Kobe University Repository : Kernel

PDF issue: 2025-12-05

High growth rate of vertically aligned carbon nanotubes using a plasma shield in microwave plasma-enhanced chemical vapor deposition

Kinoshita, Hiroshi
Kume, Ippei
Sakai, Hirokazu
Tagawa, Masahito
Ohmae, Nobuo

(Citation)
Carbon,42(12-13):2753-2756

(Issue Date)
2004-01

(Resource Type)
journal article

(Version)
Accepted Manuscript

(URL)
https://hdl.handle.net/20.500.14094/90000291

Revised Manuscript

Letters to the Editor

The e-submission number: CARBON_kinohiro.AT.mech.kobe-u.ac.jp_20031205/1
The Editorial reference number: TK-97/03

Title:

High growth rate of vertically aligned carbon nanotubes using a plasma shield in microwave plasma-enhanced chemical vapor deposition

Authors:

Hiroshi Kinoshita*, Ippei Kume, Hirokazu Sakai, Masahito Tagawa, Nobuo Ohmae

Keywords:

A. Carbon nanotubes; B. Chemical vapor deposition; C. Electron microscopy

Full postal address of all co-authors

Department of Mechanical Engineering, Faculty of Engineering, Kobe University,

ZIP code: 657-8501 Rokkodai 1-1, Nada-Ku, Kobe, JAPAN

***corresponding author**

Tel&Fax: +81-78-803-6126

E-mail address: kinohiro@mech.kobe-u.ac.jp

Since the discovery of carbon nanotubes [1], a number of researches have been made because of their high industrial potentials. Growth orientation of carbon nanotubes is increasingly studied for investigating their electronic properties, field emitters, chargeable batteries, and so on. Synthesis of vertically aligned carbon nanotubes have been realized using thermal chemical vapor deposition (CVD) [2], plasma-enhanced hot-filament CVD [3], direct-current (dc) glow discharge CVD [4], and microwave plasma-enhanced CVD [5]. Here, we report a synthesis of vertically aligned carbon nanotubes with surprisingly high growth rate (280 nm/s) using microwave plasma-enhanced CVD. The high growth rate has been achieved by avoiding the direct plasma irradiation on a substrate, in which the growth of carbon nanotubes is occurring, using a plasma shield placed between microwave plasma and the substrate. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are used to investigate the synthesis of carbon nanotubes without and with the plasma shield.

Fig. 1 presents a schematic of the microwave plasma-enhanced CVD apparatus used in this study. This apparatus consists of a quartz tube, a furnace for heating substrate, a magnetron, and a rectangular waveguide. The quartz tube passed through a hole equipped in the waveguide. A substrate holder made of molybdenum was placed in the quartz tube heated in the furnace. The quartz tube was pumped down by a rotary pump to a base pressure of 10^{-2} Torr. CH_4 and H_2 gases were introduced to the quartz tube through mass flow controllers. The apparatus was designed to install a plasma shield between microwave plasma and the substrate for the purpose of preventing the substrate from direct plasma irradiation. H-terminated Si(001) wafers were used as the substrates. Silicon oxide layers were formed on the substrates by thermal oxidation with 760 Torr O_2 gas at a temperature of 800°C for 2 h. Ellipsometric measurements showed that the oxide thickness was approximately 30 nm.

Catalytic layers of Fe with 1 nm thickness were then deposited on the silicon substrates using vacuum evaporation. The thickness of the layer was measured by a quartz crystal microbalance (QCM). The substrates were pleased in the quartz tube and annealed at 700°C for 30 min in the flowing H_2. The flow rate was 100 sccm at the pressure of 1 Torr. This provided the layers of nanoparticles with a size of below 100 nm. The silicon oxide layers acted as a diffusion barrier which prevents the Fe silicide formation during the annealing. The substrate temperature was kept at 700°C during the growth process. The total pressure in the quartz tube was kept constant at 20 Torr, while the flow rates were 10 and 100 sccm for CH_4 and H_2, respectively. Microwave plasma was ignited at 2.45 GHz and 500 W, and maintained in the quartz tube surrounded by the waveguide. The substrates were located downstream from the microwave plasma. A negative high voltage (-500V) was applied to the substrate holder by the high voltage supply when carbon nanotubes were synthesized. A gas inlet was a grounded electrode. The potential of the plasma was measured to be +50 V using a Langmuir probe. The plasma touched the substrate without the plasma shield. TEM was used to determine the microstructure of individual carbon nanotubes. For TEM measurements, carbon nanotubes were removed from the substrates and placed onto a Cu grid. SEM images of carbon nanotubes grown with and without the shield were obtained at varied growth times from 10 s to 60 s. Length of carbon nanotubes were estimated by SEM images. When the plasma was not turned on, none of growth of carbon nanotubes was observed for a growth time of 60 s, regardless of the depositing conditions with and without the shield. This indicates that only radicals and/or ions formed by the plasma synthesized carbon nanotubes in the plasma condition.

Fig.2 shows a TEM image of carbon nanotubes grown with the shield for a growth time of 60 s. The diameters of carbon nanotubes are approximately 20 nm and their wall thicknesses are approximately 6 nm, showing that carbon nanotubes synthesized are multi-walled type. The growth of multi-walled carbon nanotbues was also indicated by the Raman spectra and the high-resolution transmission electron microscopy (HRTEM) images (not shown). In Fig. 2, some carbon nanotubes have Fe catalysis (dark parts in the TEM image) at their ends, while some do not. The result indicates that the synthesis of carbon nanotubes in this study related to the tip and base growth mechanism based on effect of catalysts [5,6]. The difference in the structure of carbon nanotubes with and without the shield was not observed from TEM measurements.

Fig. 3 shows typical SEM images of carbon nanotubes grown with and without the plasma shield for a growth time of 60 s. As shown in Fig. 3, carbon nanotubes without the shield do not align vertically, while carbon nanotubes with the plasma shield are vertically aligned. Fig. 4 indicates the lengths of carbon nanotubes with and without the plasma shield as a function of the growth time. The length of the carbon nanotubes grown with the plasma shield shown in Fig. 4 appears that the synthesis process has two growth stages. One is a slow growth stage within the growth time of 20 s. The other is a fast growth stage after the growth time of 20 s. It was found that good vertical alignment was only obtained for carbon nanotubes with the shield in the fast growth stage. In the fast growth stage, the growth rate is calculated to be 280 nm/s. This high growth rate is surprising in comparison with the previously reported syntheses of carbon nanotubes, in which growth rates were ~100 nm/s in the cases of microwave plasma-enhanced CVD [5] and thermal CVD [6].

The high growth rate, and the vertical orientation of carbon nanotubes were achieved only with the plasma shield. In general, hydrocarbon-based plasma used to synthesize carbon nanotubes includes not only hydrocarbon reactants but also high-energy ions and vacuum ultraviolet ray that cause material degradation and affect reaction pathways. It is though that when the plasma shield was not used, a direct plasma irradiation to the substrates etched carbon nanotubes grown already and/or restricted the reaction pathways for growing carbon nanotubes. Namely, the direct plasma irradiation disturbed the synthesis of carbon nanotubes. The reduction of the direct plasma irradiation may cause the high growth rate and vertical alignment of carbon nanotubes.

Several experimental studies were made for synthesizing vertically aligned carbon nanotubes. Bower et al. have explained that in the microwave plasma-enhanced CVD the alignment of the nanotubes is induced by the electrical self-bias field imposed on the substrate surface from the plasma environment [5]. Mauron et al. have experimentally shown using thermal CVD without electric field that synthesis of vertically aligned carbon nanotubes requires a sufficiently high density of carbon nanotubes; more than 30~40 nanotubes/μm^2 [7]. They have explained that carbon nanotubes at high densities have spatially only one degree of freedom in which they can grow (namely perpendicular to the surface). It appears that the plasma shield disturbed the electric field. The density of carbon nanotubes grown with the shield was more than 100 nanotubes/μm^2, which is sufficiently high for aligned carbon nanotubes. In order to confirm whether the synthesis of aligned carbon nanotubes with the shield were achieved by the high density of carbon nanotubes or the electric field, more experiments of synthesizing carbon nanotubes with various densities are necessary.

The two stage growth of carbon nanotubes obtained in this study has not been reported previously. The growth rate was measured at 10 s intervals by SEM. Probably this measurement contributed to a findings of the two stage growth. We propose the two stage growth by considering the tip and base growth mechanism in which growth of carbon nanotubes is assumed to follow a supersaturation of carbon in catalysts. Since carbon nanotubes are formed from the catalysts in which the supersaturations are already occurred, the carbon nanotube density in the initial reaction is relatively low. Carbon nanotubes with a low density can freely grow in all the directions. After the carbon nanotube density is sufficiently high, carbon nanotubes should grow to the direction perpendicular to the substrate, corresponding the fast stage. With the SEM results, the carbon nanotubes at a growth time of 10 s had random orientations. Unfortunately, there is no direct experimental evidence showing the exact model of the two stage growth of carbon nanotubes.

In summary, we have shown the high growth rate of vertically aligned carbon nanotubes by microwave plasma-enhanced CVD, in which the plasma shield was used to avoid the direct plasma irradiation on the substrates. The length of carbon nanotubes with the shield was far longer than that without the shield. The synthesis process of the carbon nanotubes with the shield had two growth stages, and the growth rate in the fast growth stage was 280 nm/s.

References

[1] Iijima S. Helical microtubules of graphitic carbon. Nature 1991;354:56–58.

[2] Li WZ, Pan ZW, Xie SS, Qian LX, Chang BH, Zou BS, Zhou WY, Zhao RA, Wang G. Large-scale synthesis of aligned carbon nanotubes. Science 1996;274:1701–3.

[3] Huang ZP, Xu JW, Ren ZF, and Wang JH, Siegal MP, Provencio PN. Growth of highly oriented carbon nanotubes by plasma-enhanced hot filament chemical vapor deposition. Appl Phys Lett 1998;73(26):3845-7.

[4] Chhowalla M, Teo KBK, Ducati C, Rupesinghe NL, Amaratunga GAJ, Ferrari AC, Roy D, Robertson J, Milne WI. Growth process conditions of vertically aligned carbon nanotubes using plasma enhanced chemical vapor deposition. J Appl Phys 2001; 90(10):5308-17.

[5] Bower C, Zhu W, Jin S, Zhou O. Plasma-induced alignment of carbon nanotubes. Appl Phys Lett 2000;77(6):830-2.

[6] Ducati C, Alexandrou I, Chhowalla M, Amaratunga GAJ, Robertson J. Temperature selective growth of carbon nanotubes by chemical vapor deposition. J Appl Phys 2002; 92(6):3299-303.

[7] Mauron PH, Emmenegger CH, Zuttel A, Nutzenadel CH, Sudan P, Schlapbach L. Synthesis of oriented nanotube films by chemical vapor deposition. Carbon 2002;40:1339-44.

Figure Captions

Fig. 1 Schematic of the microwave plasma-enhanced CVD apparatus.

Fig. 2 TEM image of carbon nanotubes grown with the shield for a growth time of 60 s.

Fig. 3 SEM images of carbon nanotube grown (a) without and (b) with the shield for a growth time of 60 s.

Fig. 4 Lengths of carbon nanotubes grown with the shield (closed circle) and without the shield (open circle) as a function of growth time.

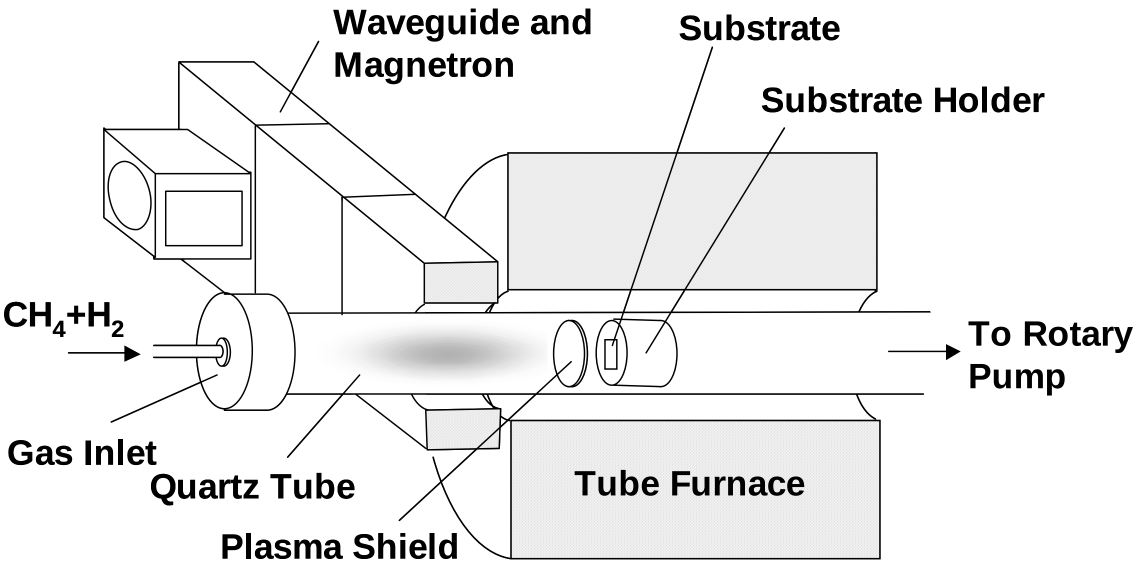


FIG.1. Kinoshita et al.

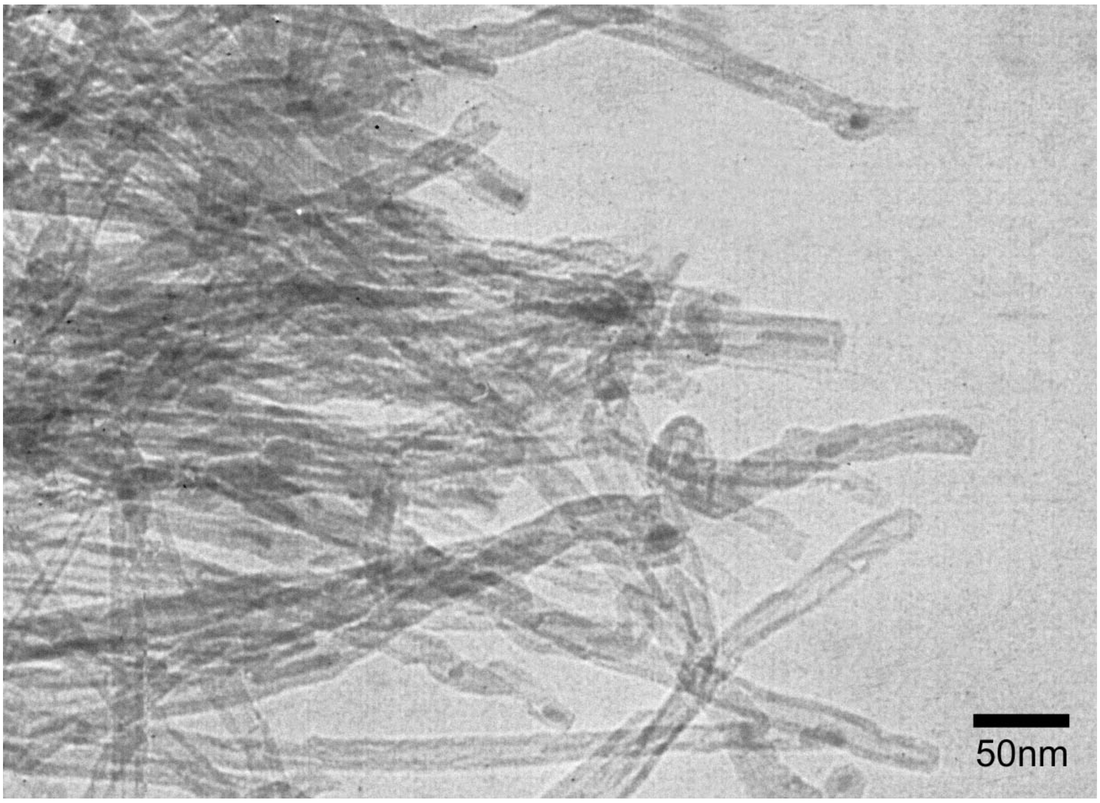
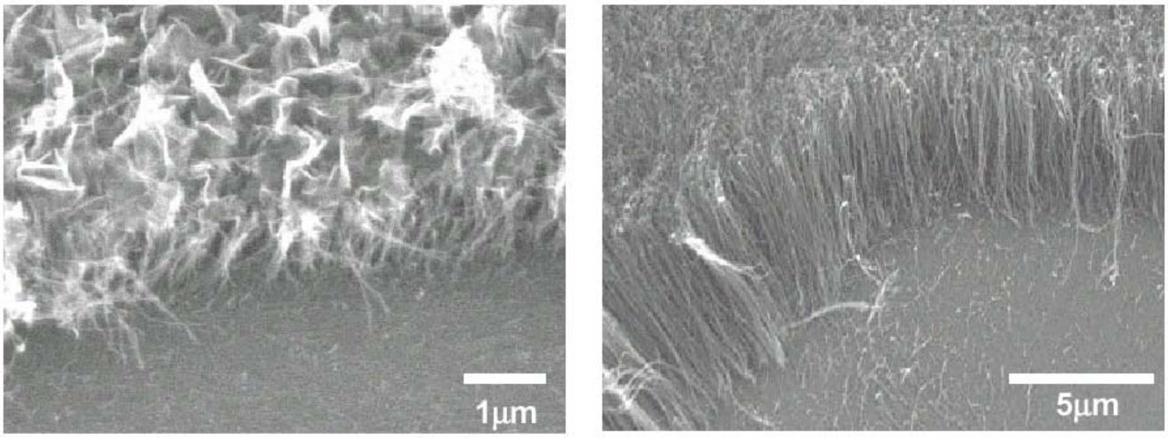


FIG.2. Kinoshita et al.



(a) Without shield (b) With shield

FIG.3. Kinoshita et al.

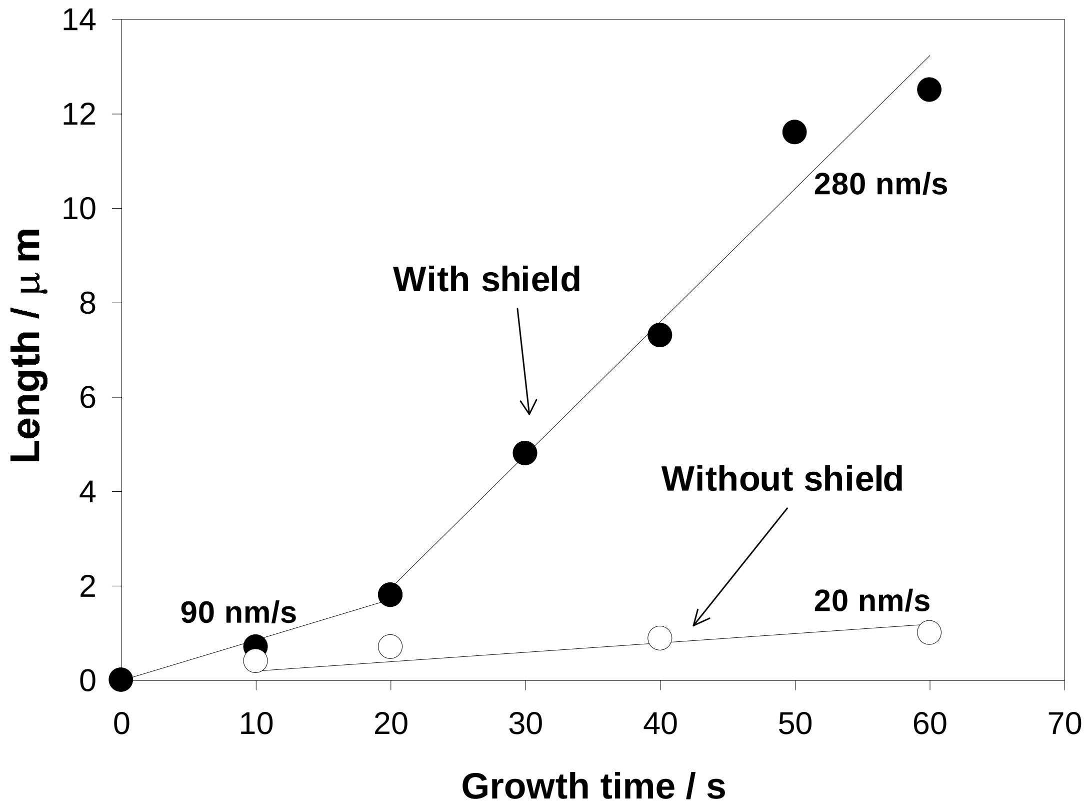


FIG.4. Kinoshita et al.