Transition between 'base' and 'tip' carbon nanofiber growth modes

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Abstract

Carbon nanofibers (CNFs) have been synthesized by catalytically controlled dc glow discharge plasma-enhanced chemical vapor deposition (PECVD). Both base-type and tip-type nanofibers have been produced on identical substrates. We have observed a sharp transition between these two growth modes by controlling the kinetics of the growth process without changing the substrate and catalyst materials. This transition is brought about by changing the parameters used in the deposition process such as the flow ratio of the carbonaceous and etchant gasses and others. This study of the initial growth stages as a function of time for both regimes provides a basis for a model of the growth mode transition. © 2002 Published by Elsevier Science B.V.

1. Introduction

Nucleation and growth of carbon nanofibers (CNFs) from catalytic particles can be a direct illustration of the concept of broken symmetry, which is one of the most important concepts of condensed matter physics and is widely used in a theory of phase transitions [1]. For a spherical catalyst particle surrounded by an isotropic environment the symmetry spontaneously breaks (from isotropic to axial) when CNF nucleation occurs. If the particle is positioned on a substrate, the symmetry of the system is already lowered, with essentially two degrees of freedom for a CNF to nucleate and grow: (1) on top of the particle, i.e., between the particle and the surrounding gas; and (2) below it, i.e., between the particle and the substrate. There are factors that can make one location preferable over the other including substrate–particle interaction [2], kinetics of the growth process, and formation of the active surfaces of the catalyst particle [3].

While the study of the catalytic growth of filamentous carbon has a 70-year history [4], interest in the growth of CNFs has resurged recently due to the

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variety of applications [5]. In particular, vertically aligned CNFs (VACNFs) produced by plasma-enhanced chemical vapor deposition (PECVD) [6–9], have numerous potential applications in scanning microscopy [10], field emission devices [11–15], nanoelectronics, and nanobiotechnology [16]. This is largely due to the ability to grow VACNFs deterministically, since the exact location, length, tip diameter, shape, and orientation all can be controlled in a large-scale synthesis process [7,17]. *Vertical alignment* in the electric field is possible for CNFs with the catalyst particle located at the end not attached to the substrate (tip-type CNF), while CNFs with the catalyst particle located at the substrate end (base-type CNF) will grow in arbitrary directions [18]. Thus, for the various potential applications it is quite important to clearly understand how to control the two CNF growth modes. Previously, it was reported that certain types of substrates lead to the base-type growth mode [8,19] whereas other types of substrates yield the tip-type growth [20–22], leading to the assumption that the growth mode is predetermined by the choice of the materials due to the particle–substrate interaction [2,23]. In this Letter we show that the growth mode can be selected by controlling the kinetics of the growth process, without changing either the substrate or catalyst material.

2. Experimental

VACNFs were grown by dc glow discharge PECVD. Continuous 10 nm thick Ni–Fe films patterned in 2 μm wide stripes were used as a catalyst, with 10 nm of Ti first deposited as a buffer layer to prevent catalyst silicide formation on Si substrates during the heating cycle. Several substrates were studied including 100 nm of Ti on Si, 100 nm of W on Si, and uncoated Si. Acetylene (C_2H_2) and ammonia (NH_3) were used as the carbon supply and etchant gases, respectively.

The synthesized VACNFs were analyzed using a Hitachi S-4700 scanning electron microscope (SEM). This microscope is equipped with two secondary electron detectors. Due to the geometry of their placement by combining the signal of these two detectors images that show compositional detail of the fibers beyond the surface morphology can produced. In this Letter this technique was used to image the shape and position of the catalyst nanoparticle within the CNF without resorting to the use of a transmission mode microscope that would require removal of the CNFs from the substrate and placement onto imaging grids.

3. Results and discussion

The SEM images of CNFs grown via tip-type and base-type growth modes are shown in Fig. 1. Both CNF growth modes were observed (for 100 nm Ti/Si) in two separate runs on *identical* substrates but under different growth conditions. The catalyst nanoparticle (brighter regions inside the CNF) was detached from the substrate (see Fig. 1a) for the smaller acetylene-to-ammonia gas flow ratio ($R(C_2H_2/NH_3) = 0.625$), while for the
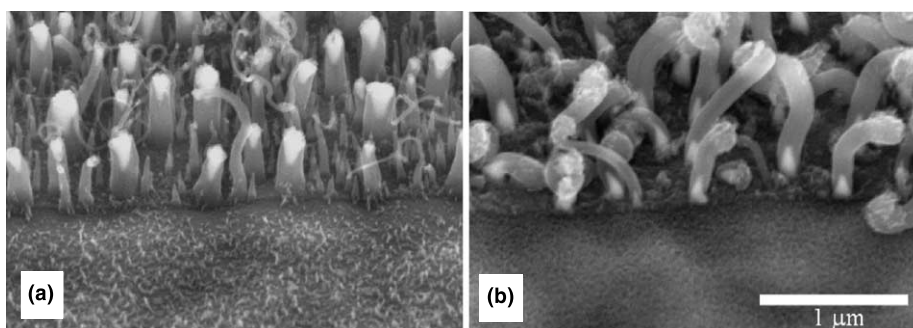

Fig. 1. Tip-type (a) and base-type (b) growth modes. All the parameters but the gas flow ratio were the same for both (a) and (b): plasma current $I = 100$ mA, bias $U = 550$ V, total pressure $P = 2$ Torr, substrate temperature $T = 750$ °C, growth time $t = 10$ min.

higher gas flow ratio of 0.688 (see Fig. 1b), the nanoparticle remained attached to the substrate. This indicates that the choice of the substrate and catalyst materials is not in itself the determining factor of the growth mode.

The following important observations can be made from a careful examination of Fig. 1:

(i) The tip-type CNFs are vertically aligned, while the base-type ones are not. The alignment is believed to be due to the interaction between the strong electric field at the substrate and the location of carbon precipitation at the base of the nanoparticle at the tip of the nanofiber as discussed in detail in our previous work [18]. Note that the presence or absence of the vertical alignment distinguishes the tip-type from the base-type CNFs here.

(ii) The catalyst nanoparticle has a conical shape with the sharper end directed into the body of the nanofiber *in both* types of the growth. It has been suggested [2] that diffusion of carbon through the nanoparticle is one of the processes involved in the CNF growth. The direction of the carbon diffusive flow has to be toward the side of the particle where the CNF forms. It also is important to note that for the base-type CNFs the elongated part of the particle follows the direction of the nanofiber precisely, that is, it bends with the nanofiber.

(iii) The substrate can be covered with a thin film of carbon. This carbon coverage is virtually zero when the acetylene-to-ammonia gas flow ratio R is sufficiently small, but increases continuously with increasing R [24]. This carbon film may obscure or completely block the entrance of free carbon into the substrate and its diffusion into and through the catalyst particle, *and thereby controls the growth mode*. A related observation is that the tips of the base-type nanofibers (Fig. 1b) have a rough ball-like shape indicating the formation of an amorphous carbon cap on the catalyst particle at the initial stages of growth. In this case, the nucleation of the CNFs is preceded by the formation of a carbon deposit around the catalyst particle, and this cap might prevent the entrance of carbon into the catalyst particle from the gaseous side, leaving carbon diffusion through the substrate as the only viable path for CNF growth.

The transition between the two growth modes as a function of acetylene content in the gas mixture is very abrupt. Fig. 2 presents SEM images for several values of the gas flow ratio: well below the transition (Fig. 2a), in the vicinity of the critical value of R, R_C, at which the transition occurs (Fig. 2b, c), and well above R_C (Fig. 2d, e). More than 90% of the CNFs are tip-type for R slightly less than R_C (Fig. 2b) and more than 90% of the CNFs are base-type for R slightly more than R_C (Fig. 2c).
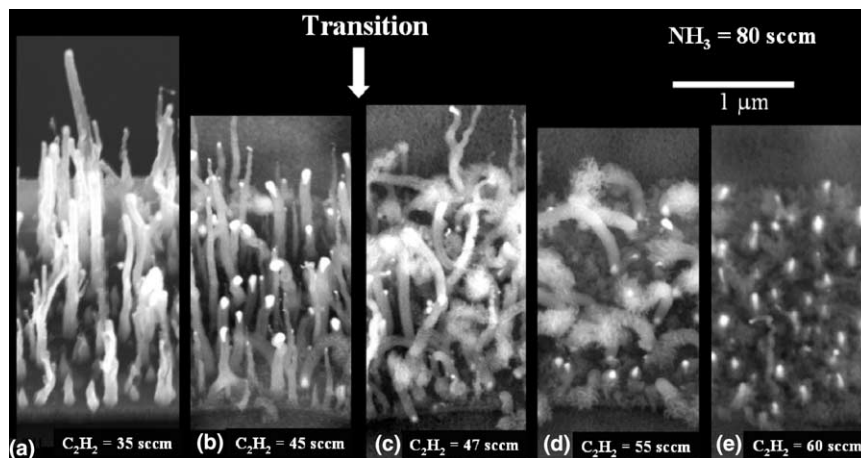

Fig. 2. Transition between growth modes as a function of the acetylene-to-ammonia gas flow ratio.

The presence of both types of nanofibers on the same sample (Fig. 2b, c) may be indicative of a local variation of the growth conditions. If the gas flow ratio is increased well above R_C, the thin film carbon coverage of the substrate increases, the size of the ball-like growth at the CNF tip increases, and the CNF growth rate decreases (Fig. 2d). Further increase of R leads to the formation of a continuous carbon film that prevents CNF growth by either mode (Fig. 2e).

We note that the value of R_C is not fixed but is a function of other growth parameters including the growth temperature, plasma power, gas pressure and the absolute value of the total gas flow. Thus, the transition can be observed along any of these axes of the multidimensional parameter space. For example, when the growth temperature is reduced

the R_C is shifted to a higher value. Consequently, variation of the growth temperature alone can bring about the growth mode transition. Also, it has been observed that increasing the plasma power had an effect similar to that of decreasing the gas flow ratio [25]. Thus, the transition could possibly occur by changing the plasma power while keeping the other parameters fixed.

A study of the time evolution of the catalyst particle and the nanofiber growth process indicates that the growth mode is determined during the first seconds of the PECVD process. SEM images of CNFs after 1 and 5 s of both base-type and tip-type growth are presented in Fig. 3, and these images demonstrate that the initial stages of the growth are crucial in determining the growth mode. The growth was initiated and terminated by
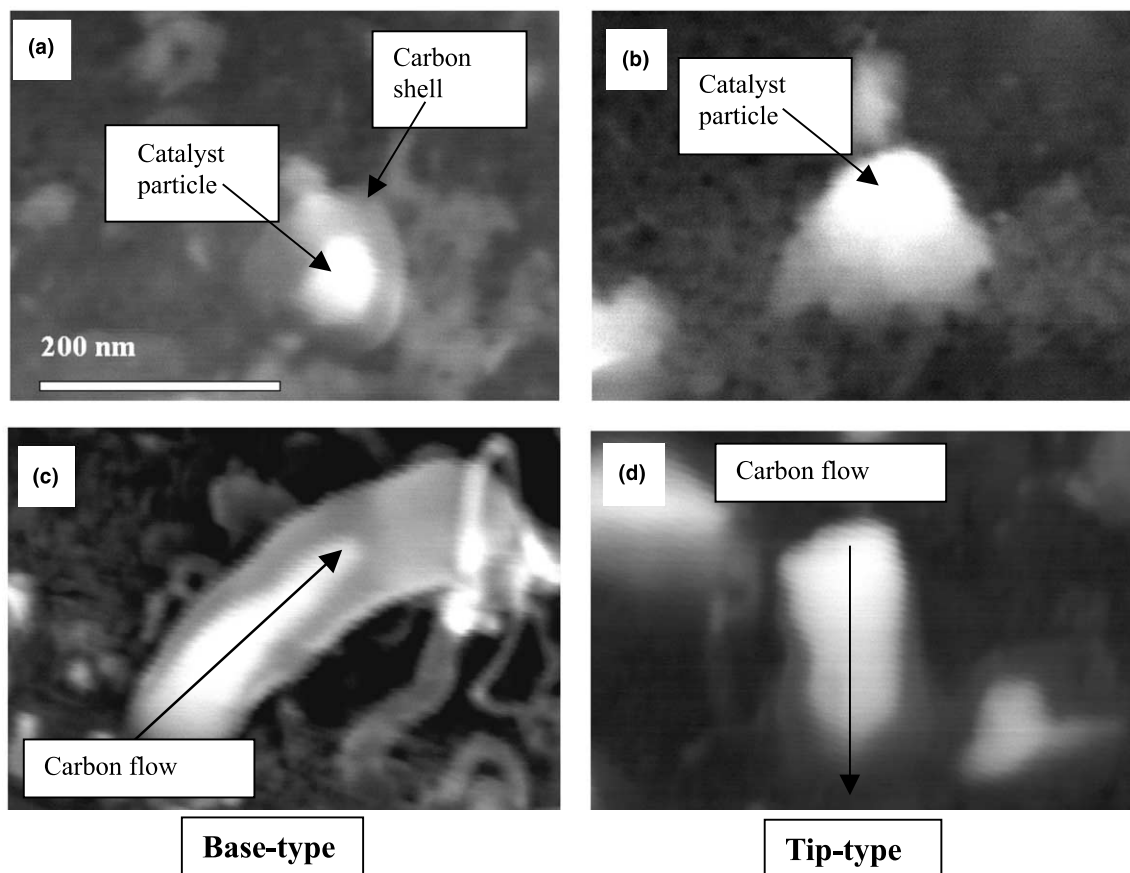

Fig. 3. Time evolution of the catalyst particle for the base- ((a) $t = 1$ s and (c) 5 s) and tip-type ((b) 1 s and (d) 5 s) growth regimes.

simply turning the glow discharge on and off, correspondingly. No additional growth was observed after the plasma was turned off. Under the base-type growth conditions, the catalyst particle becomes encapsulated in a carbon shell that prevents free carbon from reaching the catalyst particle from the top (Fig. 3a). For $R < R_C$, etching prevents formation of such a film and the top of the particle stays accessible to the free carbon (Fig. 3b). The images in Fig. 3c (base-type growth) and Fig. 3d (tip-type growth) show that the shape of the catalyst particle is determined at the very beginning of growth and reflects the *direction* of the carbon flow.

From the experimental observations presented above we propose the following three-phase model that describes how both modes of the CNF growth are established (Fig. 4). During the first phase, carbon from decomposed species diffuses into the catalyst particle through both the catalyst–gas and catalyst–substrate interfaces (Fig. 4a). During the second phase, a continuous carbon shell – the VACNF nucleation site – forms either at the catalyst–gas (Fig. 4b) or the catalyst–substrate (Fig. 4d) interface depending on whether the gas flow ratio is greater or smaller than the critical value. Formation of the carbon shell cuts off the diffusion of carbon through the interface at which it forms.

This creates a concentration gradient within the nanoparticle with very few diffusing carbon atoms at the interface where the carbon shell is formed and many diffusing carbon atoms at the interface where no carbon shell is present. The concentration gradient determines the direction of the carbon flow. During the final phase, immediately after the directed diffusive flow of carbon atoms through the catalyst nanoparticle is established, the nanofiber growth begins.

In the case of $R > R_C$, the adsorption rate of carbon atoms at the nanoparticle–gas interface due to the catalytic activity and the presence of the glow discharge is higher than the desorption rate due to etching and diffusion into the particle. As a result, the catalyst nanoparticle becomes covered with a shell of carbon from the gas side. The surrounding substrate, on the other hand, remains relatively uncovered due to the lower sticking coefficient of carbon as compared to that for the very active catalyst surface. If the adsorption rate at the nanoparticle–gas interface is higher than that for the nanoparticle/substrate interface, which is likely to occur because of the high catalytic activity of the nanoparticle and direct exposure of the former interface to the carbon species coming from the glow discharge, the carbon shell forms first at the nanoparticle–gas interface. Thus, most of the free
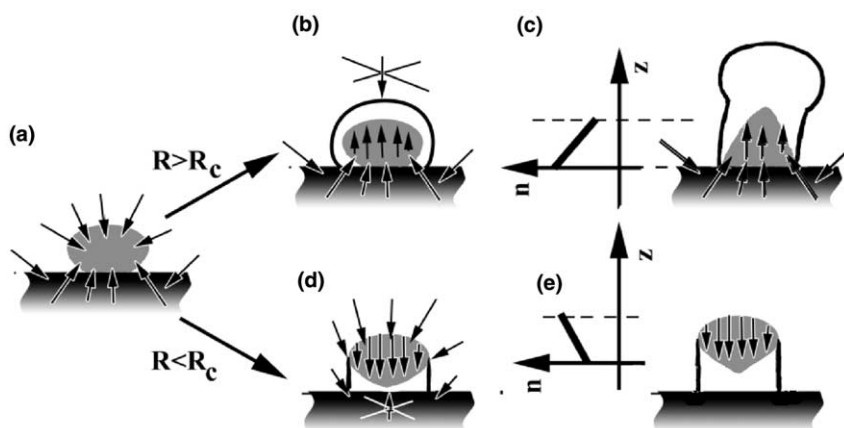

Fig. 4. Three-phase model of the mechanism for growth mode selection. (a) Phase I, the carbon diffuses into the catalytic particle from all directions; (b) and (d) phase II, a carbon shell forms on one of the interfaces and the carbon diffusive flux is established; (c) and (e) phase III, the nucleation of the fiber occurs and growth enters the steady state regime. The plots in (c) and (e) illustrate the inferred carbon concentration profile $n(z)$ inside a catalyst particle along the direction of the nanofiber growth.

carbon enters the catalyst through the nanoparticle–substrate interface (Fig. 4b) and the carbon concentration within the nanoparticle decreases with the distance away from the substrate (in Fig. 4c). Consequently, the diffusive flow, the dynamics of which prevents the formation of a continuous carbon shell at the nanoparticle–substrate interface, is created and directed away from the substrate. Thus, the base-type growth mode is established (Fig. 4c).

In the case of $R < R_C$, the etching rate at the nanoparticle/gas interface is higher. As a result, the probability of forming a continuous carbon shell at the nanoparticle–gas interface becomes smaller (and may even become virtually zero for high etching rates) than that for the nanoparticle/substrate interface. Consequently, in this case a continuous carbon layer is more likely to form first between the nanoparticle and the substrate, thus preventing carbon from entering the particle through the nanoparticle/substrate interface. This creates the carbon concentration gradient that determines the direction of the carbon diffusive flux: from the nanoparticle/gas interface toward the substrate. At this stage the nucleation of the CNF occurs and the growth enters a steady state regime (Fig. 4e). Thus, the tip-type growth mode is established.

There are two requirements on the substrate that must be satisfied for the base-type growth to occur. First, there should be a range of parameters that leaves the surface of the substrate clear of carbon film while forming a carbon cap on the catalyst particle. Second, the diffusion coefficient for carbon in the substrate material must be sufficiently large to support the growth of CNFs. We have found such conditions for a thick layer of Ti or W–Ti alloy on a Si substrate but have not observed such a behavior on Si with a thin Ti buffer layer, that is, only the tip-type growth mode was observed on this substrate. We note that prior to formation of the actual catalyst nanoparticles [7] the thin film catalyst can react with the substrate and form a surface layer, such as the catalyst/buffer layer alloy, around the nanoparticle's location. This may be the path for delivering free carbon atoms to the nanoparticle/substrate interface.

The change in the probability of CNF nucleation at a specific interface of the catalyst particle can be a universal way to control the CNF growth mode. We showed that this change is caused by the processes involved in PECVD. The results presented here indicate that the CNF growth mode is not solely determined by the particle–substrate interaction but is also controlled by the kinetic parameters of the growth process. The most general and crucial criteria for establishing a growth mode is whether a particular interface has a higher or lower probability to become a nucleation site for the CNF growth. This probability can be determined in turn by a number of factors including the particle–substrate interaction, carbon diffusion through the substrate, as well as other parameters specific to the growth method such as plasma etching with NH_3.

Acknowledgements

References

[1] M. LeBellac, Quantum and Statistical Field Theory, Clarendon Press, Oxford, 1991.
[2] R.T.K. Baker, Carbon 27 (1989) 315.
[3] I. Alstrup, J. Catal. 109 (1988) 241.
[4] F.J. Dent, J. Chem. Soc. 2 (1929) 1903.

[5] A. Cassell, L. Delzeit, C. Nguyen, et al., J. Phys. Iv 11 (2001) 401.

[6] Z.F. Ren, Z.P. Huang, J.W. Xu, et al., Science 282 (1998) 1105.

[7] V.I. Merkulov, D.H. Lowndes, Y.Y. Wei, et al., Appl. Phys. Lett. 76 (2000) 3555.

[8] C. Bower, O. Zhou, W. Zhu, et al., Appl. Phys. Lett. 77 (2000) 2767.

[9] M. Chhowala, K.B.K. Teo, C. Ducati, et al., J. Appl. Phys. 90 (2001) 5308.

[10] C.V. Nguyen, K.J. Chao, R.M.D. Stevens, et al., Nanotechnology 12 (2001) 363.

[11] H. Murakami, M. Hirakawa, C. Tanaka, et al., Appl. Phys. Lett. 76 (2000) 1776.

[12] M.A. Guillorn, M.L. Simpson, G.J. Bordonaro, et al., J. Vac. Sci. Technol. B 19 (2001) 573.

[13] V.I. Merkulov, D.H. Lowndes, L.R. Baylor, J. Appl. Phys. 89 (2001) 1933.

[14] M.A. Guillorn, V.I. Merkulov, A.V. Melechko, et al., Appl. Phys. Lett. 79 (2001) 3506.

[15] G. Pirio, P. Legagneux, D. Pribat, et al., Nanotechnology 13 (2001) 1.

[16] M.A. Guillorn, T.E. McKnight, A.V. Melechko, et al., J. Appl. Phys. 91 (2002) 3824.

[17] V.I. Merkulov, M.A. Guillorn, D.H. Lowndes, et al., Appl. Phys. Lett. 79 (2001) 1178.

[18] V.I. Merkulov, A.V. Melechko, M.A. Guillorn, et al., Appl. Phys. Lett. 79 (2001) 2970.

[19] C.J. Lee, J. Park, Appl. Phys. Lett. 77 (2000) 3397.

[20] R.T.K. Baker, J.J. Chludzinski, J. Phys. Chem. 90 (1986) 4734.

[21] M. Tanemura, K. Iwata, K. Takahashi, et al., J. Appl. Phys. 90 (2001) 1529.

[22] H. Cui, O. Zhou, B.R. Stoner, J. Appl. Phys. 88 (2000) 6072.

[23] R.T.K. Baker, J. Adhesion 52 (1995) 13.

[24] K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, et al., Appl. Phys. Lett. 79 (2001) 1534.

[25] V.I. Merkulov, D.K. Hensley, A.V. Melechko, et al., submitted to publication.