Effect of Ion Impact on Incubation Time of Single-Walled Carbon Nanotubes Grown by Plasma Chemical Vapor Deposition

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The effect of ion impact on the incubation time of single-walled carbon nanotubes (SWNTs) during plasma chemical vapor deposition (CVD) has been studied. Based on the systematic investigations, the incubation time of large-diameter SWNTs was found to be sensitive to the ion impact during plasma CVD. The incubation time difference ($\Delta t_i$) between small- and large-diameter SWNTs can increase up to 120 s with the introduction of appropriate ion impact during the growth process of the SWNTs. The selectivity of the effects of ion impact on the incubation time of small- and large-diameter SWNTs was also found to be sensitive to the hydrogen concentration during plasma CVD. This indicates that the hydrogen ion can play an important role during the nucleation period in the development of SWNTs with plasma CVD. Since the increase in $\Delta t_i$ for each chirality is important for the realization of chirality-selective growth of SWNTs, we believe that our findings can contribute to this aspect, one of the main goals in the science and application fields of SWNTs.

Keywords: single-walled carbon nanotube, ion impact, plasma CVD, incubation time, chirality

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Single-walled carbon nanotubes (SWNTs) are fabricated by fashioning a mono-layer graphene sheet consisting of hexagonal carbon networks into tubes. Due to their exceptional characteristics such as high carrier mobility, mechanical flexibility, and high current density, SWNTs are regarded as promising materials in various fields, and especially for electronic applications. Since the electrical properties of SWNTs strongly depend on their chirality [1, 2], chirality-controlled growth is still one of the major challenges in the science and application fields of SWNTs [3, 4].

Plasma chemical vapor deposition (CVD) is one of the most powerful methods for the structure-controlled growth of SWNTs [5–7]. We have previously realized narrow chirality-distributed growth of SWNTs by time-programmed plasma CVD [8]. In this method, chirality distributions of SWNTs can be contracted by controlling their process time. Since there is an incubation time difference for each chirality, the number of chirality species grown at the initial growth stage is limited, resulting in the growth of SWNTs with relatively narrow-chirality distributions. However, in order to improve the selectivity of each chirality, it is an important issue to identify the factors which strongly affect the incubation time [8–10]. The increase in the incubation time difference ($\Delta t_i$) between each chirality is also a significant topic to address.

In this study, we have investigated the effect of ion impact on the growth of SWNTs during plasma CVD. It was observed that the incubation time of large-diameter SWNTs grown with ion impact during plasma CVD can be selectively delayed compared with that without ion impact, resulting in an increase in $\Delta t_i$ between small- and large-diameter SWNTs. The $\Delta t_i$ was also found to be sensitive to the concentration of hydrogen during plasma CVD. This indicates that hydrogen ion plays an important role in the nucleation period of growth of SWNTs during plasma CVD. These findings can be useful in realizing the chirality-controlled growth of SWNTs.

Development of SWNTs was conducted in a homemade plasma CVD reactor (Fig. 1). Plasma was generated by inductively-coupled radio frequency (RF; 13.56 MHz) discharge. A gas mixture of methane and hydrogen was utilized as the carbon source. The growth conditions are...
explained in detail elsewhere [8]. A substrate was inserted into the center of the furnace with or without an ion reflector, which can control the kinetic motion of the ion entering the substrate during plasma CVD. The configuration of the ion reflector is shown in Fig. 1. Since the ion reflector was just put on the substrate without any spacer, the space between ion reflector and substrate ($d_s$) is very small ($<1\,\mu\text{m}$). In order to diffuse ions into the space between ion reflector and substrate, plasma sheath length has to be shorter than $d_s$. When we assume that the electron temperature is $0.1-1\,\text{eV}$, electron density of $10^{13}-10^{14}\,\text{cm}^{-3}$ is required to form such short plasma sheath length ($<1\,\mu\text{m}$), which is much higher than that of plasma ($10^7-10^9\,\text{cm}^{-3}$) formed in general inductively-coupled plasma discharge under low RF power condition ($\sim 25\,\text{W}$). This indicates that the ion reflector used in this study has enough ability to reflect the ions during plasma CVD. The SWNT structures were characterized by Raman scattering spectroscopy with He-Ne laser (632.8 nm wavelength) excitation.

The Raman scattering spectrum of the SWNTs was measured as a function of growth time with (Figs. 2 (a), (b)) and without the ion reflector (Figs. 2 (c), (d)). G-band intensity, which is related to the number of SWNTs, clearly increased with an increase in the growth time for both with and without ion reflector. The radial breathing mode (RBM) of the Raman scattering spectrum is known to be sensitive to the diameter of the SWNTs. In this measurement, two clear RBM peaks were obtained around $200\,\text{cm}^{-1}$ and $300\,\text{cm}^{-1}$, corresponding to the large ($\sim1.12\,\text{nm}$) and small ($\sim0.74\,\text{nm}$) diameter SWNTs, respectively. In the case of fabrication of SWNTs without ion impact (with ion reflector), both small- and large-diameter SWNTs started developing within a short growth time ($\sim40\,\text{s}$). However, a clear difference could be observed in the case of fabrication of SWNTs with ion impact (without ion reflector). Small-diameter SWNTs started their development after $20\,\text{s}$ similar to the case of growth without ion impact, whereas the development of large-diameter SWNTs was delayed up to $\sim120\,\text{s}$. In order to estimate the value of the $\Delta t$, the concentration ratio of small-diameter SWNTs to that of all SWNTs ($R_S = I_S/(I_S + I_L)$) was plotted as a function of growth time (Figs. 2 (b), (d)), where $I_S$ and $I_L$ denote the RBM intensity of small- and large-diameter SWNTs, respectively. Note that we defined $\Delta t$ as a time when $R_S$ becomes lower than $0.5$. It was found that $\Delta t$ increases from $40\,\text{s}$ to $120\,\text{s}$ when ion impact was introduced during plasma CVD. This can be explained as the result of mild ion etching. The density of hydrocarbon precursors on the surface of the catalyst decreases on the introduction of ion bombardment effects [6]. Since the number of required carbon atoms for the construction of SWNTs is proportional to the diameter of SWNTs, large-diameter SWNTs need higher amount of carbon atoms. This can result in the increase in the incubation time for large-diameter SWNTs grown with ion impact. On this assumption, the incubation time of small-diameter SWNTs should also be delayed as a result of ion impact. However, the incubation-time delay by ion impact can be obtained only for large-diameter SWNTs, as shown in Fig. 2. This can be explained as follows. There are several reasons which decide the incubation time of SWNTs, such as the time needed to reach supersaturation of carbon in a catalyst, the time for cap formation, and the time required to lift the cap from the surface of the catalyst [11]. The incubation time for small-diameter SWNTs may not be so sensitive to the supersaturation of carbon due to their small proportion of carbon in their catalysts (26-27 carbon atoms in a 1 nm size catalyst) [11], resulting in little variation of the incubation time with or without ion impact. Further studies are required to identify the detailed growth mechanism related to this issue.

To support the model mentioned above, the effects of hydrogen concentration ($R_H$) on the incubation time of
small- and large-diameter SWNTs were also investigated with relation to ion impact during the growth process. Figure 3 shows the typical Raman scattering spectra of SWNTs grown under different RH. Since a clear and sharp G-band was observed with relatively small D-band intensity, the SWNTs grown by this method are of relatively high quality, independent of RH. Interestingly, both small- and large-diameter SWNTs were grown at RH = 0% even with ion impact, whereas only small diameter SWNTs could be grown at RH = 90%. Carbon atoms are known to be etched out from the surface of the catalyst through the reaction with hydrogen. This indicates that the incubation time of large-diameter SWNTs is sensitive to the etching factor during growth. This is consistent with the model mentioned above. Based on these results, it can be conjectured that the impact of hydrogen ions should cause the mild etching of carbons on the surface of the catalyst, resulting in the difference in Δt between small- and large-diameter SWNTs.

In summary, we have investigated the effects of ion impact on the incubation time during the growth of SWNTs with plasma CVD. Based on the time evolution studies of the Raman scattering spectra, the incubation time of large-diameter SWNTs can be selectively increased by introducing ion impact during the growth process, resulting in the increase in Δt between small- and large-diameter SWNTs. This Δt between small- and large-diameter SWNTs is also found to be sensitive to RH during plasma CVD, indicating that hydrogen ions play an important role in the nucleation period of SWNTs.

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