Catalytically active nickel {110} surfaces in growth of carbon tubular structures

M. H. Kuang and Z. L. Wang[a]

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245

X. D. Bai, J. D. Guo, and E. G. Wang[a]

Institute of Physics, Chinese Academia of Sciences, Beijing 100083, China

Recent interest in the growth of aligned carbon nanotube films using transition metal catalysts has led to questions concerning the growth mechanism involved. In our experiment carbon tubules grown using Ni catalysts exhibit a preferred orientation relative to the catalytically active surfaces of Ni. The axial directions of the tubular structure are mainly parallel to the $\langle 110 \rangle$ and $\langle 042 \rangle$ directions of Ni. The faceted shape of the Ni particles determines the intrinsic structure of the tubules. A mechanism involving spiral growth is proposed to explain the nucleation and growth of such tubules. © *2000 American Institute of Physics.* [S0003-6951(00)01910-0]

Transition metal catalysts such as Fe and Ni are essential in the nucleation and growth of carbon nanotubes. The size of the catalytic particles determines the size of the carbon nanotube. It is well known that metal catalysis is the key for the formation of carbon nanotubes, but the exact role played by the catalytic particles in the growth process remains to be investigated. A possible growth mechanism for the tubular structure proposed by Tibbetts[1] involved carbon layers nucleating on certain faces of the catalytic particle such as Ni. However, it has been shown that carbon deposition is not strongly dependent on crystal orientation.[2] This discrepancy needs to be resolved if the exact growth mechanism of such carbon tubules is to be understood.

In this letter, a growth mechanism for tubules is proposed which incorporates the surface diffusion model of Oberlin *et al.*[3] It is shown that certain faces of the Ni catalyst particles are seen to be more catalytically active than other faces.

A direct current (dc) plasma assisted hot filament chemical vapor deposition was employed to grow aligned carbon nanotubes, by this apparatus the turbostratic BCN films[4] were successfully synthesized previously. The polished Ni wafers were used as substrates. A mixture of N_2 (99.999% purity), H_2 (99.999% purity), and CH_4 (99.9%) were used as the reactive gas source. After the vacuum chamber was pumped to 0.1 Pa, it was backfilled to 3.0 kPa with mixed gases. The flow rates of N_2, H_2, and CH_4 were 60, 20, and 15 sccm, respectively. A dc power supply ($500\,V \times 1\,A$) was used to generate discharge plasma between the substrate and a Mo spiral circle (anode) installed above a carbonized tungsten filament ($\phi = 0.3\,mm$). The filament was heated to about 1900 °C and a negative bias was applied to generate a dc plasma. The substrate temperature was about 700 °C during the deposition.

A typical carbon tubule is shown in Fig. 1(a). The tube is very straight, with no nodes or bends. Figure 2(a) shows the distribution of tube inner diameters for a sample of 40 tubes.

The majority of the tubes have inner diameters less than 10 nm. The inner diameter is not completely hollow, but contains many v-shaped graphitic bridges. The Ni catalyst takes on a wedge shaped side view that is a result of the growth
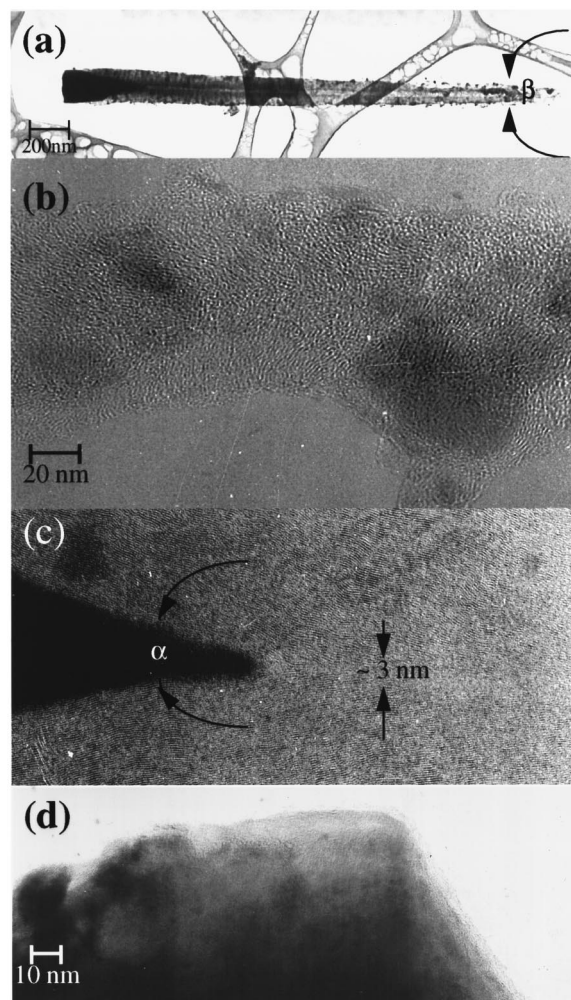

FIG. 1. (a) Low magnification TEM image of a carbon tubule. (b) and (c) high-resolution TEM images recorded from the nucleation end and the tip part of the Ni particle, respectively. (d) TEM image from the Ni particle at the growth front.

[a]Authors to whom correspondence should be addressed; electronic mail: zhong.wang@mse.gatech.edu; electronic mail: egwang@aphy.iphy.ac.cn
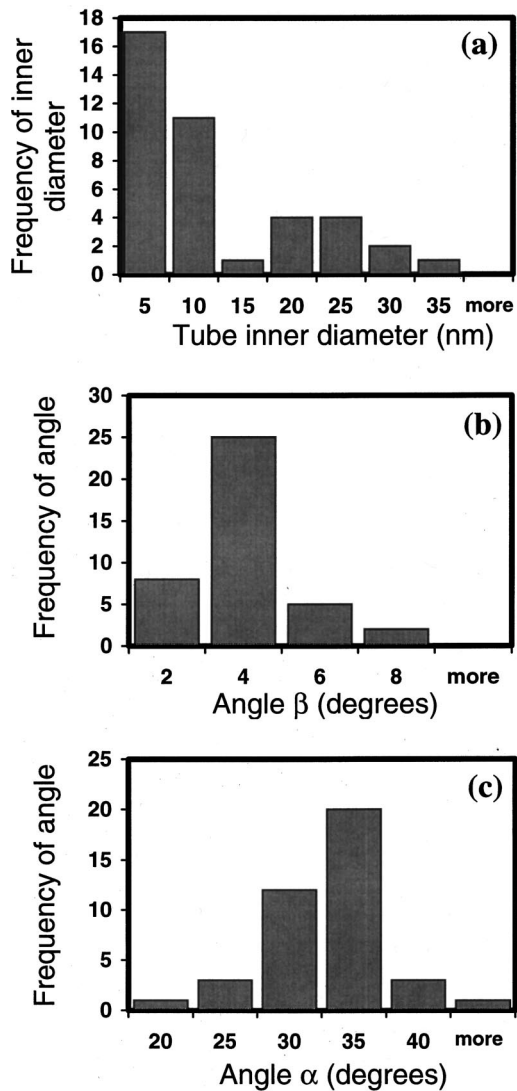
FIG. 2. (b) SEM images recorded from (a) the side and (b) from the top of carbon tubules on a Ni substrate. The irregular shape of the tubules are apparent. (c), (d), and (e) Bright-field, dark-field, and the corresponding [11 −1] electron diffraction pattern from the tip of a carbon tubule. (f) and (g) Bright-field and the corresponding [112] electron diffraction pattern from the tip of a carbon tubule.

FIG. 3. (a) Frequency of inner tube diameter, (b) the angle β, and (c) the angle α for the 40 tubules examined.

mechanism of the tubules that will be discussed later. The black dots are the trapped Ni nanoparticles that are responsible for the initiation of the tubules. The inner diameter is fairly uniform throughout the entire length, while the outer diameter of the tube is not constant and an angle β marked is defined to represent the cone angle of the tubular structure. The distribution of β is plotted in Fig. 3(b). Figure 1(b) is a high-resolution image of the tip of the tubule where the nucleation initiates. The spheroid particles are Ni catalysts. The initial growth of the tube involves a spiral growth scheme similar to that first proposed by Kroto and McKay[5] and later used to explain the growth of carbon spheres and carbon ropes.[6] Figure 1(c) is a high-resolution TEM image of the bottom tip of the Ni catalyst. The graphitc sheets are seen to align parallel to the faces of the Ni particle. Thus, the graphitic layers are not cylindrical but a ''cone'' shape with a truncated top. This is different from the microstructure of conventional carbon nanotubes.

The forefront of the Ni particle is usually a flat face [see Fig. 1(a)], which is covered by a very thin layer of carbon
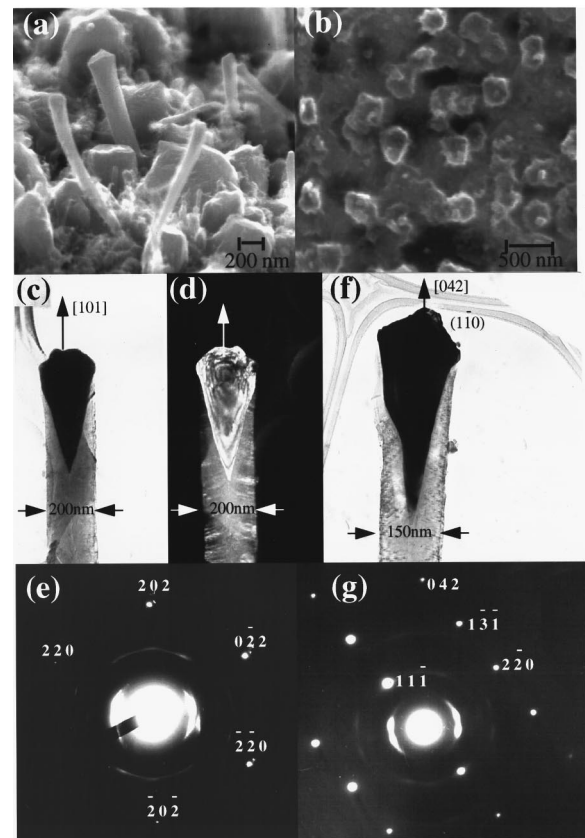
($\sim$2 nm), as shown in Fig. 1(d). It is apparent that this face is the catalytically active face and is responsible for producing carbon atoms. An α angle is defined to characterize the cone angle of the Ni particle at the tip. Figure 3(c) shows the distribution of the angle α, and it is in the range of $30°-35°$.

The morphology of the tubules is seen in the SEM images recorded from the side view [Fig. 2(a)]. The Ni particles at the end shows faceted shape, which can be seen from the SEM image at the top view of the sample [Fig. 2(b)]. It is also possible that the tubules are not cylindrically symmetric. Most of the Ni particles show a drill shape with a relatively flat top.

To identify the crystallography of the Ni particle orientation, electron diffraction together with shadow imaging were used. Among the ten particles identified, seven showed that the growth direction of carbon tubules is parallel to the $\langle 110 \rangle$ of Ni [Figs. 2(c), 2(d), and 2(e)], two of which are parallel to the [042] [Figs. 2(f) and 2(g)], and one unidentified. The two bright streaking spots very close to the central transmitted beam are the (0002) basal plane reflections from the two sides of the tubule. The double split of the (0002) reflection is due to the cone shape of the graphitic layers, and the angle between the split is just the α angle. In the $\langle 110 \rangle$ case, the angles between the two sides of the Ni particle is $\sim$30°, which does not match the angles between the {110} planes. Thus, the two side faces are likely to be high index crystal planes.

It has long been thought that the growth of such carbon tubules is largely independent of the crystal orientation of the catalyst.[2] However, in growing carbon filaments using iron carbide as catalyst, Oberlin *et al.*[3] suggested that in order to
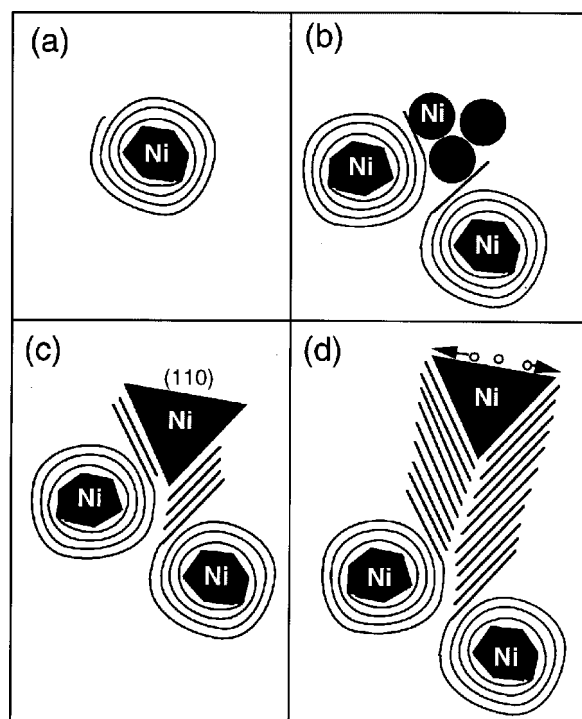
FIG. 4. Schematic diagrams showing the nucleation and growth of a carbon tubule under the catalytically active Ni (101) surface.

account for the hollow nature of such tubes it is necessary that carbon layers nucleate only on specific faces of the catalysts. Grenga and Lawless[7] found that graphitic platelets form on the {111} surfaces of Ni much faster than other surfaces when hydrocarbon gases are pyrolized over Ni. Presland and Walker[8] demonstrated that deposition of laminar graphite by the pyrolysis of acetylene at 1300 K over Ni is most effective on the {110} faces. Theoretical calculations of Yang and Chen[9] on the adsorption of graphite on Ni surfaces showed that the {110} surfaces have the highest binding energy and the largest net charge transfer than the {111}, {311}, and {100} surfaces, suggesting the unstability of carbon atoms on the Ni {110} surfaces.

Our observations suggest that the carbon tubules tend to possess certain preferred growth directions relative to the Ni crystal. The Ni (101) surfaces are catalytically active faces for producing carbon atoms. Before nucleation of the tubules occur, the Ni particle can have any shape, most likely an oval shape when Ni film is heated at temperatures adequate for pyrolysis of carbon tubules. According to Baker *et al.*,[2] when a hydrocarbon gas such as acetylene is passed over the Ni particles, the gas decomposes onto the exposed surface of the Ni particle and a large amount of heat is release, thus creating a thermal gradient on the Ni surface. Carbon atoms from the decomposed gas diffuse quickly down the thermal gradient, possibly because the diffusion on (101) surfaces is a rather rapid process. The Ni particle changes shape due to its liquid-like behavior at the growth temperatures[10] and takes on a wedge shaped side view just as we observed. There are two diffusion routes, one is on the surface of the Ni particle towards the wedge, leading to the growth of the tubules and the lifting up of the particle from the substrate. The carbon atoms tend to distribute on the surfaces with high Miller indices, thus, the (101) tip of the Ni wedge is likely to dif-

fuse the carbon atoms away, forming a hollow or nearly hollow inner diameter. The other one is towards the outer surface of the tubules, resulting in a slight increase in the diameter of the tubule as the growth proceeds.

The spiral growth mechanism introduced by Wang and Kang[6] to explain the formation of carbon nanospheres and ropes can be modified to explain the nucleation of the carbon tubules. The Ni particles in Fig. 1(b) are typically approximately 20 nm in diameter and spheroid in shape. The actual nucleation occurs when carbon atoms form graphitic sheets around a much smaller Ni particle as seen in Fig. 1(b). Graphitic sheets can grow around the Ni particle in a spiral shape as shown in Fig. 4(a). Once the Ni particle is completely engulfed by the graphitic sheets, it loses all catalytic activity. A second Ni particle must be nearby to continue the growth of the tube as shown in Fig. 4(b). It is known that when the nanoparticles are small, their melting point can be as low as 40% of the bulk value[11] (the melting point of bulk Ni is 1453 °C). Thus, some smaller liquid Ni droplets unwrapped by carbon can quickly combine to form a larger solid particle if they are not immediately enclosed by the carbon layers. With an increase in size, the particle crystallizes due to the increase in its melting point, but its shape accommodates to the shape of the adjacent graphitic layers due to the diffusion of atoms to the neck region of the particles [Fig. 4(c)]. Some Ni particles crystallize in such a way so that the catalytically active (101) plane is orthogonal to the growth direction, i.e., the direction in which carbon atoms are diffusing away, others may crystallize in other orientations. In the former case the tube will continue to grow because the (101) surface is catalytically active and the diffusion rate of carbon atoms on it is rather high. The carbon atoms are unlikely to remain on the surface and will quickly diffuse away. This explains what we observed in Fig. 2(c). In the latter case, the surfaces that are not of the (101) type will quickly be covered up by carbon atoms possibly because of higher surface adhesion to carbon atoms (i.e., slower diffusion rate), thus prohibiting further tube growth. Therefore, the only exposed surface can be (101), which will apparently be the growth front [Fig. 4(d)].

[1] G. G. Tibbetts, J. Cryst. Growth **66**, 632 (1984).

[2] R. T. K. Baker, M. A. Barber, P. S. Harris, F. S. Feates, and R. J. Waite, J. Catal. **26**, 51 (1972).

[3] A. Oberlin, M. Endo, and T. Koyama, J. Cryst. Growth **32**, 335 (1976).

[4] J. Yu and E. G. Wang, Appl. Phys. Lett. **74**, 2948 (1999).

[5] H. Kroto and K. McKay, Nature (London) **331**, 1139 (1988).

[6] Z. L. Wang and Z. C. Kang, Philos. Mag. B **74**, 51 (1996); Z. C. Kang and Z. L. Wang, *ibid.* **73**, 905 (1996).

[7] H. E. Grenga and K. R. Lawless, Proc. Of 6th Intl. Congr. on Electron Micros., Kyoto, published by the Japanese Electron Microscopy Soc. (1966), p. 551.

[8] A. Presland and P. Walker, Carbon **7**, 1 (1969).

[9] R. T. Yang and J. P. Chen, J. Catal. **115**, 52 (1988).

[10] K. Behrndt, J. Appl. Phys. **37**, 3841 (1966).

[11] Ph. Buffat, J. P. Borel, Phys. Rev. A **13**, 2287 (1976); Z. L. Wang, J. Petroski, T. Green, and M. A. El-Sayed, J. Phys. Chem. B **102**, 6145 (1998).