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High-density vertically aligned multiwalled carbon nanotubes with tubular structures

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Ammonia (NH₃) gas was thought to be essential for the growth of vertically aligned multiwalled carbon nanotubes (VA-MWCNTs) and led to the formation of bamboo-like structures. Here, we show that VA-MWCNTs with ideal tubular structures can be grown on substrates by various mixed gases with or without NH₃ gas. The growth of these VA-MWCNTs is guided by a growth model that combined the dissociative adsorption of acetylene molecules (C₂H₂) and the successive vapor-liquid-solid growth mechanism. Results indicate that the key factor for growing these VA-MWCNTs is a balance between the decomposition rate of the C₂H₂ molecules on the iron catalyst and the subsequent diffusion and segregation rates of carbon. © 2005 American Institute of Physics. [DOI: 10.1063/1.1952575]

Since their discovery in 1991,¹ multiwalled carbon nanotubes (MWCNTs) have gained significant research interest due to their unique structures, properties, and potential applications.² Recently, high-density vertically aligned (VA) MWCNTs have gained attention for innovative applications such as nanotubes membranes,³ nanotubes filter,⁴ nanotube yarns,⁵ three-dimensional microbatteries,⁶ etc. However, the growth mechanism of these VA-MWCNTs on substrates by catalytic thermal chemical vapor deposition (CVD) is still not understood. Recently, catalytic thermal CVD was also used for the growth of vertically aligned single wall carbon nanotubes.⁷

The vapor-liquid-solid (VLS) growth mechanism is well accepted for the growth of carbon nanotubes.^{8,9} However, it does not provide sufficient details on the decomposition process of the hydrocarbon molecules on the catalytic nanoparticles. The decomposition process is important for understanding how to maintain the activity of the catalyst. This is important for the growth of VA-MWCNTs by the catalytic thermal CVD technique, in which high-density growth sites are necessary so that van der Waals forces between adjacent MWCNTs can restrict their growth direction toward the free space, thus achieving vertical alignment. Ammonia (NH₃) gas was thought to be essential for the growth of these VA-MWCNTs. However, this approach leads to the formation of bamboo-like structures,^{10,11} which are not suitable for applications such as nanotube membranes, filters, and microbatteries, where tubular structures are required.

Recently, we found that carrier gases (Ar, N₂, H₂) can change the growth mode of MWCNTs from a saturated growth to a continuous growth.¹² We have explained this phenomenon by a growth model that combined the dissociative adsorption of acetylene (C₂H₂) molecules on iron (Fe) catalysts and the successive vapor-liquid-solid (VLS) growth mechanism. This model emphasizes the adsorption of C₂H₂

molecules on the Fe nanoparticles and a charge transfer from the molecule to the catalyst that will reduce the energy required for molecular decomposition. The decomposition rate must be controlled for achieving equilibrium with the rates of subsequent carbon diffusion into the catalysts and carbon segregation from the catalysts. Excessive decomposition rate will cause the formation of amorphous carbon (a-C) films on the catalyst surfaces and will prevent further adsorption and decomposition of C₂H₂ molecules. Guided by this model, we show here that high-density VA-MWCNTs with ideal tubular structures can be grown with and without the use of NH₃ gas. This result also indicates that the use of NH₃ gas is not the sole factor for the formation of bamboo-like structures.

In our experiments, catalytic Fe thin films were coated on SiO₂/Si substrates in a pulsed-laser deposition system.¹³ We used the fourth-harmonic generation of Nd:YAG laser (wavelength, $\lambda \sim 266$ nm) at an energy density of ~ 1 J cm⁻² on the Fe target. Depositions were carried out at room temperature in a vacuum ($\sim 10^{-5}$ mbar). The film thickness was determined by using an *in situ* thickness monitor. Pretreatment of these Fe/SiO₂/Si substrates was carried out for 15

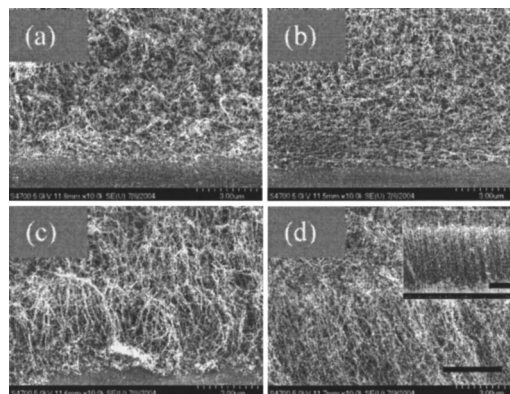


FIG. 1. SEM images of MWCNTs grown on 2.5 nm thick Fe film at (a) 800 °C, (b) 750 °C, (c) 700 °C and (d) 650 °C. Scale bar: 3.0 μ m. Scale bar for the inset: 7.5 μ m.

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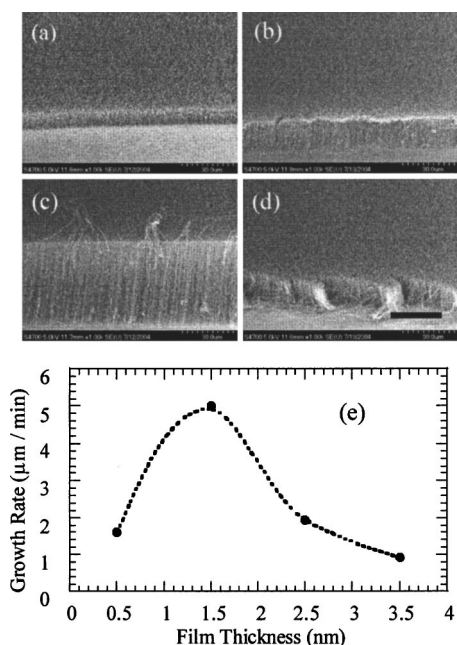


FIG. 2. SEM images of VA-MWCNTs grown at different Fe film thicknesses: (a) 3.5 nm, (b) 2.5 nm, (c) 1.5 nm, and (d) 0.5 nm. All samples were grown at 650 °C for 15 min and their growth rates are summarized in (e). Scale bar: 30 μm .

minutes in a thermal CVD system at 800 °C. This was done in the flow of hydrogen (270 sccm) and nitrogen (150 sccm) gases, although other research groups prefer to use NH_3 gas. The growth gases then replaced the pretreatment gases after the system was tuned to the growth temperature. After the growth, all samples were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and micro-Raman spectroscopy.

The VLS mechanism indicates that the growth temperature (T_g) will change the diffusion and the segregation rates of carbon. However, excessive T_g can enhance both thermal decomposition and dissociative adsorption of hydrocarbon

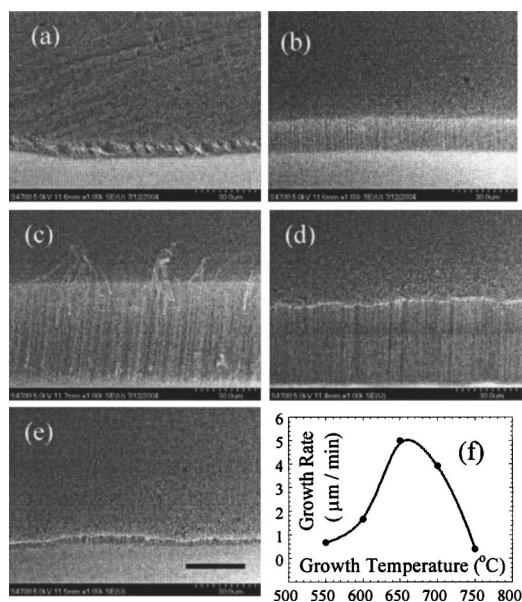


FIG. 3. SEM images of the VA-MWCNTs grown on 1.5 nm thick Fe film at (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C, and (e) 750 °C. All samples were grown for 15 min and their growth rates are summarized in (f). Scale bar: 30 μm .

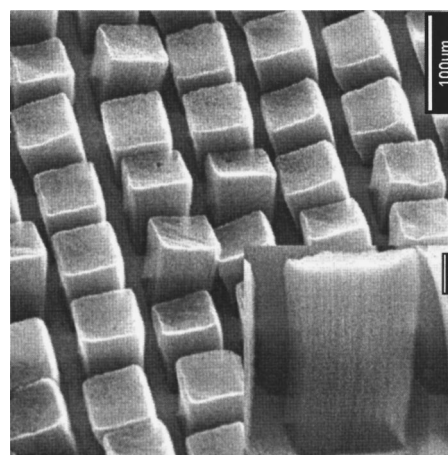


FIG. 4. Patterned growth of VA-MWCNTs with 1.5 nm thick Fe film at 650 °C for 30 min. Scale bar for the inset: 20 μm .

molecules, which have not been considered in the VLS mechanism. Thus, we scrutinize the effect of T_g by growing MWCNTs for 15 min with 2.5 nm thick Fe films and Ar (50 sccm)/ C_2H_2 (70 sccm) growth gases. At $T_g=850$ and 900 °C, random and sparse nanotubes were grown (not shown). At $T_g=800$ °C, denser but random MWCNTs were grown, as shown in Fig. 1(a). A similar growth mode was detected for the case of 750 °C, as shown in Fig. 1(b). At 700 °C, the length of the tubes and the degree of their alignment increased, as shown in Fig. 1(c). This tendency was enhanced at $T_g=650$ °C and lead to the growth of VA-MWCNTs, as shown Fig. 1(d) and its inset. We think that at $T_g > 700$ °C, thermal decomposition of C_2H_2 molecules becomes significant and causes the formation of a-C films on some catalysts, which prevent continuous dissociative adsorption, reduces the growth density, and thus results in random MWCNTs.

Once the vertically aligned MWCNTs were achieved at $T_g=650$ °C, we examined the effect of the catalyst film thickness. The SEM images of the MWCNTs grown at $T_g=650$ °C by different Fe film thicknesses are shown in Fig. 2. As shown in Figs. 2(a)–2(c), the growth rate of the VA-MWCNTs increases with the decrease of Fe film thickness of 3.5, 2.5, and 1.5 nm, respectively. According to Fick's law of diffusion, the net flux of carbon atoms (crossing unit area in unit time) is $J = -D(\Delta N/d)$.¹⁴ The minus sign means that

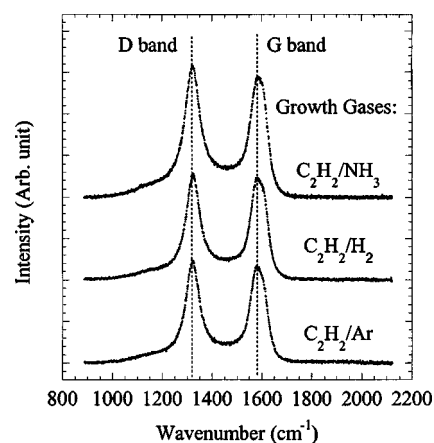


FIG. 5. Raman spectra for VA-MWCNTs grown with 1.5 nm thick Fe film at 650 °C by various mixed gases.

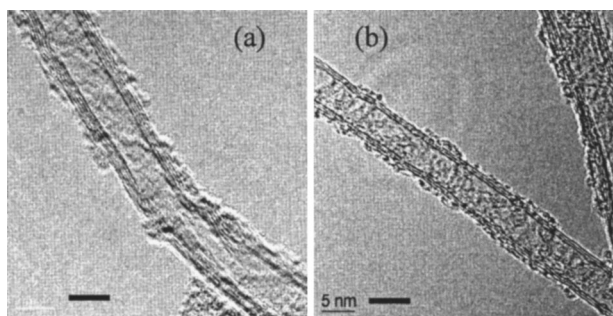


FIG. 6. TEM images of MWCNTs grown by (a) C_2H_2/NH_3 , and (b) C_2H_2/Ar mixed gases. Scale bar: 5 nm.

diffusion occurs away from regions of high concentration. D is the diffusivity and ΔN is the change of carbon concentration at the top and the bottom surfaces of the Fe particles. Both D and ΔN are constant for identical growth temperatures. Thus, faster growth rates are observed in cases with thinner Fe films (smaller particle diameter d). Besides, thinner catalyst film leads to the growth of thinner nanotubes, which require fewer carbon atoms for the growth of a unit tubular length. Thus, faster growth rates are observed in cases with thinner Fe films. However, the growth rate is reduced for the case with 0.5 nm thick Fe film [Fig. 2(d)]. This is an energy-limited phenomenon wherein the growth rates of thin nanotubes are reduced at low growth temperatures (650 °C in this case) due to the need of higher energy for growing smaller cylinders with higher curvature of graphene sheets.¹⁵ As summarized in Fig. 2(e), the optimum growth rate at 650 °C occurred for the case of 1.5 nm thick Fe film.

We further refine the optimum growth temperature (T_g) for samples grown by using 1.5 nm thick Fe films. Images in Figs. 3(a)–3(e) correspond to samples grown at 550, 600, 650, 700 and 750 °C. VA-MWCNTs were obtained for all cases and their growth rates are summarized in Fig. 3(f). As shown, the optimum growth temperature was between 650 and 700 °C. The drop of growth rate at 750 °C is due to the additional thermal decomposition of C_2H_2 molecules. The reduced growth rates at 600 and 550 °C are believed to be due to energy-limited formation at low temperatures, as discussed earlier. At the optimum growth condition ($T_g = 650$ °C, Fe films of 1.5 nm thick), VA-MWCNTs can be grown in desired patterns by using prepatterned catalyst films. As shown in Fig. 4, VA-MWCNTs are organized into microtowers of $60 \mu m \times 60 \mu m$ with uniform heights. The height of these microtowers was $\sim 150 \mu m$ after growing for 30 min.

Under this optimum growth condition, we have repeated the growth by replacing C_2H_2/Ar mixed gas with C_2H_2/H_2 or C_2H_2/NH_3 mixed gases. High-density VA-MWCNTs were grown in all these cases. We have examined the structures of these VA-MWCNTs by Raman spectroscopy (Renishaw 100, He–Ne laser excitation) and TEM (Hitachi HF2000). As shown in Fig. 5, the G band ($\sim 1580 \text{ cm}^{-1}$, zone center phonons of E_{2g} symmetry) and the disorder “ D ”

band ($\sim 1320 \text{ cm}^{-1}$, K -point phonons of A_{1g} symmetry) have similar intensity ratios (I_G/I_D), which indicates a similar graphitic order.¹³ This is confirmed by TEM; that is, all these VA-MWCNTs have an ideal tubular structure. For example, the sample grown by using C_2H_2/NH_3 mixed gas [Fig. 6(a)] is similar to that grown by C_2H_2/Ar mixed gas [Fig. 6(b)]. This means the use of NH_3 gas in the growth is not the sole factor for the formation of the bamboo-like structures. In addition, we have examined the growth of MWCNTs by changing the pretreatment gas from N_2/H_2 mixed gas to pure NH_3 gas, a reported pretreatment procedure that produced bamboo-like nanotubes.^{10,11} High-density VA-MWCNTs were obtained at our optimum growth condition with various growth gases, such as C_2H_2/Ar , C_2H_2/H_2 or C_2H_2/NH_3 . VA-MWCNTs with tubular structures are revealed in all these cases.

In summary, guided by a growth model that combined dissociative adsorption and the VLS mechanism, high-density VA-MWCNTs can be grown by various types of growth gases and pretreatment gases. Under our optimum condition, nanotubes with tubular structures are formed with similar graphitic orders. The use of NH_3 gas either in the growth or in the pretreatment process is not the only factor for the formation of bamboo-like structures.

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