Growth mechanism of vertically aligned carbon nanotubes on silicon substrates

Young Chul Choi[a], Dae Woon Kim[b], Tae Jae Lee[b],
Cheol Jin Lee[b], Young Hee Lee[a,*]

[a]*Department of Semiconductor Science and Technology, Department of Physics and Semiconductor Physics Research Center,
Chonbuk National University, Chonju 561-756, South Korea*
[b]*Department of Electrical Engineering, Kunsan National University, Kunsan 573-701, South Korea*

Abstract

We have synthesized vertically aligned carbon nanotubes by thermal chemical vapor deposition using C_2H_2 gas on a large area of transition metal-coated Si substrates. It is observed that control of nucleation sites of transition metals deposited on Si substrates by a dipping in a HF solution and/or NH_3 pretreatment is a crucial step for the growth of vertically aligned carbon nanotubes prior to the reaction of C_2H_2 gas. We show that the transition metals play as nucleation seeds and lead to further cap growth by forming a metal cap at the end of nanotubes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Transition metals; Carbon nanotubes; Thermal chemical vapor deposition

1. Introduction

Carbon nanotubes (CNTs) have been extensively investigated for the synthesis using arc discharge [1,2], laser vaporization [3], pyrolysis [4], and plasma-enhanced chemical vapor deposition (CVD) [5,6], for its unique physical and chemical properties [7–12] and for applications to nanoscale devices [13–15]. The issues in this area are the synthesis in large quantity, reproducibility, controllibility of diameters and lengths, selective growth, and its further applications to nanoscale devices such as field emission displays, electrodes for secondary battery, fuel cells, memory devices and so on.

Practical applications are still limited by the intricate sample-preparation processes, lack of synthesizing method in massive quantity and large area synthesis. Large quantity of carbon nanotubes have been obtained by arc discharge [16] and laser vaporization [3]. However, a new synthesizing method is required, since industry requires tons of nanotubes for applications. In order to apply nanotubes to field emission displays, in situ growth of vertically aligned nanotubes in a large area of substrates is always desirable, since it does not require intricate sample-preparation processes. For this purpose, vertically aligned nanotubes have been grown on

glass [5] and on porous media [17,18], although the growth mechanism is still far from being clearly understood. Here, we show that carbon nanotubes can be grown vertically on plain silicon substrates by the thermal CVD using C_2H_2 gas. We demonstrate that the surface morphology of catalyzed transition metals can be modified by a simple surface pretreatment and controls the alignment of nanotubes at an initial stage of the growth. Nanotubes are further grown by the catalyst-cap growth.

2. Experimental

The *p*-Si substrates with a resistivity of $15\,\Omega\,cm$ were thermally oxidized with the layer thickness of 300 nm. Transition metals (Co, Ni/Co, and Co–Ni alloy) with layer thicknesses of 100 nm were thermally evaporated at room temperature in a vacuum of 10^{-6} Torr. These samples were further annealed at 400°C in Ar ambient for 20 min. This annealing procedure was necessary for strong adhesion of the metal layers with oxidized Si substrates. Annealed samples were dipped for 100–400 s in a HF solution and were then loaded on the quartz boat inside the CVD quartz reactor of 60 mm in diameter. The size of the samples was $20\,mm \times 30\,mm$. The quartz boat was designed to load several samples. Ar gas was flowed into the quartz reactor in order to prevent the oxidation of transition metal during

---

Table 1
Pretreatment conditions of surface metals[a]

Sample	Metals	HF-solution ratio (HF:DI water)	HF dipping time (s)	NH3 pretreatment time (min)
A	Co	1:16	300	
B	Ni	1:16	200	10
C	Co–Ni(1:1.5)	1:12	140	10

[a]Metals are deposited by thermal evaporation method with layer thickness of 100 nm.

heating to the growth temperature. Some samples were pretreated using NH_3 gas with a flow rate of 80–300 standard cubic centimeter per minute (sccm) for 5–20 min at 800–900°C. The pretreatment conditions for catalyst metals are summarized in Table 1. Acethylene gas was then flowed into the quartz reactor with a flow rate of 15–40 sccm at 800–900°C for 10–20 min. The reactor was cooled slowly down to room temperature in Ar ambient after the growth.

3. Results and discussion

Fig. 1(a) shows the scanning electron microscope (SEM) image (JEOL, JSM-6400, 20 kV) of CNTs from the sample A. Acethylene gas was flowed with 15 sccm for 20 min. Synthesized carbon nanotubes are uniformly distributed with a relatively high density. No carbonaceous particles are observed over the entire surface area of the substrate. The figure shows quite a uniform diameters of about 200 nm. All nanotubes are laid down on the substrate with long noodle shapes. We note that all nanotube tips are terminated by the metal particles at the end, in good agreement with the previous observations [3,5,17,20]. This strongly suggests that the metal particles play a crucial role as a catalyst at the tip of the nanotube for the growth [19,20]. No nanotubes are synthesized on Co-coated Si substrates with the HF dipping time of 200 s. Instead, carbonaceous particles are formed. Nanotubes were grown uniformly over the whole area with HF dipping time of up to 300 s but catalytic layers were completely etched by the HF dipping for 400 s. The choice of HF dipping time is correlated to the thickness of catalytic layers. Although the HF dipping time of 200 s was used, nanotubes were grown after the NH_3 treatment with a flow rate of 300 sccm for 10 min at 850°C. The diameter was the same but the density of nanotubes was reduced significantly.

In order to investigate the dependence of nanotube growth upon catalyst, Ni layers of 100 nm (sample B) were further deposited on Co-coated Si substrates. The HF dipping for 200 s, followed by the NH_3 treatment of a flow rate of 300 sccm for 10 min at 850°C was done for surface treatment. Nanotubes were grown with the acethylene gas (flow rate: 40 sccm) for 10 min, as shown in Fig. 1(b). The diameter of nanotubes is about 100 nm, smaller than the
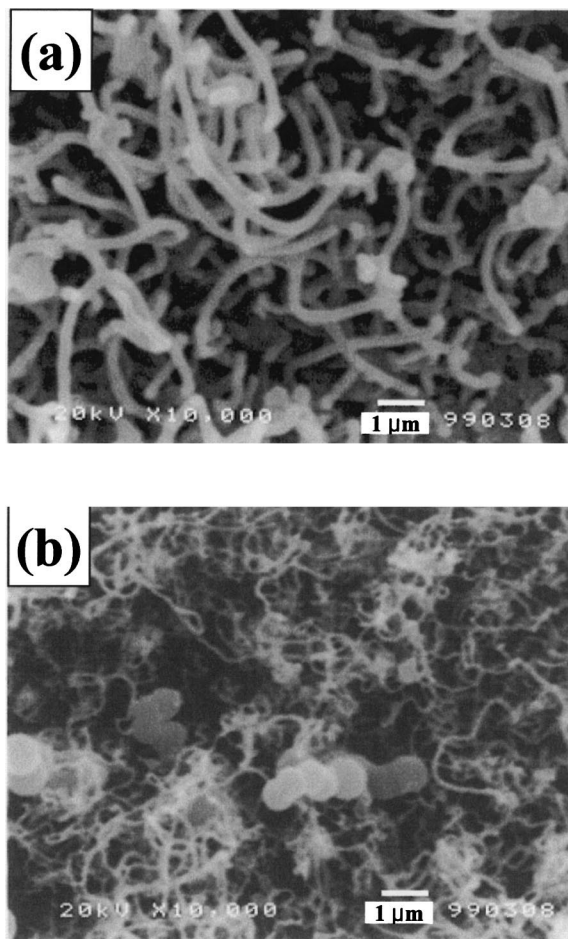

Fig. 1. SEM images of carbon nanotubes on (a) Co-coated, and (b) Ni/Co-coated substrates.

diameter of nanotubes (200 nm) on Co-coated surface. The density of nanotubes is low and the carbonaceous particles are also observed with nanotubes. We have also evaluated the effect of flow rates of NH_3 and HF dipping time on nanotube growth. The flow rates of NH_3 gas and HF dipping time controlled the densities of nanotubes but did not affect diameters of nanotubes. A keen control is required to obtain dense and uniform nanotubes. This strongly suggests that the choice of metal particles is a way to control diameters. The domain sizes of the metal particles which are directly correlated with the nanotube diameters [5] could be controlled by changing conditions of the metal evaporation.

Fig. 2 shows the SEM images of the surface morphologies of Co-coated Si substrates with different HF dipping times. The HF dipping for 100 s (Fig. 2(a)) simply etches away the Co layer and increases the surface roughness. The HF dipping for 300 s further etches away the metal surface to make microcracks on the surface, as shown in Fig. 2(b). Further dipping for 400 s completely removes the Co layers on the oxidized Si substrate. This implies that the nanotube synthesis is critically dependent on the surface morphology of metal layers. We note that carbon nanotubes can be
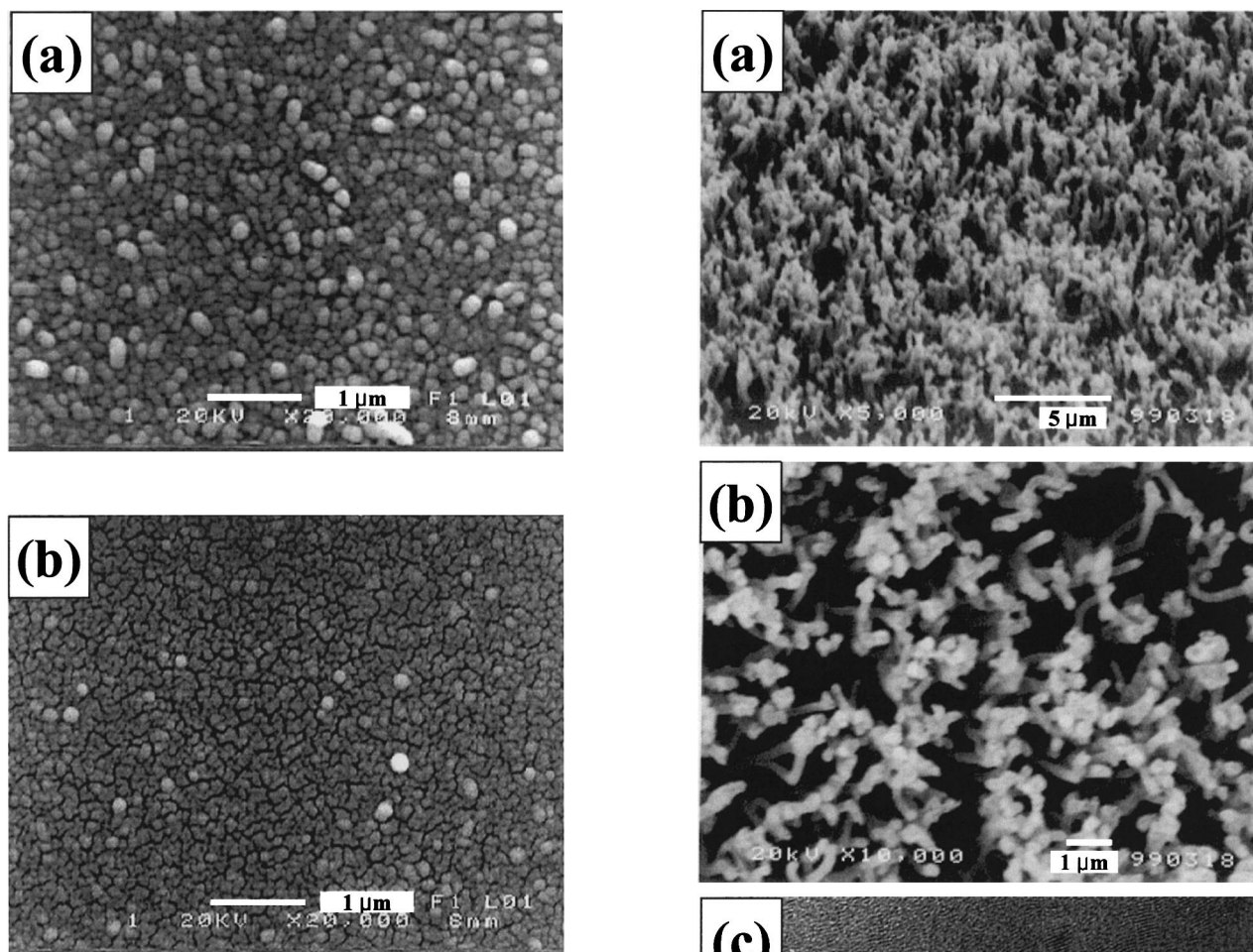
Fig. 2. SEM images of surface morphologies of Co metal layers on Si substrate, treated for different HF dipping times of (a) 100 s, and (b) 300 s.

synthesized regardless of NH_3 treatment, contrary to the previous report that the NH_3 treatment can play a crucial catalytic role for the nanotube growth [5].

Fig. 3 shows the SEM images of CNTs grown on the sample C. The HF dipping for 140 s, followed by the NH_3 treatment of a flow rate of 80 sccm for 10 min at 850°C was done for the treatment of Co–Ni surface. CNTs were grown with C_2H_2 gas flow rate of 40 sccm at 850°C for 10 min. CNTs are well aligned vertically over a large area (20 mm × 30 mm) of the substrate. The surface morphologies of CNTs are clean and uniform with the length of about 5 μm and the diameter of about 200 nm. Note that top of the aligned nanotubes is terminated by a transition-metal cap, the white spot. Fig. 3(a) reveals high density of nanotubes, where nanotubes are curly at the bottom but rather straight near the top of nanotubes [20]. The density of nanotubes is about 3×10^8 cm^{-2}, about 100 times larger than the typical density of microtips in conventional spindt-type field emission arrays. It is noted that all the nanotubes are elected on the layer of transition metals. We emphasize here that nanotubes can be aligned vertically on plain Si substrates using a simple surface treatment, in good contrast with the

Fig. 3. SEM (a,b) and TEM (c) images of carbon nanotubes grown on sample C.

previous reports that nanotubes are aligned on catalyzed porous Si [17] and CNTs are grown but not vertically aligned on catalyst-patterned Si substrates [21]. We evaluated the wall structures by the transmission electron microscopy (TEM) (Hitachi H-9000NA, 300 kV), as shown in Fig. 3(c). Peeled nanotubes were dispersed on a copper carbon-microgrid. TEM image shows long and straight multi-wall nanotube with an hollow inside, where the lattice images are shown clearly. Long range lattice images are not

formed due to relatively low growth temperature. This was also confirmed in our Raman scattering measurement that large peak near 1295 cm^{-1} was observed with the main G-peak at 1595 cm^{-1}.

Vertically aligned nanotubes were reproducibly grown with the above conditions. We have also tried various growth conditions [20]. CNTs were grown well independent of growth temperatures within the temperature range of 800–900°C, since C$_2$H$_2$ gases are highly decomposed in this range by the assistance of catalytic particles [17]. Tube lengths increased with increasing growth time, although some carbonaceous particles appeared with longer growth time. The growth rate was 30 μm h^{-1}, similar to that from the CNT growth on porous Si [17]. We note that the HF dipping and NH$_3$ pretreatment are crucial steps to obtain high density of nucleation sites. Without NH$_3$ pretreatment, CNTs were grown uniformly but not vertically aligned. Therefore, the NH$_3$ pretreatment is a very critical step in vertically aligning carbon nanotubes on Si substrates.

Fig. 4 shows SEM images of surface morphologies for Co–Ni alloys, pretreated with HF dipping and NH$_3$ treatment. The HF dipping etches metal surface and increases the surface roughness with increasing the HF dipping time, as shown in Fig. 4(b). The subsequent NH$_3$ pretreatment further etches the surface and forms small domains inside the metal cluster, as shown in Fig. 4(c), acting as nucleation seeds for vertical alignment of nanotubes. Longer HF dipping time resulted in microcracks on the surface but no small domains were formed within microcracks. The size of small domains within the metal cluster in Fig. 4(c) is about 200 nm, the same as the diameter of CNTs. This strongly suggests that carbon diffusion within the small domain is limited by the domain wall. With the absence of NH$_3$ pretreatment, nanotubes were laid down with a low density. Both HF dipping and NH$_3$ pretreatment were necessary to control the surface morphology to align nanotubes vertically in case of using the Co–Ni alloy. Our results indicate that the NH$_3$ pretreatment is a necessary step for vertical alignment of nanotubes but not responsible for nanotube growth. Nanotubes grown on Ni-coated substrates had a diameter of about 100 nm, whereas diameters of nanotubes grown on Co-coated substrates were about 200 nm. However, nanotubes were not vertically aligned in both cases [20]. In case of the Co–Ni alloy, we found that Ni particles were etched away during dry etching of NH$_3$, which resulted in the increase of the density of nucleation sites within Co particles. This was confirmed by the energy-dispersive X-ray (EDX) measurement [20]. The amount of Co left on the surface after NH$_3$ treatment was about six times larger than that of Ni. (Note that the amount of Ni was 1.5 times larger than that of Co in as-deposited samples.) When the density of nucleation sites reaches a certain value, nanotubes grown in directions other than vertical direction are prohibited from growing due to the steric hindrance from the adjacent nanotubes and then change the growth direction to further grow vertically.
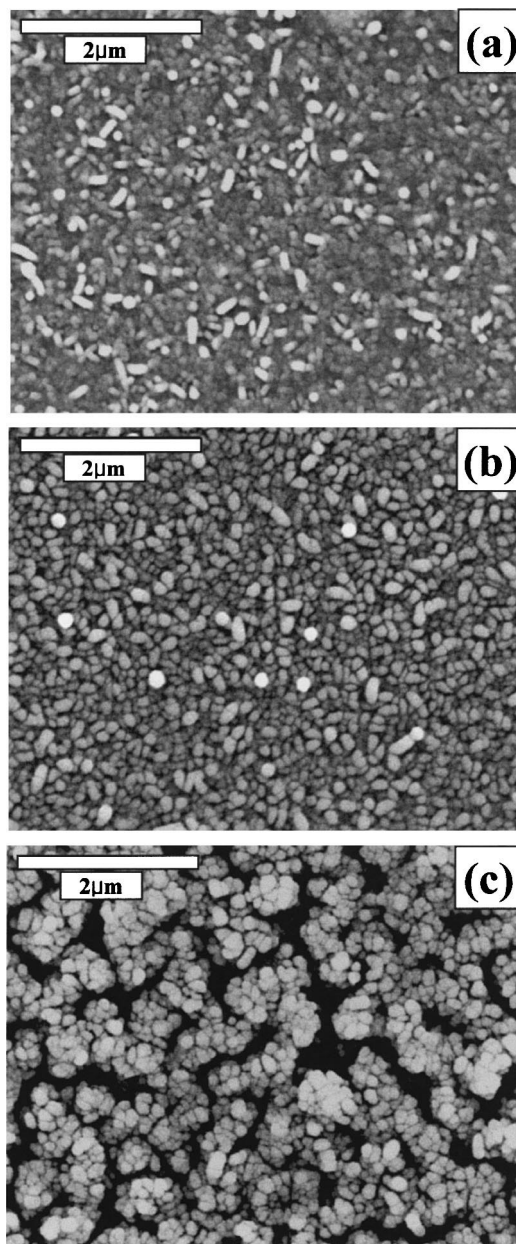
Fig. 4. SEM images of surface morphologies for Co–Ni alloys, (a) no HF dipping, (b) HF dipping for 140 s, and (c) HF dipping for 140 s, followed by NH$_3$ pretreatment for 10 min.

Fig. 5 illustrates our proposed growth model. C$_2$H$_2$ molecules are catalytically adsorbed on the metal domains. As carbon atoms are further supplied, a carbon-metal eutectic alloy can be formed, decreasing the melting temperature of the alloy. Formation of carbon-metal eutectic alloy enhances the diffusion of carbon in the metal alloy, initiating carbon aggregations which act as a nucleation seed for nanotube growth, as shown in Fig. 5(a). The carbon diffusion is limited by the domain size within the metal particles and thus the diameter of nanotubes should be smaller than the domain size. As the nanotube grows further, part of the metal domain is pushed upward, forming a metal cap, as shown in
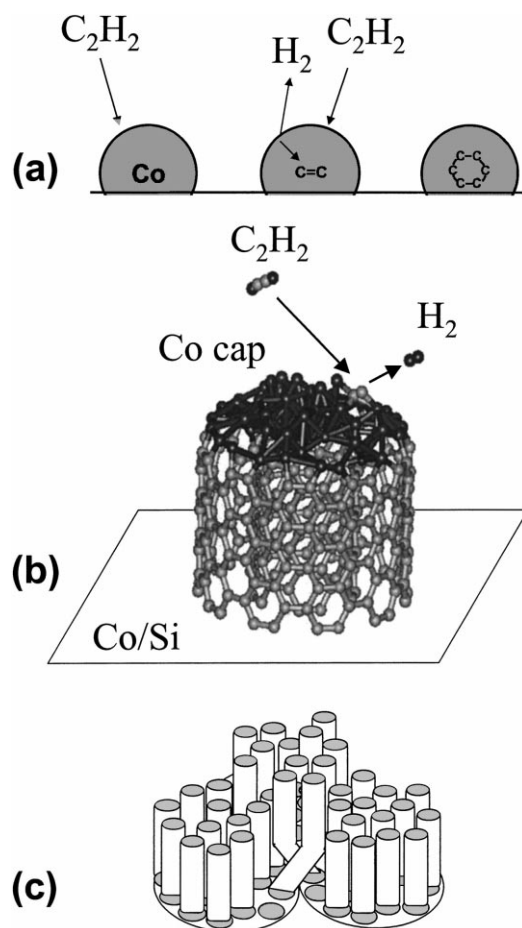
Fig. 5. Schematic diagram of proposed growth model. (a) Formation of nucleation process; (b) cap growth; (c) mechanism for vertical alignment.

Fig. 5(b). This metal cap saturates dangling bonds of the nanotube at the edge, stabilizing nanotube edges. Presuming sufficient supply of carbon atoms and high density of domains within the metal cluster, nanotubes are forced to align vertically, as shown in Fig. 5(c). Some nanotubes at the edge of the cluster may not be aligned vertically at the initial stage but will be eventually aligned vertically by the steric hindrance from other nanotubes for further growth, as shown in Fig. 5(c). The carbon atoms which are supplied from the adsorbed metal surfaces or from the tube surfaces can participate in the nanotube growth at the initial growth stage. However, as CNTs become longer, C_2H_2 gases may not easily reach the bottom of the substrate due to the compact CNTs highly populated on the surface. Instead, they will have a better chance to reach the top metal cap and then adsorbed carbon atoms can diffuse into the edge of nanotubes. Formation of complete hexagons is catalytically promoted by the assistance of the metal cap [19], giving rise to the continuous cap growth. This model is able to provide uniform height of nanotubes in large area and control the height with growth time. Uniform growth in height may not be achieved on catalyst-patterned substrates with the model

of base growth suggested in the previous work [18]. Our model can also explain the existence of the metal caps at the top of nanotubes after the growth, as observed from our SEM images and other reports [5,17].

4. Summary

In summary, we have grown vertically aligned carbon nanotubes on a large area of plain Si substrates using thermal chemical vapor deposition. Diameters of nanotubes are highly selective with different choices of transition metals. It is very essential to control the surface morphologies of transition metal layers by HF dipping and/or NH_3 pretreatment for the growth of carbon nanotubes with high quality. We proposed cap growth model for long tube growth. Formation of transition metal cap at the tip of the nanotubes promotes the adsorption of hydrocarbons and enhances the carbon diffusion in carbon-metal eutectic alloy. CNTs are grown vertically when the nucleation density reaches a certain value. Some nanotubes at the edge of the cluster may not be aligned vertically at the initial stage but will be eventually aligned vertically by the steric hindrance from the adjacent nanotubes. The current approach with the thermal CVD is expected to be easily applicable to a larger size of the substrates.

References

[1] S. Iijima, T. Ichihashi, Nature 363 (1993) 603.
[2] D.S. Bethune, C.H. Kiang, M.S. deVries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Nature 363 (1993) 605.
[3] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, D.T. Colbert, G. Scuseria, D. Tománek, J.E. Fischer, R.E. Smalley, Science 273 (1996) 483.
[4] M. Terrones, N. Grobert, J. Olivares, J.P. Zhang, H. Terrones, K. Kordatos, W.K. Hsu, J.P. Hare, P.D. Townsend, K. Prassides, A.K. Cheetham, H.W. Kroto, D.R.M. Walton, Nature 388 (1997) 52.
[5] Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, Science 282 (1998) 1105.
[6] S.L. Sung, S.H. Tsai, C.H. Tseng, F.K. Chiang, X.W. Liu, H.C. Shih, Appl. Phys. Lett. 74 (1999) 197.
[7] N. Hamada, S. Sawada, A. Oshiyama, Phys. Rev. Lett. 68 (1992) 1579.
[8] J.W. Mintmire, et al., Phys. Rev. Lett. 68 (1992) 631.
[9] T.M. Whitney, J.S. Jiang, P.C. Searson, C.L. Chien, Science 261 (1993) 1316 .
[10] M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, Science of Fullerenes and Carbon Nanotubes (Academic Press, San Diego, 1996), (Chapter 19) and references therein.
[11] M.M.J. Treacy, T.W. Ebbesen, J.M. Gibson, Nature 381 (1996) 678.

[12] P. Delaney, H.J. Choi, J. Ihm, S.G. Louie, M.L. Cohen, Nature 391 (1998) 466.

[13] W.A. de Heer, A. Chatelain, D. Ugarte, Science 270 (1995) 1179.

[14] S.J. Tans, R.M. Verschueren, C. Dekker, Nature 393 (1998) 49.

[15] S.J. Tans, R.M. Verschueren, C. Dekker, Nature 386 (1997) 474.

[16] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M.Lamy de la Chapelle, S. Lefrant, P. Deniard, R. Lee, J.E. Fischer, Nature 388 (1997) 756.

[17] W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao, G. Wang, Science 274 (1996) 1701.

[18] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Casell, H. Dai, Science 283 (1999) 512.

[19] Y.H. Lee, S.G. Kim, D. Tomanek, Phys. Rev. Lett. 78 (1997) 2393.

[20] C.J. Lee, D.W. Kim, T.J. Lee, Y.C. Choi, Y.S. Park, W.S. Kim, Y.H. Lee, W.B. Choi, N.S. Lee, J.M. Kim, Chem. Phys. Lett. 312 (1999) 461.

[21] J. Kong, H.T. Soh, A.M. Cassell, C.F. Quate, H. Dai, Nature 395 (1998) 878.