Corn-shape carbon nanofibers with dense graphite synthesized by microwave plasma-enhanced chemical vapor deposition

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Corn-shape carbon nanofibers (CCNFs) with metal-free tips have been synthesized by a microwave plasma-enhanced chemical-vapor deposition method using CH_4 and H_2 gasses. The CCNFs were grown on $Ni/SiO_2/Si$ and Ni/Mo mesh substrates using a bias-enhanced growth method, and they were analyzed by scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy. The cones are composed of cylindrical pure graphite sheets, and have nanometer-sized tips and roots. The tips' apex angles of CCNFs have cone angles of 20°, 39°, and 60° depending on the growth conditions such as substrate temperature. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1666998]

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have recently received large attention for industrial applications, since a new generation of nanoscopic science and engineering is fully dependent on them.[1] Both theoretical and experimental results revealed that these nanostructures could lead to further improvements in electronic devices, in particular. Both CNTs and CNFs can be fabricated by various types of plasma-enhanced chemical vapor deposition (PECVD) method.[2] The plasma produced CNTs, with shapes being straight or corn-shape (or conical) depending on growth parameters, consist of tubular graphite walls.

Recently, we have produced the corn-shape carbon nanofibers (CCNFs) with cylindrical graphene cones with small cylindrical structure by a bias-enhanced microwave PECVD (BE-MPECVD) method. Despite the morphological similarity, the structure of CCNFs with concentric graphene cones and funnels was quite different from that of CNTs with concentric graphene cylinders. Since corn-shape structure provides higher mechanical and thermal stability than a narrow cylinder,[3] therefore, CCNFs have potential for use not only as FE device but as a rigid tip for scanning probe microscopy. Tsai *et al.* reported the carbon nanotips with a large aspect ratio grown on Pt films by a PECVD method without discussing the structures of carbon nanotips, and they showed that carbon nanotips had a solid body made of graphite with good field emission property.[4]

Here we report the detailed characterization of BE-MPECVD grown CCNFs by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and Raman spectroscopy, and propose the growth model of them.

The BE-MPECVD system used to grow the CCNFs consists of a 2.45 GHz, 1.5 kW microwave power supply with a rectangular waveguide that is coupled to a stainless cylindrical growth chamber and molybdenum substrate holder with a radio-frequency graphite heater that allows control of the substrate temperature independent of the plasma power. A negative bias voltage of 450 V was applied to the substrate holder. To obtain an effective substrate bias, a Ni/Si substrate or a Ni/Mo TEM mesh mounted on Si substrate was surrounded by a quartz shield to conducting parts of substrate holder. Prior to growth, a thin film of Ni metal was deposited on the thin barrier layer of SiO_2 formed on Si surface to prevent the formation of silicide, and Mo TEM mesh substrates were used. The sample was then transferred into the growth chamber and then heated to 750 °C gradually and kept for 20 min in vacuum, and then hydrogen (H_2) gas was flown into the chamber at a pressure of 20 Torr at that temperature. A microwave plasma was turned on to 600 kW. The feed gas, methane (CH_4), was introduced and the H_2 gas was adjusted to achieve the optimum CH_4/H_2 ratio at a total pressure of 20 Torr during setting of the desired growth temperature. In this experiment, the substrate temperature was varied from 350 to 750 °C. The growth period was about 10 min, and the CCNF lengths ranges from 0.4 to 1.1 μm depending on the substrate temperature.

Two high-resolution TEMs (JEOL JEM-400EM and FEI's TECNAI-20) were used to determine the structure of the CCNFs. The Raman spectra were measured in the backscattering geometry using the 514.5 nm line of an Ar^+ ion laser at room temperature in the spectral range from 900 to 1800 cm^{-1} with a resolution of 1.0 cm^{-1}, and the signals were separated by a monochromator.

Although the formation of nanometer- to micrometer-sized graphite cones have been reported recently,[5,6] they were composed of cone-shaped or polyhedral graphite sheets with a nonometer-sized tube. HRTEM studies of CCNFs revealed that they are composed of dense graphene wall layers and with cylindrical shape. A technique that enables one to control synthesis of nanoscale carbon structures with conical and cylinder-on-cone shapes have been reported and provides the capability of changing the nanostructure shape during the synthesis process.[3] The nanotips have a higly disordered ''bamboo'' structure, and is completely different from those of CCNFs. It has been found that there is a similar

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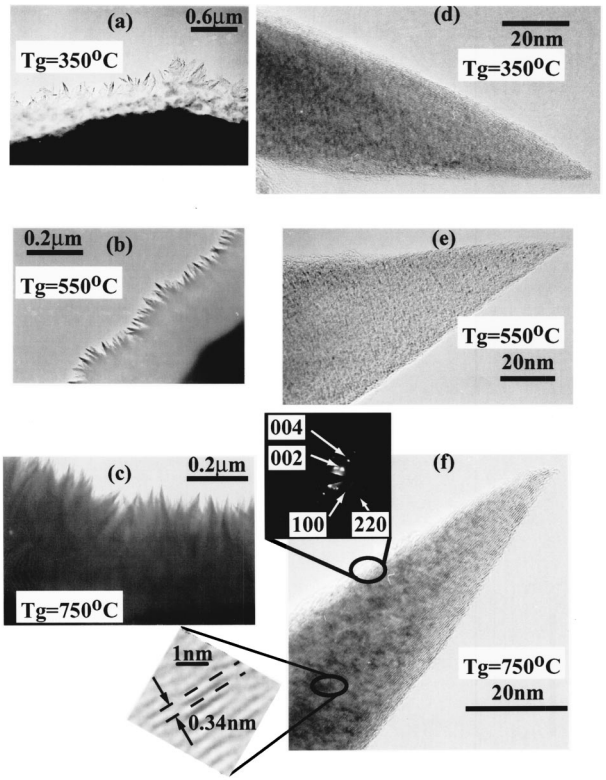

FIG. 1. Low-magnification TEM images of CCNFs grown at 350 °C (a), 550 °C (b), and 750 °C (c). High-resolution TEM (HRTEM) images of CCNFs grown at 350 °C (d), 550 °C (e), and 750 °C (f). The insets in (f) are selected area electron diffraction taken on the longitudinal edge of a CCNFs and magnified image and interlayer space of CCNFs grown at 750 °C.

carbon nano-structure reported by Koshio *et al.*,[7] in which the metal-free multiwall CNTs (MWCNTs) with the innermost tubes having a diameter of 0.4 nm was produced by radio-frequency plasma.

Although their sizes are different, CCNFs maintained their shape as turbostratic and grown directly from Ni catalyst particles, which are not observed on their tips. Figure 1 shows typical low- and high-magnification TEM images of aligned CCNFs after 10 min of growth at different growth temperature. As the substrate temperature increases from 350 to 750 °C, CCNFs become well aligned and dense at higher temperatures, seen from the low-magnification TEM images, Figs. 1(a)–1(c). It should be noted that most of the vertex of the cone is located on the center axis of the CCNFs, just like a pencil point. Moreover, there is no significant difference among the corn-shape structure of samples grown with different substrate temperatures, as shown in Figs. 1(d)–1(f). The results obtained by electron dispersive x-ray spectroscopy shows that tips of CCNFs consist of carbon atoms and no Ni metal on the tips.

Based on symmetry of a graphite sheet and Euler's theorem, the cone-shape tip can be made from a continuous sheet of graphite corresponding to values of pentagons (P) between 1 and 5. The corn angle θ is given by $\sin(\theta/2)=1-(P/6)$.[5] The θ can be deduced from the projected dimensions of the tilted cones. The HRTEM images indicate that the cone angles of $\theta \sim 20°$, 39°, and 60° depending on the substrate temperature, as shown in Fig. 2. These angles correspond closely to those expected for solid angles which are multiples of an integer number (5, 4, and 3) of pentagons.

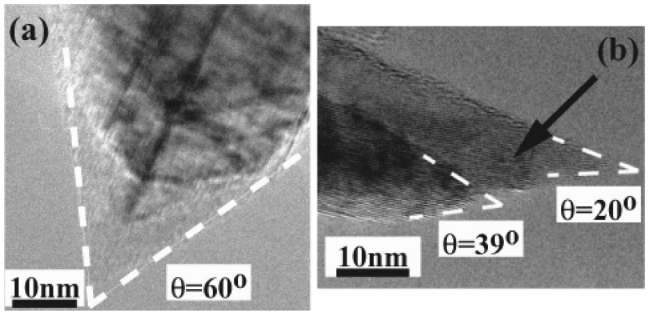

FIG. 2. HRTEM images of three types of corn angles (20°, 39°, and 60°) observed in the experiment. CCNFs grown at 350 °C (a) and 550 °C (b). The pointing arrows indicate the overlapped cones of CCNFs.

Statistical distribution of measured cone angles among microstructures indicates that the cone angle roughly decreases with increase in the substrate temperature. A typical selected area electron diffraction pattern, taken on the edge of CCNFs where the graphite layers are quasiparallel to the electron beam, is shown in the inset in Fig. 1(f). The diffraction spots and rings indicated a typical graphitic stacking and a cylindrical tubular structure, respectively. The average innermost tube spacing measured from the HRTEM image was ~0.34 nm, as shown in the inset in Fig. 1(f), which is close to that of the graphite crystal (0.3354 nm).[8]

The first-order Raman spectrum of CCNFs consists of two sharp peaks located at 1582 cm^{-1} (the G peak) and 1355 cm^{-1} (the D peak), as shown in Fig. 3. The G and D peaks are attributed to the in-plain symmetric C–C stretching (E_{2g}) and the graphite materials with small crystallite sizes or so-called disordered graphite, respectively. Raman spectra show an additional peak at about 1620 cm^{-1} (D'). The origin of the D and D' bands in other forms of carbon materials has been explained as disorder-induced features, caused by the finite particle size effect or the lattice distortion.[9] In our case, CCNFs contain some amorphous impurities at near Pt/Si substrate surface. The D' intensity relative to the G peak decreases as the substrate temperatures increase. As the substrate temperature increase from 350 to 550 °C, the Raman intensity ratio between D and G bands (I_D/I_G) decreases from 1.5 to 1.0 due to the decrease of amorphous carbon. Then, the I_D/I_G decreases gradually with further increase in temperature. Thus, the optimum growth temperature of the CCNFs is estimated to be above 550 °C.

In most reports so far, catalyst particles were encapsu-

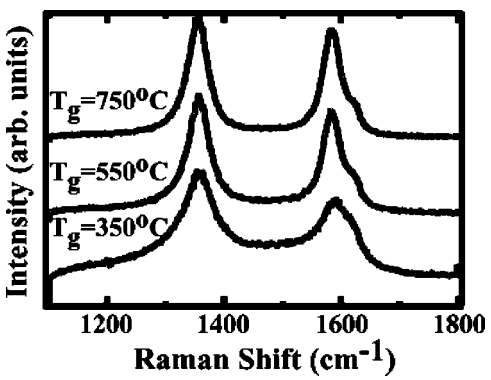

FIG. 3. Normalized micro-Raman spectra for CCNFs grown at 350, 550, and 750 °C.

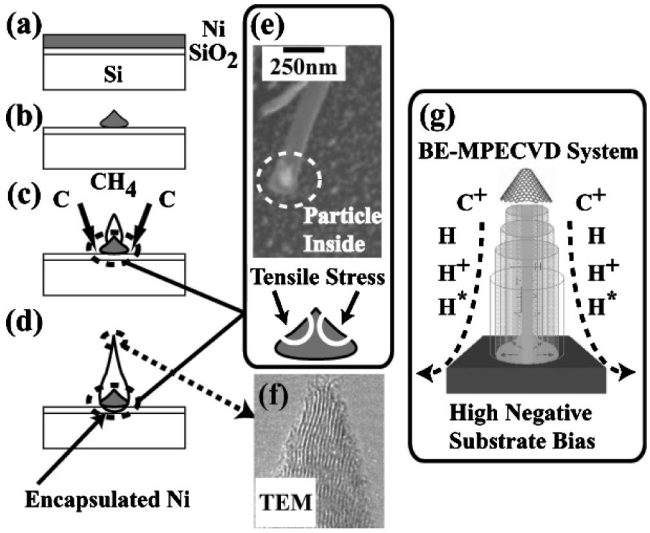

FIG. 4. Summary of the proposed growth model of the CCNFs. (a) Si substrate with a thin SiO_2 barrier layer and the Ni catalyst layer, (b) fragmentation of catalyst into nano-particles by sintering and electrostatic force, (c) decomposition of CH_4 on the surface of the Ni nanoparticle, and (d) growth of CCNF. (e) and (f) The high resolution SEM and TEM images, respectively. (g) The alignment process of CCNFs during growth.

lated on the tip of the MWNTs. The question arises as to why there was no catalyst particle on the tip of CCNFs. The previous works done by Ren *et al.*[10] may provide the mechanism of the catalyst particle reduction, where the fibers lose the particle at the tip during the growth. In this experiment, the shorter growth period of 10 min was applied, which results in the length of CCNFs being short. Thus, their proposed growth mechanism is not applicable in this case.

We propose the following model to explain the vertical alignment of BE-MPECVD-grown CCNFs, as shown in Fig. 4. After Ni layer deposition [Fig. 4(a)], the fragmentation of Ni catalyst into nanoparticles with sharp tip took place by sintering and electrostatic force [Fig. 4(b)]. The growth of CCNFs is believed to occur via decomposition of the carbonaceous gas molecules at Ni-catalyst surface, diffusion of carbon atoms through the Ni particle, and subsequent precipitation at the particle/fiber interface [Fig. 4(c)]. During the initial growth state, CCNFs nucleate and grow from the Ni particle with plasma-induced alignment. The catalyst transforms into a conical shape due to the applied electrostatic force, which creates uniform tensile (not compressive) stress across the entire catalyst particle including the base and fiber interface.[11] The shape of Ni catalyst was assumed to be conical shape, determined from HRSEM image, Fig. 4(e), which may provide a key clue to explain the nature of the corn shape of CCNFs. The fibers grow continuously until the conical Ni particles, are completely enclosed, as shown in Figs. 4(d) and 4(e). The corn-shape tip may be defined by an amount of carbon induced by both an electrostatic force and a substrate temperature. Also, the tips' apex angle, as shown in Fig. 4(f), probably reflects the shape of Ni particles. Although the optimum plasma temperature is hard to determine, the decomposition ratio of carbonaceous gas molecules around Ni surface depends on the substrate temperature.

During the CCNFs' growth, an atomic hydrogen, hydrogen ions, and hydrogen radicals, as shown in Fig. 4(g), are in the plasma. We have reported the effect of these species during the growth of nanostructure diamond by the same method.[12] At a high electric field, the hydrogen ions rather than atomic hydrogen takes an important role of surface modification due to attraction of positively charged energetic ions beside the carbon ion. The hydrogen ion etches off the carbon atoms from the surface and forms hydrocarbon clusters or as-grown particles. CCNFs' growth, or the thickening of cylindrical CCNFs, is a combined process of growth and etching taking place concurrently at the outer surface. The etching process is more significant than the growth process in the experiment, therefore the length of CCNFs is short.

In conclusion, we have produced metal free CCNFs with a high-purity multiwall on Pt/Si and Pt/Mo substrate using a BE-MPCVD method by controlling the substrate temperature and the electrostatic force. The CCNFs have a vertex on the center axis of the tube. Based on the statistical distribution of measured cone angles, the number of pentagons consisting of curvatures of the tips roughly increases from three to five as the substrate temperature increases from 350 to 750 °C. They are composed of dense and co-axially grown multiwall graphite walls with innermost tube diameters of 0.34 nm corresponding to the smallest possible CNT.[8] The Raman result indicates the optimum substrate temperature should be above 550 °C to grow. The growth model of the CCNFs is proposed based on these experimental results.

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