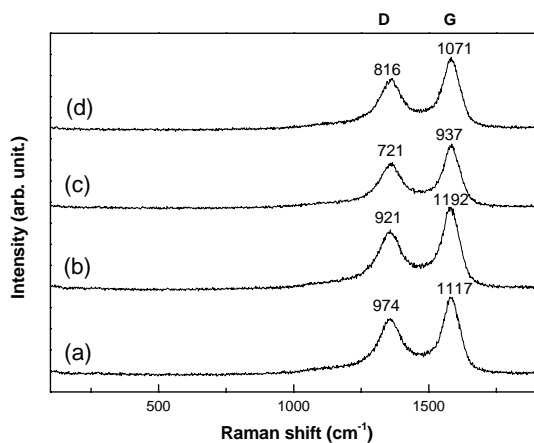


Fig. 5. Raman spectra of the grown CNTs according to the Fe catalyst thickness; (a) 5, (b) 10, (c) 20, and (d) 40 nm.

Figure 6 presents the SEM images of Fe catalyst and CNTs as a function of pre-treatment and growth temperature from 700 to 900°C. With increasing pre-treatment and growth temperature, Fe catalyst gradually changed from a continuous film to island

particles, resulting in significant improvement of CNT density. When the Fe catalyst did not form island shape all over the area, CNTs were grown only on island particles (Fig. 6(b)) and the rest of Fe catalyst area except island parts was covered with amorphous carbons. High intensity of D peak at 800°C in Raman spectra (Fig. 7(a)) proved that there are a lot of amorphous carbons when Fe catalyst did not form a perfect shape of island. Island formation of Fe catalyst as well as growth temperature increased the crystallinity and length of CNTs (Fig. 6(c) and 6(f)).

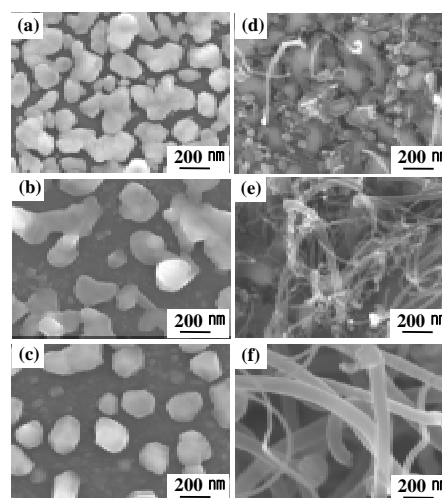


Fig. 6. SEM images of Fe catalyst (40nm) pre-treated at (a) 700, (b) 800, (c) 900°C and CNTs ((d)-(f)) grown at the corresponding temperature.

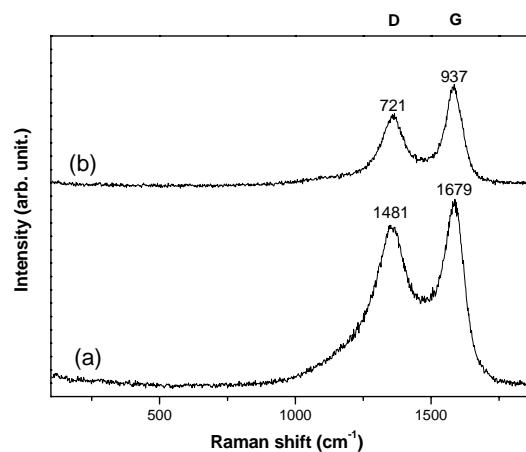


Fig. 7. Raman spectra of the grown CNTs according to the growth temperature; (a) 800°C and (b) 900°C

4. Summary

Effects of several factors such as ammonia gas in hydrocarbon gas, growth time, Fe catalyst thickness, and CVD growth temperature on the characteristics of CNTs were investigated. Firstly, the addition of NH_3 gas in C_2H_2 gas helped to improve CNT quality, but increasing total flow rate to $\text{NH}_3/\text{C}_2\text{H}_2=20/60$ worsened CNT quality. Only use of C_2H_2 gas for growth of CNTs thickened the diameter of CNT with amorphous carbons. The inner diameters of CNTs were decided by catalyst particle size. Secondly, as the thickness of Fe catalyst films decreased, the diameter and density of grown CNTs became smaller and higher, respectively. Finally, with increasing pre-treatment and growth temperature, Fe catalyst film changed to island particles, leading to the growth of CNTs. Unless the Fe catalyst film formed as an island shape, CNT growth could not occur.

5. References

1. S. Iijima, *Nature*, **354**, 56 (1991).
2. S. Iijima and T. Lchihashi, *Nature*, **363**, 603 (1993).
3. Philip G. Collins, and Phaedon Avouris, *Sci. Am.*, **283**, 62 (2000).
4. Min-Feng Yu, Tomasz Kowalewski and Rodney S. Ruoff, *Science*, **287**, 637, (2000).
5. C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, P. Deniard, R. Lee, and J. E. Fisher, *Nature*, **388**, 756 (1997).
6. A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, Y. H. Lee, and R. E. Smalley, *Science*, **273**, 483 (1996).
7. Chris Bower, Wei Zhu, Sungho Jin, and Otto Zhou, *Appl. Phys. Lett.*, **77**, 830 (2000).
8. Ta-Tung Chen, Yih-Ming Liu, Yuh Sung, Ha-Tao Wang, and Ming-Der Ger, *Mater. Chem. Phys.*, **97**, 511 (2006).
9. J. Li, C. Papadopoulos, J. M. Xu, and M. Moskovits, *Appl. Phys. Lett.*, **75**, 367 (1999).
10. S. H. Tsai, C. W. Chao, C. L. Lee, and H. C. Shih, *Appl. Phys. Lett.*, **74**, 3462 (1999)
11. Z. W. Pan, S. S. Xie, L. F. Sun, and G. Wang, *Chem. Phys. Lett.*, **299**, 97 (1999).
12. C. J. Lee, J. H. Park, and J. Park, *Chem. Phys. Lett.*, **323**, 560 (2000)
13. S. Amelinckx, X. B. Zhang, D. Bernaerts, X. F. Zhang, V. Ivanov, and J. B. Nagy, *Science*, **265**, 635 (1994).
14. W. Li, H. Zhang, C. Wang, Y. Zhang, L. Xu, K. Zhu, and S. Xie, *Appl. Phys. Lett.*, **70**, 2684 (1997).