Effects of spatial separation on the growth of vertically aligned carbon nanofibers produced by plasma-enhanced chemical vapor deposition

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Vertically aligned carbon nanofibers (VACNFs) with vastly different spacing were grown by catalytically controlled dc glow discharge chemical vapor deposition. Both densely packed VACNFs and essentially isolated VACNFs were studied using scanning electron microscopy and x-ray energy dispersive spectroscopy. The morphology and chemical composition of isolated VACNFs were found to have a strong dependence upon the growth conditions, in particular on the C_2H_2 /NH_3 gas mixture used. This is attributed to the sidewalls of isolated VACNFs being exposed to reactive species during growth. In contrast, the sidewalls of densely packed VACNFs were shielded by the neighboring VACNFs, so that their growth occurred mainly in the vertical direction, by diffusion of carbon through the catalyst nanoparticle and subsequent precipitation at the nanofiber/nanoparticle interface. These striking differences in the growth process result in the formation of flattened carbon nanostructures (carbon nanotriangles) and also are quite important for the realization of VACNF-based devices. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1433905]

Vertically aligned carbon nanofibers (VACNFs) produced by plasma-enhanced chemical vapor deposition (PECVD)[1–4] are a material that has numerous potential applications in scanning microscopy, field emission devices,[5–7] nanoelectronics, and biology. Both densely packed and well-separated (isolated) VACNFs can be produced. For example, using a thin metal film (e.g., Ni) as a catalyst results in growth of densely packed forests of randomly positioned VACNFs. On the other hand, electron beam lithography (EBL) can be used to pattern well-separated catalyst dots leading to the growth of essentially isolated VACNFs,[2,8] i.e., the growth of an individual VACNF is not influenced by neighboring VACNFs. Changing the growth conditions, such as the discharge power, gas mixture, temperature, etc., have been found to affect the properties of the resultant VACNFs.[4,9,10] In this letter we report the results of studies that reveal significant differences between the growth of densely and sparsely packed VACNFs. The spacing among VACNFs is shown to have a profound effect on their properties because of the quasi-two-dimensional nature of VACNF growth[10] combined with mechanical and perhaps electrostatic shielding effects. These results are quite important for potential practical applications as well as fundamental understanding of the growth process.

VACNFs were grown by dc glow discharge PECVD. Continuous Ni thin films and 100-nm-diameter Ni dots were used as a catalyst. In the case of Ni thin films, 100 nm of W or W–Ti alloy was used as a buffer layer on the Si substrate to prevent the formation of Ni silicide. 10 nm of Ti was used as the buffer layer for the patterned Ni dots. The Ni thickness was 10 nm for all samples. Acetylene (C_2H_2) and ammonia (NH_3) were used as carbon source and etchant gases. In some cases, helium was used as a buffer gas. The growth temperature was ~700 °C. The synthesized VACNFs were analyzed using Hitachi S4700 and Philips XL30/FEG scanning electron microscopes equipped with x-ray energy dispersive spectroscopy (EDS) detectors. More details on the apparatus and experimental conditions can be found elsewhere.[2,5,10]

We find that the morphology of well-separated VACNFs has a strong dependence on the gas mixture used in PECVD. Figure 1 shows how the shape of isolated VACNFs varied as
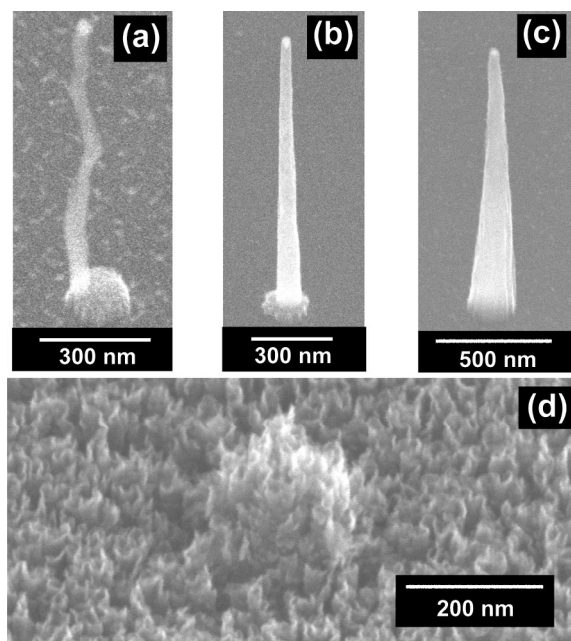

FIG. 1. SEM images of isolated carbon nanofibers grown with C_2H_2 /NH_3 ratios of (a) 0.38, (b) 0.50, (c) 0.59, and (d) 0.75. The ammonia flow for all samples was 80 sccm and the total pressure was ~2.5 Torr. The discharge current and voltage were 100 mA and 555–575 V, respectively. All images were taken using a Hitachi S4700 SEM at 10 kV and a tilt angle of 45°.

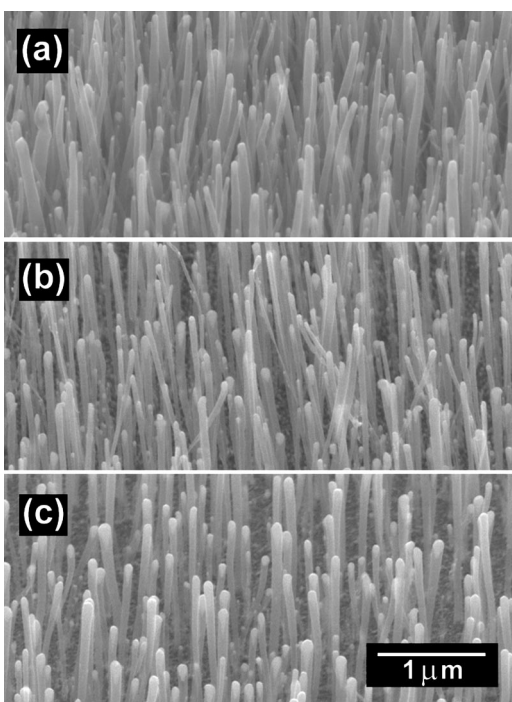[a]Electronic mail: merkulovvi@ornl.gov

FIG. 2. SEM images of forests of densely spaced carbon nanofibers grown with C_2H_2/NH_3 ratios of (a) 0.50, (b) 0.25, and (c) 0.15. A mixture of ammonia (10%) and helium (90%) with a flow of 200 sccm was kept constant for all samples, and the total pressure was ~6 Torr. The discharge current was 50 mA and the voltage was 480–550 V. All images were taken using a Phillips XL30 SEM at 15 kV and a tilt angle of 50°.
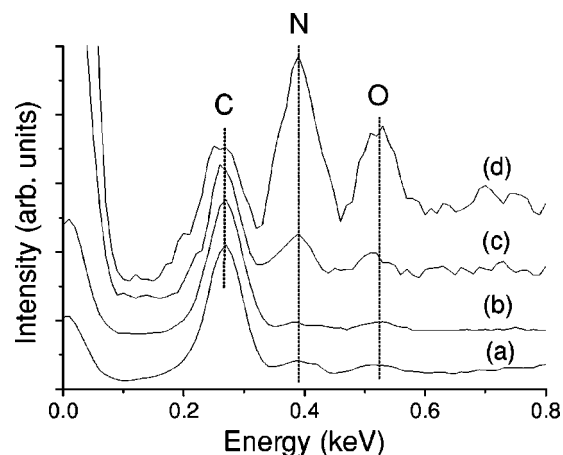

FIG. 3. EDS spectra for (a) a dense VACNF forest grown with a C_2H_2/NH_3 ratio of 0.15 and for isolated VACNFs grown with C_2H_2/NH_3 ratios of (b) 0.59, (c) 0.46, and (d) 0.38. All spectra are normalized to the C peak.

a function of the C_2H_2/NH_3 ratio. With relatively low acetylene content, isolated VACNFs with kinks and significantly damaged walls resulted [Fig. 1(a)]. With increasing acetylene content, the VACNFs became much straighter with significantly less damage to the walls [Figs. 1(b) and 1(c)]. Furthermore, the nanofibers assumed a conical shape as we reported previously.[10] Finally, if the acetylene content is increased even further, a continuous nanostructured carbon film, rather than VACNFs, was formed [Fig. 1(d)].

If a continuous thin film Ni catalyst was used, high acetylene content once again produced a continuous carbon film. However, when the acetylene content was reduced below a threshold value, essentially cylindrical, densely packed VACNFs were obtained [Fig. 2(a)]. In striking contrast to isolated VACNFs, further reduction of the C_2H_2/NH_3 ratio had no significant effect on the morphology of individual VACNFs in a densely packed array [Figs. 2(b) and 2(c)]. While a careful examination of the images in Fig. 2 reveals a subtle change in VACNF shape as a function of C_2H_2/NH_3 ratio (namely, slightly wider bases with higher C_2H_2/NH_3 ratio [Fig. 2(a)] and slightly narrower bases with lower C_2H_2/NH_3 ratio [Fig. 2(c)]), this effect is quite small as compared that for isolated VACNFs.

EDS was utilized to study the chemical composition of VACNFs. We found that the nitrogen content of isolated VACNFs was significantly increased as the acetylene content of the gas mixture was decreased, as shown in Figs. 3(b)–3(d). When the C_2H_2/NH_3 ratio was low [Fig. 3(d)], the nanofibers appeared damaged and, although still vertically oriented, exhibited kinks as shown in Fig. 1(a). In contrast, the C_2H_2/NH_3 ratio had little effect on the nitrogen content of densely packed VACNFs. Even very high relative concen-

trations of ammonia resulted in quite small amounts of nitrogen in the nanofibers [Fig. 3(a)]. We could also observe an oxygen peak in the EDS spectra, which may originate either from water adsorbed on the VACNF surface after growth or from oxygen incorporated into the films due to water coming off of the chamber walls during the PECVD process.

The significant differences in morphology and chemical composition between densely packed and isolated VACNFs can be explained as follows. During PECVD growth, isolated VACNFs have their sidewalls exposed to the reactive species emanating from the glow discharge. The reactive species are responsible for two competing processes: etching and adsorption. The balance of these processes is controlled by the C_2H_2/NH_3 ratio. If there is a slight excess of acetylene, i.e., adsorption exceeds etching, additional carbon precipitates at the walls of VACNFs leading to the formation of carbon nanocones rather than nanocylinders.[10] However, as the C_2H_2/NH_3 ratio is reduced (the relative ammonia content is increased) extra etchant species begin to attack the walls of the nanofibers, which leads to a damaged structure such as that shown in Fig. 1(a). At the same time, substantial nitrogen incorporation occurs in the nanofibers, although the exact mechanism of this incorporation is not completely understood. Possible mechanisms include continuous sorption/implantation of atomic nitrogen and/or the attachment of nitrogen-containing carbon species onto the VACNFs. *In situ* spectroscopy studies during PECVD would be useful to elucidate the nitrogen-containing species present and the exact mechanism of nitrogen incorporation.

For densely packed VACNFs, the growth process is quite different in that the sidewalls of VACNFs are shielded by neighboring VACNFs. As a result, ionized or neutral reactive species cannot easily reach the outer walls of the VACNFs and consequently their growth occurs mainly via C diffusion through the catalyst nanoparticle (riding upward on the nanofiber tip) and precipitation of C at the nanoparticle base.[11] This results in essentially cylindrical VACNFs. Nitrogen incorporation is also quite small in this case. We note that in addition to purely mechanical shielding by neighboring VACNFs, electrostatic shielding is also present if the separation among VACNFs becomes small compared to their height.[5,12] As a result, the equipotential surface is only gently
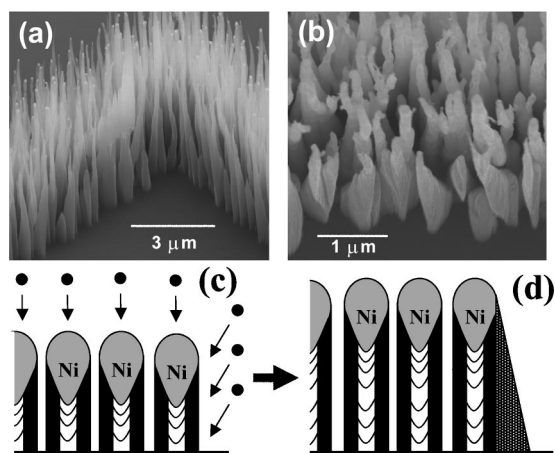
FIG. 4. SEM images of carbon nanotriangles taken at (a) 45° and (b) 30° tilt angle. A schematic representation of nanotriangle formation is shown at (c) the beginning and (d) near the end of growth.

undulating above the tips of closely spaced VACNFs and the electric field at the tips is significantly lower than that for isolated VACNFs, which also may lead to substantial changes in the growth process.

An interesting consequence of the differences between the growth of densely packed and isolated VACNFs is the formation of flat carbon nanostructures at the boundary of a dense VACNF forest, as shown in Fig. 4. While the walls of the inner VACNFs are fully shielded by their neighbors, the outward-facing walls of VACNFs on the boundary are exposed to the incoming carbon species. However, in contrast to completely isolated VACNFs, at the forest boundary only a part of each VACNF wall is exposed. As a result, the lateral growth occurs only in one direction yielding the formation of flat carbon nanostructures (right nanotriangles), rather than the nanocones that result from isotropic growth over the entire wall surface.[10]

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