

Research Article

Effect of Catalytic Layer Thickness on Diameter of Vertically Aligned Individual Carbon Nanotubes

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The effect of catalytic thin film thickness on the diameter control of individual carbon nanotubes grown by plasma enhanced chemical vapor deposition was investigated. Individual carbon nanotubes were grown on catalytic nanodot arrays, which were fabricated by e-beam lithography and e-beam evaporation. During e-beam evaporation of the nanodot pattern, more catalytic metal was deposited at the edge of the nanodots than the desired catalyst thickness. Because of this phenomenon, carbon atoms diffused faster near the center of the dots than at the edge of the dots. The carbon atoms, which were gathered at the interface between the catalytic nanodot and the diffusion barrier, accumulated near the center of the dot and lifted the catalyst off. From the experiments, an individual carbon nanotube with the same diameter as that of the catalytic nanodot was obtained from a 5 nm thick catalytic nanodot; however, an individual carbon nanotube with a smaller diameter (~40% reduction) was obtained from a 50 nm thick nanodot. We found that the thicker the catalytic layer, the greater the reduction in diameter of the carbon nanotubes. The diameter-controlled carbon nanotubes could have applications in bio- and nanomaterial scanning and as a contrast medium for magnetic resonance imaging.

1. Introduction

Recently, various nanomaterials have been widely used in nanoscience, engineering, and technology. In particular, carbon nanotubes (CNTs) are the most popular material in the nanotechnology field. Since discovered in the soot of an arc discharge apparatus [1], CNTs have been used in many nanotechnology applications such as transistors and chemical or biosensors, and as atomic force microscopy tips because of their remarkable electrical, mechanical, chemical, and thermal properties [2–6]. In many cases, however, it is difficult to control the nanotubes' locations and orientations. Recently, an attempt to manipulate nanotubes has been made by polymer encapsulation [7].

In the last decade, chemical vapor deposition (CVD) techniques, particularly plasma enhanced chemical vapor deposition (PECVD), have been widely used to grow CNTs

[8]. The controlled synthesis of CNTs is an essential step for realizing CNT-based devices and technologies. In particular, vertically aligned carbon nanotube growth is important for applications such as field emission displays (FEDs) and scanning probe microscopy (SPM) [9]. However, because of the complicated coupled parameters that are required to grow CNTs [10, 11], it is not easy to control the synthesis of CNTs. Moreover, vertically aligned individual carbon nanotubes are not easily grown because of the lack of knowledge about the mechanism of interaction between the thin catalytic layer and individual dots. Several papers have shown that the growth depends on parameters such as substrate temperature, gas ratio of hydrocarbon gas and dilution gas, pretreatment using plasma, and catalyst film thickness [12–17]. For growing individual carbon nanotubes, a single nanodot is needed to control the CNT's diameter and to make a catalytic island without undergoing etching [18, 19]. Although patterned dots

are used in CNT growth, CNTs grown by PECVD still have various diameters depending on the growth conditions.

In this paper, we report the effect of the catalytic layer thickness on the diameter of individual carbon nanotubes grown using direct current PECVD (DC-PECVD). Specifically, we show that the thickness of the catalytic nanodots affects the diameter of the resulting vertically aligned individual carbon nanotubes. From the field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) images, we verified the relation between the carbon nanotube diameter and the catalytic layer thickness of nanodots.

2. Experimental Section

2.1. Fabrication Processes for Catalytic Nanodots. Co, Fe, Mo, and Ni are generally used as catalysts for carbon nanotube growth. In this study, we used Ni as the catalytic metal. For growing CNTs at determined locations, we patterned nanodots with diameters of 400 nm on a p-type, boron-doped silicon (100) wafer. Titanium nitride (TiN) with 200 nm thickness was deposited before catalytic layer deposition to provide a buffer layer on the SiO₂/Si substrate in order to prevent catalyst silicide formation under high growth temperature conditions. To make small nanodots, electron beam lithography (Raith 150) was used on an e-beam resist (3% 950,000-MW (molecular weight) PMMA (polymethyl methacrylate) in chlorobenzene) deposited on the titanium nitride/silicon dioxide/silicon wafer. Through a series of e-beam exposures, we found that an e-beam area dose of 150 $\mu\text{As}/\text{cm}^2$ was needed for making dots with 400 nm diameters. Next, the patterns were developed for 80 seconds in a mixed solution of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) with a ratio of 1:3. Subsequently, Ni with 5~50 nm thickness was deposited by electron beam evaporation. Finally, Ni nanodots were produced after metal lift off in acetone or *N*-methylpyrrolidone (NMP). Figure 1 shows a schematic diagram of the microfabrication processes for nanodot arrays and subsequent carbon nanotube growth by PECVD.

2.2. Vertically Aligned Carbon Nanotube Growth by Plasma Enhanced Chemical Vapor Deposition. Vertically aligned CNTs were grown on the patterned metal catalyst (in this case, Ni) by PECVD. The PECVD instrument had a DC plasma chamber consisting of a pair of electrodes in which one electrode was grounded and the other was connected directly to a power supply. The negative DC bias voltage applied to the cathode dissociates the feedstock hydrocarbon gas and generates many carbon-bearing radicals for CNT growth.

Figure 2 shows a schematic diagram of PECVD and the generated plasma (inset). The CNT growth equipment had the following components: a rotary pump to obtain a pressure of 10^{-2} Torr, turbo-molecular pump to obtain a pressure of 10^{-6} Torr, vacuum chamber to withstand high temperature, mass flow controller (MFC) to measure the flow of acetylene and ammonia gases, vacuum gauge to sense the pressure,

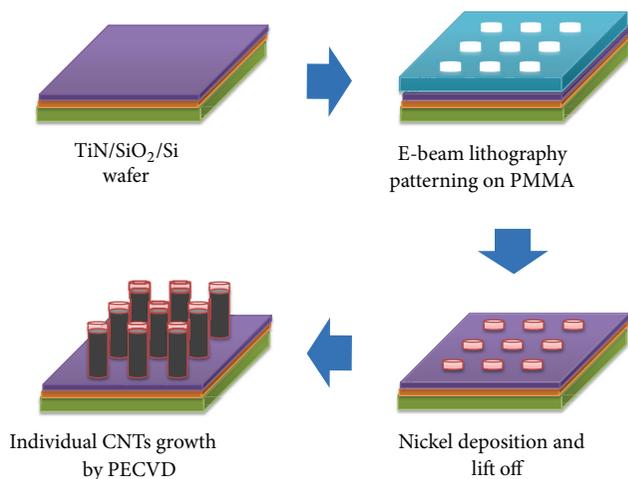


FIGURE 1: Schematic diagram showing microfabrication processes for nanodot arrays and carbon nanotube growth by plasma enhanced chemical vapor deposition (PECVD).

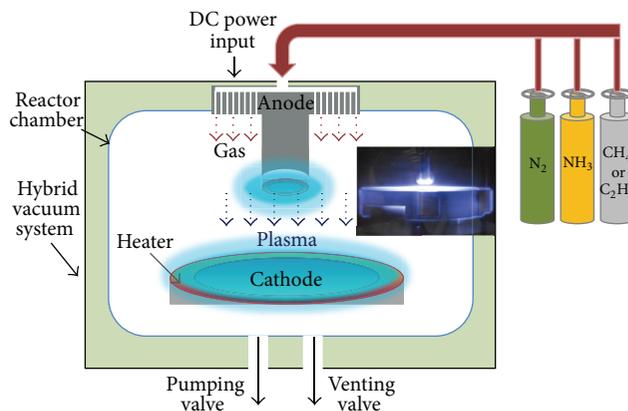


FIGURE 2: Schematic diagram of plasma enhanced chemical vapor deposition and generated plasma (inset).

plasma power supply to ignite the plasma, ceramic heater to obtain temperatures up to 800°C, heater controller to vary the temperature, cathode chuck on which a wafer piece or whole wafer is placed, and tube fittings for gases and water flow. At the bottom of the cathode chuck, two thermocouples were mounted to measure the temperature of the substrate, which was controlled by the heater controller. Plasma was formed between anode and cathode by applying a DC voltage.

A patterned sample was loaded in the PECVD chamber evacuated by rotary and turbo-molecular pumps to a base pressure ($<10^{-6}$ Torr), which was needed for eliminating the impurities and water vapor. When the pressure reached the desired value, the temperature of the heater beneath the cathode was gradually increased to 580°C. When the temperature became 580°C, ammonia (NH₃) gas was introduced into the chamber for 5~15 min without igniting the plasma to etch the catalyst. After subjecting the catalyst to preetching without plasma, acetylene (C₂H₂) was injected into the chamber and the plasma was ignited to initiate CNT growth. After the CNT growth time, the plasma was turned off and the heater was

cooled down slowly to prevent CNT damage from a sudden change in temperature. During the CNT growth process, amorphous carbon was deposited on the cathode and heater, which may have caused fluctuations in the plasma. To form stable plasma, the heater and cathode were cleaned after several experiments. Figure 3(a) shows the FESEM images of catalytic nanodot arrays and Figure 3(b) shows the vertically aligned individual carbon nanotube arrays on top of the catalytic nanodot arrays.

3. Results and Discussion

3.1. Edge Bead Effect of E-Beam Evaporation. Nanodots were fabricated by e-beam lithography and e-beam evaporation as a catalyst for vertically aligned carbon nanotube growth. In the e-beam process, the edge bead effect generally appears with very small patterns. The edge bead effect occurs when evaporated material is preferentially deposited toward the edge of a pattern compared to the center. Figure 4(a) shows a field emission scanning electron microscopy (FESEM, Zeiss Supra-40 and FEI/Philips XL30 FEG ESEM) image of a Ni nanodot with a diameter of 400 nm and a thickness of 5 nm obtained by e-beam lithography and e-beam evaporation. Because the surface roughness is not easily observed in the FESEM image, the nanodot was scanned by AFM (Figure 4(b)). The figure shows that the catalytic metal was deposited uniformly on the top of the nanodots. Because the deposited layer was thin, no edge bead effect was observed on the nanodot. However, the phenomenon observed for the thick-layered nanodots was different. Figure 4(c) shows an FESEM image of a nanodot with a diameter of 400 nm and a thickness of 50 nm. From the image, a difference in height was observed at the edge of the nanodot. The AFM scan is shown in Figure 4(d). An unexpected profile with a peak of approximately 5 nm was observed at the edge of the nanodot (indicated by the white circle). This profile was caused by the edge bead effect during e-beam evaporation. This ~5 nm peak was obtained in the thicker catalytic layered nanodots and increased the travel distances for carbon atoms in order to reach the interface between the catalytic layer and diffusion barrier in the carbon diffusion process to grow CNTs.

3.2. Brownian Diffusion Distance of an Atom of Particle. A carbon atom of particle is diffused onto or into a metal layer. These atoms of particles are diffused according to the Brownian diffusion distance [20]. The root-mean-square net displacement (x_{rms}) along any axis during a time (t) is

$$x_{\text{rms}} = \sqrt{2Dt}, \quad (1)$$

where D = diffusion coefficient [cm^2/s], t = time [s]. From this formula, the thicker a layer, the longer diffusion time of an atom of particle.

3.3. Carbon Atom Diffusion and Lift-Off Catalyst. CNTs can be grown by following a three-step procedure as follows: (1) decomposition of the hydrocarbon gas (in this study, acetylene (C_2H_2)) over a catalytic metal (Ni), (2) diffusion of

the carbon atoms through the bulk and surface of the catalyst, and (3) subsequent precipitation of the carbon atoms beneath the catalyst [17, 19]. In the second step, carbon atoms must reach the interface of the catalytic layer and the diffusion barrier. Figure 5(a) shows the 3D AFM image of the catalytic nanodot with a thickness of 50 nm and a diameter of 400 nm. As mentioned above, the unexpected over deposition at the edge of the nanodot was clearly observed as shown in Figure 5(a) (the white circle). This unexpected peak made the catalytic layer thicker at the edge of the nanodot compared with its center. Figure 5(b) shows a schematic diagram of a carbon atom's diffusion in the catalytic nanodot. As shown in Figure 5(b), carbon atoms diffuse to the interface between the catalytic layer and the diffusion barrier through a bulk or surface diffusion process. Carbon atoms at the center of the nanodots could diffuse faster than those at the edge of the dot because of the thicker catalytic layer at the edge of the nanodot. Carbon atoms accumulated earlier in the center of the nanodot caused a specific catalytic area to lift off, as shown in Figure 5(b). Consequently, the resulting carbon nanotube has a smaller diameter than expected with the thick catalytic nanodots.

3.4. Vertically Aligned Individual Carbon Nanotubes and Relation between Carbon Nanotube Diameter and Catalyst Thickness. The CNT's electric dipole, accruing from the electric field exerted on the CNT, interacts with the DC electric field and experiences an alignment torque, developing stresses at the interface between the CNT and the catalyst particle. Because the diffusion flux depends on the stress gradient as well as the concentration gradient, stress-induced fluctuations in the diffusion rate can be primary mechanism for the vertical alignment of the CNTs. Figures 6(a), 6(b), and 6(c) show the vertically aligned individual carbon nanotubes made using catalyst thicknesses of 5, 30, and 50 nm, respectively. The individual carbon nanotube from a 5 nm thick catalyst had the same diameter as that of the initial nanodot, that is, a diameter of 400 nm. In the case of 30 nm and 50 nm catalyst thicknesses, individual carbon nanotubes with small diameters were synthesized. For the 30 nm thick catalytic nanodot, the resulting carbon nanotube had a 30% smaller diameter. Furthermore, the diameter of the individual carbon nanotube was reduced by 40% when 50 nm thick catalytic nanodots were used. Figure 6(d) shows the relation between the thickness of the catalyst layer and the diameter of the individual carbon nanotubes. From this work, we found that the thickness control of catalytic nanodots is a very important parameter for obtaining vertically aligned individual carbon nanotubes with predictable diameter.

4. Conclusions

In this work, the effect of catalyst layer thickness on the diameter of vertically aligned individual carbon nanotubes produced by PECVD was investigated. For the growth of individual carbon nanotubes, catalytic nanodot arrays were fabricated by e-beam lithography and e-beam evaporation. During e-beam evaporation, the edge effect was observed in

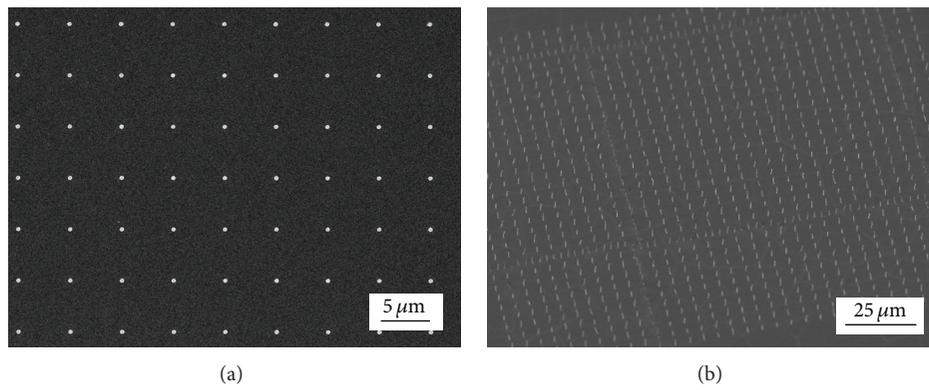


FIGURE 3: Field emission scanning probe microscopy (FESEM) images of (a) catalytic nanodot array and (b) vertically aligned individual carbon nanotube array.

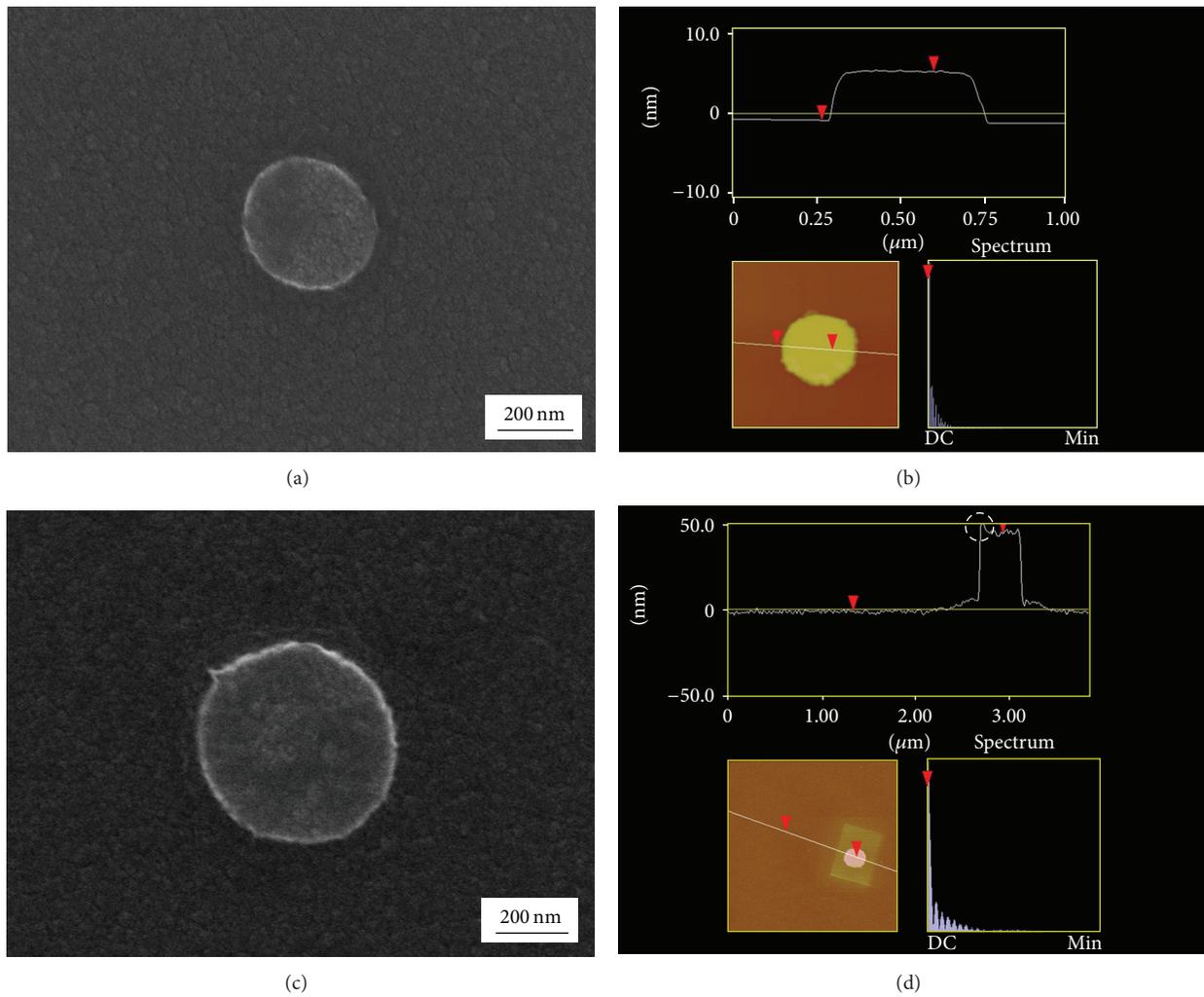


FIGURE 4: (a) Scanning electron microscopy (SEM) image and (b) atomic force microscopy (AFM) scanning profile of catalytic nanodot with a thickness of 5 nm; (c) SEM image and (d) AFM scanning profile of catalytic nanodot with a thickness of 50 nm.

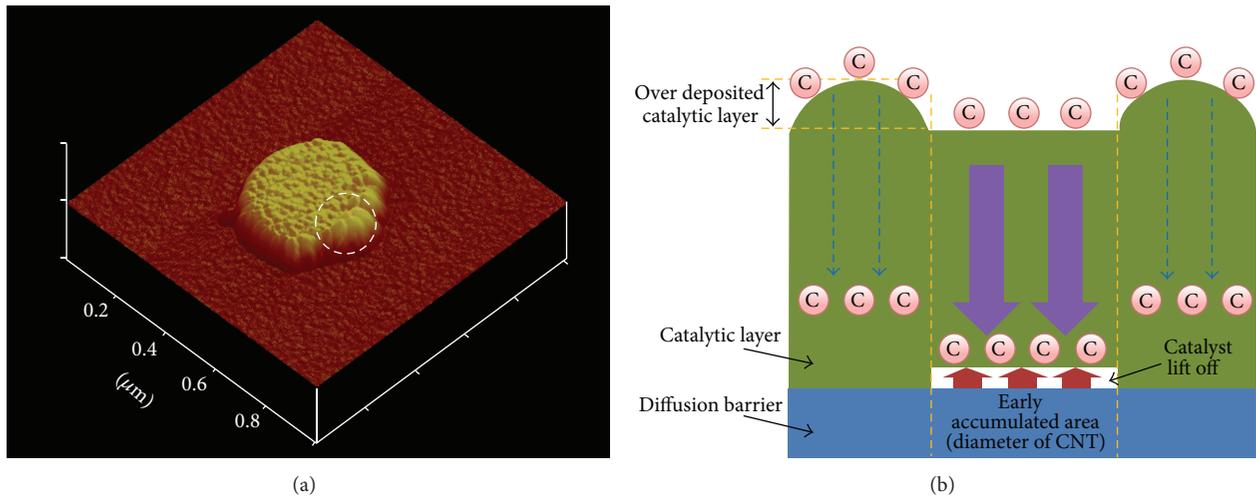


FIGURE 5: (a) Three-dimensional (3D) atomic force microscopy (AFM) scanning image of 50 nm thick nanodot and (b) schematic diagram of carbon atoms' diffusion.

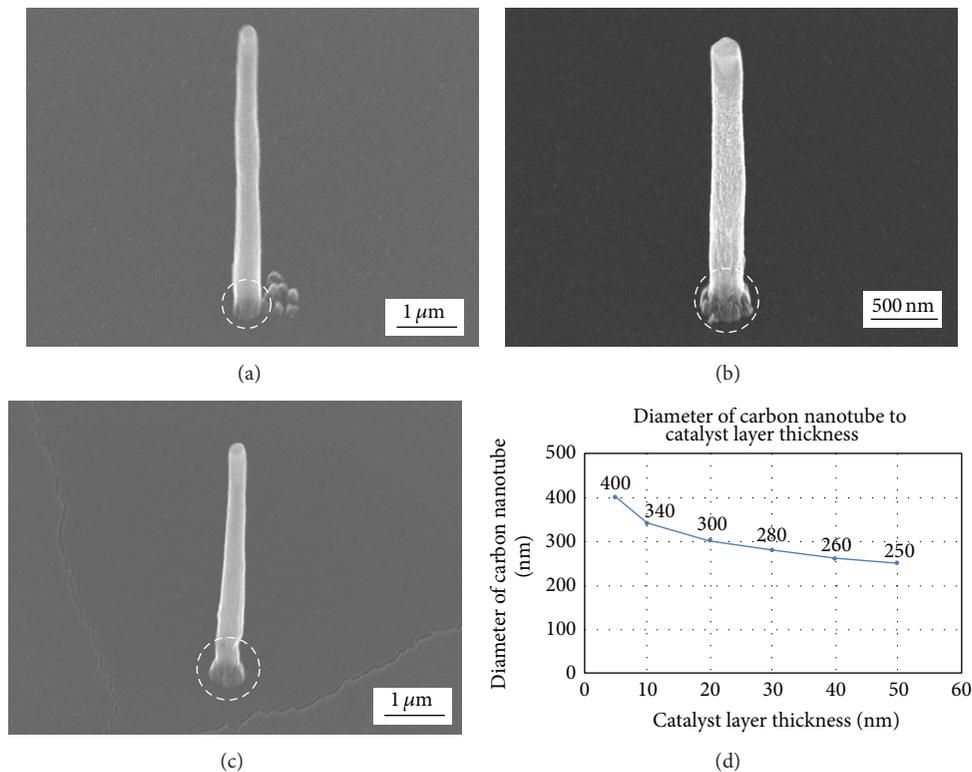


FIGURE 6: Scanning electron microscopy (SEM) images of vertically aligned carbon nanotubes from catalytic nanodots with thicknesses of (a) 5 nm, (b) 30 nm, and (c) 50 nm; (d) relation between thickness of catalytic nanodots and diameter of carbon nanotubes.

catalytic nanodots, because the diameters of the dots were very small. Because of the edge effect, the catalytic metal was deposited preferentially toward the edge of the dot resulting in a larger thickness than desired. When growing vertically aligned individual carbon nanotubes by PECVD, thick catalytic nanodots reduced the diameter of the synthesized carbon nanotubes. The reduction occurred because carbon atoms diffused faster near the center of dots than at the edges. The carbon atoms diffused to the interface between the

catalytic nanodot and the diffusion barrier and accumulated near the center, causing the center of the catalytic nanodot to lift off faster than the edge of the dot.

From the experiments, individual carbon nanotubes with the same diameter as that of the catalytic nanodots (400 nm) were obtained when the catalyst thickness was 5 nm. For 50 nm thick catalytic nanodots, a carbon nanotube with diameter of 260 nm (reduction by ~40%) was obtained. We found that the thicker the catalytic layer, the greater the

reduction in the diameter of the individual carbon nanotubes. From the FESEM and AFM images, we verified the relation between the diameter of the carbon nanotubes and the catalytic layer thickness of the nanodots.

Diameter control of vertically aligned individual carbon nanotubes is very important and useful for the application of CNTs in electric and energy-based devices and for scanning bio- and nanomaterials. Furthermore, the diameter-controlled carbon nanotubes could be applied to a contrast medium for magnetic resonance imaging.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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