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Growth rate of plasma-synthesized vertically aligned carbon nanofibers

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Abstract

Vertically aligned carbon nanofibers (VACNFs) were synthesized by direct-current plasma enhanced chemical vapor deposition using acetylene and ammonia as the gas source. The mechanisms responsible for changing the nanofiber growth rate were studied and phenomenological models are proposed. The feedstock for VACNF growth is suggested to consist mainly of radicals formed in the plasma and not the unexcited acetylene gas molecules. The growth rate is shown to increase dramatically by changing the radical transport mechanism from diffusive to forced flow, which was accomplished by increasing the gas flow in the direction perpendicular to the substrate. © 2002 Elsevier Science B.V. All rights reserved.

Vertically aligned carbon nanofibers (VACNFs) prepared by plasma enhanced chemical vapor deposition (PECVD) [1–7] are an important material for various applications including electron field emitters [8,9], tips for scanning microscopy [10], and biological probes [11], among others. Despite the morphological similarity, the structure of VACNFs, which are composed of concentric graphene funnels and cones, is quite different from that of carbon nanotubes (CNTs), which consist of concentric graphene cylinders. To date, the crucial advantage of using PECVD-grown VACNFs is the ability to synthesize them *deterministically* [12], i.e., their location, height, tip and base diameters [12–14], and, to some extent, shape [15], orientation [10], and chemical composition [2,16] can all be controlled, and mechanically and electrically reliable contact to the substrate can be established. It has been suggested [17] that in PECVD only VACNFs grown from the tip are aligned specifically due to the presence of the plasma electric field in the growth process, whereas VACNFs grown

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from the base are aligned mainly due to the crowding effect. Consequently, in the case of the *base-type* growth, deterministic synthesis of *isolated* VACNFs is expected to be rather difficult.

The ability to control the VACNF growth rate is an important practical aspect of the synthesis process because some applications require high growth rates, whereas others would benefit from a lower growth rate but a high degree of uniformity and control over the final VACNF length. Thus understanding the factors that determine the growth rate is essential not only from the fundamental science point of view, but also from the point of view of practical applications. In the present letter we address this issue and illuminate the mechanisms underlying the VACNF growth rate. We also demonstrate how the growth rate can be drastically altered in a controllable way by changing some of the growth parameters.

VACNFs were prepared using dc plasma-enhanced chemical vapor deposition (PECVD) in a vacuum chamber evacuated to a base pressure of $\sim 1 \times 10^{-5}$ Torr. Nickel (Ni) was used as the catalyst and n-type (100)-oriented Si wafers were utilized as the substrates. 10 nm thick catalyst thin films evaporated directly onto Si substrates were used to form "forests" of chaotically placed CNFs. A thin film of native oxide on the Si substrates served as a buffer layer to prevent the catalyst silicide formation at elevated growth temperatures ($\sim$700 °C). For synthesis of individual CNFs, 10 nm thick catalyst dots of 100 nm in diameter with a 10 nm thick Ti buffer layer were produced using electron beam lithography and metal evaporation. The plasma current was 150 mA for VACNF forests and 120 mA for individual VACNFs, and the discharge voltage was $\sim$550–570 V. A mixture of acetylene (C_2H_2) and ammonia (NH_3) was used as the gas source, and the total pressure was $\sim$3 Torr. The NH_3 flow was kept constant at 80 sccm and the C_2H_2 was varied to produce different gas mixtures. To obtain different gas flows towards the sample surface, a showerhead located $\sim$6 cm above the substrate holder and two nozzles with $\sim$1 mm and $\sim$5 mm diameter orifices located $\sim$1.5 cm above the sample were used. The substrates were heated directly by placing them on a heater plate (the cathode of the plasma discharge). A simplified schematic of the experimental setup is shown in Fig. 1. Post-growth imaging of VACNFs was carried out using a Hitachi S4700 high-resolution scanning electron microscope (SEM).

In conventional thermal CVD the growth of carbon nanofibers/nanotubes occurs in three main steps [18]: (i) decomposition of the carbonaceous gas molecules at the surface of the catalyst nanoparticle, (ii) diffusion of the resultant carbon atoms through the catalyst nanoparticle from the nanoparticle/gas interface towards the nanoparticle/nanofiber interface due to the concentration gradient, and (iii) precipitation of carbon atoms at the nanoparticle/nanofiber interface. Each of these steps can be a complex process by itself [19,20] and the whole picture is not completely understood, mainly due to the difficulty of conducting imaging and surface analysis in situ during the growth. In thermal CVD, the carbon feedstock is the molecules of the carbonaceous gas used in the growth process. The growth rate is determined by all of the three steps, but under typical growth conditions appears to be diffusion limited as suggested by the equality of the activation energies for the nanofiber growth rate and for the diffusion of carbon atoms through the catalyst [21]. This is in contrast to PECVD growth, in which case the activation energies were found to be different [3] and the growth rate was suggested to be limited by the supply of carbon from the gas phase [2].

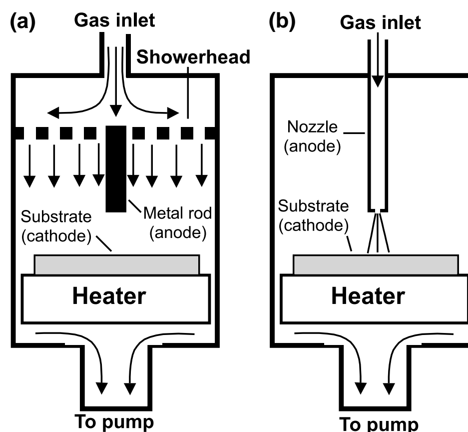

Fig. 1. A schematic representation of two experimental setups for PECVD growth employing (a) a showerhead and (b) a nozzle.

Studies by our group [2] as well as other researchers [3,22] revealed that the VACNF growth rate depends quite strongly upon the gas mixture and plasma power used in the PECVD process. This was attributed to changes in the chemical composition of the excited gas species [2]. These species include (i) simple radicals created in the plasma as a result of direct dissociation of C_2H_2 and NH_3 molecules and (ii) larger radicals that form due to collision and consequent attachment of radicals to each other as they move towards the substrate. It was suggested that changing the gas mixture or plasma power changes the chemical distribution of the excited species. Since different species are expected to have different decomposition rates at the catalyst surface, the nanofiber growth rate also changes. The fact that *reduction* of the C_2H_2 content resulted in a several-fold *increase* of the growth rate [2,3] as well as a dramatic increase of the nitrogen content within the nanofibers [2] strongly suggests that the growth occurs mainly due to the species created in the plasma, not due to unexcited C_2H_2 molecules.

In a typical plasma, ions constitute only 1 part-per-million of the total number of the gas species, whereas the fraction of neutral radicals is of the order of 1% [23]. Therefore, the growth is essentially due to the neutral radicals (and species that form due to mutual collisions of these radicals as they move towards the substrate across the dark space). Since the neutral radicals constitute only a small fraction of the total gas molecules, the relatively low (of the order of 100 nm/min) growth rate for VACNFs as compared to that of purely thermal CVD, which is of the order of μm/min, also is consistent with the idea of the growth occurring mostly from the radicals.

Our further studies also suggest that the presence of the radicals from the plasma is critical for the growth of VACNFs. We find that VACNF growth appears to cease immediately after the plasma is turned off. We have already demonstrated that pre-grown VACNFs can be re-grown further if loaded back into the growth chamber and exposed to a plasma with the standard parameters required for the VACNF growth [14]. However, we find that if the plasma is not present, i.e., the process is purely thermal, the re-growth of VACNFs does not occur. Fig. 2 shows the SEM image of a sample for which VACNFs were first grown using a plasma, then the plasma was turned off, the NH_3 flow was stopped, and C_2H_2 was flowed over the sample that was kept at the same high temperature as during the PECVD part of the growth (~700 °C). During the purely thermal phase, the VACNFs did not seem to increase in length. However, interestingly enough, very long thin non-aligned CNFs/CNTs that were not present during the PECVD part of the growth were produced. The non-aligned CNFs seemed to originate from the bases of VACNF, where perhaps some of the catalyst was still left. This demonstrates that the catalytic activities are quite different for the base- and tip-type growth modes. While the base-type catalytic growth can produce CNFs in the purely thermal process, the tip-type growth, for our growth conditions, requires the presence of radicals. The inability to re-grow VACNFs using only thermal CVD supports the idea of the feedstock for the VACNF growth consisting mainly of radicals and not C_2H_2 molecules.

We note, however, that there is another possible scenario for VACNFs not being able to re-grow by purely thermal CVD. A carbon shell may form

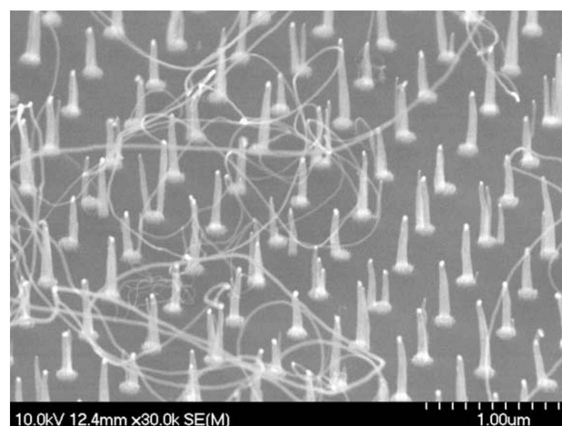

Fig. 2. SEM image of an array of VACNFs grown by PECVD for 5 min and of randomly oriented CNFs/CNTs produced after the plasma was turned off and the growth run continued via purely thermal CVD (~700 °C). The thermal growth was conducted at ~5 Torr of C_2H_2 for 10 min.

around the catalyst nanoparticles sitting at the tips of VACNFs after the plasma is turned off, which prevents decomposition of carbonaceous species at the catalyst surface and consequently the VACNF growth. In fact, a thin carbon shell covering catalyst nanoparticles is indeed observed by transmission electron microscopy (TEM) [3,12]. However, it is quite likely that the shell is formed due to precipitation of carbon from the particle when the sample is cooled down to room temperature for TEM measurements. This makes the TEM evidence inconclusive. More work is underway to elucidate this issue more completely.

As was suggested previously, the VACNF growth rate is proportional to the number of radicals impinging on the catalyst surface and to the decomposition rate of these radicals at the surface. (Here, by decomposition we mean a complex process involving adsorption and fragmentation of the radicals at the catalyst surface as well as desorption of the reaction byproducts from the surface). Different types of radicals are expected to have different decomposition rates. One way to increase the growth rate is to change the gas mixture and plasma power to create more radicals or to shift the radical distribution towards those with higher decomposition rates. We note that simply increasing the C_2H_2 content increases the growth rate only up to a certain value, which is still substantially lower than that for thermal CVD, after which the growth rate begins to decrease [3]. We believe this happens because above a critical C_2H_2 content, which depends upon a particular set of experimental conditions such as plasma power, pressure, temperature, etc., more radicals with lower decomposition rates and less radicals with higher decomposition rates are produced. Moreover, the radicals with lower decomposition rate may start forming a shell encapsulating the catalyst particle, thereby limiting the carbon supply, and can also permanently attach to the substrate surface. This results in reducing the growth rate and, if the C_2H_2 content is increased even further, leads to the formation of a thick carbon film covering the entire substrate, which has been experimentally observed in several studies [13,16]. Since some applications may require very long VACNFs, it is highly desirable to develop controllable ways to further increase the growth rate. In the present work we demonstrate an additional way to boost the growth rate of VACNFs, namely by increasing the gas flow directed *towards* the substrate.

If the feedstock for VACNF growth is mainly carbon-containing radicals, then the growth rate will be governed by the diffusion of these radicals from the plasma across the dark space to the catalyst particle surface. The growth rate may thus be approximately estimated from the radical flux F as follows: $F = -D(\mathrm{d}C/\mathrm{d}z)$, where D is the diffusion coefficient of radicals in the gas and $\mathrm{d}C/\mathrm{d}z$ is the concentration gradient of the carbon containing radicals in a direction z perpendicular to the substrate [23]. For our growth parameters, namely the gas density of the order of 10^{16} molecules/cm^3, and therefore the neutral radical density of the order of $\sim 10^{14}$ cm^{-3}, the dark space width of a few mm, and D of the order of several tens of cm^2/sec (a typical diffusion coefficient for our pressure range) [23], the growth rate can be estimated as several μm/hr. This agrees quite well with the experimentally observed nominal growth rate in our system, which is of the order of 100 nm/min.

We note that some researchers report growth rates for PECVD of VACNFs that are noticeably higher than that achieved in our system under nominal growth conditions. We believe this occurs because of the different growth parameters and/or experimental setups used by other researchers. For example, Huang et al. [22] used a hot-filament and perhaps a higher gas pressure (up to 20 Torr). In the case of Delzeit et al. [4], Bower et al. [6], and Cui et al. [7] inductively coupled and microwave plasmas, different gas mixtures, and higher gas pressures were utilized. Also, in [6,7] the growth was base-type, which is quite different from the tip-type growth (in [4] it was both base- and tip-type). Finally, even though Chhowalla et al. [3] employed growth conditions quite similar to ours, the difference in the growth rate could result from a different reactor setup, in particular different anode size and geometry; PECVD is notoriously sensitive to reactor configuration.

One way to relax the limit for the VACNF growth rate, imposed by the process of radical diffusion towards the substrate, is to change the

radical transport mechanism from diffusive to forced flow by applying a pressure gradient perpendicular to the substrate surface to force more radicals to impinge on the surface [23]. The radical flux in this case will be given by $F = Cv$, where C is the radical concentration and v is an average velocity towards the substrate. Thus, by increasing the gas flow and therefore the radical velocity one can expect to achieve substantial increase in the VACNF growth rate.

In our system, increasing the gas flow was accomplished by replacing a showerhead (Fig. 1a) with a capillary-type gas nozzle with a variable orifice (Fig. 1b). The experiments were carried out with two orifice diameters: ~1 mm and ~5 mm. Fig. 3 shows how the growth rate is affected by replacing the showerhead with the 5 mm and then with the 1 mm nozzle. One can see that the maximum growth rates increase significantly as one shifts to smaller nozzle sizes and consequently higher local gas flows. The maximum growth rate for the 1 mm nozzle is more than two times higher than that for the 5 mm nozzle and about five times higher than that for the showerhead.

Of course, the gas chemistry, i.e., mutual interactions among the gas species, also is a very important factor affecting the growth rate. This is demonstrated in Fig. 4, which shows the growth rate for 1 mm and 5 mm nozzles as a function of the C_2H_2/NH_3 gas ratio. Clearly, the growth rates

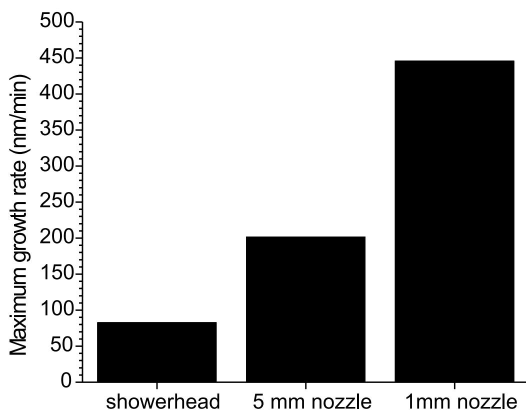

Fig. 3. Maximum VACNF growth rates for different experimental setups and therefore different gas flows to the substrate surface.

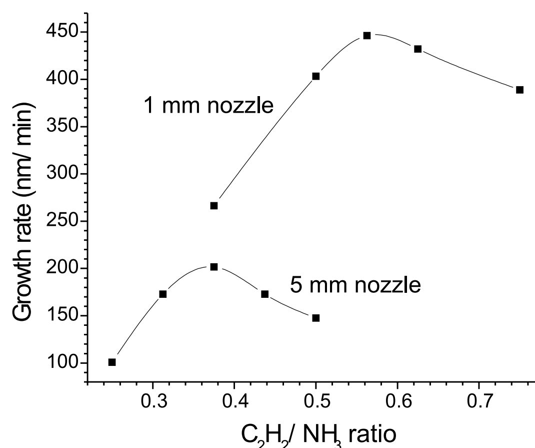

Fig. 4. VACNF growth rate as a function of C_2H_2/NH_3 gas ratio for two nozzle diameters of ~1 mm (upper curve) and ~5 mm (lower curve).

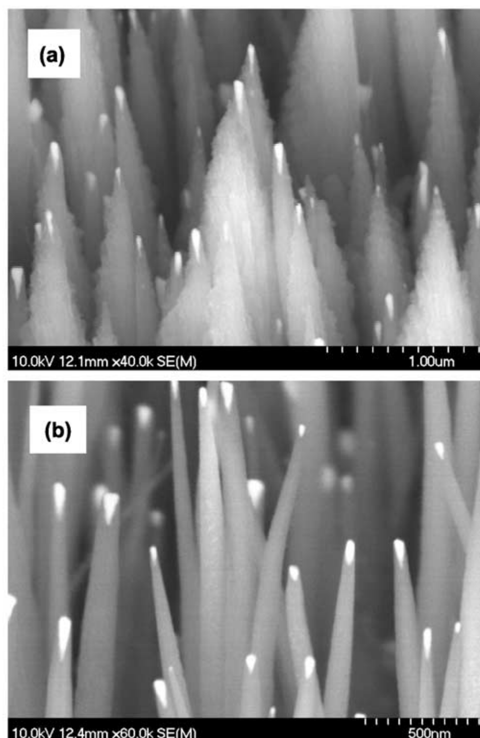

Fig. 5. SEM images of dense forests of (a) highly conical and (b) substantially less conical VACNFs prepared using 1 mm diameter nozzle and the C_2H_2/NH_3 gas ratios of ~0.75 and 0.56, respectively.

in both cases depend strongly upon the gas mixture and exhibit a well-defined maximum. Moreover, the maximum growth rates for the two nozzle sizes correspond to different values of the C_2H_2/NH_3 gas ratio. We believe this occurs because orifices with different diameters produce different gas flow velocities, which affects the interaction among the gas species within the flow. This results in modification of the chemical composition of the resultant species that reach the sample surface and consequently changes the growth rate.

An interesting consequence of the high gas flow during the growth is the fact that highly conical structures can be produced even for *dense* forests of VACNFs. We have shown recently that isolated VACNFs tend to assume conical shape during the growth due to reactive species emerging for the discharge and attaching to the sidewalls of the nanofibers [15,16]. In contrast, dense VACNF forests nominally consist of essentially cylindrical nanofibers due to the shielding of the sidewalls by neighboring VACNFs [16]. However, if the velocity of the incoming radicals is high enough, they will be able to penetrate the inter-fiber space for even densely-spaced VACNFs and precipitate at the sidewalls thus forming conical structures, as shown in Fig. 5a. Similar to our previous observations, the degree of conicity can be modified by changing the gas mixture. Fig. 5b shows a VACNF forest grown at a lower C_2H_2/NH_3 gas ratio as compared to that used in the growth run depicted in Fig. 5a. Lowering the C_2H_2 content clearly results in VACNFs becoming substantially more cylindrical. Again, this emphasizes the importance of the plasma chemistry in determining the resultant properties of VACNF and demonstrates the possibility of controlling these properties by changing the growth parameters.

To conclude, we have shown that increasing the gas flow toward the substrate by using small-diameter gas inlets can drastically increase the VACNF growth rate. We believe that substantially higher growth rates may be achieved by using even smaller-diameter orifices and therefore higher effective gas flows. Despite the fact that using nozzles limits the deposition area, employing multiple nozzles can solve this problem and should be especially effective if only parts of the substrate need to be covered with VACNFs. Alternatively, a showerhead that has small holes and is located close to the substrate surface (which is analogous to using multiple nozzles) can be used for large-area depositions.

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