1. Introduction

Carbon nanotubes (CNTs) have been intensively studied because of many featured characteristics such as high electric conductivity, high permissible current density and high mechanical strength in spite of high flexibility [1]–[5]. These characteristics are available to prepare various kinds of nano structured devices such as field emitters, high-densely integrated circuits and so on [6]–[10]. Especially, the CNT rolled with a graphene sheet was called single-walled carbon nanotubes (SWNTs). The SWNTs are characterized as metals or semiconductors depending on their diameter and chirality [3]. For applying the SWNTs to the nanoscale electronic devices, the preparation volume, the diameter, the alignment, the chirality and the growth position must be controlled [11]–[22]. A dip-coat method is provided for uniform size of and/or dense coating of catalyst particles [23], [24]. The SWNTs grew selectively from catalyst particles using chemical vapor deposition (CVD) and its diameter depends on that of the catalyst particles. The alignment of the SWNTs growth in-plane was reported in the growth on sapphire and quartz substrates [17], [25]. The research concerning about the chirality control is roughly classified on sapphire and quartz substrates [17], [25]. The research of the SWNTs growth in-plane was reported in the growth of the separation method for nano-scale devices.

2. Experimental

2.1 Surface Treatment

A schematic diagram of the surface treatment is shown in Fig. 1. In Fig. 1(a) the triangle Au/Cr electrodes were deposited on SiO$_2$(300nm)/Si substrate using photolithography and lift-off technique. The size of the electrodes and the gap is described in the Fig. 1. In Fig. 1(b) a ribbon-type hole was patterned by a photolithography. And then the surface of the electrodes and the area between the electrodes were treated to be hydrophilic by exposure to the ozone atmosphere. (d) The resist was removed.
Table 1  Catalyst preparation conditions.

<table>
<thead>
<tr>
<th>Concentration (wt%)</th>
<th>C₄H₆CoO₂·4H₂O (mg)</th>
<th>[(C₂H₂O₂)₂Mo₂] (mg)</th>
<th>C₂H₅OH (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 1</td>
<td>67.6</td>
<td>35.6</td>
<td>20</td>
</tr>
</tbody>
</table>

ozone atmosphere for 30 min using UV/Ozone cleaner (Pro-CleanerTM110, BIOFORCE NANOSCIENCES) as shown in Fig. 1(c). The resist was removed using remover of diethylene glycol monobutyl ether 65%-monoethanol amin 35% (00413020, Tokyo Ohka Kogyo Co., Ltd) as shown in Fig. 1(d). The electrodes surface and the area between the electrodes were more hydrophilic.

2.2 SWNT Growth Process

2.2.1 Deposition of Catalysts

Two ethanol solutions containing cobalt(II) acetate tetrahydrate (C₄H₆CoO₂·4H₂O) and molybdenum(II) acetate dimer ([(C₂H₂O₂)₂Mo₂]) were prepared as shown in Table 1. The concentration of catalysts was 0.1wt%. After the surface of the electrodes deposited substrate was treated by ozone, immediately the catalysts particles were formed using a dip coat technique. The substrate was soaked in solution for 10 min, and then drawn with the speed of 600 μm/s. Molybdenum particles were deposited and annealed first, and subsequently the Co particles were deposited and annealed. The annealing condition after dipping was 400°C in air for 5 min.

2.2.2 Setting of an Equipment for the SWNT Growth

The SWNTs growth was carried out by alcohol chemical vapor deposition (ACCVD) method. The schematic view of the ACCVD equipment is illustrated in Fig. 2. The fabricated equipment was a cold-wall type CVD in which only the substrate was heated by the heater under the substrate. The growth condition of the equipment was set in advance as follows. The chamber was evacuated using a rotary pump (c) down to approximately 0.5Pa without the substrate. The valve position was set to obtain a growth condition, a flow rate of ethanol (C₂H₅OH) 1000 ccm and a process pressure 1000 Pa through (a) process line using (d) rotary pump. The flow line was switched to (b) waiting line evacuated with (d) rotary pump. After leaking the chamber back to an atmospheric pressure, the substrate was set on the heater at a tilting angle of approximately 5°, and then the chamber was evacuated again.

2.2.3 Growth of the SWNT

Argon (Ar, 200 ccm) and hydrogen (H₂, 20 ccm) mixture gases were introduced into the chamber as the carrier and reducing agents, respectively, as shown in Fig. 3(a), (b) processes for approximately 30 min. The substrate temperature was increased by heating at the same time up to 1050°C. The flow rate of Ar and H₂ gases were controlled using mass flow controllers (STEC, SEC-400MK3). At the process of Fig. 3(c), ethanol was introduced into the chamber as a carbon source by switching flow line back from (b) waiting line to (a) process line as shown in Fig. 3, and its flow rate was controlled using a flow monitor at 1000 ccm. The FEL was irradiated through the quartz window set up foreside of the substrate as shown in Fig. 2. After stopping the flow of ethanol gas, Ar gas was flowed at the rate of 200 ccm and the substrate temperature was decreased to room temperature in the process of Fig. 3(d).

The FEL used was irradiated at the Laboratory for Electron Beam Research and Application (LEBRA), Institute of Quantum Science, Nihon University [33]. The FEL was extracted from vacuum through a CaF₂ window to the
air. The extracted laser passed through a nonlinear crystal, \(\beta\)-BaB\(_2\)O\(_4\) (BBO), to obtain the second harmonics for 800 nm FEL. The 800 nm FEL is the most influenced wavelength for chirality control in our previous report [34], [35]. A prism was inserted in an optical path when fundamental and the other harmonic wavelengths were excluded.

The synthesized CNTs were characterized by micro- and resonance-Raman scattering spectroscopy (NRS-3000, JASCO Corp.) The micro-Raman spectra for excitation with the second harmonic of diode laser (at 785 nm), He-Ne laser (at 632 nm), YAG laser (at 532 nm), and He-Cd laser (at 442 nm) to obtain CNTs were characterized. The surface morphology was observed by a scanning probe microscopy (SPM, NanoNavi Station, SPA-400, SII).

3. Results and Discussion

Figure 4 shows the \(2 \times 2 \mu\)m\(^2\) surface images of the specimen grown with the 800 nm FEL irradiation. The image of Fig. 4(a) is of the area between electrodes, where the surface was the hydrophilic area due to the treatment of the ozone. The image of Fig. 4(b) is of the other substrate area, where no treatment was done. The image of Fig. 4(c) was detected at the electrodes. In the Fig. 4(a), a lot of tube-like materials were dispersed in the plane with a random direction. The height, corresponding to the diameter, of the tubes was approximately 1.4 nm. Similar tubes were detected on the no treatment substrate surface as shown in Fig. 4(b), but the tubes were not the SWNTs confirmed by the Raman spectra mentioned below. On the electrodes three dimensional grains grew without any tubes. The specimen grown without the FEL irradiation showed similar results, but the tube-like materials were not detected at the no treated substrate area.

The detected height of 1.4 nm is expected to be due to the growth of the SWNTs. On the electrodes, the growth temperature of 1050\(^\circ\)C, which is a little bit lower than an Au melting temperature, makes the Au and catalysts be an alloy. The alloy does not work as a catalyst any more. Therefore no CNTs grew on the electrodes as shown in Fig. 4(c). It is noticed that we can find the difference of the SWNTs growth at the points of the ozone treated, no treated, and electrodes area.

Figure 5 shows the resonant Raman spectra related to a radial breathing mode (RBM) of the specimen grown without the FEL irradiation detected at the area between electrodes. The used excitation lasers were (a) 442, (b) 532, (c) 632, and (d) 785 nm, respectively. In all Raman spectra, the G-band at approximately 1590 cm\(^{-1}\) and the D-band at approximately 1350 cm\(^{-1}\), not shown here, were observed, indicating the growth of the CNTs. The RBM peaks in Fig. 5 revealed the growth of the SWNTs, the diameter of which was estimated by the Eq. (1) [12], [36]–[38]. On the no treated substrate area and electrodes, both of G- and D-bands were not observed, indicating that the CNTs did not grow, corresponding with the results of surface image.

\[
d(\text{nm}) = 248/\text{RBM}(\text{cm}^{-1})
\]  

The excitation laser of 532 nm is resonantly absorbed in the SWNTs with the energy gap between van Hove singularities (vHs) in the nanotube density of state (DOS), so-called \(E_{31}^S, E_{22}^M, E_{22}^S\), where the superscript \(S\) and \(M\) mean the semiconductor and metal [36]. The relationship between series of the energy gap for resonance absorption and the diameter of the SWNTs is referred from the Kataura plot [12], [36]–[38]. The RBM peaks of the SWNTs at 187, 236,
Table 2  Summary of the results from the RBM peaks of Raman spectra for the specimens without the FEL irradiation and with the 800 nm FEL irradiation. The detected points were of the area between electrodes where the ozone treatment was done to be hydrophilic.

<table>
<thead>
<tr>
<th>FEL (nm)</th>
<th>Excited wavelength for Raman</th>
<th>Peaks of RBM (cm⁻¹)</th>
<th>Diameter of SWNT (nm)</th>
<th>Notation of energy gap and electric property</th>
<th>Chiral index</th>
</tr>
</thead>
<tbody>
<tr>
<td>532</td>
<td>187.3</td>
<td>E₈₂²</td>
<td>1.32</td>
<td>(14,4) (15,6) (12,7) (10,9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>235.7</td>
<td>1.05</td>
<td>E₈₂²</td>
<td>(9,6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>283.7</td>
<td>0.87</td>
<td>E₈₂²</td>
<td>(11,0) (10,2)</td>
</tr>
<tr>
<td>632</td>
<td>194.1</td>
<td>E₈₂²</td>
<td>1.28</td>
<td>(12,6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>250.7</td>
<td>0.99</td>
<td>E₈₂²</td>
<td>(12,1) (9,5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280.1</td>
<td>0.89</td>
<td>E₈₂²</td>
<td>(11,1) (10,2) (7,6)</td>
</tr>
<tr>
<td>785</td>
<td>151.6</td>
<td>E₈₂²</td>
<td>1.64</td>
<td>(20,6) (16,7) (12,12)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>219.7</td>
<td>1.13</td>
<td>E₈₂²</td>
<td>(13,2) (12,4) (10,6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>235.4</td>
<td>1.05</td>
<td>E₈₂²</td>
<td>(12,2) (11,4) (10,5)</td>
</tr>
<tr>
<td>800</td>
<td>785</td>
<td>220.9</td>
<td>1.12</td>
<td>E₈₂²</td>
<td>(14,0) (13,2) (10,6) (8,7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>237.7</td>
<td>1.04</td>
<td>E₈₂²</td>
<td>(13,0) (12,2) (10,5) (8,7)</td>
</tr>
</tbody>
</table>

Fig. 6  The Raman spectra of the treated area between electrodes were detected using four different excitation lasers, (a) 442, (b) 532, (c) 632, (d) 785 nm. The specimen was grown with the 800 nm FEL irradiation. The RBM peaks were detected only in the spectrum (d).

We can see the peaks only in the spectrum detected using excitation laser of 785 nm as shown in Fig. 6(d). The RBM results revealed that the grown SWNTs were only semiconductor. The results are summarized in Table 2. From the results of the SPM, the tube-like materials with the height of approximately 1.4 nm grew with random direction in the plane at the area. The tube-like materials are sure to be the SWNTs. At the other area, any SWNTs were not found in the Raman spectra and the SPM analysis.

Figure 7 shows the graphene honeycomb lattice for estimating the chiral index. The chiral vector \( C_h \) is defined as the vector from the origin to the crystallographically equivalent site on the graphene sheet. Since the SWNT was formed by rolling up the sheet to fit the origin and the equivalent site, the diameter and the chirality of the SWNT are determined by \( C_h \). The \( C_h \) is described by Eq. (2), where \( n_1 \) and \( n_2 \) are integer. The magnitude of the \( C_h \), \( |C_h| \), is the diameter of the SWNT. The \( a_1 \) and \( a_2 \) are unit vectors, described in Fig. 7. A pair of integers \( (n_1, n_2) \) is the chiral index.

\[
C_h = n_1a_1 + n_2a_2
\]  

The chiral index is estimated as follows. i) The diameter of the SWNTs is estimated from the wavenumber of the RBM peak and Eq. (1). ii) Since the absorbance energy gap is known from the used excitation laser, we can find out whether the SWNT is semiconductor or metal from the estimated diameter using the Kataura plot, as shown in the column of “notation of energy gap and electric property” in
Table 2. iii) An arc of the estimated diameter is illustrated in the graphene sheet. In Fig. 7 the arc is described when the diameter, $\phi$, of the SWNT is 1.04 and 1.12 nm. Those SWNTs were obtained when the 800 nm FEL was irradiated during growth. iv) Since we know that the SWNT is semiconductor or metal at the process ii), the possible chiral index is turned out from the intersection between the arc and open circles (semiconductor) or closed circles (metal). The notation of energy gap and electric property as well as the chiral index are summarized in Table 2. The 22 kinds of chiral indices in the SWNTs grown without the FEL irradiation were much reduced to 8 chiral indices with 800 nm FEL irradiation as shown in Table 2. It is also noticeable that only semiconducting SWNTs grew when the FEL was irradiated, though the mixture of semiconducting and metallic SWNTs grew without the FEL irradiation. Since the 800 nm FEL is expected to be resonantly absorbed at the gap energy of $E_{22}$, the semiconducting SWNTs is enhanced to grow.

4. Conclusion

For applying SWNTs to the nanoscale electronic devices, we propose a novel technique to control the growth position as well as the chirality of the SWNTs using the free electron laser (FEL) irradiation and the surface treatment. The SWNTs were grown by the ACCVD method with ethanol as a feeding gas. The chirality controlled SWNTs grew at only the area between electrodes, where the ozone treatment was done to be hydrophilic, using the 800 nm FEL irradiation and surface treatment technique. The number of possible chirality was 22 when the FEL was not irradiated during the ACCVD process, however, the number was much reduced to be 8 in the SWNTs grown with the 800 nm FEL irradiation. The mixture growth of semiconducting and metallic SWNTs was limited to the growth of semiconducting one because of the FEL irradiation.

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References


