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Effect of Factors on Growth of Carbon Nanotubes by Thermal CVD

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The characteristics of carbon nanotube obtained by thermal chemical vapor deposition (CVD) process were investigated as a function of ammonia (NH_3) gas in hydrocarbon gas, growth time, growth temperature, and Fe catalyst thickness. Fe catalyst was prepared on Si by DC magnetron sputtering with thickness of 5–40 nm and pre-treated with NH_3. CNTs were then grown with ammonia-acetylene gas mixture by thermal CVD. From our results, it was found that NH_3 in C_2H_3 gas positively acted to improve CNT quality. The density and diameter as well as quality of CNTs were strongly affected by catalyst shape and thickness.

Keywords: ammonia gas; carbon nanotubes; Fe catalyst; hydrocarbon gas; thermal chemical vapor deposition

INTRODUCTION

Carbon nanotubes (CNTs), which have a nano-scale sharpness [1], high chemical stability [2], thermal conductivity [3], and mechanical strength [4], have been attracting a great deal of attention. They are expected to be applied to electron field-emitter arrays [5,6], energy industry [7,8], bio-technology [9], and photoelectronic engineering [10]. There exist several techniques for fabricating CNTs such as arc discharge [11], laser ablation [12], and CVD [13,14]. Among these

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techniques, CVD is the most effective method for the 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 [15–17]. 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. The catalytic particles can stay at the tip of the growing nanotube during the growth process [18], or remain at the nanotube base [19], depending on the adhesion between the catalytic particle and the substrate [20]. 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.

EXPERIMENTAL

Synthesis of Carbon Nanotubes

Fe thin films with thickness of 5–40 nm were prepared on Si substrate using DC magnetron sputtering. The power of DC magnetron sputtering is 50 W (320 V, 0.15 A) under Ar pressure of 5×10^{-3} Torr. The thermal CVD system used in our experiments has a quartz tube having dimension of 66 mm $\phi \times$ 1000 mm L into with a movable quartz boat. After the quartz chamber reached to a background pressure below 20 mTorr, Ar gas was applied at 200 sccm in order to prevent the oxidation of the Fe catalytic film while increasing the temperature. Before growing CNTs, Fe catalytic films were pretreated using NH_3 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 a mixture of C_2H_2 and NH_3 gases with a total flow ratio of 40 sccm for 10 min at the same temperature as pretreatment temperature. After the growth, the reactor was cooled down to room temperature.

MEASUREMENTS

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[21].

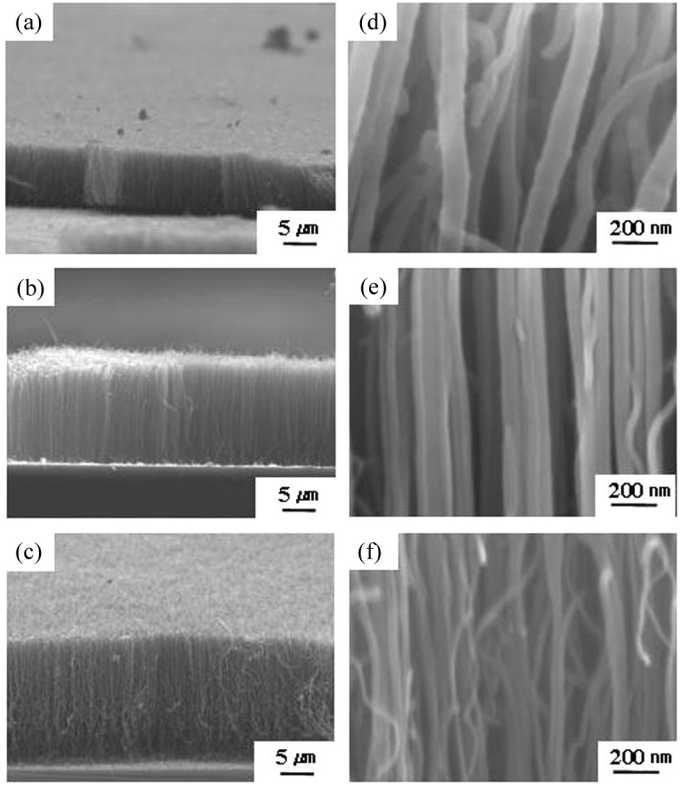

FIGURE 1 SEM images of CNTs synthesized on 40 nm Fe thin film at 800°C using $NH_3 - C_2H_2$ mixture gas. (a), (d) NH_3:C_2H_2 = 0:40 sccm, (b), (e) NH_3:C_2H_2 = 10:30 sccm, and (c), (f) NH_3:C_2H_2 = 20:20 sccm.

RESULTS AND DISCUSSION

The effect of the addition of NH_3 to C_2H_2 gas on CNT growth at 800°C was observed by SEM (Fig. 1) and TEM (Fig. 2). The gas mixture ratio of NH_3 to C_2H_2 was varied at total flow rate of 40 sccm. In Figure 1, as the amount of NH_3 in C_2H_2 ratio increased, CNTs were thinner and longer. In case of using only C_2H_2 gas (Figs. 2(a) and 2(d)), the wall of CNT was quite thick and amorphous carbon was significantly deposited on the outerwall of CNT. In TEM study, the outer diameter of CNT walls became smaller, reducing amorphous carbons on the outerwall of CNT with addition of NH_3 in C_2H_2 gas (Figs. 2(b) and 2(c)). The inner diameters of CNTs were almost same irrespective of gas composition. That means that the inner diameter of CNTs depend on the size of Fe catalytic particles. From Raman spectra result in Figure 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 Karpov *et al.* [22] reported that NH_3 actively

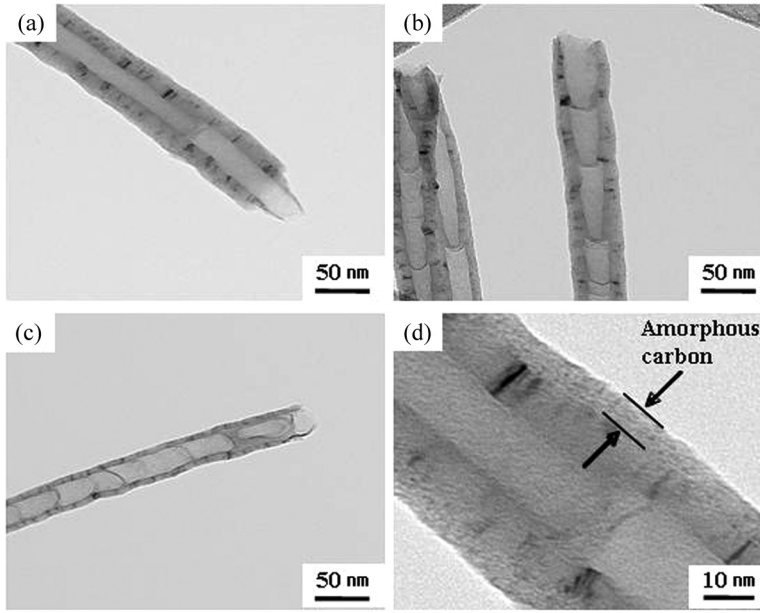

FIGURE 2 TEM images of CNTs grown on Fe catalyst using NH_3–C_2H_2 mixture gas. (a) NH_3:C_2H_2 = 0:40 sccm, (b) NH_3:C_2H_2 = 10:30 sccm, (c) NH_3:C_2H_2 = 20:20 sccm, and (d) the magnified view of (a).

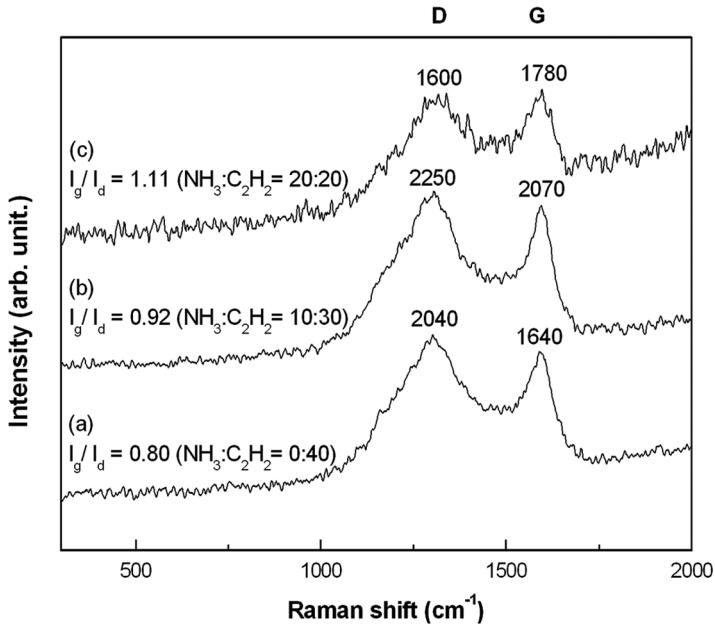

FIGURE 3 Raman spectra of CNTs with use of NH_3–C_2H_2 mixture gas.

begins to decompose and generates atomic hydrogen at a temperature of 800°C. This atomic hydrogen would react with amorphous carbon to form volatile CO_x gas and keep catalytic metal surface clean and active for carbon diffusion, which also matches the other report [23].

Figure 4 shows the CNT images as a function of growth time from 1–60 min at 800°C with $NH_3/C_2H_2 = 10/30$. The pretreatment on Fe catalyst was applied at 800°C for 10 min. using NH_3 gas before CNT growth process. The growth of CNTs occurred up to the growth time of 10 min. However, over 10 min, the CNTs stopped growing and its diameter was rather thickened. The reason may be that as the CNTs grow denser and longer, the mass transport of carbon atoms in C_2H_2 gas to Fe catalyst is more difficult because there is not much space among dense CNTs for gas to penetrate into. Therefore, carbon atoms appeared to be directly deposited on the surface of CNTs, forming amorphous carbons.

Figure 5 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

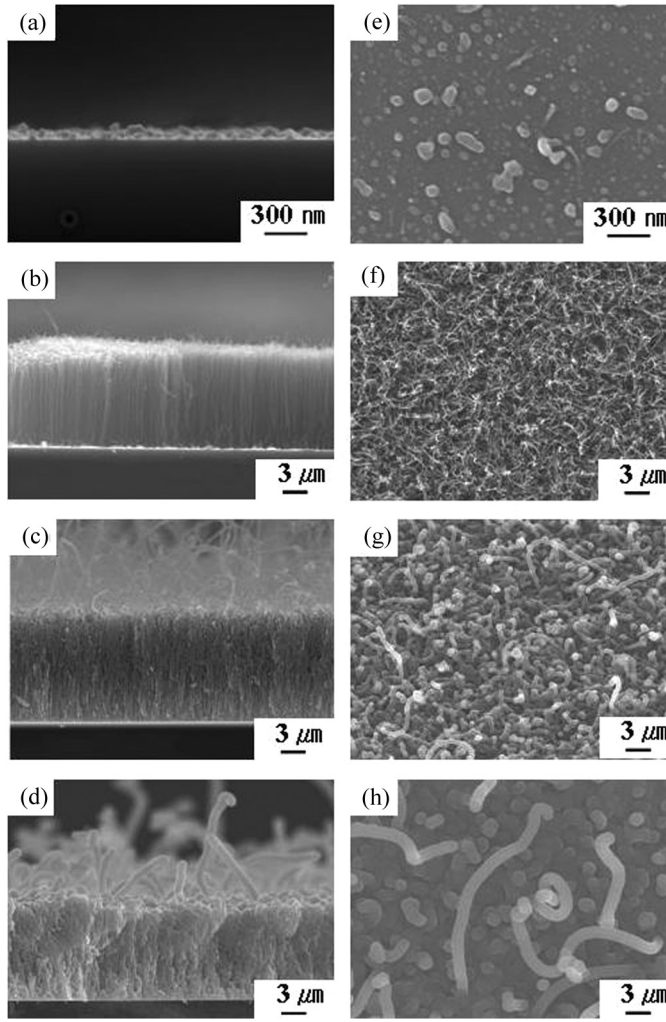

FIGURE 4 The morphologies of CNTs grown on 20 nm Fe catalyst using a mixture gas ($NH_3/C_2H_2 = 10/30$) at 800°C for (a), (b) 1 min, (c), (d) 10 min, (e), (f) 30 min, and (g), (h) 60 min.

catalyst did not form island shape all over the area, CNTs were grown only on island particles (Fig. 5(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. 6) 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

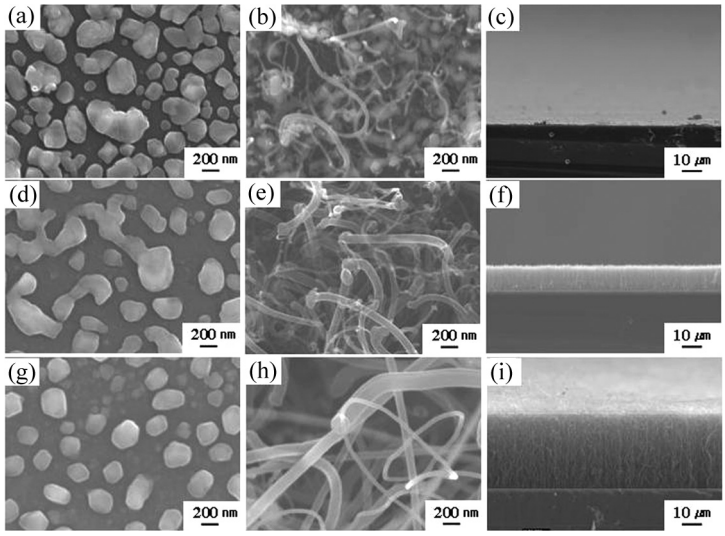

FIGURE 5 SEM images of Fe catalyst (20 nm) and CNTs at pretreatment and growth temperature of (a)–(c) 700, (d)–(f) 800, and (g)–(i) 900°C.

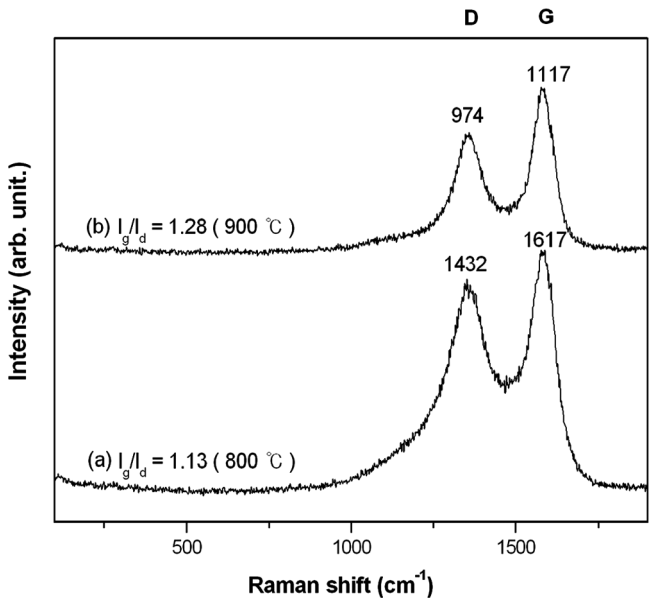

FIGURE 6 Raman spectra of CNTs with different growth temperature.

temperature increased the crystallinity and length of CNTs (Figs. 5(c), 5(f), and 5(i)).

Figures 7(a)–7(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 min. As the sputtered

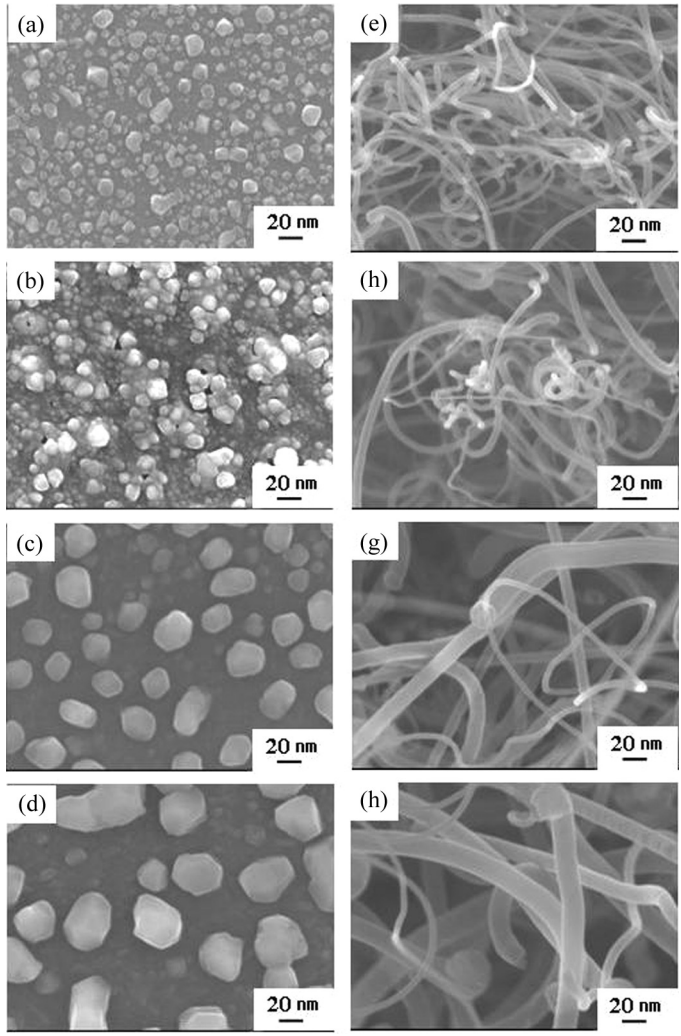

FIGURE 7 SEM images of the pre-treated (900°C, 10 min) Fe catalyst films having thickness of (a) 5, (b) 10, (c) 20, and (d) 40 nm and the corresponding CNTs images ((e)–(h)) grown on each Fe catalyst film at 900°C.

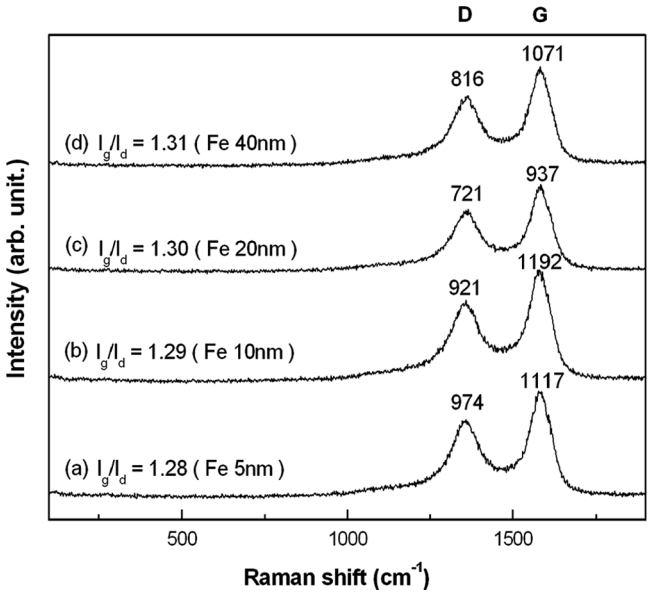

FIGURE 8 Raman spectra of CNTs grown on Fe catalyst having different thickness.

Fe film was thinner, the pre-treated Fe catalytic particles were smaller and denser. The diameter of the grown CNTs was directly affected by the size of Fe particles (Figs. 7(e)–7(h)). The crystallinity of CNTs from Raman spectra (Fig. 8) was a little improved with increase in CNT size, but almost negligible.

CONCLUSIONS

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. First, the addition of NH_3 gas in C_2H_2 gas helped to improve 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, CNTs stopped growing over 10 min at 800°C and then its diameter was rather thickened. It might be a mass transport problem of carbon as CNTs got denser and longer. As a result, the diameter was only increased by adsorption of amorphous carbon. Thirdly, 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. Finally, as the thickness of Fe catalyst films decreased, CNTs grew thinner and denser.

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