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Distortion of carbon nanotube array and its influence on carbon nanotube growth and termination

Jun Wu, Yanfeng Ma, Yi Huang, Zunfeng Liu, Yongsheng Chen *

Center for Nanoscale Science and Technology and Institute of Polymer Chemistry,
College of Chemistry, Nankai University, Tianjin 300071, China

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Abstract

Well-aligned carbon nanotubes (CNTs) were produced by thermal chemical vapor deposition (CVD) of $C_2H_4/H_2/Ar$ on Fe/Al catalyst films. CNT growth kinetics and the array microstructure were investigated for the densely grown CNT films. A new CNT curling-controlled growth model is presented for the CNT growth kinetics. In this curling-controlled base-growth model, the initial CNT growth rate is relatively stable but the rate decreases dramatically after the initial period. It is found that, instead of the CNT film height, the curling of freshly grown CNTs is the essential cause of the CNT growth rate decrease and termination and this is in consistent with the Knudsen-diffusion theory.

Keywords: Carbon nanotubes; Array; Growth; Mechanism

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1. Introduction

Vertically aligned carbon nanotubes (VACNTs) synthesized by catalytic chemical vapor deposition (CCVD) has been extensively investigated since 1996 [1] because of their paramount importance for making CNTs-based devices [2–6] and many theories have been proposed to account for their growth mechanism. The main mechanisms are based on tip-growth [6–9] and base-growth [10–14]. The growth mechanism is most often identified as base-growth if the catalysts are deposited on substrates preciously and gaseous hydrocarbons are used as carbon source. In this model, the carbon source must diffuse through the CNTs array and reach the surface of the catalyst [13–19], therefore, diffusion of the carbon source is an important step in the growth of CNTs array. Recently [13] the temperature influence on the diffusion is investigated considering that the whole structure of the array is homogeneous and it is pointed out that the CNT growth is reaction-rate-controlled below 740 °C and the growth rate is independent of the array height; above 740 °C the growth is Knudsen-diffusion-controlled and the densely packed CNT film acts as a diffusion barrier to the carbon precursor, increase in array height will hinder the diffusion of the carbon source and then leading to the decrease in growth rate [14–16,18,19].

In this study we found that the significant growth rate decrease was caused by the increasing curly and densely packing of the freshly grown CNTs which decrease the interspace among the CNTs. By use of the Knudsen-diffusion theory [20], it is proposed that the curling of freshly grown tubes is the essential cause of the growth rate decrease and termination of the CNTs array. A new CNT curling-controlled growth model is presented for the CNT growth kinetics.

2. Experiment

The substrate used in this study is a silicon wafer coated with Si_3N_4 by plasma CVD. The catalyst layer of Al (10 nm)/Fe (3 nm) was formed on the silicon wafer by sequential e-beam evaporation. The growth of CNTs was performed in a single-zone atmospheric pressure quartz tube furnace. The reaction temperature was ramped to the set point 775 °C in 12 min under 350 sccm Ar. Then the growth was carried out at 775 °C with ethylene (150 sccm) as the carbon source and hydrogen (200 sccm) and Argon (350 sccm) as carrier gases. After reaction, Ar flowing (250 sccm) was kept for 5 min at the reaction temperature before the furnace cooled down. The samples were

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* Corresponding author. Tel.: +86 22 2350 0693; fax: +86 22 2349 9992.
E-mail address: yschen99@nankai.edu.cn (Y. Chen).

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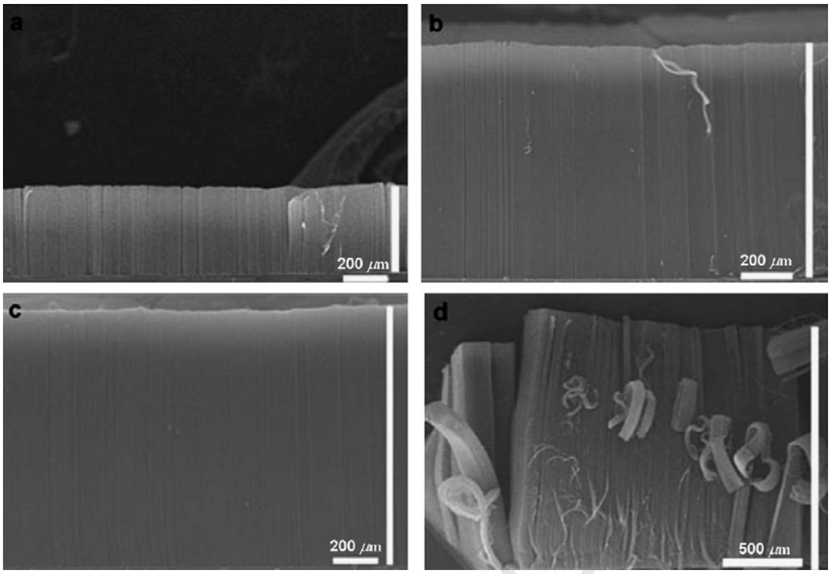

Fig. 1. Side view of aligned carbon nanotubes, growth time: (a) 15 min (scale bar 200 μm); (b) 30 min (scale bar 200 μm); (c) 45 min (scale bar 200 μm); (d) 90 min (scale bar 500 μm).

characterized by scanning electron microscopy (SEM, Hitachi S-3500N) at 20 keV.

3. Results and discussion

VACNTs films are grown from the Fe/Al film in $C_2H_4/H_2/Ar$ (150/200/350 sccm) at 775 °C. Fig. 1 shows VACNTs with different growth time. The side view shows that the CNTs are oriented primarily perpendicular to the substrate. It can be seen that the height of CNTs array increases with the growth time. It gets nearly 370 μm at 15 min, and increases to 910 μm in 30 min, and then to 1500 μm in 90 min.

By investigating the CNTs array height (thickness) as a function of time (shown in Fig. 2), we can find that the array grows rapidly at the initial time and the growth rate is relatively stable. Afterwards, the growth rate decreases, which agrees well with the literatures [14–16,18,19]. These researches suggest that the CNTs films act as densely packed nanoporous layers that present a diffusion barrier to the ethylene precursor and its diffusion will be increasingly hindered as the array height increases, leading to the decrease in the growth rate.

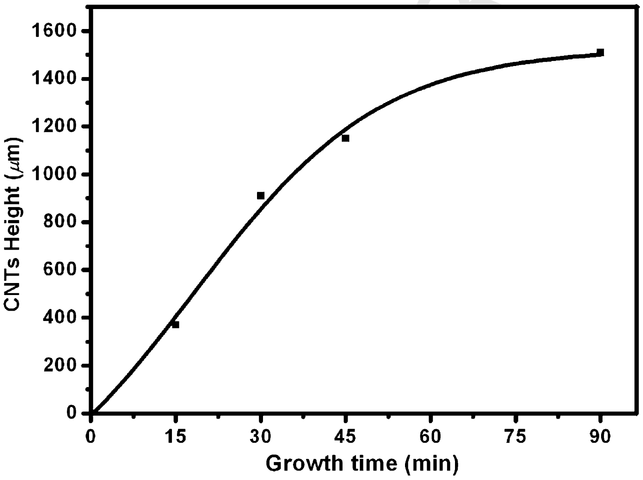

Fig. 2. CNTs height as a function of growth time.

In our CNT film growth, we found (Fig. 2) in the initial 30 min the growth rate (the slope of the curve) kept almost a constant value nearly 26 μm/min. As the growth time increases from 30 to 45 min, we can see a dramatic decrease in the average growth rate (17 μm/min) and further to a much smaller value (7 μm/min) from 45 to 90 min. We were wondering what were the intrinsic reasons for the accelerated decrease in the growth rate with the increase of the array height.

The growth of CNTs array includes two steps [13,21]. Firstly, the carbon source molecules diffuse to the catalyst surface; secondly, C atoms nucleate on the catalyst particles to form CNTs. Therefore, the growth rate of the CNTs array depends on both the diffusion rate of the carbon source and its reaction rate on the catalyst particle. Recent report [13] indicates for the system using Fe/Ai_2O_3 as catalyst and ethylene as the carbon source the reaction rate is relatively low below 740 °C and the growth of CNTs array is the reaction-rate-controlled; when the growth rate temperature exceeds 740 °C, the reaction rate is high and the growth of CNTs array mainly depends on the diffusion rate of the carbon source, i.e. the CNTs growth is diffusion-controlled. In our work the reaction system is the same as that of and the reaction temperature (775 °C) is higher than 740 °C, therefore, we argue that the CNT growth is also diffusion-controlled.

In such a growth system, the feeding of carbon source and growth of VACNTs can be considered as a porous system [13,20]. Diffusion through porous materials is typically described as either bulk or Knudsen-diffusion [22]. Bulk diffusion occurs when the pore diameter is large in comparison to the mean free path of the gas molecules. Molecular transport through pores that are small in comparison to the mean free path of the gas is described as Knudsen-type diffusion. The mean

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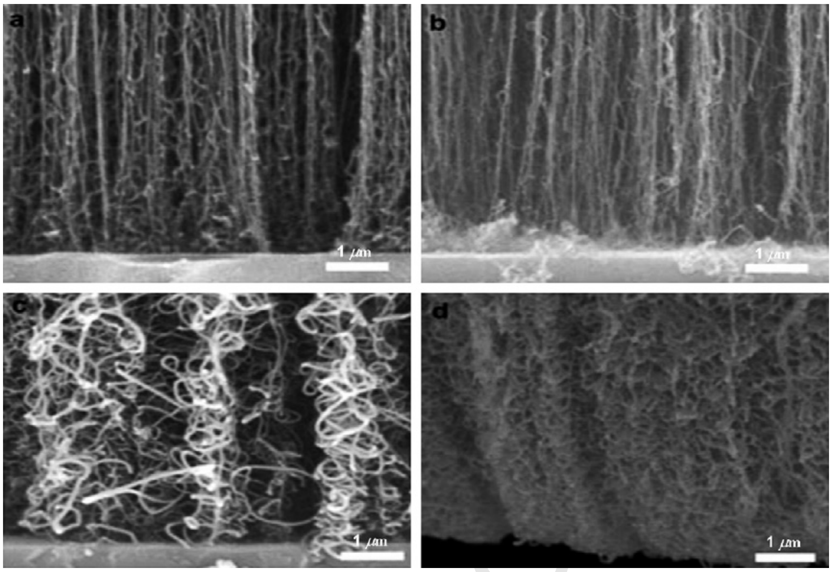

Fig. 3. SEM micrographs of aligned CNTs array root of different growth time: (a) 15 min; (b) 30 min; (c) 45 min; (d) 90 min (all scale bar 1 μm).

free path (λ) of ethylene is about 201 nm at the same temperature and pressure as our system [13,20], and the channel radius (λ_t, the distance among the tubes) is about 20 nm. Because $\lambda \gg \lambda_t$, the diffusion of carbon source is Knudsen-type in our reaction system [23].

In general, the diffusion rate is described using the diffusion coefficient, which is defined as the diffusion flux per concentration gradient. The bigger the value of diffusion coefficient, the faster the diffusion rate will be [20], which shall yield higher growth rate in the diffuse-controlled growth. In Knudsen-diffusion system, it can be expressed as

$$D_{A,K,e} = 97.0 r \frac{\varepsilon}{\tau} \left(\frac{T}{M_A} \right)^{1/2} \quad (1)$$

where $D_{A,K,e}$ is the effective Knudsen-diffusion coefficient, ε porosity of the solid, r the channel radius, τ the tortuosity factor, T the temperature, M_A the molecule weight of the gas. In the case of our CNT growth, r lies on the diameter and the neighboring distance of the CNTs, ε is the fraction of the bulk volume of the porous sample that is occupied by pore or void space. In the random pore model the medium tortuosity factor (τ) can be described as $1/\varepsilon$ [24], Eq. (1) can thus be expressed as

$$D_{A,K,e} = 97.0 r \varepsilon^2 \left(\frac{T}{M_A} \right)^{1/2} \quad (2)$$

In our study, T and M_A can be regarded as constant, therefore, $D_{A,K,e}$ depends on r and ε, which are determined by the microstructure of the CNTs array. Thus we observed the microstructure of the CNT array at different growth time. Interestingly we found that the microstructure of the CNT array root changed significantly with the growth time, as shown in Fig. 3. Fig. 3a is the root part after 15 min growth, we can see that most of the CNTs are straight and there is relatively large clear room among the tubes in the array and only few tubes are slightly curved. As the growth time prolongs to 30 min (Fig. 3b), the amount of curved tubes increases and the gap among the tubes decreases. Fig. 3c shows the array root after 45 min growth, it can be seen that almost all the tubes curve very much and are entangled together. Furthermore, only partial alignment was kept with an increased CNT density. After growth of 90 min (Fig. 3d), the tubes are densely packed to form a “blanketry”, almost no interstice or single tube can be seen. The alignment is almost lost completely. Furthermore, we have found the curly extent of the tubes in VACNTs show an increase trend from top to the root of the array. Fig. 4 shows the SEM pictures of the middle part and the root of the arrays at the growth time of both 30 and 90 min. Clearly it can be seen that the tubes in the middle part of the array are much straighter than those in the root.

From Fig. 3a and b we can see that the CNTs are straight and the interspace among the tubes should not have significant change in the initial period, so the r and ε can be regarded as constant in the Knudsen-diffusion model. It has been mentioned previously that T and M_A in Eq. (2) keep as constant in our study, so from Eq. (2) the effective Knudsen-diffusion coefficient $D_{A,K,e}$ shall change little in this period. Therefore, the CNT growth rate will be almost a constant in this period as observed in Fig. 2. With the growth time prolonging, the freshly grown tubes become more and more curly and densely packed as shown in Fig. 3c and d, especially for them after 45 min growth. During this period, the diffuse channel of the freshly grown part gets more crowded due to the increased curling of the tubes, which will result in the decrease in r and ε. Consequently, the $D_{A,K,e}$ of carbon source through the CNT film decreases gradually. Therefore, in the later growth period, the growth rate shall decrease at an accelerated mode as shown in Fig. 2. As the CNTs get so curly and densely packed, the much decreased r and ε will get $D_{A,K,e}$ close to zero and the CNT growth become practically terminated.

As mentioned previously, Wong and co-workers [13] has pointed out that the CNT growth is reaction-rate-controlled below 740 °C and the growth rate is independent of the array

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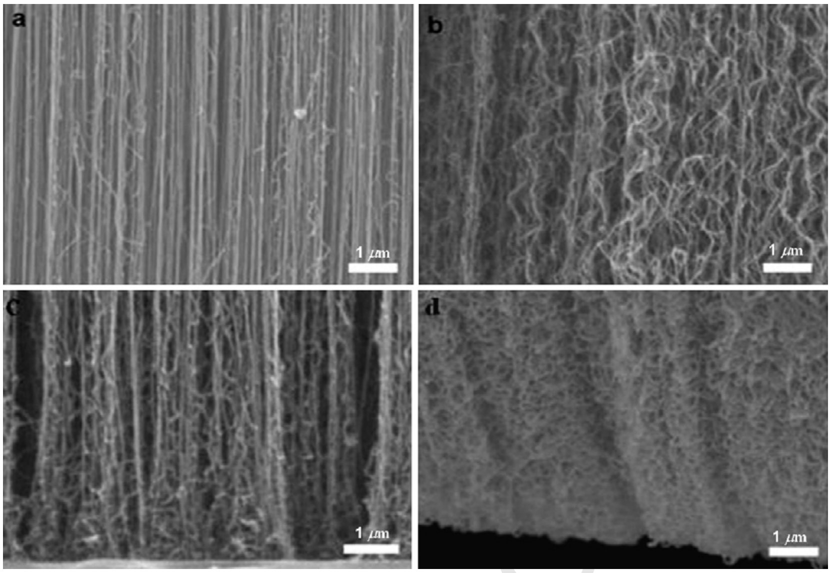

Fig. 4. Side view of middle part and the root of the CNTs array at different growth time: (a) middle part at 30 min; (b) middle part at 90 min; (c) root at 30 min; (d) root at 90 min (scale 1 μm).

height; above 740 °C it is Knudsen-diffusion-controlled and the densely packed CNT film acts as a diffusion barrier to the carbon precursor, increase in array height will hinder the diffusion of the carbon source and then leading to the decrease in growth rate [14–16,18,19]. In fact, in the Knudsen-diffusion-controlled system, the effective Knudsen diffusivity is independent of the array height if the CNTs array is uniform (r and ε are constant), which can be seen from Eq. (2). In other words, the diffusion rate at different height shall be the same from Knudsen-diffusion theory. Thus the CNT growth rate will keep unchanged with the increase of the array height in such a simplified uniform array diffusion CNT system. But our study indicated the commonly observed growth rate decrease of CNTs array was caused by the decrease of $D_{A,K,e}$ induced by shrink of r and ε. Because shrink of r and ε occurs accompany the increase in the array height, apparently it is easily mistaken that the decrease in growth rate is caused by increase of height. Just the array height increase will not influence the growth rate of CNTs array in neither reaction-rate-controlled nor Knudsen-diffusion-controlled system. Therefore, the curling of the CNTs is the essential cause of the growth rate decrease and even of the termination in the CNTs array growth.

The curling of the CNTs during the growth is an often-happened phenomenon, which is caused by the defects such as five- or seven-membered rings in the C framework instead of the normal six-membered ring defect formation on the tube walls [25,26]. As for the cause for the bent and twist of the carbon nanotubes, there have been some reports in recently [27,28]. Q1 Anastasios [27] reported that outside force in the process of produced VACNTs affects the degree of CNTs alignment greatly. Zhua et al. [28] reported that the bending and twisting of CNTs may result from both defect growth and gravity effects. In our growth system no mechanical pressure was applied on the CNT array, therefore we believe that the gravity of CNTs might be one of the possible causes leading to the distortion of the CNTs. The increasing curly shall also cause more densely CNT packing with increased growth time. Other possible factors might include the slight different growth rate of individual CNTs and the interaction (attraction, friction, etc.) among the CNTs. Thus in our base-growth model, with the growth of tubes, the array becomes thicker and thicker, the CNTs will bear bigger and bigger weight of the tubes themselves and possible forces in other forms; which then cause the CNTs get curlier and curlier.

4. Conclusion

In summary, in the synthesis of the VACNTs we found that after a period of growth time the freshly grown tubes gets more and more curly and densely packed, and the curly extent of tubes in the array increases gradually from top to the bottom. At the same time, the growth rate shows an accelerated decrease with growing time. By use of the Knudsen-diffusion theory, it can be seen that the more densely packing of CNTs due to the increased curling with growing time and that from the top to the bottom of the CNTs array will decrease the diffuse rate of the carbon source to reach the growth sites at the bottom and thus the CNT growth rate. Therefore, the curling of the CNTs is the essential cause of the CNT growth rate decrease and termination in this base-growth “curling-controlled growth model”. The increased curling from top to the bottom is proposed to be caused by the increased weight of CNTs themselves.

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