Specific conditions for Ni catalyzed carbon nanotube growth by chemical vapor deposition

Masako Yudasaka, Rie Kikuchi, Takeo Matsui, Yoshimasa Ohki, Susumu Yoshimura et al.

Citation: Appl. Phys. Lett. **67**, 2477 (1995); doi: 10.1063/1.114613
View online: http://dx.doi.org/10.1063/1.114613
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v67/i17
Published by the American Institute of Physics.

Specific conditions for Ni catalyzed carbon nanotube growth by chemical vapor deposition

Masako Yudasaka, Rie Kikuchi, Takeo Matsui, Yoshimasa Ohki, and Susumu Yoshimura
Yoshimura Pi-Electron Materials Project, ERATO, JRDC, c/o Matsushita Research Institute Tokyo, Inc., 3-10-1 Higashimita, Tama-ku, Kawasaki 214, Japan

Etsuro Ota
Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan

(Received 15 June 1995; accepted for publication 18 August 1995)

Chemical vapor deposition using 2-methyl-1,2′-naphthyl ketone as a starting material has been done between 1000 and 600 °C on Ni particles with diameters ranging from 10 to 500 nm. The Ni particles were prepared by annealing Ni thin film deposited on quartz glass substrates. The size of the Ni particle was controlled by the thickness of the Ni film. Carbon nanotubes were obtained at 700 °C when the diameter of the Ni particles was about 20–30 nm. © *1995 American Institute of Physics.*

A carbon nanotube comprises, according to Ebbesen,[1] cylindrical shells of graphitic sheets. The length of the nanotube is greater than 1 μm and the aspect ratio (length over diameter) is greater than 100. The interlayer distance of the sheets is about 0.34 nm. Carbon nanotubes have been formed in the arc plasma with the subsequent purification for separating the graphite tubes from the carbon soot.[2] The formation mechanism in the arc has been studied but is still open to question.[3] While much work has been devoted to arc-discharge-based nanotubes, metal-catalyzed growth of nanotubes has been recognized for some time.[5,6] Here we report the formation of multilayer graphite nanotubes by chemical vapor deposition (CVD) under a very specific reaction condition. The specific condition includes the temperature of 700 °C and the size of a Ni catalyst with a round shape of 20 to 30 nm in diameter, which is noted for the first time and may help to clarify the growth mechanism. Precise knowledge on roles of Ni in low-temperature graphitization found by the authors[7,8] is also useful.

Ni films with various thicknesses (1–100 nm) were vacuum-deposited (10^{-6} Torr) on quartz–glass substrates. Ni particles were formed by heat treating the Ni film under vacuum (10^{-7} Torr). Immediately after the heat treatment, carbon was deposited on the Ni particles by CVD without breaking the vacuum. The starting material for vacuum CVD was 2-methyl-1,2′ naphthyl ketone which has been found to be appropriate for graphite film formation on Ni at temperatures above 600 °C.[5–7] The vacuum CVD and the detailed deposition conditions were described previously.[7]

The Ni films with a thickness of 5 nm were transformed into Ni droplets by heat treatment at 700 °C for 2 h, whose diameter was 10–250 nm [Fig. 1(a)]. Long carbon tubes with length more than several μm and the carbon particles with round shape were obtained by CVD at 700 °C on the Ni droplets [Fig. 1(b)]. It was confirmed that the carbon nanotubes and particles were composed of graphite with small basal domain dimensions, using a Raman scattering spectrum [Fig. 2(b)] that exhibited two peaks at 1585 and 1350 cm^{-1}.[9] The transmission electron microscopy (TEM) images of the nanotubes are shown in Fig. 3. The TEM image of Fig. 3(a) shows straight carbon nanotubes with uniform diameter. The outside and inside diameters of the carbon nanotubes are 17–27 nm and 10–17 nm, respectively [Figs. 3(a) and 3(b)]. About 10 sheets of graphite layers can be clearly seen in Fig. 3(b). A selected area diffraction pattern of the carbon nanotube is shown in Fig. 4. The diffraction spots (Fig. 4), corresponding to a layer distance of 0.34 and 0.17 nm, are considered to be of the graphite (002) and (004) diffractions, respectively. The graphite ⟨001⟩ is known to be perpendicular to the tube axis. In Fig. 4 can also be seen halolines with spots corresponding to layer distances of 0.21 and 0.12 nm. The former corresponds to (100) and the latter to (110) of graphite. This means that ⟨100⟩ and ⟨110⟩ of the graphite tube is parallel with the tube axis.

There is evidence of materials appearing as black shadows in Fig. 3, not only at the top end but also in the middle of the carbon nanotubes. They were found to be Ni by energy dispersive spectrometry. Many of the Ni particles take a cylindrical shape with diameter of about 10–13 nm and length of 40–100 nm, whose volume is 4500–11 000 nm^3, which corresponds to the volume of a sphere with diameters ranging from 20–28 nm. There are many Ni droplets with diameters around 20–30 nm in the scanning electron microscope (SEM) image for the heat-treated Ni film with an initial thickness of 5 nm [Fig. 1(a)]. The Ni cylinder was found to be crystallized because the electron diffraction spots corresponding to (111) and (100) of Ni could be observed. Besides the carbon nanotubes, graphite particles with Ni particles inside can also be seen in the TEM images of Fig. 3(c). The diameter of the Ni particle is larger than 50 nm and the thickness of graphite is less than 10 nm. When the diameter of the Ni particle is above 50 nm, the graphite prefers to take a round particle shape.

The above results indicate that the carbon nanotubes are able to grow from the Ni droplets with specific diameter, which is confirmed in the experiments shown below where the Ni droplet size is changed. After the Ni film with the initial thickness of 1 nm [written as Ni (1 nm) film] was heat treated at 700 °C, its SEM image did not show any Ni droplets. The carbon deposit obtained by CVD on the heat treated

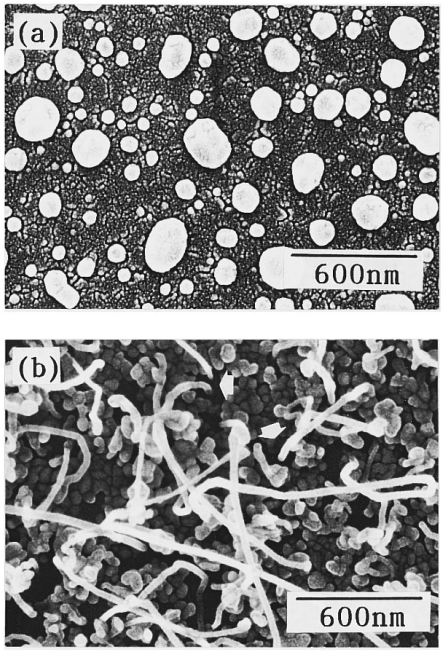

FIG. 1. Scanning electron micrographs of (a) heat-treated Ni film with thickness of 5 nm and (b) deposit obtained by CVD on Ni droplets appearing in (a). Temperature of heat treatment and CVD was 700 °C. Gold film with thickness about 10 nm was deposited for SEM observation.

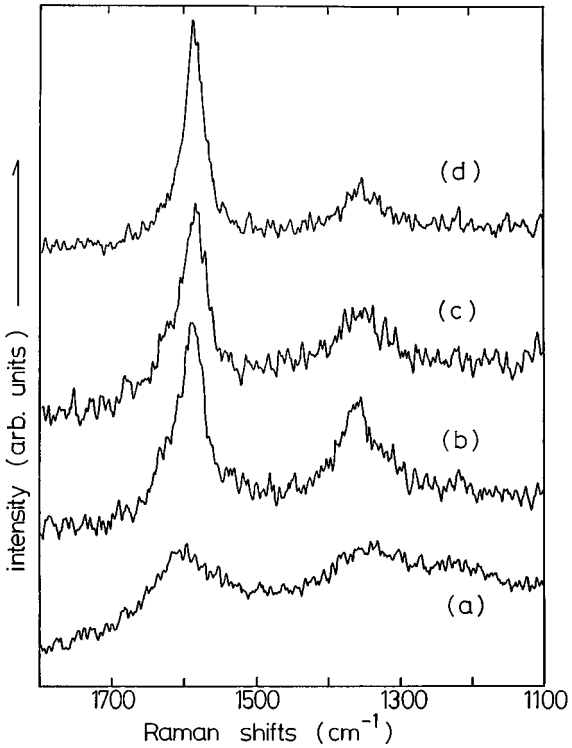

FIG. 2. Raman spectra of deposits obtained by CVD on heat-treated Ni films with initial thicknesses of (a) 1, (b) 5, (c) 10, and (d) 100 nm.

Ni (1 nm) film [written as C/Ni (1 nm)] was amorphous carbon, which is apparent from the Raman spectrum showing broad peaks at around 1600 and 1350 cm^{-1} [Fig.2(a)].[9] When the Ni (10 nm) film is used, the sizes of the Ni droplets generated by the heat treatment were in the range of 10–500 nm. The number of Ni droplets with diameter around 20–28 nm are much smaller than that observed in the case of Ni (5 nm). The C/Ni (10 nm) achieves a graphite structure as is apparent from the Raman spectrum of Fig. 2(c). SEM images of the C/Ni (10 nm) showed only a few carbon tubes among many carbon particles. The SEM images of the heat-treated Ni (100 nm) film and C/Ni (100 nm) showed a continuous structure. The Raman spectrum of the C/Ni (100 nm) [Fig. 2(d)] is characteristic of graphite.[9] It is concluded that the size of the Ni droplet suitable for carbon nanotube growth is limited to around 20–30 nm.

Furthermore, the optimum temperature range for the carbon nanotube formation was investigated. At 1000 °C, no carbon nanotube was generated even though various thicknesses of Ni films were applied. The SEM images of graphite

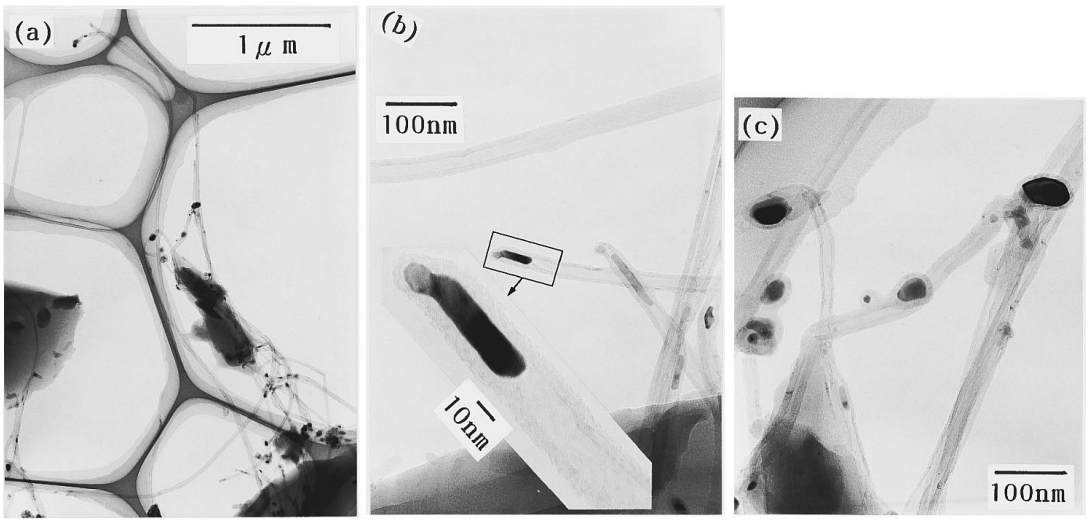

FIG. 3. Transmission electron micrographs of (a) carbon nanotubes and particles, (b) carbon nanotubes, and (c) carbon particles grown by CVD at 700 °C using Ni thin film with thickness of 5 nm. The thick network is a microgrid made of organic material. Large dark islands are broken pieces of quartz glass.

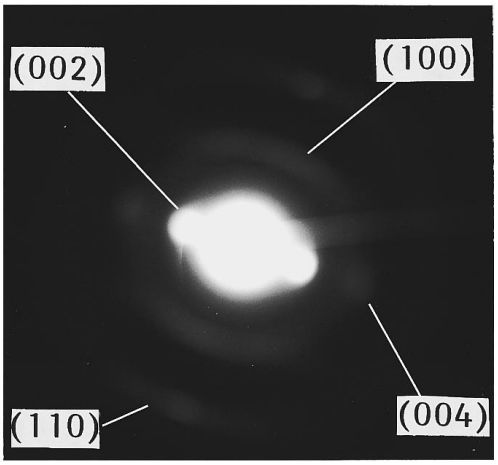

FIG. 4. Selected-area diffraction pattern of carbon nanotube inserted in Fig. 1(b).

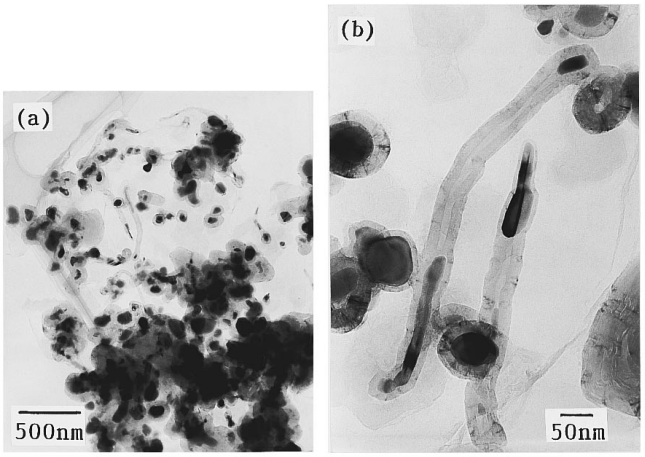

FIG. 5. Transmission electron micrographs of (a) carbon nanotubes and particles and (b) carbon tubes grown by CVD at 800 °C using an Ni thin film with thickness of 5 nm. The thick network is a microgrid made of organic material. Transparent carbon sheets are considered to be amorphous carbon.

deposited on the Ni films at 800 °C showed a few carbon tubes among round graphite particles. The carbon nanotubes were featured by an outside diameter of 17–27 nm, a length of less than 1 μm, and a bending structure. The diameters of the tube are not constant along the tube (Fig. 5). At 600 °C, the Ni film could not be transformed into round droplets by the heat treatment.

It is concluded that the optimum temperature and the diameter of the Ni droplet for the carbon nanotube formation are 700 °C and 20–30 nm, respectively. The temperature of 700 °C is understood to be significant for the graphite thin film formation on Ni by CVD; Ni can assist the graphite formation via dehydrogenation of the starting material used in this study.[8] Since Ni and carbon do not make a solid solution at 700 °C,[8] the Ni cylinder and the carbon nanotube can exist independently. The temperature of 700 °C is sufficiently high for Ni to change its shape from thin films to droplets and then to cylinders. At temperatures above 800 °C, carbon and Ni dissolve into each other, leading to recrystallization of carbon as graphite. This phenomenon is suitable for the formation of graphite thin films by CVD[8] but is not suitable for the nanotube formation. The interdissolution possibly prohibits the formation of long straight carbon nanotubes with uniform diameter.

Finally, we give a picture for the mechanism of the carbon nanotube formation and explain the specific sizes of the Ni droplets and unique sizes of the carbon nanotubes and the Ni cylinders. First, the Ni film with a thickness of 5 nm transforms into the Ni droplets with 10–250 nm in diameter by heat treatment. Then, as the CVD begins, the graphite starts to cover the Ni droplets. When the Ni droplets are 20–28 nm in diameter and the number of graphite sheets covering the Ni droplets reaches around 10, the mechanical stress of the graphite exceeds the elastic limit. This causes the round shape of the graphite and the Ni droplets to concurrently transform into the carbon nanotube and the Ni cylinders, respectively. One end of the cylinder must be rooted on the substrate surface, which was actually recognized through the SEM observation [Fig. 1(b)]. During the growth of the carbon nanotube by CVD at 700 °C, the Ni cylinder is likely to exist at the end of the carbon nanotube so that additional stability can be gained by contact with newly forming nanotube fragments at the nanotube edge.[5] The carbon nanotube may be closed when the temperature is sufficiently lowered, causing five-membered carbon rings to become sufficiently stable to cap the nanotube.[10]

We thank T. Kohzaki of Matsushita Technoresearch, Inc. for his measuring the TEM, the energy dispersive spectra, and the selected-area diffraction.

[1] T. W. Ebbesen, Annu. Rev. Mater. Sci. **24**, 235 (1994).
[2] M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi, and H. Kroto, J. Phys. Chem. Solids **54**, 1841 (1993).
[3] M. José-Yacamán, M. Miki-Yoshida, and L. Rendón, Appl. Phys. Lett. **62**, 657 (1993).
[4] C. Gurret-Plécourt, Y. Le Bouar, A. Loiseau, and H. Pascard, Nature **372**, 761 (1994).
[5] A. Oberlin, M. Endo, and T. Koyama, J. Cryst. Growth **32**, 335 (1976).
[6] M. Yudasaka, R. Kikuchi, T. Matsui, H. Kamo, Y. Ohki, E. Ota, and S. Yoshimura, Appl. Phys. Lett. **64**, 842 (1994).
[7] M. Yudasaka, R. Kikuchi, T. Matsui, Y. Ohki, E. Ota, and S. Yoshimura, Appl. Phys. Lett. **65**, 46 (1994).
[8] M. Yudasaka, R. Kikuchi, T. Matsui, Y. Ohki, E. Ota, and S. Yoshimura, J. Vac. Sci. Technol. A **13**, 2142 (1995).
[9] K. Kinoshita, *Carbon, Electrical and Physicochemical Properties* (Wiley, New York, 1988).
[10] M. Endo and H. Kroto, J. Phys. Chem. **96**, 6941 (1992).