

High Density Growth of Horizontally Aligned Single-Walled Carbon Nanotubes on Quartz by Variation of Incubation Time

Taiki Inoue, Daisuke Hasegawa, Saifullah Badar, Shinya Aikawa¹, Shohei Chiashi, Shigeo

Maruyama*

Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku,

Tokyo 113-8656, Japan

Abstract

We studied the influence of gas pressure on the growth of horizontally aligned single-walled carbon nanotubes (SWCNTs) on R-cut crystal quartz substrates by alcohol chemical vapor deposition. The density of horizontally aligned SWCNTs was found to depend highly on gas pressure. Time evolution of horizontally aligned SWCNT growth revealed that the density of horizontally aligned SWCNTs continued to increase for 10 min at reduced pressure, whereas the density saturated rapidly at higher pressure even though catalysts were not deactivated. We concluded that variation of incubation time for low-pressure CVD is key for independent growth of aligned SWCNTs and hence higher density growth.

*Corresponding author. Fax: +81-3-5800-6983.

E-mail address: maruyama@photon.t.u-tokyo.ac.jp (S. Maruyama).

¹ Current address: International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

1. Introduction

Because single-walled carbon nanotubes (SWCNTs) [1] have outstanding electrical, thermal, and mechanical properties, many research efforts have been done to control SWCNT growth. For many applications, alignment control of SWCNTs is critically important. Both post-growth alignment techniques and direct growth of aligned SWCNTs have been studied. The former requires dispersing SWCNTs in solutions [2], and causes degradation of SWCNTs due to encapsulation by surfactants and cutting into short segments by sonication. In contrast, the latter methods cause no degradation and accordingly enable us to use the full potential of SWCNTs. Direct-growth alignment methods include chemical vapor deposition (CVD) using an applied electric field [3], gas-flow [4], or surface structure of crystalline substrates [5-8]. Among these, aligned growth of SWCNTs on crystalline substrates such as sapphire [7, 9] and crystal quartz [8] is promising because high-density, highly aligned SWCNTs can be obtained. The mechanism of this alignment growth is explained by van der Waals interactions between SWCNTs and the surface atomic structure of crystal substrates for sapphire [7, 9] and for crystal quartz [10, 11]. In other words, SWCNTs grow along the periodic potential valleys on the substrate surface.

Direct growth of horizontally aligned SWCNTs is desirable for the fabrication of field effect transistors (FETs) [12], and density enhancement of horizontally aligned SWCNTs is necessary for improving the performance of FETs [13]. High-density growth has been studied focusing on CVD conditions [14-16], catalyst preparation [15, 17-21], and surface treatment of quartz [22-24]. Furthermore, in addition to single-cycle growth, multiple-cycle CVD growth [25, 26] and multiple-cycle transfer of SWCNTs [27, 28] have been performed to increase the density.

By the CVD method, SWCNTs with various morphologies, such as randomly oriented SWCNTs [29], vertically aligned SWCNTs [30], and gas-flow induced aligned SWCNTs [4] have been grown. Although the underlying growth mechanism of individual SWCNTs should be the same, different growth morphologies have specific influences on SWCNT growth due to interactions with the substrate, with the gas flow, or among SWCNTs. In order to control the density of horizontally aligned SWCNTs on quartz we need to understand the overall behavior of growing many SWCNTs, as well as the growth mechanism of each SWCNT.

In this study, we investigated the effects of CVD conditions on the morphology of horizontally aligned SWCNTs grown on quartz substrates. Although CVD includes various parameters such as carbon source gas species, growth temperature, and gas pressure, we

focused on the gas pressure as an important factor. For example, the growth temperature simultaneously affects the decomposition rate of carbon source gas in gas phase, the diameter distribution of catalyst nanoparticles, and the reactivity of catalyst nanoparticles, making it difficult to examine the growth mechanism. On the other hand, gas pressure is mainly related to the feeding rate of carbon atoms to the catalyst nanoparticles, and does not significantly affect other aspects of the growth. By changing the growth time we investigated the time evolution of horizontally aligned SWCNT growth and discuss the important aspect of aligned growth mechanism for high-density SWCNTs.

2. Experimental Methods

R-cut crystal quartz substrates (Kyocera Crystal Device Co.) were used for the growth of horizontally aligned SWCNTs. R-cut quartz substrates are cut parallel to the natural R-plane, upon which we recently reported aligned growth of SWCNTs [11]. The R-cut quartz substrates were treated by chemical etching with ammonium hydrogen fluoride, and followed by annealing in air at 900 °C for 12 h. These processes improve the crystallinity of the quartz surface and enhance the degree of alignment of SWCNTs [22-24]. Iron with nominal thickness of ~0.2 nm was prepared as catalyst in a stripe pattern using photolithography, thermal evaporation, and lift-off. Stripes with width of 3 μm and intervals of 50 μm were patterned perpendicular to the alignment direction. After the lift-off process, the substrates

were rinsed by distilled water, and then annealed in air at 550 °C for 10 min in order to remove any residual photoresist.

Horizontally aligned SWCNTs were grown by the alcohol catalytic CVD method [31] using ethanol as the carbon source gas. The CVD apparatus was composed of a quartz tube with an inner diameter of 26 mm surrounded by an electric furnace with a length of 60 cm. A substrate was placed in the chamber at the center of the heating zone, and the catalysts were reduced under flowing Ar/H₂ (3 %) gas while increasing the temperature to 800 °C. After reaching 800 °C, the Ar/H₂ gas flow was stopped and ethanol gas was introduced. The flow rates of the gases were controlled by digital mass flow controllers. For certain experiments, the Ar/H₂ mixture was also introduced as a carrier gas in addition to ethanol so as to keep the gas flow rates at the same order for each gas pressure condition. This is because the decomposition of carbon source in the gas phase, which is affected by flow rate, is also related to the net carbon feeding rate and SWCNT growth [32]. The partial pressure of ethanol was determined by both flow rates and total pressure.

SWCNTs were characterized by scanning electron microscopy (SEM, Hitachi S-4800), atomic force microscopy (AFM, SII SPI3800N), and resonance Raman spectroscopy (homemade system based on Seki Technotron STR-250) with an excitation laser wavelength

of 488 nm. For AFM measurements, horizontally aligned SWCNTs were transferred using poly(methyl methacrylate) film [33] onto silicon substrates in order to precisely measure the tube diameter.

3. Results and discussion

3-1. Effect of CVD gas pressure

To investigate the effect of the CVD gas pressure, horizontally aligned SWCNTs were grown under different ethanol partial pressures. The growth time was fixed at 10 min and the CVD gas pressure was varied from 60 to 1300 Pa. Figure 1 (a) shows SEM images of SWCNTs grown at each gas pressure. SWCNTs grew from the patterned catalyst stripes and aligned horizontally along the direction of the quartz x-axis. The number density of SWCNTs for each gas pressure is plotted in Figure 1 (b). The number density was determined at a distance of 10 μm away from the edge of the catalyst area. We find that as the partial pressure of carbon source gas decreased, the density of horizontally aligned SWCNTs increased.

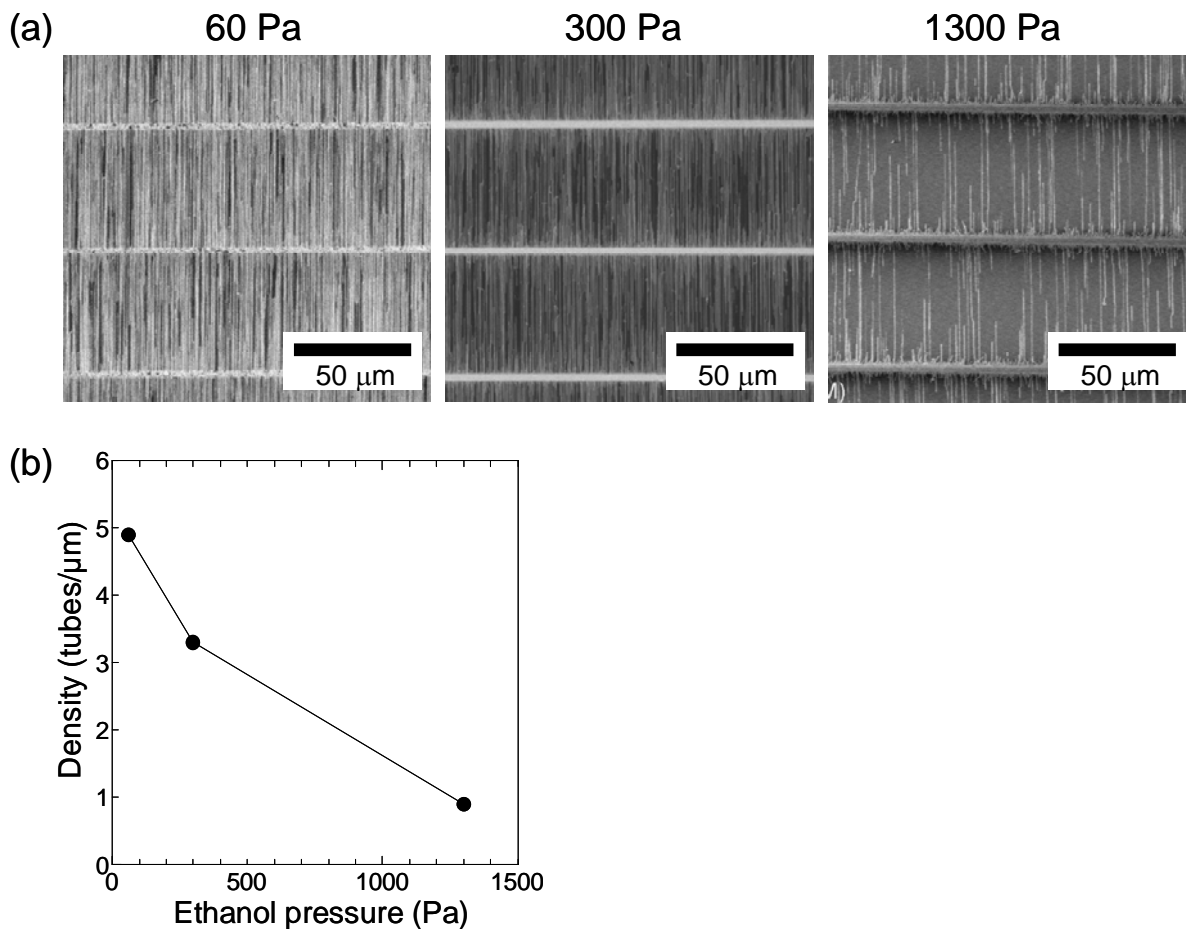


Figure 1 (a) SEM images and (b) density of horizontally aligned SWCNTs grown on quartz substrates under 60, 300, and 1300 Pa of ethanol.

Horizontally aligned SWCNTs were characterized by resonance Raman spectroscopy. Figure 2 shows Raman spectra of SWCNTs measured at several points along the alignment direction with different distance from the catalyst area. The excitation wavelength was 488 nm. Radial breathing mode peaks and split G-band peaks clearly show the existence of SWCNTs. Additionally, we found up-shifts of the G-band feature measured at points away

from the catalyst area. These up-shifts are considered as the indication of strong interaction between SWCNTs and the surface structure of crystal quartz [34]. G-bands of aligned SWCNTs which are strongly bound on quartz substrates show up-shifts compared to those of randomly oriented, weakly interacting SWCNTs. Accordingly, these position dependent up-shifts of G-bands indicated that SWCNTs were randomly oriented near the catalyst area and aligned away from the catalyst area.

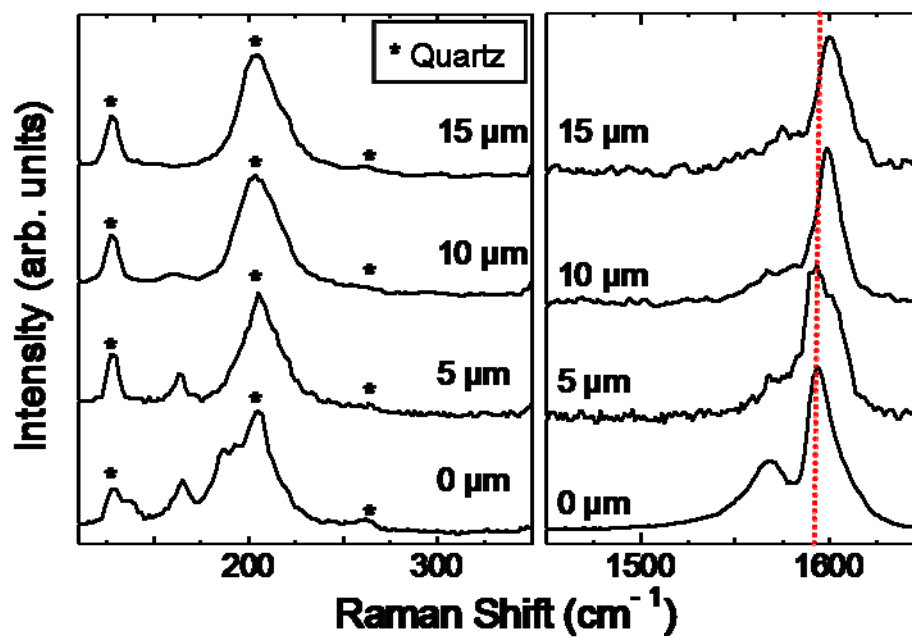


Figure 2 Raman spectra of SWCNTs measured at four points along the alignment direction: on the catalyst area (0 μm) and positions of 5, 10, and 15 μm away from the catalyst area.

3-2. Growth process of horizontally aligned SWCNTs

Next we investigated the time evolution of horizontally aligned SWCNT growth in order to obtain more detailed information about the growth process. SWCNTs were grown for different times under two gas pressure conditions of 60 and 1300 Pa. SEM images of SWCNTs grown at each growth time are shown in Figure 3 (a). The growth of aligned SWCNTs at the higher gas pressure was nearly saturated within 0.5 min, while aligned SWCNTs at the lower gas pressure continued to grow even after 5 min of CVD. At lower gas pressure, aligned SWCNTs grow at a slower rate, but eventually attain higher density than was achievable at higher pressure. Length distributions per unit area of horizontally aligned SWCNTs were measured for the space between the catalyst patterns, and are plotted in Figure 3 (b). These data clearly show that the number and length of SWCNTs continued to increase for 10 min in the low pressure condition.

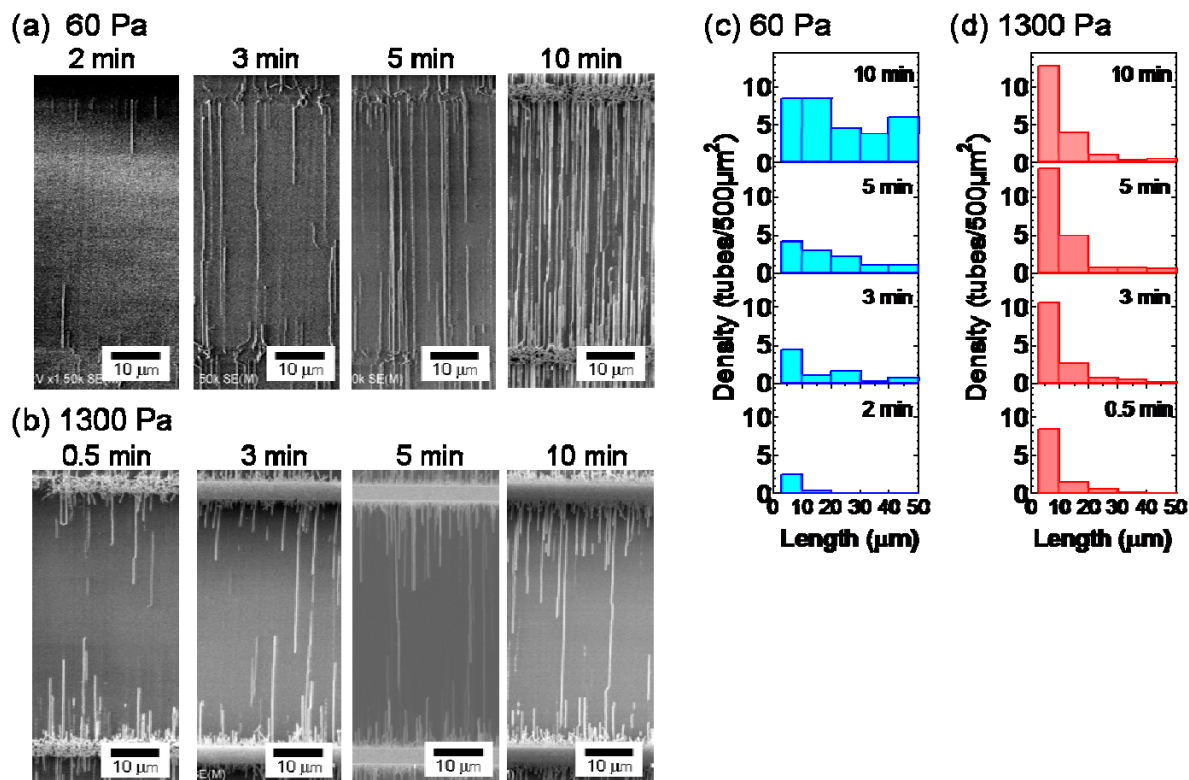


Figure 3 Time evolution of horizontally aligned SWCNT growth at different pressures. (a, b) SEM images and (c, d) length distributions of horizontally aligned SWCNTs grown at (a, c) 60 and (b, d) 1300 Pa.

Gas pressure of the carbon source at a certain temperature is proportional to the carbon feeding rates into the catalysts nanoparticles. Figure 3 showed that higher feeding rates caused a higher growth rate and rapid termination of aligned SWCNT growth. One may then assume that the high feeding rate caused rapid encapsulation and deactivation of the catalyst nanoparticles. To examine this possibility, we measured Raman spectra of SWCNTs in the catalyst area grown at 1300 Pa and plotted the G-band intensity in Figure 4 as a function of

growth time. Since the G-band intensity is considered to be roughly proportional to the amount of SWCNTs in the Raman excitation laser spot area, the data indicate the temporal evolution of SWCNT amount in the catalyst area. The data were fitted by an equation derived by assuming exponential decay of growth rate [35].

$$L(t) = \gamma_0 \tau \left\{ 1 - \exp\left(-\frac{t}{\tau}\right) \right\}$$

where γ_0 represents the initial growth rate and τ represents a time constant (the catalyst life time). The curve revealed that the amount of SWCNTs continued to increase, even though SEM images showed almost no change of horizontally aligned SWCNTs after 0.5 min. The time constant τ is calculated to be 4.9 min, which is close to the value obtained for vertically aligned SWCNTs grown under similar conditions [35]. Therefore, we conclude that the high-pressure condition did not prematurely terminate the growth, but the SWCNTs did not grow away from the catalyst area, thus did not contribute to the increase in horizontally aligned SWCNTs.

3-3. Effect of incubation time

Now we consider the incubation time of SWCNT growth. A certain period of time before the onset of SWCNT growth has been observed by in situ measurements [36-41], and the time delay was interpreted as the time necessary for nucleation of SWCNTs. Figure 3 shows that for the high pressure case a large number of SWCNTs grew within 0.5 min, whereas in

the low partial pressure case few SWCNTs grew within 2 min, but more continued to grow even after 5 min. A likely explanation for these observations is that the incubation time is longer at lower pressure conditions.

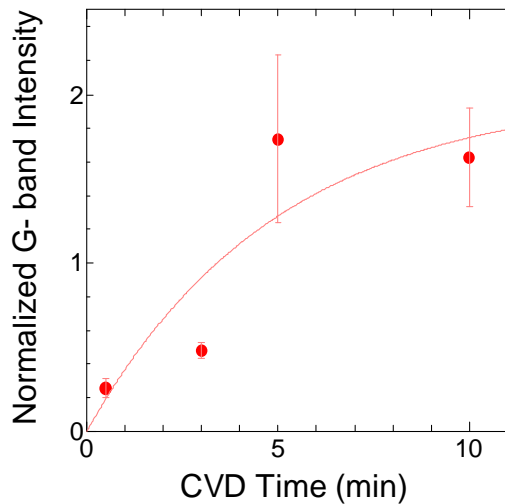


Figure 4 CVD time dependent G-band intensity on catalyst area for SWCNTs grown at 1300 Pa.

Previous studies showed an inverse relationship between incubation time and gas pressure [40, 41]. Our recent study on in situ Raman measurement [42] of SWCNT growth under low-pressure cold wall CVD also indicated similar results, which will be reported elsewhere. The origin of incubation time has been explained by the necessity of certain carbon atoms dissolving into catalyst nanoparticles before supersaturation, nucleation, and lift-off as described in the literature [43]. Note that gas pressure may affect not only the catalyst

supersaturation by carbon atoms, but also the time duration of the reduction and the deformation of catalysts by surrounding gas [44]. Here we discuss the growth mechanism of horizontally aligned SWCNTs based on the relationship between the incubation time and gas pressure.

From Figure 1, we found that the density of horizontally aligned SWCNTs increases with decreasing partial pressure of the carbon source gas. When a SWCNT starts growing, it is considered to grow in a direction away from the substrate [45]. As the SWCNT increases in length it moves around above the substrate due to thermal vibration. At some point, when the SWCNT touches the substrates, it starts growing along the substrate, and in the case of crystal quartz will align itself along the crystal structure. Here we consider two SWCNTs growing from neighboring catalysts nanoparticles. When two growing SWCNTs touch each other, they could entangle each other above the substrate by van der Waals interactions and form a bundle of SWCNTs. Bundling prior to alignment is considered to prevent aligned growth. One of the reasons for this is that two SWCNTs with different growth rates pull on each other, and the other is that an increase in the effective diameter of SWCNTs prevents the fitting of SWCNTs into the atomic scale potential valleys of the quartz surface [46]. Entangled and misaligned SWCNT bundles further prevent the growth of other SWCNTs grown later, thus reducing the final density of horizontally aligned SWCNTs. On the other

hand, when two aligned SWCNTs grow independently without forming bundles, one SWCNT touches the substrate and starts aligned growth, followed later by another one. Thus, the difference in the incubation time decreases the possibility of forming bundles just after SWCNT nucleation.

The experimental results reported here show that a decrease in gas pressure extends the incubation time of SWCNTs, thus extending the average incubation time and enhancing the difference in the onset of growth for different SWCNTs. Therefore, decreasing the gas pressure reduces the probability that neighboring SWCNTs start growing simultaneously, which results in more aligned SWCNT growth. Vertically and horizontally aligned nanotubes were grown separately by changing growth conditions [47], and this can be explained by critical importance of the incubation time for each morphology. A distinct incubation time has been hardly observed in the growth of vertically aligned SWCNTs [48], indicating that very small incubation time is the necessary condition for vertical growth. Hence, achieving vertical alignment requires that many nanotubes start growing simultaneously in order to bundle and form a self-supporting structure, whereas non-simultaneous nucleation of SWCNTs is necessary to grow horizontally aligned SWCNTs in high density.

3-4. Diameter distribution and expected highest density growth

Because the diameters of SWCNTs affect the degree of alignment of SWCNTs on crystal substrates [46], it could be possible that differences in gas pressure vary the diameter distributions of SWCNTs, which then affects the degree of alignment and SWCNT density. In order to examine the diameter difference, we performed AFM measurement of SWCNTs grown at two different gas pressures. Figure 5 shows the diameter distribution of aligned SWCNTs grown at 60 and 1300 Pa. Average diameters of 1.47 and 1.76 nm were obtained for SWCNTs grown at 60 and 1300 Pa, respectively. This slight difference can be explained by the relation between the SWCNT diameter and feeding rates of carbon source gas [49]. However, since aligned growth of SWCNTs with average diameter of 2.4 nm was reported previously [26], we consider the difference in diameter distribution in the present study is sufficiently small that it does not affect the density of horizontally aligned SWCNTs.

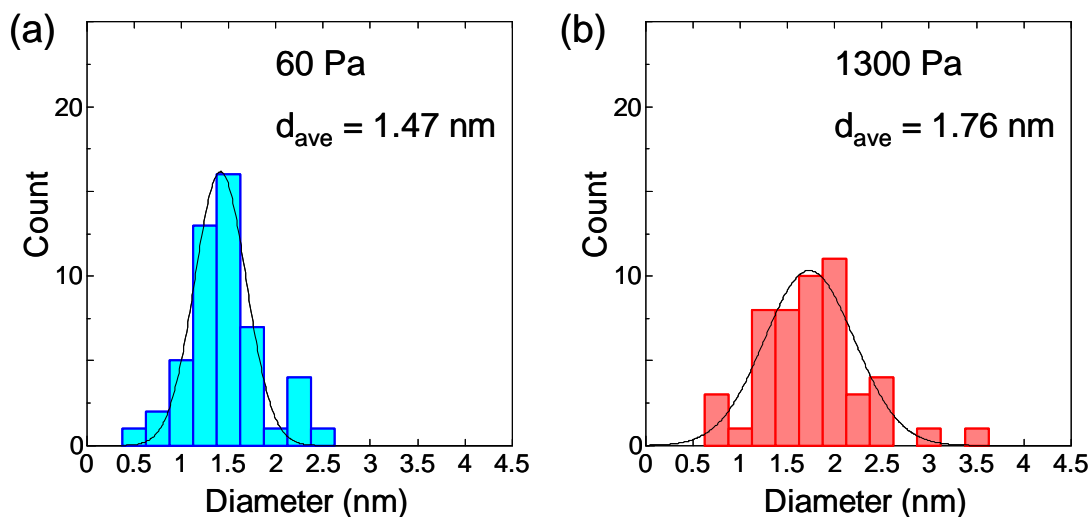


Figure 5 Diameter distributions of SWCNTs grown at (a) 60 and (b) 1300 Pa measured by AFM.

Finally, we observed SWCNTs with the highest density in this study (grown at 60 Pa) under high magnification. SEM and AFM images are shown in Figure 6. The SWCNT density was about 10 tubes/ μm at several different points. Furthermore, the shortest distance between two adjacent SWCNTs shown in the AFM image is about 15 nm, which corresponds to a local density of > 60 tubes/ μm . In this study, we did not optimize conditions for the catalyst deposition and the surface treatment of substrates, and left these aspects unchanged in order to investigate the effect of gas pressure. Because these conditions can significantly affect the degree of alignment and the density of horizontally aligned SWCNTs [17-24], it is possible to further enhance the density of SWCNTs by optimizing the conditions.

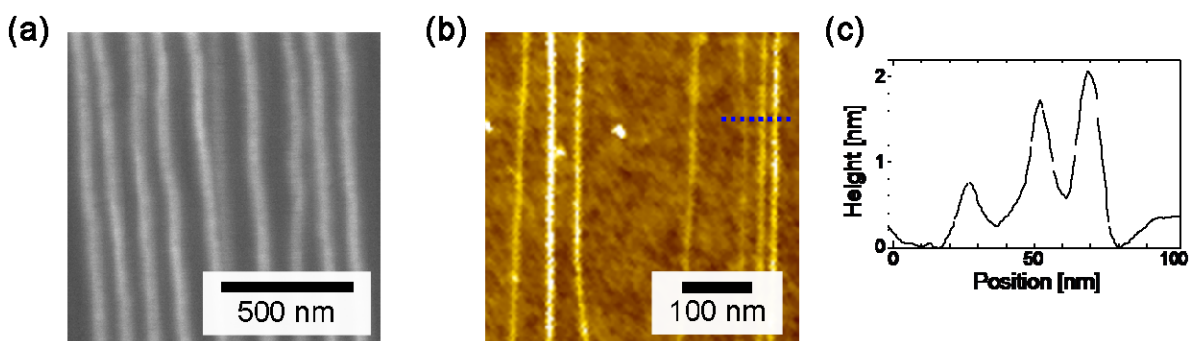


Figure 6 (a) SEM and (b) AFM images of horizontally aligned SWCNTs. (c) Cross section profile along the dashed line in the AFM image.

4. Conclusions

In summary, we investigated the growth of horizontally aligned SWCNTs on quartz substrates. We demonstrated that the density of horizontally aligned SWCNTs depends on the partial pressure of the carbon source gas. We also examined the time evolution of horizontally aligned SWCNT growth, and found that density of horizontally aligned SWCNTs continued to increase for longer time at lower pressure, in comparison with rapid saturation at higher pressure. Based on incubation time, growth mechanisms of aligned SWCNTs were discussed. By extending the average incubation time and causing larger variations in nucleation times, SWCNTs grew without forming bundles and high-density growth was achieved. AFM measurements revealed that the difference in diameter distribution by CVD pressures is small, and we discussed the possibility of further enhancement of SWCNT density.

Acknowledgement.

We thank Dr. E. Einarsson at the University of Tokyo for useful discussion. Part of this work was supported by Grants-in-Aid for Scientific Research (22226006 and 23760179), JSPS Core-to-Core program, and Global COE Program “Global Center of Excellence for Mechanical Systems Innovation”. One of the authors (TI) was financially supported by a JSPS Fellowship (23-8717). This work was also supported by the VLSI Design and

Education Center (VDEC), The University of Tokyo, in collaboration with Cadence Corporation.

Reference

- [1] Iijima S; Ichihashi T. Single-shell carbon nanotubes of 1-nm diameter. *Nature* 1993;363(17):603-5.
- [2] Lay MD, Novak JP, Snow ES. Simple route to large-scale ordered arrays of liquid-deposited carbon nanotubes. *Nano Lett* 2004;4(4):603-6.
- [3] Zhang Y, Chang A, Cao J, Wang Q, Kim W, Li Y, et al. Electric-field-directed growth of aligned single-walled carbon nanotubes. *Appl Phys Lett* 2001;79(19):3155-7.
- [4] Huang S, Cai X, Liu J. Growth of millimeter-long and horizontally aligned single-walled carbon nanotubes on flat substrates. *J Am Chem Soc* 2003;125(19),5636-7.
- [5] Su M, Li Y, Maynor B, Buldum A, Lu JP, Liu J. Lattice-oriented growth of single-walled carbon nanotubes. *J Phys Chem B* 2000;104(28):6505-8.
- [6] Ismach A, Segev L, Wachtel E, Joselevich E. Atomic-step-templated formation of single wall carbon nanotube patterns. *Angew Chem Int Ed* 2004;43(45):6140-3.
- [7] Ago H, Nakamura K, Ikeda K, Uehara N, Ishigami N, Tsuji M. Aligned growth of isolated single-walled carbon nanotubes programmed by atomic arrangement of substrate surface. *Chem Phys Lett* 2005;408(4-6):433-8.

- [8] Kocabas C, Hur SH, Gaur A, Meitl MA, Shim M, Rogers JA. Guided growth of large-scale, horizontally aligned arrays of single-walled carbon nanotubes and their use in thin-film transistors. *Small* 2005;1(11):1110-6.
- [9] Han S, Liu X, Zhou C. Template-free directional growth of single-walled carbon nanotubes on a- and r-plane sapphire. *J Am Chem Soc* 2005;127(15):5294–5.
- [10] Xiao J, Dunham S, Liu P, Zhang Y, Kocabas C, Moh L, et al. Alignment controlled growth of single-walled carbon nanotubes on quartz substrates. *Nano Lett* 2009;9(12):4311-9.
- [11] Chiashi S, Okabe H, Inoue T, Shiomi J, Sato T, Kono S, et al. Growth of horizontally aligned single-walled carbon nanotubes on the singular R-plane (10–11) of quartz. *J Phys Chem C* 2012;116(12):6805–8.
- [12] Kang SJ, Kocabas C, Ozel T, Shim M, Pimparkar N, Alam MA, et al. High-performance electronics using dense, perfectly aligned arrays of single-walled carbon nanotubes. *Nat Nanotechnol* 2007;2(4):230-6.
- [13] Patil N, Deng J, Mitra S, Wong H-SP. Circuit-level performance benchmarking and scalability analysis of carbon nanotube transistor circuits. *IEEE Trans Nanotechnol* 2009;8(1):37-45.
- [14] Kocabas C, Kang SJ, Ozel T, Shim M, Rogers JA. Improved synthesis of aligned arrays of single-walled carbon nanotubes and their implementation in thin film type transistors. *J Phys Chem C* 2007;111(48):17879-86.

- [15] Ago H, Nakamura Y, Ogawa Y, Tsuji M. Combinatorial catalyst approach for high-density growth of horizontally aligned single-walled carbon nanotubes on sapphire. *Carbon* 2011;49(1):176-86.
- [16] Shi D, Tennyson WD, Keay JC, Sanchez ES, Johnson MB, Resasco DE. Role of water on the surface-guided growth of horizontally aligned single-walled carbon nanotubes on quartz. *Chem Phys Lett* 2012;525-526:82–6.
- [17] Kocabas C, Shim M, Rogers JA. Spatially selective guided growth of high-coverage arrays and random networks of single-walled carbon nanotubes and their integration into electronic devices. *J Am Chem Soc* 2006;128(14):4540–1.
- [18] Ding L, Yuan D, Liu J. Growth of high-density parallel arrays of long single-walled carbon nanotubes on quartz substrates. *J Am Chem Soc* 2008;130(16):5428-9.
- [19] Phokharatkul D, Ohno Y, Nakano H, Kishimoto S, Mizutani T. High-density horizontally aligned growth of carbon nanotubes with Co nanoparticles deposited by arc-discharge plasma method. *Appl Phys Lett* 2008;93(5):053112-1-3.
- [20] Zhou W, Rutherglen C, Burke PJ. Wafer scale synthesis of dense aligned arrays of single-walled carbon nanotubes. *Nano Res* 2008;1(2):158-65.
- [21] Akinwande D, Patil N, Lin A, Nishi Y, Wong H-SP. Surface science of catalyst dynamics for aligned carbon nanotube synthesis on a full-scale quartz wafer. *J Phys Chem C* 2009;113(19):8002-8.

- [22] Rutkowska A, Walker D, Gorfman S, Thomas PA, Macpherson JV. Horizontal alignment of chemical vapor-deposited SWNTs on single-crystal quartz surfaces: further evidence for epitaxial alignment. *J Phys Chem C* 2009;113(39):17087-96.
- [23] Hata K, Ohno Y, Kishimoto S, Mizutani T. Improvement in alignment of single-walled carbon nanotubes grown on quartz substrate. *Phys Status Solidi C* 2011;8(2):561-3.
- [24] Ibrahim I, Bachmatiuk A, Börrnert F, Blüher J, Wolff U, Warner J, et al. Optimizing substrate surface and catalyst conditions for high yield chemical vapor deposition grown epitaxially aligned single-walled carbon nanotubes. *Carbon* 2011;49(15):5029-37.
- [25] Hong SW, Banks T, Rogers JA. Improved density in aligned arrays of single-walled carbon nanotubes by sequential chemical vapor deposition on quartz. *Adv Mater* 2010;22(16):1826–30.
- [26] Zhou W, Ding L, Yang S, Liu J. Synthesis of high-density, large-diameter, and aligned single-walled carbon nanotubes by multiple-cycle growth methods. *ACS Nano* 2011;5(5):3849-57.
- [27] Wang C, Ryu K, De Arco LG, Badmaev A, Zhang J, Lin X, et al. Synthesis and device applications of high-density aligned carbon nanotubes using low-pressure chemical vapor deposition and stacked multiple transfer. *Nano Res* 2010;3(12):831–42.
- [28] Shulaker MM, Wei H, Patil N, Provine J, Chen HY, Wong H-SP, et al. Linear increases in carbon nanotube density through multiple transfer technique. *Nano Lett*

2011;11(5):1881–6.

[29] Murakami Y, Miyauchi Y, Chiashi S, Maruyama S. Direct synthesis of high-quality single-walled carbon nanotubes on silicon and quartz substrates. *Chem Phys Lett* 2003;377(1-2):49–54.

[30] Murakami Y, Chiashi S, Miyauchi Y, Hu M, Ogura M, Okubo T, et al. Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy. *Chem Phys Lett* 2004;385(3-4):298–303.

[31] Maruyama S, Kojima R, Miyauchi Y, Chiashi S, Kohno M. Low-temperature synthesis of high-purity single-walled carbon nanotubes from alcohol. *Chem Phys Lett* 2002;360(3-4):229–34.

[32] Xiang R, Einarsson E, Okawa J, Thurakitserree T, Murakami Y, Shiomi J, et al. Parametric study of alcohol catalytic chemical vapor deposition for controlled synthesis of vertically aligned single-walled carbon nanotubes. *J Nanosci Nanotechnol* 2010;10(6):3901–6.

[33] Jiao L, Fan B, Xian X, Wu Z, Zhang J, Liu Z. Creation of nanostructures with poly(methyl methacrylate)-mediated nanotransfer printing. *J Am Chem Soc* 2008;130(38):12612–3.

[34] Ding L, Zhou W, McNicholas TP, Wang J, Chu H, Li Y, et al. Direct observation of the strong interaction between carbon nanotubes and quartz substrate. *Nano Res*

2009;2(11):903–10.

[35] Einarsson E, Murakami Y, Kadowaki M, Maruyama S. Growth dynamics of vertically aligned single-walled carbon nanotubes from in situ measurements. *Carbon* 2008;46(6):923–30.

[36] Lin M, Tan JPY, Boothroyd C, Loh KP, Tok ES, Foo YL. Direct observation of single-walled carbon nanotube growth at the atomistic scale. *Nano Lett* 2006;6(3):449–52.

[37] Wako I, Chokan T, Takagi D, Chiashi S, Homma Y. Direct observation of single-walled carbon nanotube growth processes on SiO₂ substrate by in situ scanning electron microscopy. *Chem Phys Lett* 2007;449(4-6):309–13.

[38] Marchand M, Journet C, Guillot D, Benoit JM, Yakobson BI, Purcell ST. Growing a carbon nanotube atom by atom: “And Yet It Does Turn”. *Nano Lett* 2009;9(8):2961–6.

[39] Li-Pook-Than A, Lefebvre J, Finnie P. Phases of carbon nanotube growth and population evolution from in situ Raman spectroscopy during chemical vapor deposition. *J Phys Chem C* 2010;114(25):11018–25.

[40] Eres G, Rouleau CM, Yoon M, Puretzky AA, Jackson JJ, Geohegan DB. Model for self-assembly of carbon nanotubes from acetylene based on real-time studies of vertically aligned growth kinetics. *J Phys Chem C* 2009;113(35):15484–91.

[41] Geohegan DB, Puretzky AA, Jackson JJ, Rouleau CM, Eres G, More KL. Flux-dependent growth kinetics and diameter selectivity in single-wall carbon nanotube

arrays. ACS Nano 2011;5(10):8311–21.

[42] Chiashi S, Murakami Y, Miyauchi Y, Maruyama S. Cold wall CVD generation of single-walled carbon nanotubes and in situ Raman scattering measurements of the growth stage. Chem Phys Lett 2004;386(1-3):89–94.

[43] Latorre N, Romeo E, Cazana F, Ubieto T, Royo C, Villacampa JI, et al. Carbon nanotube growth by catalytic chemical vapor deposition: A phenomenological kinetic model. J Phys Chem C 2010;114(11):4773–82.

[44] Picher M, Anglaret E, Jourdain V. High temperature activation and deactivation of single-walled carbon nanotube growth investigated by in situ Raman measurements. Diam Relat Mater 2010;19(5-6):581–5.

[45] Takagi D, Homma Y, Suzuki S, Kobayashi Y. Vertical growth of individual single-walled carbon nanotubes on silicon and SiO₂ substrates. Jpn J App Phys 2005;44(4A):1564–8.

[46] Liu X, Ryu K, Badmaev A, Han S, Zhou C. Diameter dependence of aligned growth of carbon nanotubes on a-plane sapphire substrates. J Phys Chem C 2008;112(41):15929–33.

[47] Zhou W, Ding L, Yang S, Liu J. Orthogonal orientation control of carbon nanotube growth. J Am Chem Soc 2010;132(1):336–41.

[48] Maruyama S, Einarsson E, Murakami Y, Edamura T. Growth process of vertically aligned single-walled carbon nanotubes. Chem Phys Lett 2005;403(4-6):320–3.

[49] Lu C, Liu J. Controlling the diameter of carbon nanotubes in chemical vapor deposition

method by carbon feeding. J Phys Chem B 2006;110(41):20254-7.