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Kinetics of reactive ion etching upon single-walled carbon nanotubes

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The remarkable etching reaction of single-walled carbon nanotubes (SWNTs) has been observed in their growth of the parameter-controlled plasma chemical vapor deposition (CVD). The time evolution study of the SWNTs growth leads to establishing a growth equation which can completely express the growth kinetics of SWNTs in the plasma CVD. The growth equation is found to reveal that there are several key parameters which directly affect the etching reaction of SWNTs. Furthermore, such kinetics of the SWNT etching in plasmas can perfectly be explained with a reactive ion etching model. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2837463]

In the last several decades, plasma etching technologies[1] strongly contributed to improving a device performance in a semiconductor application stage from the viewpoint of downscaling. Those outstanding developments of the etching process had been brought through the basic understanding of the etching kinetics.[2] Single-walled carbon nanotubes (SWNTs) have attracted a great deal of attention due to their prominent scaling advantages and exceptional properties and are expected to be as a potential candidate in the post silicon-based semiconductor device stage. Recently, significant findings have been reported about the selective etching of metallic SWNTs based on a plasma reaction.[3] Since the selective removal of metallic SWNTs from bulk samples is one of the critical problems for the SWNT application in a semiconductor device field, this pursuit appears to provide us a practical scenario toward the realization of the logical circuit integration with semiconductor SWNTs. Unfortunately, the etching reaction of SWNTs has, however, not been deeply understood and, especially, the elucidation of plasma effects has never been attacked so far. Since the etching reaction is also closely linked to the defect formation which profoundly influences basic electrical transport properties of SWNTs, an understanding of the etching kinetics is an inevitable and crucial issue for the future development of the high-performance SWNT device.

In this letter, we report a crucial finding of remarkable etching reaction of SWNTs during the plasma chemical vapor deposition (CVD) and key parameters for such etching reaction are also revealed with a numerical analysis of the experimentally established SWNT-growth equation. A reactive ion etching model is also developed to explain the etching reaction of SWNTs in plasmas.

The SWNT growth is performed with a home made diffusion plasma CVD system. Detailed experimental conditions are described in elsewhere.[4] The radio-frequency (rf, 13.56 MHz) power (P_{rf}), ion energy (U_i), and growth time (t_g) are systematically varied to discuss the growth kinetics of SWNTs. Principal plasma parameters such as electron-density, electron temperature, plasma potential, radical species, and radical density are measured by an rf-compensated Langmuir probe and optical emission spectroscopy (OES), respectively.[5]

Figure 1 presents typical Raman scattering spectra of SWNTs as a function of t_g. Raman scattering spectroscopy has been known as one of the powerful tools to characterize the SWNTs structure such as diameter, chirality, quality, and so on. In addition to these structural information, the absolute value of G-band intensity (I_G) at 1593 cm^{-1} originating from a graphite nature in the SWNTs is sometimes utilized to discuss the amount of SWNTs.[6] As information of the amount of SWNTs, therefore, we utilize the absolute value of I_G measured under the almost same experimental conditions; laser power of $\sim$0.2 mW/μm^2, laser wavelength of 488 nm, laser spot size of 4 μm^2, and accumulation time of 60 s. When P_{rf} is 40 W, I_G gradually increases with an increase in t_g [Fig. 1(a)]. On the other hand, I_G suddenly decreases when the growth time is longer than 50 s under the 100 W P_{rf} condition [Fig. 1(b)]. These results indicate that the growth kinetics of SWNTs is strongly influenced by the plasma conditions and several specific factors in plasmas cause the strong etching of SWNTs, as shown in Fig. 1(b).

In the case of the thermal CVD, it has been reported that the growth kinetics of SWNTs can be expressed with a following equation (normal equation):[7] $I_G = I_0[1-\exp[-(t_g - \Delta t)/\tau_{gro}]]$, where I_0, Δt, and τ_{gro} denote saturated I_G, incubation time, and relaxation time of the growth, respectively. Our experimental results of damage free growth [Fig. 1(a)] well match with this equation, which denotes our estimation

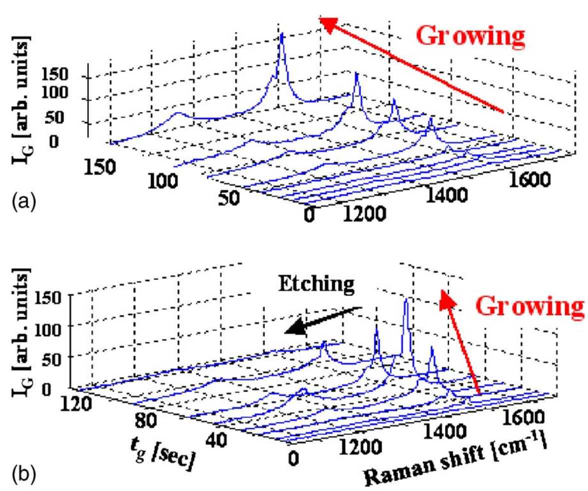

FIG. 1. (Color online) Raman spectra of SWNTs as a function of t_g. (a) P_{rf}=40 W and (b) P_{rf}=100 W, respectively.

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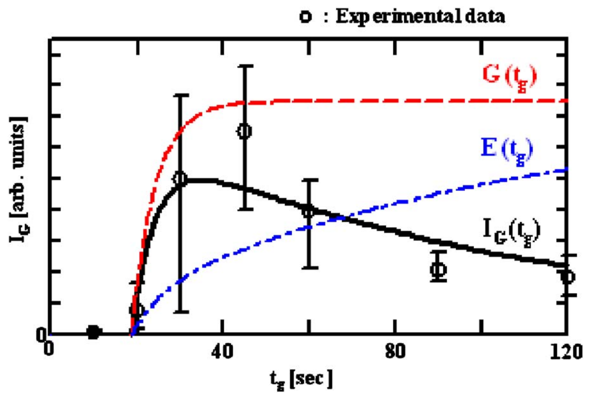

FIG. 2. (Color online) The comparison between the experimental data and fitting curve of Eq. (1).

of SWNTs amount with I_G is reliable. However, there is obviously no formula which can describe the growth kinetics including the etching effect as described in Fig. 1(b). On purpose to express this phenomenon, therefore, we assume that the growth mode can be described with a following 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 kinetic has to be described with the above-mentioned normal equation, which means that $G(t_g)$ is the same as the normal equation. One of the most important points in this study is how to describe $E(t_g)$. Since carbon atoms are etched out 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. The Langmuir's adsorption isotherm is known as one of the most basic ones, and to be expressed by the following form: $d\theta/dt = \alpha P(1-\theta)$, where θ, t, α, and P indicate the percentage of covered area, reaction time, adsorption efficiency, and pressure of adsorbate, respectively. Actually, the Langmuir's equation has been utilized in the wide range of fundamental scientific studies to understand chemical adsorption reactions.[8] In our study, θ corresponds to the etched area against the area of the graphite sheet of SWNTs, i.e., $\theta = E(t_g)/G(t_g)$. Since the solution of the Langmuir's equation is $\theta(t_g) = 1 - \exp(-t_g/\tau_{\mathrm{etc}})$, where $\tau_{\mathrm{etc}} = 1/\alpha P$ is the relaxation time of the etching reaction, $E(t_g)$ results in the following equation: $E(t_g) = G(t_g)[1 - \exp(-t_g/\tau_{\mathrm{etc}})]$. According to the above mentioned equations, an advanced growth equation can be established as

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

Figure 2 shows a comparison between the experimental result of Fig. 1(b) and fitting curve with Eq. (1). The fitting curve gives good agreement with the experimental result, indicating that the advanced equation established enables us to discuss a more detailed correlation between plasma parameters such as ion energy U_i and species density and growth parameters such as Δt and etching efficiency [$k = 1/(\tau_{\mathrm{etc}}\text{-}\tau_{\mathrm{gro}})$].

Based on the advanced growth Eq. (1), we attempt to understand effects of U_i coming to the substrate during the SWNT growth. Figure 3(a) gives a counterplot of I_G as functions of t_g and U_i. Since U_i is determined by a potential drop between the plasma and substrate, the substrate bias voltage is changed to adjust U_i. When U_i is fairly low (~1 eV), I_G gradually increases and saturates with an increase in t_g. The similar tendency can also be found under the condition of $U_i = 30$ eV. When $U_i = 10$ eV and over 50 eV, on the other hand, a sudden decrease of I_G can be found after the specific t_g progress ($t_g > 150$–200 sec). This decrease of I_G indicates that the etching reaction arises at these specific energy window of ions as similar to the result in Fig. 1(b). The I_G/I_D plot also supports the evidence of etching reaction in such a specific energy range, where I_D is D-band intensity around 1350 cm^{-1} in Raman spectroscopy. Only under the U_i condition of 10 and >50 eV, the SWNTs quality remarkably decreases independently of t_g [Fig. 3(b)]. These lead us to conclude that several significant damages are likely caused via energetic ions ranging around 10 and >50 eV.

A further quantitative and practical analysis is also performed upon the fitting of experimental results with the advanced growth equation [Eq. (1)]. Figure 4(a) shows a plot of estimated k under the different U_i condition. As similar to the result in Fig. 3, the clear increment of k is recognized

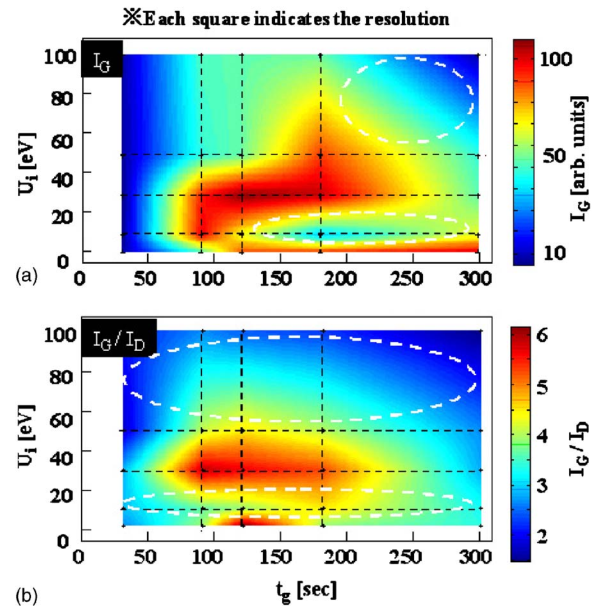

FIG. 3. (Color online) Contour plot of I_G (a) and I_G/I_D (b) as functions of U_i and t_g. Each dot indicates the condition, where experiments have been done. For visual help, all of data between each dot are computationally compensated.

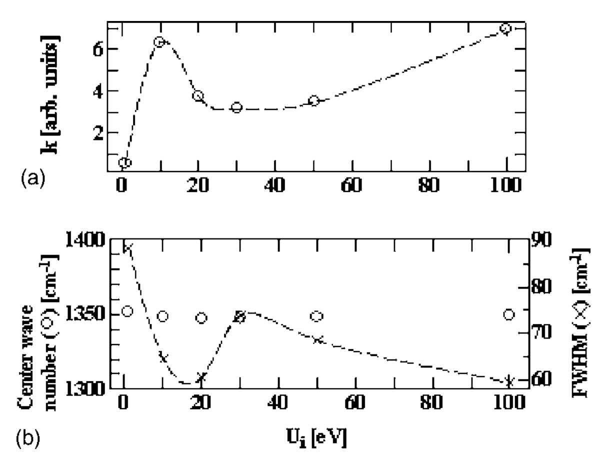

FIG. 4. (a) Etching efficiency k as a function of U_i. (b) Center wavelength and FWHM of D-band spectra as a function of U_i.

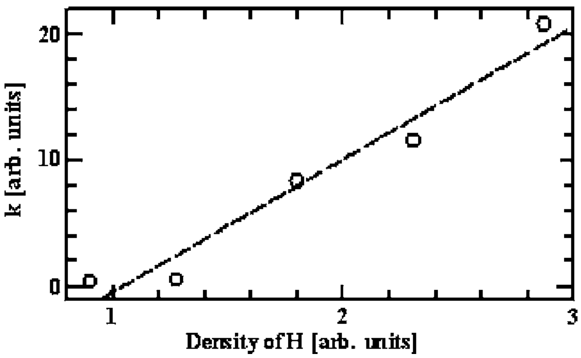

FIG. 5. Etching efficiency k as a function of relative density of H.

under the specific energy condition of $U_i=10$ and >50 eV.

Figure 4(b) describes a plot of the center wavelength and full width at half maximum (FWHM) of D band as a function of U_i. Although, the center wavelength of D band is independent of U_i, a clear difference can be found about the FWHM of D band, i.e., it obviously decreases under the specific U_i (10 and >50 eV) condition. Since the narrow width of D band is known as the origin of defects in SWNTs,[9] the observation described just above also suggests the existence of significant damage on the carbon network in SWNTs under the specific U_i condition (10 and >50 eV). This structure deconstruction in the specific energy range is also confirmed with the other kind of ion irradiation experiment.[10]

In addition to the ions, there are many kinds of factors causing significant impacts on the structure of SWNTs in hydrocarbon plasmas. Especially, the density of radicals is much higher than that of ions in reactive plasmas. Thus, we attempt to reveal a correlation of k with several radical densities. The relative densities of radicals are measured by an actinomery method with OES.[5] When k is plotted as a function of H density, it is surprising that a clear liner correlation is found as displayed in Fig. 5. Although the dependence of H on etching reactions has already been mentioned by several groups without any direct measurement of H density,[11] our time-evolution results combined with the systematical H-density measurement afford more direct evidence for the primal factor determining k during the growth of SWNTs.

Based on the above mentioned experimental results, a consistent reactive ion-etching model can be established as follows. In our study, the etching efficiency k is expressed by the following equation:

$$k = 1/(\tau_{\text{etc}} - \tau_{\text{gro}}) \approx 1/\tau_{\text{etc}} = \alpha P. \tag{2}$$

The linear dependence of k on H density shown in Fig. 5 indicates that the density of H corresponds to P in Eq. (2). Since the density of H is kept constant during the experiment of ion energy effects, on the other hand, the supplied amount of etching elements (P) must be constant. Hence, the variation of k depending on U_i [Fig. 4(a)] originates from the difference of α. Under the specific U_i condition, the carbon-carbon bond is considered to be broken, and the efficiency of adsorption between the carbon and etching element (H) resultantly comes to increase. After all, the direct factor causing the etching of SWNTs is the H and the specific energy of ions enhances those etching reactions by changing the adsorption efficiency between the carbon and hydrogen atoms.

In summary, the remarkable etching reaction of SWNTs has been found in the growth experiment by the parametrically well-controlled plasma CVD. The time evolution of SWNTs Raman scattering spectra enables us to establish an advanced growth equation which can completely express the growth kinetics of SWNTs in the plasma CVD. Owing to the growth equation, it is also revealed that there are several key parameters which directly affect the etching reaction of SWNTs. Furthermore, such etching reaction of SWNTs in plasmas can perfectly be explained with a reactive ion etching model. These basic knowledge about the SWNTs etching kinetics is increasingly indispensable for setting an issue for the industrialization of high performance SWNT-based electrical applications.

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