Review Article

Growth of Single-Walled Carbon Nanotubes by Plasma CVD

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Recent research in plasma chemical vapor deposition (CVD) for single-walled carbon nanotube (SWNT) growth has achieved low-temperature synthesis, individually freestanding formation, and structure control of diameter, chirality, and length. Detailed growth kinetics of SWNTs are revealed using a combination of techniques for plasma control and nanomaterial analysis. Plasma CVD also allows tube metallicity to be controlled by tuning the mean diameter of SWNTs. This plasma CVD progress contributes to the next stage of nanotube fabrication, which is required for practical use of SWNTs in a variety of applications.

1. Introduction

One-dimensional single-walled carbon nanotubes (SWNTs) are potential materials for future nanoelectronics [1–5]. Since the electronic and optical properties of SWNTs strongly depend on their structure, such as diameter, chirality, and length, the selective synthesis of SWNTs with desired structures is a major challenge in nanotube science and applications. SWNT growth was first achieved by arc discharge in 1993 [1]. Several growth techniques have been developed since then, including laser ablation [6] and chemical vapor deposition (CVD) [7]. Since it is possible to grow SWNTs at a specific position on a substrate by patterning a catalyst, CVD has attracted much attention in nanoelectronics applications. In general, CVD can be divided into two types: thermal CVD [7–9] and plasma CVD [10–13]. Due to the strong electric fields in plasma sheaths, nanotubes grown by plasma CVD tend to have an individually and vertically freestanding shape [11, 14–16]. Thermal CVD decomposes carbon source gases using thermal energy. In contrast, in plasma CVD, the source gas decomposition is effectively carried out by electron impact with no additional thermal energy; hence, the growth temperature is significantly lower compared to that of thermal CVD [17–19]. Despite these benefits of plasma CVD, it is difficult to control the structure of SWNTs by plasma CVD because there are many unknown factors in plasma, such as ion density, ion energy, radical species,

radical densities, and sheath electric field, which restrict the potential application of plasma CVD in nanotube science. Based on previous studies, SWNT growth by plasma CVD has been significantly improved in recent years. Here, we give a brief overview of recent achievements in SWNT growth by plasma CVD.

2. Freestanding Single-Walled Carbon Nanotube Growth

The potential of plasma CVD for nanotube growth was first demonstrated by Ren et al. in 1998 [11]. Vertically and individually aligned multiwalled carbon nanotubes (MWNTs) are grown by plasma CVD. Since carbon nanotubes (CNTs) grown by thermal CVD are known to form a spaghetti-like entangled shape, the well-aligned growth of CNTs by plasma CVD makes it an attractive CNT-growth method that may solve the integration issue in CNT-based nanoelectronics. However, plasma CVD is limited to the production of MWNTs; SWNTs, which have superior electrical and optical characteristics compared with MWNTs, have not been successfully produced by plasma CVD. The growth of SWNTs by plasma CVD was first reported by our group in 2003 [20]. SWNTs are grown by plasma CVD using a zeolite as a catalyst support. Zeolites are nanoporous materials known to maintain small catalyst particle sizes on their rough surfaces, even under high-temperature conditions.

FIGURE 1: (a) SEM and (b, c) TEM images of freestanding individual SWNTs. (d) Raman scattering spectrum of freestanding individual SWNTs. The inset of (d) shows the RBM region. (e) PLE map from as-grown freestanding SWNTs with no dispersion process.

Thus, certain plasma effects might enhance catalyst particle aggregation during plasma CVD, which could be the main reason why SWNTs could not be grown by plasma CVD. It is thought that catalyst particle aggregation is enhanced due to high-energy ions attacking the catalyst. In general, ions in plasma are accelerated through the potential drop between space potentials in the plasma and substrate biases. The minimum value of this potential drop is determined by the electron temperature in the plasma. Thus, low electron-temperature plasma can significantly decrease the energy of ions arriving at the substrate. Since the diffusion region in plasma is known to have very low electron temperatures, we used the diffusion plasma to decrease the energy of ions attacking the catalyst to below a few eV. SWNT growth under the diffusion plasma region occurs on a flat substrate without using catalyst support materials [21–23]. Thus, the critical element promoting catalyst aggregation is high-energy ion bombardment. Interestingly, SWNTs grown by diffusion-plasma CVD have the well-aligned freestanding form, that is, all SWNTs are individually and vertically standing on the flat substrate. Figures 1(a)–1(d) show a typical scanning electron microscope (SEM) image (Figure 1(a)), low-magnification (Figure 1(b)) and high-magnification (Figure 1(c)) transmission electron microscope (TEM) images, and Raman scattering spectra (Figure 1(d)) of freestanding SWNTs. Relatively high-quality SWNTs were grown with the individually freestanding form, and this alignment can be obtained by the plasma-sheath electric field. Based on our estimation, the rotation energy of the dipole moment in SWNTs is much higher than the thermal energy, which disturbs the tube

alignment [23]. This indicates that individual SWNTs can be aligned along the electric field. Owing to their unique as-grown state, it is possible to directly detect photoluminescence (PL) spectra from the as-grown freestanding SWNTs on the substrate (Figure 1(e)) [24]. This is a remarkable advantage for optoelectrical applications and fundamental studies toward chirality control, which will be discussed later.

3. Low-Temperature Growth

In addition to the alignment control of CNTs, low-temperature growth is another benefit of plasma CVD [17–19]. Since the carbon source gases are decomposed by the electron impact in plasma, the growth temperature can be lower than that of conventional thermal CVD. Although the quality of the graphite network in a tube structure is not high and a carbon nanofiber-like structure can be formed, the growth temperature of MWNTs is below 120°C with plasma CVD [17]. For SWNTs, the lowest reported growth temperature is ~400°C [18]. Low-temperature growth enabled us to directly grow CNTs on low-melting point materials, such as plastics and polymers. Hence, the application field of CNTs is broadened by improving the low-temperature growth of CNTs using plasma CVD.

4. Growth Mechanism

To achieve structure-controlled growth of SWNTs by plasma CVD, it is important to understand the growth kinetics of

FIGURE 2: Raman spectra of SWNTs as a function of growth time. (a) $P_{RF} = 40$ W and (b) $P_{RF} = 100$ W. (c) Comparison between the experimental data and the fitting curve of (1).

SWNTs during plasma CVD and elucidate the effects of plasma in detail.

For thermal CVD, it is reported that the growth kinetics of SWNTs can be expressed by $I_G = I_0[1 - \exp\{-(t_g - \Delta t)/\tau_{gro}\}]$ (normal equation) [25], where I_G , I_0 , t_g , Δt , and τ_{gro} denote the G-band intensity in Raman scattering spectra ($\sim$ amount of SWNTs), saturated I_G , growth time, incubation time, and relaxation time of the growth, respectively. Figures 2(a) and 2(b) show typical Raman scattering spectra of SWNTs as a function of growth time under different radio frequency (RF; 13.56 MHz) power (P_{RF}) conditions. The experimental results of the damage-free growth (Figure 2(a)) match well with this equation, indicating that our estimation of the amount of SWNTs with I_G is reliable. However, there is obviously no formula that can describe growth kinetics by including an etching effect, as shown in Figure 2(b). To express this phenomenon, we assumed that the growth mode could be described with a balance equation, $I_G = G(t_g) - E(t_g)$, where $G(t_g)$ and $E(t_g)$ are growth and etching functions, respectively. When the etching effect is weak and negligible, the growth kinetics can be described with the aforementioned normal equation, indicating that $G(t_g)$ gives results that are similar to the normal equation. One of the most important outcomes of this study is the description of $E(t_g)$. Since carbon atoms are etched only when atoms or molecules attach themselves to the carbon atoms in SWNTs,

the probability of the etching reaction can be simplified in terms of an adsorption reaction. Langmuir's adsorption isotherm, a well-known equation, can be expressed as $d\theta/dt = \alpha P(1 - \theta)$, where θ , t , α , and P denote the percentage of covered area, reaction time, adsorption efficiency, and pressure of the adsorbate, respectively. The Langmuir's equation has been used in a wide range of fundamental scientific studies to understand chemical adsorption reactions [26]. In our study, θ corresponds to the etched area against the graphite sheet of SWNTs, that is, $\theta = E(t_g)/G(t_g)$. Since the solution of the Langmuir's equation is $\theta(t_g) = 1 - \exp(-t_g/\tau_{etc})$, where $\tau_{etc} = 1/\alpha P$ is the relaxation time of the etching reaction, $E(t_g)$ results in the following equation: $E(t_g) = G(t_g)\{1 - \exp(-t_g/\tau_{etc})\}$. According to the aforementioned equations, an advanced growth equation can be established as

$$I_G = I_0 \left[1 - \exp\left\{-\frac{(t_g - \Delta t)}{\tau_{gro}}\right\} \right] \left\{ \exp\left(\frac{-t_g}{\tau_{etc}}\right) \right\}. \quad (1)$$

Figure 2(c) compares the experimental result of Figure 2(b) with the fitting curve from (1). The fitting curve agreed well with the experimental result.

Since there are several important fitting parameters related to growth kinetics of SWNTs in (1), such as Δt ,

etching efficiency, and catalyst lifetime, it is possible to precisely understand the correlation between plasma parameters and growth parameters, leading to improved structure-controlled growth of SWNTs by plasma CVD [27]. Our systematic experiment, combined with this growth-equation study, reveals that unique reactive-ion etching occurred during the growth of SWNTs under specific plasma conditions in plasma CVD [27].

5. Structure-Controlled Growth of SWNTs

The structure of SWNTs, including diameter, chirality, and length, strongly influences their electrical and optical properties; therefore, it is important to precisely control the structure of SWNTs. Here, we discuss recent progress in the structure-controlled growth of SWNTs by plasma CVD.

5.1. Diameter Control. The band gap is known to be inversely proportional to tube diameter; thus, controlling the tube diameter is very important for electrical and optical applications. Here, we present our experimental results for diameter tuning of SWNTs based on gas-phase control in plasma CVD [28].

Figures 3(a)–3(d) show photoluminescence-excitation (PLE) maps of as-grown SWNTs produced at different gas pressures. Note that all PLE measurements were carried out immediately after the growth process to prevent the freestanding SWNTs from forming bundles, which cause significant PL changes [24]. Peaks in the PLE map at high growth pressures (Figure 3(a)) appeared in the range of long excitation and emission wavelengths. The peak positions shifted to the region of short excitation and emission wavelengths with decreasing growth pressure (Figures 3(b)–3(d)). Since each peak corresponds to a different chirality in the sample, and smaller-diameter SWNTs appeared in the shorter wavelength region, the peak-position shifts in the PLE map indicate that the diameter distribution of SWNTs is strongly influenced by growth pressure. Thus, lower pressure results in smaller SWNT diameters. This diameter dependence on the growth pressure is also reflected in Raman scattering spectra of SWNTs grown at different growth pressures. Figure 3(e) shows that peak positions of the radial breathing mode (RBM) clearly shifted from higher to lower wavenumbers with increasing growth pressure. The RBM peak position and the SWNT diameter are known to have a close correlation, $\omega = 248/d$ [29], where ω and d are the RBM peak position (cm^{-1}) and diameter (nm), respectively. This result is fairly consistent with the PLE result shown in Figures 3(a)–3(d). The typical pressure range where SWNTs can be grown is from 30 Pa to 650 Pa and depends on the P_{RF} used for the plasma generation. Although the absolute intensity of the G-band in Raman scattering spectra decreased in the low- or high-pressure range, the G-band to D-band ratio was almost constant. This indicates that the quality of SWNTs should be independent of the pressure range, whereas the density of SWNTs depends on the pressure. When we increased the input P_{RF} , it was possible to grow SWNTs, even below 30 Pa, indicating that a

lack of hydrocarbon supply is significant under low-pressure conditions. Hence, an additional input P_{RF} is required to increase the density of active species used for the growth of SWNTs. Since the pressure during the heating and growth was the same in our growth process, the process pressure affected both the heating and the growth process. Based on this systematic investigation, we believe that the catalyst particle size increased due to aggregation after high-pressure annealing, which resulted in the growth of large-diameter SWNTs. The density of reactive hydrocarbon radicals and ions should increase under higher growth pressure conditions. Under high carbon supply conditions, a small catalyst can be deactivated by an oversupply of hydrocarbons, causing the population of small-diameter SWNTs to decrease. Therefore, the heating pressure is an important parameter that controls the catalyst particle size distribution, which directly influences the diameter of SWNTs. The pressure during plasma CVD is also important for a narrow SWNT diameter distribution [28].

5.2. Chirality Distribution Control. The chirality of SWNTs directly determines their electronic and optical properties; thus, selective synthesis of SWNTs with desired chiralities is a major challenge in nanotube science and applications [3, 30, 31]. Some progress has been made with silica-supported CoMo [32] and zeolite-supported FeCo [33] catalysts. FeRu [34] and FeNi [35] catalysts have also been developed to achieve narrow chirality distributions. Interestingly, all syntheses resulting in narrow chirality distributions have involved magnetic catalysts. The main obstacle to research on intrinsic magnetic properties of SWNTs is residual ferromagnetic catalyst particles; thus, SWNT growth with nonmagnetic catalysts is beneficial. Despite recent improvements in SWNT growth with nonmagnetic catalysts [36–39], diameter and chirality (n, m) distribution control with nonmagnetic catalysts is still required for fundamental studies and a variety of applications [40].

In this subsection, we discuss a recent achievement in the growth of SWNTs with narrow chirality distributions using an Au catalyst and plasma CVD [41, 42]. PLE mapping [43] was used to assign (n, m) of SWNTs grown from the Au catalyst at different H_2 concentrations (Figures 4(a)–4(c)). The total pressure was kept at 50 Pa by adjusting the pumping rate of the rotary pump throughout this experiment. Lower H_2 concentrations (0 and 3 sccm) led to larger diameters and wider (n, m) distributions with (6,5), (7,5), (7,6), (8,4), (8,6), and (8,7) (Figures 4(a) and 4(b)). On the other hand, the 7-sccm H_2 concentration yielded the narrowest (n, m) distribution with a dominant peak corresponding to the (6,5) tube (Figure 4(c)). The UV-Vis-NIR optical absorbance spectra of Au-plasma CVD SWNTs grown at the 7-sccm H_2 flow rate showed one dominant peak in the first van Hove E_{11} range (900–1400 nm) corresponding to SWNTs with (6,5) chirality (Figure 4(d)). Since clear metallic SWNT peaks were not observed in the UV-Vis-NIR spectra (Figure 4(d)), the concentration of metallic SWNTs was lower than that of the generally grown SWNTs. The RBM in the Raman spectra measured with 632.8-nm and 778-nm lasers on the same

FIGURE 3: (a)–(d) PLE maps of as-grown freestanding SWNTs grown under different pressures ((a) 550 Pa, (b) 300 Pa, (c) 100 Pa, and (d) 40 Pa). (e) Dependence of the RBM in Raman scattering spectra on growth pressure for as-grown freestanding SWNTs.

SWNT sample also confirmed the growth of the (6,5) SWNTs (Figure 4(e)). This is the first result showing narrow chirality distributions for SWNTs grown from a nonmagnetic catalyst.

To elucidate the effects of Au and plasma CVD on the narrow chirality distribution, other combinations of catalysts

and CVD methods were systematically investigated. Based on the PLE analysis, SWNTs grown by the Fe catalyst with plasma CVD (Fe-plasma CVD) did not show a clear correlation between the H_2 flow rate and the chirality distribution, which was broader than that of SWNTs grown by Au-plasma

FIGURE 4: (a)–(c) PLE maps of SWNTs grown from an Au catalyst by plasma CVD under H_2 flow rates of (a) 0 sccm, (b) 3 sccm, and (c) 7 sccm. (d) UV-Vis-NIR spectrum of SWNTs grown from an Au catalyst under a 7-sccm H_2 flow rate and (e) Raman spectra of as-synthesized SWNTs grown from an Au catalyst under a 7-sccm H_2 flow rate using excitation laser wavelengths of 632.8 nm and 778 nm.

CVD. This indicates that H_2 -assisted Au catalyzation is a critical factor for achieving narrow chirality distributions, which is in good agreement with theoretical predictions. The first-principle calculation by Yazyev and Pasquarello reveals that coinage metals, such as Cu, Ag, and Au, produce narrow chirality distributions [44]. Ding et al. have reported that the SWNT diameter is larger on the surfaces of Fe, Co, and Ni particles than on Cu, Pd, and Au particles because of the different bond energies on the catalyst surfaces [45]. Based on these theoretical models, we can explain the effect of H_2 -assisted Au catalyzation on the narrow chirality distribution as follows. Since the binding energy of hydrocarbons on the Au surface is much weaker than on the Fe surface, it is difficult to achieve cap formation for large-diameter Au catalysts [45]. Additional H_2 also enhances the etching of the carbon precursor from the catalyst surface, which strongly suppresses the growth of large-diameter SWNTs; hence, the chirality distribution of SWNTs grown from the Au catalyst should be narrower than those grown from the Fe catalyst. The stability of the cap structure is

a possible reason why the (6,5) tube was dominant in the small-diameter Au-plasma CVD SWNTs. The number of cap structures, which satisfies the isolated pentagon rule, is highly limited for small-diameter SWNTs, and (6,5) is known to have a stable cap structure in this diameter range [33]. A comparison between Au-plasma CVD and Au-thermal CVD was also carried out. Although the chirality distribution became relatively narrow for SWNTs grown by Au-thermal CVD under appropriate H_2 concentrations, it was much broader than that of SWNTs grown by Au-plasma CVD. Comparison of the Au-plasma CVD and Au-thermal CVD processes showed that there were two significant differences in the SWNT growth conditions: growth temperature and incubation time. The lower limit of growth temperature for Au-plasma CVD was $700^\circ C$, which was lower than that of Au-thermal CVD by $50^\circ C$. The initial SWNT growth occurred 1 min after the growth substrate was exposed to the plasma for Au-plasma CVD, whereas 15 min were required for the growth of SWNTs with Au-thermal CVD. These results suggest that the low-temperature and short-time

growth with Au-plasma CVD prevents aggregation of catalyst particles during SWNT growth, which suppresses the growth of large-diameter SWNTs and results in a narrow chirality distribution.

5.3. Length Control. Length is another important factor that determines the SWNT properties. Recently, length-controlled SWNTs, especially short SWNTs, have attracted attention because of their unique properties, such as ballistic electron transport [46] and blue-shifted optical band gap due to quantum confinement along the axial direction [47]. These properties have led to applications in high-frequency mechanical resonators [48], molecular sensing [49], biological imaging [50], and drug delivery [50]. However, compared to studies on radial structure control, including tube diameter and chirality, very few efforts have been devoted to axial structure control, that is, length control of SWNTs, especially short SWNTs. Furthermore, simultaneous control of both the radial (diameter and chirality) and axial (length) structure remains a major challenge in fundamental studies and applications of SWNTs.

There are two main approaches used to obtain short SWNTs. One is direct growth, and the other is based on posttreatments, such as cutting [51] and chemical separation [52]. Almost all work reported thus far has used the latter approach, which is based on the top-down process. Ultra-short (<10 nm) SWNTs [47] are fabricated by the combination of chemical cutting and separation. However, SWNTs obtained by these top-down approaches are contaminated by abrasive materials used in some processes, and the use of chemicals and surfactants inhibits the intrinsic property characterization of SWNTs due to reactions and interactions. On the other hand, directly grown short SWNTs can maintain their original high quality and clean surface with no chemical impurities, making it possible to fully utilize their capabilities in various applications. Very recently, the direct growth of short SWNTs [53] has been reported. However, control of the diameter and chirality of the directly-grown short SWNTs, which is necessary for the fabrication of high-performance electrical and optical devices, has not yet been achieved.

In this subsection, we report a novel direct-growth approach for short SWNTs based on time-programmed plasma CVD. By precisely adjusting the growth time (t_g), the length distribution is narrowed, and short (<100 nm) SWNTs are successfully grown with very short growth times (2–5 sec). Furthermore, the direct PL study revealed that short SWNTs have the (6,5)-rich or (7,6)- and (8,4)-dominant narrow chirality distribution. This is the first report for direct growth of short SWNTs with a narrow chirality distribution [54].

Recent progress in *in situ* TEM observation during SWNT growth revealed that metal-catalyzed SWNT growth is initiated by the formation of a carbon-cap structure on the surface of a catalytic nanoparticle with a certain incubation time (t_i) [55]. Although the detailed mechanism of this incubation period is still debated, it is thought that there might be a correlation between the t_i and SWNT structure, such as diameter and chirality. By assuming that

the t_i of the small-diameter (or specific-chirality) SWNTs is shorter than that of the large-diameter (or other chiralities) SWNTs, it should be possible to selectively grow SWNTs with narrow diameter (or chirality) distributions by strictly controlling the t_g of the initial growth stage. Since the length of SWNTs should be proportional to the growth time at the initial growth stage, very short SWNTs can be obtained by adjusting the growth time. For thermal CVD, SWNT growth gradually starts and stops after the feeding and pumping of the hydrocarbon gas, respectively. It is difficult to use thermal CVD for precise growth-time control because there are uncertainties in the growth time. For plasma CVD, on the other hand, reactive ions and radicals are the main species involved in nanotube growth, and SWNT growth occurs only when plasma is generated. This suggests that the growth time can be controlled by tuning the electric power supply used for the plasma generation, and precise t_g control on the order of microseconds is possible in plasma CVD. Based on this strategy, we attempted to grow short SWNTs with narrow diameter and chirality distributions by precisely adjusting the t_g with time-programmed plasma CVD. Although plasma CVD is a well-known SWNT growth method with advantages of low-temperature growth [17–19] and freestanding growth [14–16], there have been no reports of highly controlled growth time.

The length distribution of SWNTs was carefully investigated by TEM and atomic force microscopy (AFM). For relatively long (~60 sec) growth times, the length distribution of SWNTs was broad (Figures 5(a) and 5(c)). On the contrary, when the growth time was carefully controlled on the order of a few seconds, almost all the SWNTs were very short (<100 nm), and the distribution also narrowed, as confirmed by direct TEM observation (Figure 5(b)) and AFM characterization (Figure 5(d)). This indicates that it is possible to directly grow short SWNTs by precisely adjusting the growth time with time-programmed plasma CVD. Interestingly, the PLE map of SWNTs grown for long (Figure 5(e)) and short (Figure 5(f)) times showed that the main chirality species were limited to (7,6) and (8,4) (Figure 5(f)) only for short growth times. This indicates that the chirality distribution at the initial growth stage was very narrow.

5.4. Metallicity Control. Thin-film transistors (TFTs) are promising candidates for SWNT nanoelectronics applications. Although high mobility and flexibility make SWNT films ideal for use in various industrial applications, the low on/off current ratio in SWNT TFTs caused by a mixture of metallic and semiconducting SWNTs strongly restricts the practical use of SWNTs in TFTs applications. Recent progress in chemical separation enables us to fabricate high-quality devices with on/off ratios of $\sim 10^4$ and gate-effective mobility of $\sim 52 \text{ cm}^2/\text{Vs}$ [56]. Impurities and defects are occasionally induced in the chemically treated nanotubes during the separation process, which significantly decreases the device performance. Since the as-grown SWNTs maintain their original high quality with low impurity concentrations, the selective growth of semiconducting SWNTs is

FIGURE 5: (a, b) TEM images of freestanding SWNTs produced by long (a) and short (b) growth times. (c, d) Length distributions of SWNTs produced by long (c) and short (d) growth times. The inset shows a typical AFM image of SWNTs used for length estimation. (e, f) PLE map of SWNTs grown for long (e) and short (f) times.

an important topic. li et al. reported the preferential growth of semiconducting SWNTs by plasma CVD [57]. Although several similar studies of plasma CVD [58–60] and thermal CVD [61] have also been reported, elucidation of this selective-growth mechanism remains an open question that requires further investigation. Here, we present our recent experimental results on the clear correlation between the performance of semiconducting devices fabricated by plasma CVD-grown SWNTs and the SWNT mean diameter, which might explain the preferential growth of semiconducting SWNTs by plasma CVD.

Figure 6(a) shows typical Raman scattering spectra of SWNTs grown under different growth temperatures. The high G-peak to D-peak ratio indicates that the quality of SWNTs was comparable to that of the conventionally CVD-grown SWNTs. The RBM in the lower wave number region shows the clear down-shift with increasing growth temperature. It is well known that the RBM peak position and tube diameter have a correlation of $\omega = 248/d$, that is, the mean diameter of SWNTs increases with increasing growth temperature. Note that all Raman measurements were carried out for the as-grown SWNTs. The density of SWNTs grown by our system is not so high and they form individual or thin bundled shapes. Thus, the equation for individual SWNTs ($\omega = 248/d$) is utilized for the diameter estimation. This correlation is thought to be due to

the catalyst particle size effect. Higher growth temperatures cause catalyst particle aggregation and increasing catalyst particle size, which result in large-diameter SWNTs. Figures 6(b)–6(d) show a source-drain current (I_{ds}) versus gate bias voltage (V_g) curve (Figure 6(b)), an I_{ds} -source drain voltage (V_{ds}) curve (Figure 6(c)), and an SEM image (Figure 6(d)) of TFT devices fabricated with SWNTs grown under 800°C. The on/off ratio was on the order of 10^4 (Figure 6(b)) with a 3- μ A on-current (I_{on}) at $V_{ds} = 1$ V (Figure 6(c)). The linear I_{ds} - V_{ds} characteristic indicates good contact between electrodes and nanotubes. The channel length and width were 2 μ m and 50 μ m, respectively. A clear dependence was observed from the plot of I_{on} versus on/off ratio as a function of SWNT growth temperature. The on/off ratio of each device clearly decreased with decreasing growth temperature (Figure 6(e)). The concentration of the working devices, which had on/off ratios greater than 5, was counted and plotted as a function of growth temperature (Figure 6(f)). Interestingly, the working device concentration was only 2.5% for the 600°C-grown (small-diameter) SWNTs, whereas more than 90% of the devices worked for the 800°C-grown (large-diameter) SWNTs. The densities of SWNTs grown under different growth temperatures were similar.

To explain this dependence of the working device concentration on diameter, Ar plasma was irradiated on the devices consisting of small- and large-diameter SWNTs,

FIGURE 6: (a) Raman scattering spectra of SWNTs grown at different growth temperatures. (b) I_{ds} - V_g and (c) I_{ds} - V_{ds} characteristics of TFT devices fabricated with SWNTs grown at 800°C. (d) Typical SEM image of TFT devices with random-network SWNTs grown at 800°C. (e) I_{on} - I_{on}/I_{off} plot of TFT devices with SWNTs grown at different growth temperatures. (f) Histogram of working device concentration for TFT devices with SWNTs grown at different growth temperatures.

and a defect formation rate was estimated from the current change before and after plasma treatment. For small-diameter SWNT devices, the on/off ratio did not change, and on- and off-current significantly decreased after Ar-plasma irradiation. In contrast, the on/off ratio increased with increasing Ar-plasma irradiation time, and the off-current depression was significant compared to that of the on-current for large-diameter SWNT devices. Based on these results, the following model can be developed to explain the dependence of the working device concentration on diameter. Due to the curvature effect, small-diameter SWNTs are less stable than large-diameter SWNTs. Hence, both metallic and semiconducting SWNTs are easily deformed by Ar-plasma irradiation with no change in the tube metallicity. On the other hand, in the weak curvature range, metallicity depends on the defect formation rate, which might correlate with reactivity, binding energy between carbon atoms, and a healing process. This model is consistent with the selective etching of metallic SWNTs by a gas-phase reaction, which was previously reported in [62]. Further detailed studies on the selective damage of metallic SWNTs might provide

insight on the preferential growth of semiconducting SWNTs by plasma CVD.

6. Conclusions

Recent progress in SWNT growth was presented, with a special emphasis on plasma CVD. Due to the strong plasma-sheath electric field, it is possible to grow freestanding individual SWNTs by plasma CVD. The growth temperatures for MWNTs and SWNTs were lowered to ~ 120 and 400°C , respectively, by the effective decomposition of carbon source gasses due to energetic electron impact in plasma. Based on the time-evolution study and the detailed plasma parameter measurements, the growth kinetics of SWNTs in plasma CVD were well established. Diameter-, chirality-, and length-controlled growth also achieved by adjusting the plasma conditions. Moreover, the concentration of semiconducting SWNTs in FET devices can be increased by tuning the mean diameter of SWNTs, and this effect is attributable to selective damage of metallic SWNTs during plasma CVD.

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