Effect of Carrier Gas on the Growth Rate, Growth Density, and Structure of Carbon Nanotubes

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ABSTRACT

We attempt to understand the fundamental factors that determine the growth rate of carbon nanotubes. In a series of experiments on growing multiwall carbon nanotubes (MWNTs) by thermal chemical vapor deposition, we found that the addition of carrier gas and the type of carrier gas can change the growth rate, growth density, and structures of MWNTs. We explain these results based on the dissociative adsorption of C_2H_2 on Fe nanoparticles and the vapor-liquid-solid (VLS) growth model. Finally, high-density, vertically aligned MWNTs were grown when decomposition and segregation rates of carbon were balanced.

INTRODUCTION

Carbon nanotubes (CNTs) [1, 2] are among the promising materials for applications in future nanotechnology. Chemical vapor deposition (CVD) is a convenient technique for growing both singlewall, and multiwall CNTs. However, it is still fundamentally unclear on the factors that will determine the growth rate and structure of carbon nanotubes. Sustaining the growth of carbon nanotubes to unlimited lengths is still technologically impossible. Why does the growth of carbon nanotubes stop or saturate under certain growth conditions? What are the factors that cause the formation of bamboo-like multiwall carbon nanotubes (MWNTs) that are often produced by CVD techniques? We will attempt to answer some of these questions in this paper.

The well-accepted growth mechanism of CNTs by thermal CVD involves the decomposition of hydrocarbon gas on the surface of the catalyst, the diffusion of carbon into the catalyst until saturation, and subsequent segregation of carbon from the catalyst as a tubular structure. The catalytic decomposition of hydrocarbon gases is known as dissociative adsorption [3-5]. The subsequent steps can be described by using the vapor-liquid-solid (VLS) model [6, 7]. Ideally, CNTs will continue to grow if every carbon atom that adsorbed on the catalyst's surface can be added to CNTs. This is valid if the catalyst remains active. Such an ideal condition has not been achieved due to the lack of control over the decomposition, diffusion, and segregation processes.

Here we report our original finding on controlling the decomposition of C_2H_2 on the Fe catalyst during the growth of MWNTs. We found that the use of carrier gases can either suppress or enhance the decomposition rate of C_2H_2 on Fe nanoparticles. Furthermore, the growth density and the structure of these MWNTs vary when different carrier gases are used. These results suggest a rational route to control the growth rate, the growth density, and the structures of CNTs produced by thermal CVD.

EXPERIMENTAL DETAILS

We used the thermal CVD technique for growing MWNTs because of its simplicity. As mentioned, this process involves decomposition of hydrocarbon gas on the catalyst surface at high temperatures. It can produce MWNTs at 600-900 °C from pure C_2H_2 gas on SiO_2/Si substrates coated with Fe films. It is notable that ammonia gas is often required for pretreatment, and growing MWNTs by this technique results in bamboo-like structures [8].

All Fe films used in these experiments were coated using a pulsed-laser deposition (PLD) system [9, 10]. In this work, we used the fourth harmonic generation of Nd:YAG laser at a wavelength of 266 nm. Fe coating was done at room temperature in a vacuum. These films had a thickness of ~4 nm as verified by atomic force microscopy (AFM). The thickness of Fe films was controlled either by the deposition time or laser pulse energy.

The SiO_2/Si substrates coated with Fe films were then loaded into the quartz tube of the thermal CVD system. The tube was evacuated to a pressure of 10^{-3} mbar and purged by the flow of H_2 (270 sccm) and N_2 (150 sccm) gases. The temperature of the reaction zone was then raised to 800 ^{o}C and maintained for 1 hour. During this heating period, Fe films were converted to Fe catalytic nanoparticles. The formation of effective nanoparticles cannot be obtained by heat treatment in a vacuum. Hydrogen may act to reduce the surface oxide of the iron films. After such a pretreatment process, the system was evacuated again before the growth of MWNTs.

We used C_2H_2 as the carbon source gas, which is known to decompose on Fe surfaces at high temperatures [5]. After the pretreatment, MWNTs were grown at 800° C by using (a) pure C_2H_2, (b) C_2H_2 and Ar, (c) C_2H_2 and H_2, or (d) C_2H_2 and N_2. In all cases, the flow rate of C_2H_2 was fixed at 60sccm so that the source of the carbon is the same in all experiments. In this way, the effect of the addition of the carrier gases on the growth of MWNTs can be determined. The growth of MWNTs was carried out for two hours in all cases. After the growth, the CVD system was cooled to room temperature in the flow of carrier gases [cases (b), (c), (d)], or Ar gas for case (a). All MWNTs were than examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy.

DISCUSSION

As shown in figures 1 and 2, the growth rate and the growth density of MWNTs are different when grown from different gas mixtures. We describe these images by

comparing the images of MWNTs grown by pure C_2H_2. As shown in figure 1a, MWNTs grown by pure C_2H_2 gas are typically 2 µm long with a growth rate of ~ 1 µm /hour. The addition of Ar gas [figure 1b] led to a thicker deposit due to the stacking of individual tubes. The MWNTs were significantly longer (estimated as ~10µm under dynamic SEM imaging) than those observed in the case of pure C_2H_2. Subsequent experiments had shown that the growth pattern of MWNTs from pure C_2H_2 gas for two hours is similar to that of a sample grown for only 15 minutes. This means, the growth of MWNTs from pure C_2H_2 gas has terminated after ~15 minutes. We think that the flow rate of C_2H_2 gas under the selected growth condition has caused excessive adsorption and decomposition of C_2H_2 on the surfaces of Fe nanoparticles. This could lead to the formation of a carbon layer on the surface of catalyst particles and prevent further contact of C_2H_2 molecules with Fe. Thus, the supply of carbon stopped and resulted in growth termination. This happened because the decomposition rate of C_2H_2 was higher than the carbon diffusion rate into the Fe nanoparticles and the segregation rate of carbon from the nanoparticles.
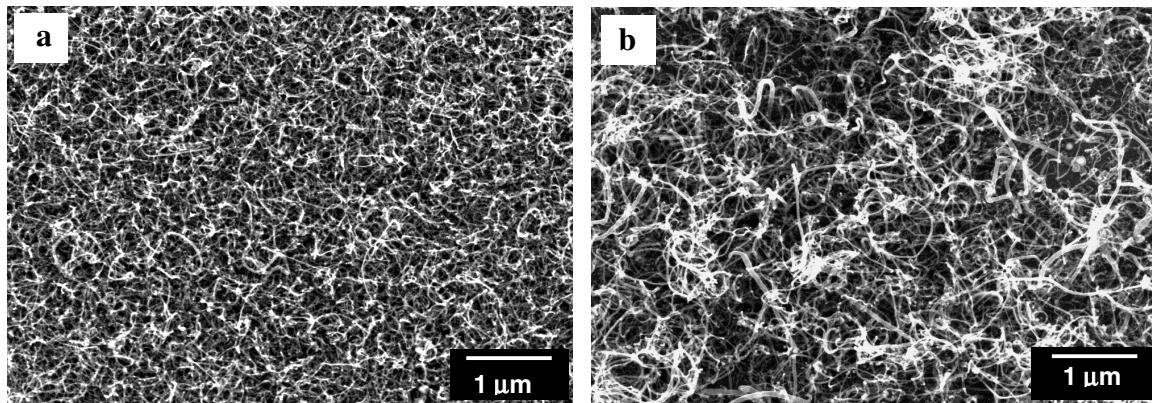

Figure 1. MWNTs grown from (a) pure C_2H_2 gas and (b) C_2H_2 / Ar mixed gas.

We then examined the growth of MWNTs from the C_2H_2 /Ar mixture at periods shorter than two hours. Results indicate that the growth of MWNTs continued for two hours. This means, the addition of Ar has diluted C_2H_2 in the growth chamber. Thus, coverage of C_2H_2 on the surface of Fe nanoparticles is lower than in case of pure C_2H_2. This decreased the supply rate of carbon into the catalyst nanoparticles. Thus, the rate of carbon supply and carbon segregation was balanced for continued growth.

The addition of H_2 gas to C_2H_2 induced a different effect on the growth of MWNTs. As shown in figure 2a, the growth of MWNTs did not occur on all Fe nanoparticles. Some bare particles are clearly seen on the surface of the substrate. We explain this result by referring to the dissociative adsorption of H_2 on Fe surface [3, 4]. Like C_2H_2, H_2 is known to dissociate on the surface of Fe at high temperatures. This means, it is possible that C_2H_2 and H_2 molecules are competing to adsorb and dissociate on the surfaces of Fe nanopartcles. Two effects occurred: First, the growth density of MWNTs was reduced since some particles were occupied for the decomposition of H_2 and resulted in insufficient carbon supply for growing MWNTs. This may explain the observed smaller growth density in figure 2a. Second, the concentration of C_2H_2 is

decreased, similar to the effect that induced by Ar gas, as discussed earlier. As shown in figure 2a, MWNTs grown from this mixed gas were longer than those grown from pure C_2H_2. In fact, additional experiments confirmed that MWNTs continued to grow for two hours from C_2H_2 / H_2 mixture.
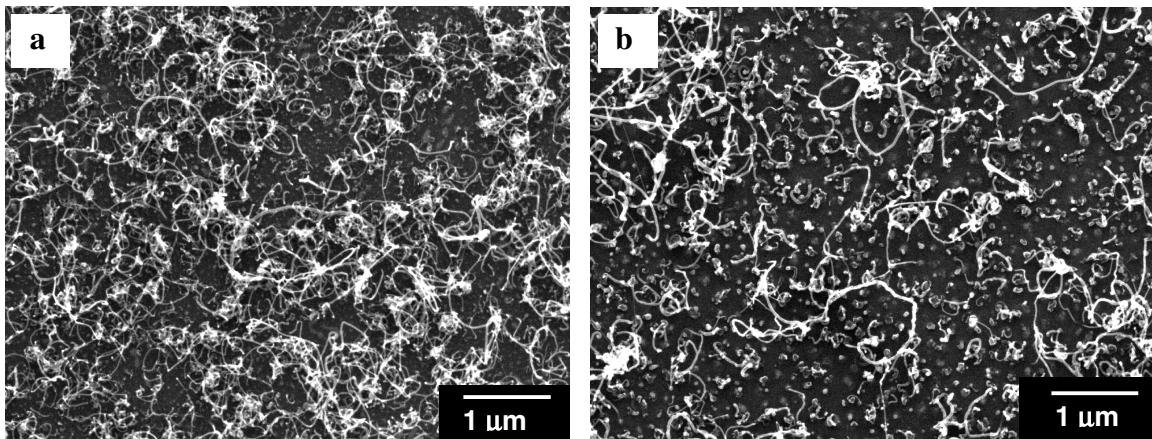

Figure 2. MWNTs grown from (a) pure C_2H_2 / H_2, and (b) C_2H_2 / N_2 mixed gases.

The addition of N_2 gas induces similar effects as the addition of H_2. As shown in figure 2 (b), the growth density is further suppressed. Many Fe nanoparticles are seen on the substrate surface are not involved in the growth of MWNTs. This could be explained by the formation of iron nitride films on the surface of Fe particles [11]. The effect of F-N films on the growth of CNTs is not well documented. Another possibility could be the cross interaction between C_2H_2 and N_2 molecules on the Fe surface. There could be a possibility of forming CN^- radicals, which are volatile at high temperatures. This could reduce the diffusion of carbon into the Fe nanoparticles and thus reduce the chances of MWNT formation. The actual reason for our observation is subjected to further investigations.
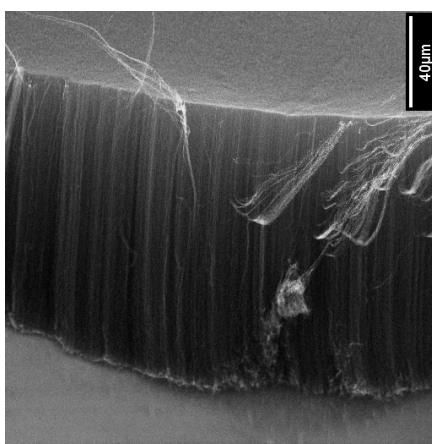

Figure 3. High-density vertically aligned MWNTs grown from C_2H_2 / Ar gas mixture for 15 minutes.

We then attempted to optimize the growth of MWNTs, as we understood the need of balancing the carbon supply and segregation rate. We used C_2H_2 / Ar gas mixture, which promotes continued growth without reducing the growth density, and then optimized the growth temperature for such a gas mixture. As a result, we were able to grow high-density MWNTs at 650 $^\circ$C, as shown in figure 3. As shown, these MWNTs are vertically aligned, most likely due to the high growth density and van der Waals forces between adjacent MWNTs, which help in restricting the growth toward the free space (vertically upward). The sample in figure 3 is grown for 15 minutes with a length of ~100 µm.

Besides affecting the growth rate and growth density of MWNTs, we found that carrier gases could change the structures of MWNTs. For instance, we frequently observed branching tubes on samples grown from the C_2H_2 / Ar gas mixture. The TEM image of such a branching MWNT is shown in figure 4a. On the other hand, we detected mostly dome-capped MWNTs in samples grown from the C_2H_2 / H_2 gas mixture. As shown in figure 4b, Fe catalyst particles were often found captured inside the nanotubes. Besides, we detected bamboo-like MWNTs in samples grown from the C_2H_2 / H_2 / N_2 mixtures. Such a structure is shown in figure 4c.

The reasons for the formation of various structures are related to the growth rate induced by different carrier gases. This is consistent with the interpretation that the carbon supersaturation during growth will determine the formation of carbon fibers, bamboo-like MWNTs, and SWNTs [12]. Likewise, there are several reports on the formation of carbon nanotubes with T-, Y-, and X-junctions (see for example a recent review in [13]). However, the mechanisms involved are still not clear. We think that this is related to the growth rate, supersaturation, and the structural properties of the catalytic nanoparticles. On the other hand, gases like H_2 and N_2 could induce addition chemistry that changed the structures of nanotubes. For instance, we think that H_2 might work to stabilize the dangling bonds of carbon during growth and selectively etch the amorphous carbon phase. The present of N_2 could form CN bonds within the graphitic rings of nanotubes. These CN bonds can bend the graphitic network [14] and induce bamboo-like structures.
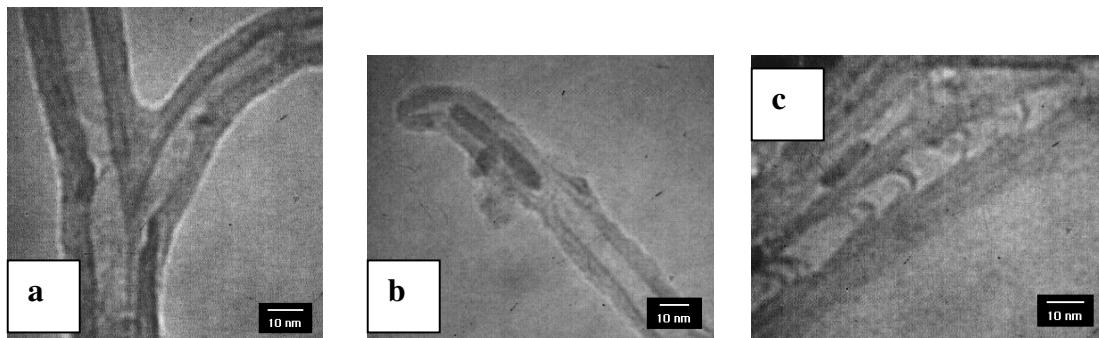

Figure 4. (a) Branching, (b) dome-capped, and (c) bamboo-like MWNTs.

CONCLUSIONS

We found that carrier gas can change the growth rate, growth density, and structures of MWNTs. The addition of Ar dilutes C_2H_2 and reduces the number of C_2H_2 molecules reacting on the Fe catalyst surface. Both H_2 and N_2 reduce the growth density of MWNTs. A balance between the carbon supply rate and segregation rate is required for high-density and high growth rate of MWNTs. The mechanism for structural change is still not clear but is related to the growth rate, carbon supersaturation, and addition chemistry induced by H_2 and N_2 gases.

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