I. INTRODUCTION

Since the discovery of carbon nanotubes (CNTs), much interest has been concentrated on their application to electronic devices such as field emitters, transistors, and electrochemical systems as well as structural composite materials. For the practical application to such devices, chemical vapor deposition (CVD) using plasma is normally used to synthesize CNTs on substrates at low temperatures although a large number of structural defects cannot be excluded. Many researchers have investigated that the structural order and morphologies of CNTs are crucial factors in determining their characteristics of field emission, hydrogen storage, and capacity. It was reported that the field emission property of multiwalled nanotubes (MWNTs) was enhanced by controlling the atomic structure at their tip surface, which was modified by introducing a high density of defects by plasma treatment or producing protrusions during field emission. For the hydrogen storage of MWNTs, the difference in capacity was closely related to the structure and crystallinity of MWNTs. It was also observed that higher amounts of Li ions were electrochemically inserted in defective MWNTs than in more crystalline MWNTs.

Electron cyclotron resonance (ECR)-CVD is one of the promising routes for the low-temperature synthesis of CNTs, since the plasma zone in the ECR-CVD is far from the substrate, giving rise to the benefit of maintaining the low substrate temperature during deposition. If incorporated in the process, moreover, radio-frequency (rf) or direct-current (dc) biasing can impart ion bombardment energy to the substrate without disturbing the ECR plasma. Hence, we can control the kinetic energy of ion bombardment to the growing surface, decoupled from the ECR plasma. It is well known that negative biasing to the substrate plays a crucial role in determining the physical properties of as-grown films. In diamondlike carbon (DLC) films, the ion bombardment to the growing films decreases the amount of bonded hydrogen, thus affecting the film properties, such as optical band gap and refractive index. CNT synthesis using ECR-CVD, however, has not been often investigated until now even though ECR-CVD possesses many advantages as described above. Moreover, the synthesis process of CNT is very similar to that of DLC, implying that bonded hydrogen has a certain effect on the structure and properties of MWNTs synthesized using ECR-CVD.

In our previous work, various kinds of carbonaceous materials were synthesized, including well-graphitized MWNTs at temperature as low as 500 °C using ECR-CVD with rf biasing to the substrates. The structures of carbonaceous materials were observed to develop from the amorphous phase to defective nanorods, and progressively to...
well-graphitized MWNTs as the applied rf bias voltages increased. In this study, the structural differences are investigated between defective carbon nanorods formed at lower rf bias voltages and well-graphitized MWNTs at higher rf bias voltages. It is noted that the distance between two graphene layers of carbon nanorods is much larger than that of MWNTs. It is also shown that the $D$ (~1350 cm$^{-1}$) and $G$ (~1580 cm$^{-1}$) peaks in Raman spectra shift toward higher wave numbers as the applied rf bias voltages increase, probably resulting from the shortening of C—C bonds which is considered to be related to the lower concentration of $sp^3$ C—C bonds. Electron-energy-loss spectroscopy (EELS) spectra obtained from carbon nanorods and well-graphitized MWNTs are presented to compare the electronic configurations of carbon atoms constituting nanorods and nanotubes. The position of the bulk plasmon $\pi + \sigma$ peak from carbon nanorods is seen to shift toward a lower energy, compared to well-graphitized MWNTs, and the low-energy plasmon loss peak due to $\pi$ electrons, clearly defined for well-graphitized MWNTs, is not observed for defective carbon nanorods. This is also confirmed by x-ray photoelectron spectroscopy (XPS), in which the delocalization of $\pi$ electrons becomes more pronounced with the structural evolution from carbon nanowalls to MWNTs with increasing rf bias voltages. Using plasma diagnosis, an ion kinetic energy was estimated for the synthesis of well-graphitized MWNTs by the removal of hydrogen from C—H bonding. These results seem to lead us to understand the role of ion bombardment in the synthesis of CNTs and, therefore, the effect of bonded hydrogen within CNTs on their morphologies and properties. Moreover, the growth mechanism is proposed for carbon nanorods and highly crystalline MWNTs at low temperatures with the aid of ion bombardment.

II. EXPERIMENT

Carbonaceous materials were synthesized on Ni/Cr-coated glass substrates using a gas mixture of CH$_4$ and Ar by ECR-CVD. A 1000 Å thick Cr layer was coated on the Corning glass 1737 by magnetron dc sputtering to improve adhesion between the glass substrate and a Ni layer. Ni serves as a catalytic layer with 600 Å in thickness, deposited using electron-beam evaporation (Balzers, BAV1250). The 800 W of microwave with 2.45 GHz was guided through a rectangular waveguide and introduced into an excitation chamber through a quartz window. Two magnets attached to the chamber generated a magnetic field of 875 Gauss. The system was evacuated down to a base pressure below 10$^{-5}$ Torr by a turbomolecular pump, and a gas mixture of CH$_4$ and Ar with the flow rates of 50 and 10 sccm, respectively, was fed into the chamber to achieve a pressure of 10 mTorr. The substrate was heated to 400 °C by an infrared light and sustained at this temperature during the process, monitored by a thermocouple. In particular, a rf power was supplied to the substrate holder to induce negative self-bias voltages to the substrate from $-50$ to $-200$ V (the variation of rf biases from $-50$ to $-200$ V will be described as an increase of the rf biases below). The plasma diagnostics were carried out using a computerized double Langmuir probe (Plasmart, DLP 2000) to measure electron temperatures, ion saturation currents, and plasma potentials. The cylindrical Langmuir probe, made of a tungsten tip 0.5 mm in diameter and 10 mm in length, was positioned in the center of discharge 4 cm above the substrate holder. The growth continued for 20 min.

As-grown samples were examined by scanning electron microscopy [(SEM) Philips, XL30SFG] and high-resolution transmission electron microscopy [(HRTEM) Philips, UT-30]. Micro-Raman spectroscopy with an excitation wavelength of 632.8 nm using a He–Ne laser (Renishaw System 3000) was also employed to investigate the structural characteristics of as-deposited samples. EELS spectra were measured with a high-resolution 300 keV electron-energy-loss spectrometer having an energy resolution of 1 eV, fitted to HRTEM. For EELS measurement, the as-deposited samples were scrapped off from the substrate, dispersed in an ethanol ultrasonic bath, and then placed on copper grids. The spectra from each sample were obtained using a nanometer-sized electron probe. XPS measurement was also performed using Q2000 spectrometer (PHI, Q2000) with Al Kα(1486.6 eV) line, analyzing approximately a few tens of Å from the top of the film.

III. RESULTS

A. Properties of carbon nanorods and nanotubes

Figure 1 shows SEM images of as-deposited samples with different rf biases from $-50$ to $-200$ V at 10 mTorr.

![SEM images of carbon materials deposited with rf bias voltages of (a) $-50$, (b) $-100$, and (c) $-200$ V. Carbon nanowalls were formed at $-50$ V, while carbon filaments were grown at $-100$ and $-200$ V.](image-url)
while keeping the other deposition parameters the same. As presented in Fig. 1(a), a translucent carbonaceous material with a wavy fencelike shape was grown at the rf bias of −50 V, called as carbon nanowalls hereafter. Different with the morphology of carbon nanowalls at −50 V, filamentous carbon with vertical alignment began to grow at the rf bias voltages equal to or higher than −100 V [Figs. 1(b) and 1(c)]. It was found, in particular, that the carbon filaments synthesized at −100 V [Fig. 1(b)] were curved and bent in their shapes, while they became straighter when the rf bias voltage increased to −200 V [Fig. 1(c)]. We have already reported such a morphological evolution with rf bias voltages under a similar experimental condition.12

HRTEM images of the very samples of Fig. 1 are presented in Fig. 2. As shown in Fig. 2(a), a carbon nanorod formed at the rf bias of −50 V is mainly composed of amorphous carbon, in which the graphene layers are locally observed around the Ni catalytic particles. For the sample grown at −100 V [Fig. 2(b)], a carbon nanorod, not a hollow tube, is obtained in which Ni catalyst resides on top of the carbon nanorod. At a low magnification of a transmission electron microscope, it is observed that most carbon nanorods are curved and bent, as already seen in Fig. 1(b). The HRTEM image in Fig. 2(b) clearly shows the crystalline walls constituting the carbon nanorod, but the graphene layers are disordered and a little slanted about the rod axis with their ends terminated at the rod surface, surrounding the Ni catalyst particle. The distance between two graphene layers is measured to be about 0.385 nm on average, even larger than 0.4 nm in a highly distorted area, which is much larger than the typical value of 0.344 nm of graphite. A halo diffuse diffraction pattern given in an inset, obtained by fast Fourier transformation (FFT), indicates that the distance between adjacent graphene layers has a wide spread in its value. On the other hand, the well-graphitized MWNTs grown at the rf bias of −200 V are found to have fewer defects in their structure. As shown in Figs. 2(c) and 2(d), the graphene layers line up, in most cases, along the tube axis to form a hollow tube, of which the inner and outer diameters are about 8 and 30 nm, respectively. The distance between adjacent layers is measured to be 0.356 nm, which is fairly uniform over a large area, verified by diffraction spots in Fig. 2(d). It is emphasized that ECR-CVD could produce highly crystalline MWNTs by rf biasing even at temperatures as low as 400 °C, while in thermal CVD, high temperatures above 700 °C are needed to synthesize MWNTs having such a high crystallinity.

Raman spectroscopy is a versatile tool for characterizing carbon materials, providing information about the structural properties of the materials examined. Micro-Raman spectroscopic analyses of the carbonaceous materials grown by ECR-CVD clearly show the G peaks at 1580–1588 cm⁻¹ and the D peaks at 1323–1327 cm⁻¹ with the various rf bias voltages in Fig. 3. Here, it is to be noted that the D and G peaks in Raman spectra shift to higher wave numbers as the negative rf bias voltages increase from −50 to −200 V. As already discussed in our previous study,12 such an upshift in the D and G peaks can be explained to originate from the shortening of C—C bonds due to the structural change from carbon nanowalls to nanorods, and progressively to well-graphitized MWNTs as the rf bias voltages increase. In DLC films, it has been known that a downshift of the D and G peaks is attributed to an increase in the average C—C bond length at higher concentrations of sp³ C—C bonds. Therefore, it can be thought that shorter C—C bond length at higher rf biases is related to the lower concentration of sp³ C—C bonds for highly crystalline MWNTs.

EELS measurement was carried out on the very samples shown in Figs. 2(b) and 2(c), which provide information on the chemical bonding nature in a very small region of the material examined. In order to eliminate the curvature effect...
of graphene sheets on the nature of chemical bonding, in particular, EELS was performed in the center of an individual nanorod and MWNT having almost the same diameter. As shown in Fig. 4(b), the well-graphitized MWNT exhibits two distinct plasmon peaks at 6.0 and 25.5 eV, corresponding to the collective excitation due to \( \pi \) electrons (\( \pi \) plasmon) and whole valence electrons (\( \pi + \sigma \) bulk plasmon), respectively. Here, the energy-loss peaks of graphite were used as a reference. On the other hand, an EELS spectrum of the carbon nanorod is quite different from that of the well-graphitized MWNT. For the nanorod, as shown in Fig. 4(a), the \( \pi \) plasmon peak at 6.0 eV was not seen and one prominent peak of \( \pi + \sigma \) bulk plasmon shifts toward a lower energy of 23.3 eV in comparison with the well-graphitized MWNT. Since the \( \pi + \sigma \) bulk plasmon peak position is directly related to the number of electrons that take part in the excitation, it shifts toward a lower energy with a decrease in the density of the material examined. This also agrees with the HRTEM observation described above, showing a much larger distance between adjacent graphene layers of the carbon nanorod than that of the well-graphitized MWNT. It is likely, therefore, that the reduction in the density of material gives rise to the effective decrease in contribution of \( \pi \) electrons in the carbon nanorod, thus making the shift of \( \pi + \sigma \) bulk plasmon peak toward a lower energy. Another possibility to explain the lower shift in \( \pi + \sigma \) bulk plasmon peak in the carbon nanorod is less delocalization of valence \( \pi \) electrons around carbon atoms, effectively decreasing their contribution to the collective plasma oscillations. In addition, the invisible \( \pi \) plasmon peak in the carbon nanorod means that there is only a small amount of valence \( \pi \) electrons excited.

Here, XPS results of carbonaceous materials synthesized at different rf bias voltages suggest that the shift of \( \pi + \sigma \) bulk plasmon peak toward a lower energy is due to the less delocalization of valence \( \pi \) electrons. Figure 5 is normalized XPS C 1s core energy loss spectra for the very samples shown in Fig. 1. The as-deposited samples shown in Figs. 1(b) and 1(c) exhibit relatively sharp energy loss peaks at 6.4 eV and very broad loss features around 28 eV, corresponding to \( \pi \) and \( \pi + \sigma \) plasmons, respectively. These are the typical values of the plasmon energy loss obtained from graphitized carbon, and thus these two samples are thought to consist of mostly graphene layers. However, in the carbon nanowall formed at the rf bias of \(-50\) V, a broad loss feature is observed around 23 eV, which usually appears in amorphous carbon. In addition to the difference in the position of \( \pi + \sigma \) plasmon peak, it is to be noted that the lower part of \( \pi \) plasmon peak at 6.4 eV broadens in shape, and this may be due to the enhancement of the extra low-energy transition at 5.4 eV with the rf bias voltages. This low-energy transition is known to come from the delocalization of 2\( p_\pi \) electrons. Fink et al. observed the low-energy transition in the EELS of hydrocarbon plasma-produced carbon films due to the \( \pi \) electrons being delocalized over several benzene rings. Chen et al. also investigated the dispersion coefficient of 2\( p_\pi \) electrons for CNTs by the comparison of intensity of low-energy transition in graphite and C60. Therefore, it is suggested that the valence \( \pi \) electrons around carbon atoms become more delocalized when the structure of the carbonaceous materials develops from the carbon nanowalls to the carbon nanorods, and progressively to the well-graphitized MWNTs as the rf bias voltages increase.

B. Evaluation of ionic bombardment energy

It has been well known that the ion bombardment to the growing films has a significant effect on the characteristics of DLC films due to the release of hydrogen from the surface. However, the role of ion kinetic energy in determining the physical properties of CNTs is not yet investigated until now since ECR-CVD has been rarely employed for the synthesis of CNTs.

First of all, the mean-free path of molecules and the sheath thickness above the substrate are to be considered in order to exactly estimate the ion kinetic energy. The mean-free path between adjacent collisions \( \lambda \), is given by

\[
\lambda = \frac{1}{n_g \sigma},
\]

where \( \sigma \) is the collision cross section and \( n_g \) the...
density of gas molecules. Since $\sigma$ is calculated to be $2.8 \times 10^{-15}$ cm$^2$ with an atomic diameter of 3 Å for Ar and $n_e$ is $3.54 \times 10^{14}$ cm$^{-3}$ at 10 mTorr, the mean-free path is estimated approximately to be 10 mm. In addition, the sheath thickness above the substrate $s$ is given as follows:

$$s = \frac{2}{3} \left[ \frac{2}{\exp(-1)} \left( \sqrt{\frac{-eV_o}{kT_e}} - \frac{1}{\sqrt{2}} \right) \right] \times \left( \sqrt{\frac{-eV_o}{kT_e} + \frac{1}{2}} \right),$$

where $\lambda_D$ is Debye length, $k$ is the Boltzmann constant, $T_e$ is the electron temperature, and $V_0$ is the potential on the substrate with respect to plasma potential. Here, the Debye length, which is useful for defining length scales in plasma, is expressed by $\lambda_D = (kT_e\varepsilon_0/n_ee^2)^{1/2}$, where $\varepsilon_0$ is the permittivity of free space, and $n_e$ is the electron density. In order to evaluate sheath thickness $s$, Debye length $\lambda_D$, and plasma parameters of $T_e$, $n_e$, and $V_0$ are measured using a double Langmuir probe, and presented in Table I. Here, the $V_0$ is estimated by adding the difference between plasma and floating potentials $V_p - V_f$ to the rf bias voltage applied to the substrate. Using the plasma parameters, the sheath thickness is calculated to range from $1.69 \times 10^{-2}$ cm to $2.28 \times 10^{-1}$ cm with the rf bias voltages, as shown in Table I. Since the sheath thickness $s$ is shorter by more than one order of magnitude than the mean-free path $\lambda$, ion collisions would rarely occur within the sheath region during the flight to the substrate. It may be then assumed that ions are accelerated to have a kinetic energy of $eV_0$ when they arrive on the substrate. According to the kinetics of inelastic collision, the internal energy $\Delta U$ transferred from the kinetic energy of a colliding particle to a stationary particle is given by

$$2m_iu_i u_i \cos \theta = \frac{m_i}{m_t} (m_i + m_t) u_i^2 + 2\Delta U,$$

where $m_t$ is the mass of a colliding particle with a velocity of $u_i$ to a stationary particle of mass $m_t$ with an incident angle $\theta$, and $u_i$, $u_f$, $u_i$, $u_f$ are the velocities of $m_i$, $m_t$ after collision, respectively. In this study, CH$_4^+$ and Ar$^+$ ions can be assumed as colliding particles to neutral CH$_3$ radicals deposited on the substrate since it is known that CH$_4$/Ar glow discharge consists of mainly single-charged ions such as CH$_4^+$ and Ar$^+$ and neutral CH$_3$ radicals. The internal energy transferred from the initial kinetic energy of a CH$_4^+$ or Ar$^+$ ion to a CH$_3$ radical molecule is a function of the incident angle $\theta$ and the velocity $u_i$ of a CH$_4$ molecule after collision, as plotted in Fig. 6. Here, CH$_4$ radicals on the substrate cannot move freely after collision in real. Hence $u_f$ is determined to maximize $\Delta U$ from Eq. (2), and the fraction of the kinetic energy of the incident particle that transferred to the stationary molecules, has a maximum value of

$$\frac{\Delta U}{1/2m_t\nu_i^2} = \frac{m_t}{m_t + m_i} \cos^2 \theta.$$

Since the incident angle $\theta$ is the only variable in Eq. (3), the internal energies averaged over the incident angle $\theta$ for different rf bias voltages are presented in Table I. Here, it is to be noted that the maximum internal energies are larger than the C—H bonding enthalpy of 4.3 eV when the rf bias voltages applied to the substrate are equal to or larger than $-50$ V. Therefore, it can be explained that the formation of graphite layers from the rf bias voltage of $-50$ V, but only amorphous carbon without rf biasing to the substrate, comes from the insufficient internal energy necessary for dehydro-

TABLE I. Plasma parameters of CH$_4$/Ar discharge determined from the current–voltage characteristics using a double Langmuir probe, and average internal energies transferred from the ion kinetic energies at various rf bias voltages. The internal energies obtained from a colliding ion of CH$_4^+$ and Ar$^+$ to a stationary CH$_3$ molecule are calculated using the inelastic collision kinetics.

<table>
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<th>rf self-bias (V)</th>
<th>$T_e$ (eV)</th>
<th>$n_e$ (#/cm$^3$)</th>
<th>$V_p - V_f$ (eV)</th>
<th>$V_0$ (eV)</th>
<th>$\lambda_D$ (cm)</th>
<th>$s$ (cm)</th>
<th>Max. $\Delta U$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.10</td>
<td>$1.70 \times 10^{11}$</td>
<td>14.50</td>
<td>14.50</td>
<td>$3.17 \times 10^{-3}$</td>
<td>$1.69 \times 10^{-2}$</td>
<td>3.50</td>
</tr>
<tr>
<td>-50</td>
<td>3.06</td>
<td>$1.84 \times 10^{11}$</td>
<td>14.31</td>
<td>64.31</td>
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<td>$7.19 \times 10^{-2}$</td>
<td>15.56</td>
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<tr>
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<td>$1.87 \times 10^{11}$</td>
<td>14.50</td>
<td>114.50</td>
<td>$3.03 \times 10^{-3}$</td>
<td>$12.41 \times 10^{-2}$</td>
<td>27.70</td>
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<tr>
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</tr>
<tr>
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<td>51.94</td>
</tr>
</tbody>
</table>
gernation from C—H bonding. On the other hand, as discussed in the deposition of DLC film, it is instructive to evaluate the flux of ions and neutral species to the substrate to understand the deposition process on surface. The ion saturation current measured by a Langmuir probe is in the range of 4–5 mA/cm², not influenced by the rf bias voltages. This value approximately corresponds to \(3 \times 10^{16} \text{ions cm}^{-2} \text{s}^{-1}\). The flux of neutral species is also estimated from \(I = n_n \nu_n A/4\), where the density of neutral species \(n_n\) and the average neutral velocity \(\nu_n\) are obtained from the ideal gas law and mean speed calculation. This value estimated at a gas temperature of 600 K and a pressure of 10 mTorr is approximately \(4 \times 10^{18} \text{neutrals cm}^{-2} \text{s}^{-1}\) when \(\text{CH}_3\) molecules are assumed as neutral species. Comparing the flux of ions and neutrals estimated, it is considered that one or a few ions would arrive at the substrate when 100 or more neutrals deposit on the surface. Hence, some of \(\text{CH}_3\) molecules would be chemically activated to be dehydrogenated by ions only if the kinetic energy of ions is large enough to remove hydrogen from C—H bonding.

### IV. DISCUSSION

We have suggested that ion bombardment to the substrate would enhance the crystallization of MWNTs synthesized using ECR-CVD at low temperatures due to the dehydrogenation from C—H bonding. In DLC films, it is well known that the ion bombardment to the growing surface decreases the amount of bonded hydrogen incorporated into DLC films, and thus critically affects physical properties of DLC films. On the other hand, other experimental efforts for decreasing the amount of bonded hydrogen caused the same results in the properties of DLC film, including an increase of the substrate temperatures, a usage of source gases with high ratios of C/H, and an addition of Ar gas. Hydrogen incorporation during the CNT growth, however, has not been considered yet even though the environment for CNT growth is very similar to that for DLC films. In the basic growth model of CNTs, hydrocarbon molecules decompose into carbon atoms on the catalyst surface and the carbon atoms then diffuse inside the catalyst particle or along the surface toward the bottom of the particle due to the temperature and concentration gradients, consequently precipitating at the cold bottom. Hydrocarbon molecules, however, may not be completely decomposed into carbon atoms, in which cases hydrocarbon molecules such as \(\text{CH}_3\), \(\text{CH}_2\), and \(\text{CH}\) and carbon atoms diffuse through the surface or the bulk of the catalyst particle to its bottom. Then, they would precipitate at the cold bottom of the Ni catalyst particle and form a CNT wall. When this process happens, hydrocarbon species combine with carbon atoms precipitated from the Ni catalyst and form a graphite segment, bonding at the end of graphite layer, as described in Fig. 7. Otherwise, \(\text{CH}_3\) radicals in the plasma can also arrive on the CNT wall during the CNT synthesis and join graphite layers newly formed from the Ni catalyst. This mechanism can explain the results of other researchers too, in which very defective CNTs similar to carbon fibers were usually synthesized when a hydrogen-rich gas mixture was used as a carbon source or synthesis temperatures were too low. It can be explained by providing a number of hydrocarbon species arriving on the catalyst or CNT wall and insufficient energy for dehydrogenation of hydrogen from hydrocarbon molecules. It was also reported that carbon nanorods were formed on Cu particles using \(\text{C}_2\text{H}_2\) through the surface diffusion of carbon atoms since Cu has low solubility of carbon. It can be thought, however, that hydrocarbon species as well as carbon atoms are likely to diffuse through the surface of Cu particles, and thus form carbon nanorods composed of short graphite segments at the cold bottom. It was also reported that carbon nanowalls were grown on an insulating substrate, but MWNTs on a conductive substrate, by microwave plasma-enhanced CVD using a \(\text{CH}_3/\text{H}_2\) gas mixture. This result is thought to originate from the insufficient ion kinetic energy investigated in this study previously. The ion bombardment to the growing surface would occur on a conductive substrate because the self-bias has to occur spontaneously on the substrate due to the difference between the flux of electrons and positive ions. On the contrary, the self-bias cannot be sustained on an insulating substrate due to the accumulation of the charged particles on the substrate, not flowing away through the substrate.

Based on the EELS and XPS results, the formation of carbon nanorods and well-graphitized MWNTs by the ion bombardment can be modeled at low temperatures, in which the \(\sigma\) characteristics of carbon nanorods indicate the hydrogen bonded at the end of the graphite segment, while the \(\pi\) characteristics is predominant in the well-graphitized MWNTs. As already shown in Fig. 2, graphite layers begin to form at the rf bias voltage of \(-50\ \text{V}\) when the maximum internal energy transferred from the ion kinetic energy 15.56 eV and 8.76 eV are comparable to the C—H bonding enthalpy 4.3 eV. Moreover, the crystallinity of MWNTs is improved with an increase of the ion kinetic energies to the substrate. It is noticeable, on the other hand, that completely graphitized MWNTs are not obtained at the rf bias voltages of \(-50\) and \(-100\ \text{V}\) even though the internal energies trans-
ferred from the ion kinetic energy at $-50$ and $-100$ V are larger than $C-H$ bonding enthalpy as indicated in Table I. Here, it should be considered that ratios of the number of neutrals to that of ions are calculated to be more than 100 in our experiments, and one ion collision can activate only one or a few hydrocarbon molecules, leaving most of hydrocarbons on the substrate nonactivated. For the synthesis of the well-graphitized MWNTs, thus, the ion kinetic energy should be large enough to supply the internal energy needed for releasing hydrogen from hydrocarbon as many as possible with one ion collision. Therefore, it can be suggested that the well-graphitized MWNTs are synthesized at low temperatures only when sufficient energy for dehydrogenation of hydrocarbon molecules is provided by other methods except thermal energy, one of which corresponds to an ion kinetic energy supplying to the growing surface, as investigated in this study.

V. CONCLUSION

Different types of carbonaceous materials were synthesized by ECR-CVD on Ni-coated glass substrates with rf biasing using a gas mixture of CH$_4$ and Ar. It was observed that vertically aligned carbon nanorods and MWNTs were synthesized at the rf bias voltages of $-100$ and $-200$ V, respectively. The distance between two graphene layers of carbon nanorods was measured to be about 0.382 nm, which is much larger than that of well-graphitized MWNTs having a typical value of 0.356 nm. In our previous report,$^{12}$ Raman spectroscopic analysis indicated that the shortening of $C-C$ bonds within the graphene layer of an as-deposited film occurred as the rf bias voltages increased, which was considered to be related to lower concentrations of $sp^3$ C-C bonds due to the bonded hydrogen. In EELS, the energy of $\pi + \sigma$ plasmon peak for carbon nanorods shifted to a lower value of 23.8 eV, in comparison to 25.5 eV of well-graphitized MWNTs, and $\pi$ plasmon loss peak at 6 eV, which was clearly defined for well-graphitized MWNTs, was not observed for carbon nanorods. XPS investigations also showed that the delocalization of $\pi$ electrons became more pronounced as the structure evolved from carbon nanowalls to nanorods and eventually to well-graphitized MWNTs with increasing rf biases. It is thought that the bonded hydrogen within graphite layers, which is originated from incorporation of less dehydrogenated hydrocarbon molecules into the graphene sheets, causes the differences in structural characteristics between carbon nanorods and well-graphitized MWNTs. According to the plasma diagnosis, the maximum internal energy transferred from the ion kinetic energy is comparable to or larger than $C-H$ bonding enthalpy at the rf bias voltages of $-50$ V or higher, probably leading to the graphitization within the carbon materials grown. Based on these results, it is concluded that the hydrocarbon species, not completely dehydrogenated because of the insufficient internal energy, as well as carbon atoms diffuse through the surface of Ni catalyst particles and precipitate at the cold bottom of the particles, forming CNT walls. Therefore, it is suggested that the ion kinetic energy to the substrates should be large enough to provide a sufficient internal energy for releasing hydrogen from $C-H$ bonding of hydrocarbon molecules in order to synthesize well-graphitized MWNTs at low temperatures.

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