**Abstract**—Single-walled carbon nanotubes (SWCNTs) are generally synthesized by chemical vapor deposition (CVD) using Fe, Co, and Ni as catalysts. However, due to the Ostwald ripening of metal catalysts, the diameter distribution of the grown SWCNTs is considerably wide (>2 nm), which is not suitable for electronics applications. In addition, reduction in the growth temperature is desirable for fabricating SWCNT devices compatible with the LSI process. Herein, we performed SWCNT growth by alcohol catalytic CVD using platinum-group metal catalysts (Pt, Rh, and Pd) because these metals have high melting points, and the reduction in the Ostwald ripening of catalyst particles is expected. Our results revealed that web-like SWCNTs were obtained from Pt and Rh catalysts at growth temperature between 500 °C and 600 °C by optimizing the ethanol pressure. The SWCNT yield from Pd catalysts was considerably low. By decreasing the growth temperature, the diameter and chirality distribution of SWCNTs from Pt and Rh catalysts became small and narrow. In particular, the diameters of most SWCNTs grown using Pd catalysts were below 1 nm and their diameter distribution was considerably narrow. On the contrary, SWCNTs can grow from Rh catalysts even at 300 °C by optimizing the growth condition, which is the lowest temperature recorded for SWCNT growth. Our results demonstrated that platinum-group metals are useful for the growth of small-diameter SWCNTs and facilitate low-temperature growth.

**Keywords**—Carbon nanotube, chemical vapor deposition, catalyst, Pt, Rh, Pd.

**I. INTRODUCTION**

SWCNTs [1] are one-dimensional materials with unique properties [2], [3] and have various potentials for future nanoelectronics applications [4-6]. SWCNTs exhibit a number of properties, including ballistic transport [7], high mobility [8], and high current-carrying density (~10^6 A/cm^2) [9], so they have a huge potential in electronics applications, including field-effect transistors (FET) [10], [11], LSI interconnects [12], [13], and energy conversion devices [14], [15]. Because the electronic and optical properties of SWCNTs strongly depend on their chirality [2], the selective growth of SWCNTs having uniform chirality and diameter is one of the most important issues in this field. To date, the most versatile techniques for synthesizing SWCNTs are based on catalyst-assisted CVD. In these techniques, metal-based nanoparticles serve as catalysts in both assisting carbon feedstock cracking and facilitating the nucleation of SWCNTs. In general, transition metal catalysts, including Fe [16], [17], Co [18], [19], and Ni [20], are widely used for SWCNT growth via CVD because of both high efficient production and wide growth windows. However, the chirality of SWCNTs grown using these catalysts is distributed to some extent. Additionally, their diameters are distributed between approximately 1 and 3 nm because of the enlargement of catalyst particles caused by surface migration and/or Ostwald ripening at the growth temperature. To avoid this problem, various bimetal catalysts are used, and SWCNTs having narrow diameter distributions are obtained [21], [22]. However, it is desirable to grow SWCNTs having narrow diameter distributions using only one metal for the simplicity of growth process.

Recently, several groups have attempted SWCNT growth using noble metals as catalysts. Ghorannevis et al. demonstrated SWCNT growth having a narrow chirality distribution from Au catalysts using a plasma CVD method [23]. By controlling the H2 concentration in CH4, they demonstrated selective growth of (6,5) SWCNTs. Lie et al. reported that the addition ofPt into Co catalysts in alcohol CVD growth dramatically reduced the diameters of SWCNTs and narrowed their chirality distributions [24]. These results suggest that nanoscale noble metals might have some advantages in the growth of SWCNTs having uniform chirality and diameter.

Herein, we focused on platinum-group metals as catalysts for SWCNT growth. Compared with Fe, Co, and Ni, many platinum-group metals have high melting points, which could suppress the aggregation of catalysts, leading to narrow diameter distributions. We conducted SWCNT growth using the Rh, Pt, and Pd catalysts under various growth conditions via a cold-wall ultrahigh vacuum (UHV) CVD system. Rh and Pt have 8 and 9 d-electrons (4d^8 and 5d^5), respectively, which are suitable for SWCNT growth [25]. On the contrary, Pd has 10 d-electrons (4d^10), which is considered to exhibit low activity against feedstock gas containing carbon atoms. We conducted SWCNT growth using these three metals as catalysts and...
compared the differences in SWCNT growths.

II. EXPERIMENTAL PROCEDURE

Pt catalysts were deposited on SiO2(100 nm)/Si substrates using a pulsed arc plasma gun. Rh catalysts were deposited on Al2O3(10 nm)/SiO2(100 nm)/Si substrates using electron beam evaporation because SWCNT yields were enhanced by the deposition of Rh catalysts on Al2O3 support layers. In the case of Pd catalysts, Al2O3 (0.2 nm)/Pd/Al2O3 (4 nm)/SiO2 (100 nm)/Si structures were used for SWCNT growth because the amount of grown SWCNTs was considerably low from Pd on the SiO2/Si and Al2O3/SiO2/Si substrates.

During SWCNT growth, only ethanol gas was supplied without any carrier gas. The ethanol pressure was monitored using an ion gage on the inside wall of the UHV chamber. The ethanol pressure in this study was much smaller than that at the catalysts on the substrates. During heating, the substrate temperature was monitored using a pyrometer, which can measure the sample temperature between 200 °C and 2000 °C.

SWCNT growth was conducted in a UHV chamber equipped with a stainless-steel nozzle for introduction of the ethanol gas. The details of the equipment used for SWCNT growth are available shown in previous research [26], [27]. Before SWCNT growth, the base pressure was below 1 × 10−6 Pa. The substrate temperature was increased to the growth temperature under H2 gas flow at a pressure of 1 × 10−3 Pa to prevent the oxidation of the catalysts. The growth time was 1 h for all samples.

The samples were characterized using a field-emission scanning electron microscope (SEM; JSM-6700F, JEOL) and Raman spectroscopy (inVia Reflex, Renishaw). High-resolution transmission electron microscope (TEM, JEM-3100) images were obtained at an accelerating voltage of 200 kV. The TEM samples were prepared using SiO2 membrane TEM grids to investigate the catalyst particle size.

III. RESULTS AND DISCUSSION

A. SWCNTs Grown Using Pt Catalysts

Figs. 1 (a)–(e) show the SEM images of the samples grown using Pt catalysts on SiO2/Si substrates at a growth temperature between 400 °C and 700 °C. The ethanol pressures used for the growth of these samples were 1 × 10−3 Pa for 400 °C, 450 °C, 500 °C, 600 °C, and 1 × 10−5 Pa for 700 °C. These ethanol pressures were optimized to maximize the SWCNT yield for each growth temperature. Fibrous structures were observed between 500 °C and 700 °C, and their densities increased as the growth temperature increased. However, only a small amount of products was observed at 400 °C and 450 °C. Fig. 1 (f) shows a TEM image of a sample grown at 700 °C under an ethanol pressure of 1 × 10−3 Pa. Several SWCNT bundles were observed, accompanied by Pt particles (black particles in the image), indicating that SWCNTs were grown using Pt catalysts. Fig. 1 (f) also shows that the diameters of most SWCNTs contained in the bundle were below 2 nm. Moreover, some SWCNTs had diameters less than 1 nm.

Figs. 2 (a) and (b) show the Raman spectra of the samples grown using Pt catalysts on SiO2/Si substrates between 400 °C and 700 °C under the optimal ethanol pressures. The excitation wavelength used for Raman measurements was 785 nm. The Raman spectra of these samples exhibited both G band peaks at 1594 cm−1 and radial-breathing-mode (RBM) peaks, indicating that SWCNTs were grown in this temperature range. At a growth temperature of 700 °C, the intensity ratio of G band to D band in the Raman spectrum (G/D ratio) was ~4. When the growth temperature was reduced to 400 °C, the G band intensity decreased, indicating the reduction in the SWCNT yield. In addition, G band became broad and G/D ratio became less than 1. This result demonstrated that the crystallinity of SWCNTs deteriorated as the growth temperature was reduced.

In general, the Raman shift of an RBM peak is related to the SWCNT diameter. The relation between the Raman shift of an RBM peak and the SWCNT diameter is well known, i.e., \( d (\text{nm}) = 248/\omega \text{ cm}^{-1} \), where \( d \) is the diameter of the SWCNT and \( \omega \) is the Raman shift [28]. Thus, RBM peaks shown in Fig. 2 (a), which were distributed between 375 and 175 cm−1 at a growth temperature of 700 °C, correspond to SWCNTs having diameters between 0.66 and 1.4 nm. On the contrary, when the growth temperature was less than 450 °C, the RBM peaks were distributed between 250 and 375 cm−1, which corresponded to
diameters in the range 0.66–0.69 nm. Both SWCNT diameters and their diameter distributions thus became small and narrow, respectively, as the growth temperature was reduced.

B. SWCNTs Grown Using Rh Catalysts

Figs. 3 (a)–(c) show the SEM images of samples grown using Rh catalysts on Al$_2$O$_3$/SiO$_2$/Si substrates at 600 °C, 500 °C, and 400 °C, respectively. The ethanol pressures used for the growth of these samples were 1 × 10$^{-3}$, 1 × 10$^{-4}$, and 1 × 10$^{-5}$ Pa, respectively, which were optimized to maximize the SWCNT yield. When the growth temperature was 600 °C, fibrous structures were observed, which formed a web-like structure. However, the density of these structures was fairly reduced at 500 °C. At 400 °C, only a small amount of products was observed. Fig. 3 (d) shows the TEM image of a sample grown using Rh catalysts at 600 °C under an ethanol pressure of 10$^{-3}$ Pa. In addition, SWCNTs were observed, accompanied by Rh particles (black particles in the image). This result also indicates that SWCNTs were grown using Rh catalysts.

C. SWCNT Grown Using Pd Catalysts

Figs. 5 (a) and (b) show the SEM images of the samples grown using Pd catalysts in Al$_2$O$_3$/Pd/Al$_2$O$_3$/SiO$_2$/Si substrates at 600 °C and 500 °C, respectively. The optimized ethanol pressure used for the growth of both samples was 1 × 10$^{-4}$ Pa. At both temperatures, only a few fibrous structures were observed on the substrates. Figs. 5 (c) and (d) show the Raman spectra of the samples at 600 °C and 500 °C, respectively. The excitation wavelength used for the Raman measurements was 633 nm. Both the G band (at 1594 cm$^{-1}$) and distinct RBM peaks were observed at 141 cm$^{-1}$ for both growth temperatures, indicating that SWCNTs were grown using Pd catalysts. The G/D ratio was greater than 10, indicating that the crystalline quality of SWCNTs was considerably good. However, SEM images revealed that the amount of SWCNTs grown using Pd catalysts was considerably lower than the amount of SWCNTs grown using the Pt and Rh catalysts. Thus, Pd catalysts are not suitable for SWCNT growth at low temperatures.
D. Comparison between the Pt and Rh Catalysts

In the previous section, we showed that Pt and Rh catalysts were suitable for SWCNT growth at growth temperatures below 600 °C. Therefore, in this section, we compared these two catalysts with regard to SWCNT growth. In our samples, SWCNTs wither formed web-like structures or were sparsely grown on the substrates. Therefore, the intensity ratio of the G band peak to the Si peak at ~520 cm\(^{-1}\) (G/Si intensity ratio) in the Raman spectra roughly corresponded to the SWCNT yield. Fig. 6 shows a plot of G/Si intensity ratio versus the growth temperature for SWCNTs grown using the Rh and Pt catalysts. The samples used for this plot were grown under the optimal ethanol pressures, so the SWCNT yields were maximized at each growth temperature. For both catalysts, the G/Si intensity ratio decreased as the growth temperature was reduced, indicating that the SWCNT yield decreased as the growth temperature decreased, as stated in previous sections. It is worth noting that the G/Si intensity ratio for Rh catalysts was similar to or stronger than that for Pt catalysts, regardless of the growth temperature. Therefore, among these two catalysts, Rh was found to be effective and suitable for SWCNT growth at low temperatures.

![Graph showing the relation between intensity ratio and growth temperature](image1)

To compare the structural properties of SWCNTs grown from these two catalysts, we performed Raman measurements for SWCNTs grown using the Pt and Rh catalysts at 400 °C by employing lasers at four excitation wavelengths (488, 532, 633, and 785 nm) because the RBM peak was found to have strongly enhanced under the resonance condition wherein the incident laser energy coincided with an electronic transition energy in the SWCNT. Fig. 7 shows the RBM regions of the Raman spectra of SWCNTs grown using the Pt and Rh catalysts at 400 °C under the optimal ethanol pressures. For the samples grown using Pt catalysts, RBM peaks were observed in the Raman spectra measured using only 633- and 785-nm lasers [Figs. 7 (c) and (d)]. In the Raman spectrum using the 633-nm laser [Fig. 7 (c)], weak RBM peaks were observed at 251, 283 and 351 cm\(^{-1}\), while relatively strong RBM peaks appeared at 349 and 369 cm\(^{-1}\) in the Raman spectrum measured using the 785-nm laser (Fig. 7 (d)). These results revealed that the diameters of SWCNTs grown using Pt catalysts were mainly distributed between 0.67 and 0.99 nm. In the other words, the diameters of SWCNTs grown using Pt catalysts were relatively small and their distribution was narrow. As for Rh catalysts, RBM peaks were observed in Raman spectra for all excitation wavelengths. In particular, strong RBM peaks appeared at 196 and 235 cm\(^{-1}\) in the Raman spectra measured using 633- and 785-nm lasers, respectively. In addition, the Raman spectra measured using 488-, 532-, and 633-nm lasers exhibited that weak RBM peaks were distributed between 172 and 282 cm\(^{-1}\). This indicates that the diameters of SWCNTs grown using Rh catalysts were distributed in the range 0.88–1.44 nm. Compared with the Pt and Rh catalysts in the low-temperature growth, SWCNTs grown using Pt catalysts exhibited small diameters and narrow diameter distribution, while the SWCNT yield obtained using Rh catalysts was higher than that obtained using Pt catalysts.

![Graph showing Raman spectra](image2)

Previously, Vesselli et al. reported that the dissociation barrier of the C–C bond of an ethanol molecule on the Rh(111) surface was only 0.6 eV [29]. Later, a study employing density functional theory (DFT) also showed that the maximum activation energy was ~1.0 eV in the dissociation route of ethanol molecules on the Rh(111) surface, which is smaller than that on other transition metal surfaces [30]. From these simulations, we found that the dissociation of an ethanol molecule could easily occur on the Rh surface, thereby enhancing SWCNT growth at low temperatures. As for the SWCNT diameter, it is considered that the SWCNT diameter decreases as the catalyst particle size decreases [31], [32]. However, our TEM observation revealed that catalyst particle sizes were similar between the Pt and Rh catalysts; however, the diameters of SWCNTs grown using Pt catalysts were much smaller than those of SWCNTs grown using Rh catalysts. At
present, the reason for this phenomenon is unclear. There is a possibility that the nucleation mechanism of carbon nanocaps at the catalyst particles is different between the Pt and Rh catalysts.

IV. CONCLUSION

SWCNT growth was conducted via alcohol catalytic CVD using the Pt, Rh, and Pd catalysts. Compared with the Pt and Rh catalysts, the SWCNT yield from Pd catalysts was considerably low. On the contrary, SWCNTs were grown using Rh catalyst even at 300 °C. Furthermore, SWCNTs grown using Pt catalysts had small diameters and exhibited narrow diameter distributions. We demonstrated that the Pt and Rh catalysts are useful catalysts for SWCNT growth.

ACKNOWLEDGMENT

This research was partially supported by the Program for the Strategic Research Foundation at Private Universities and the Meijo University Research Branding Project, which was supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. Part of this research was conducted at the Institute for Molecular Science (IMS), supported by the “Nanotechnology Platform” of MEXT, Japan. We thank Dr. Nakao of IMS for providing the SEM facility.

REFERENCES