Growth of carbon nanofibers on metal-catalyzed substrates by pulsed laser ablation of graphite

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Abstract. Carbon nanofibers (CNFs) were grown on metal-catalyzed Si substrates by pulsed laser ablation of graphite. Metal catalysts, Ni, NiCo, Pd and PdNi, were respectively deposited on Si substrates with a SiO₂ layer of 200 nm thickness by a dip coat method, and the substrates placed in a laser oven apparatus. By pulsed laser ablation of graphite for 2 hours, CNFs were grown at oven temperatures ≥ 1000°C. Diameters of grown CNFs were about 20–30 nm by scanning electron microscopy, and increased with oven temperature. The difference of CNF growth by the catalysts was shown. Pd-contained catalysts grew thicker CNFs than the other catalysts; while PdNi and NiCo yielded a higher number density of CNFs than the other catalysts. CNF diameter and length changed according to the substrate position from the target. We also discussed the growth mechanism of CNFs with this method.

1. Introduction

Pulsed Laser ablation (PLA) is well known to produce high-quality single-walled carbon nanotubes (CNTs) with a wide range of diameters [1, 2]. CNTs have excellent physical and electronic properties, such as a field emission property, high electrical conductivity and high tensile strength; therefore, they are widely studied for their various applications to field electron emitters, scanning probes and electronic devices [3]. To grow CNTs by PLA, a laser oven apparatus consisting of an electric furnace and furnace tube is used [1]. CNTs are grown in a gas phase and deposited on the inner wall of the furnace tube. Recently, we have grown carbon nanofibers (CNFs) on Ni- and Fe-coated Si substrates placed in a laser oven apparatus [4, 5]. CNFs and CNTs are promising materials, and are expected to be applied to field-emission electron sources, intercellular gene delivery devices and nanoporous membranes [6]. We have shown that the number density of CNFs grown from a Ni catalyst was about 2 times higher than that from an Fe one [4]. We also found that the diameter of CNFs increased with catalyst film thickness as mentioned in chemical vapor deposition of CNTs [7]. This is explained by that the catalyst film thickness is correlated with size of catalytic nanoparticles on which CNF growth occurs [5]. We have confirmed that no CNFs were grown on a pure Si substrate when a pure graphite target was used; consequently speculating that CNFs did not grow in a gas phase but grew on metal-catalyzed substrates by feeding on the carbon from a laser ablation plume of graphite. We named this technique laser-thermal chemical vapor deposition (LTCVD).

In this paper, the results of LTCVD experiments by varying the catalyst, oven temperature and substrate position are presented. The CNFs grown are analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and an energy dispersive X-ray analysis (EDX).
2. Experimental setup and procedure

LTCVD was described in detail in our previous reports [4, 5]. Briefly, the set-up (AL039, SUGA Co., Ltd.) consists of an alumina tube (furnace tube) of 60 mm inner diameter, an electrical furnace (350 mm length) operated at 950–1100°C, and an ArF excimer laser (LAMBDA PHYSIK Co. Ltd., COMPex 205: λ = 193 nm, fluence = 2 J/cm², repetition rate = 10 Hz). A sintered graphite target (purity = 99.999%) was mounted at the center of the furnace and rotated at 40 rpm. The temperature at different substrate positions from the target surface in the furnace tube (T_{sub}) was measured to be −1090°C at +0 mm, −1060°C at +30 mm, −1020°C at +80 mm and −818°C at +130 mm (+: upstream of Ar gas flow in the furnace tube) when the oven temperature T was set to 1100°C. The experimental procedure is as follows. Metal-catalyzed Si substrates were placed between +130 mm and 0 mm from the target surface in the furnace tube. The tube was first evacuated down to < 10⁻⁵ Torr by a turbo-molecular pump followed by a rotary pump, and then Ar gas was introduced from the laser irradiation window side and pumped out through an angle valve while the tube was heated up to T over a period of 2.5 hours. During the heating, the Ar gas flow rate and gas pressure were 100 sccm and 300–500 Torr, respectively. After reaching T, H₂ gas with a flow rate of 7 sccm was added for 10 min to reduce the catalyst, which decreases the deposition of amorphous carbon particles and increases the purity of CNFs. Total pressure was kept at 500 Torr. After reduction, the Ar gas flow rate was raised to 750 sccm. Then the ArF excimer laser beam irradiated the target for 2 hours. Metal catalysts were deposited on a Si substrate with a 200-nm SiO₂ layer (SiO₂/Si) by a dip coat method [8] and DC sputtering. The dip coat method is almost the same as Murakami et al performed [8]. We deposited thin films of Ni, NiCo, Pd and PdNi using nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Kanto Chemical Co., Inc.), cobalt acetate (Co(CH₃COO)₂·4H₂O, Kishida Chemical, Co., Ltd.) and palladium chloride (PdCl₂, Kishida Chemical, Co., Ltd.). Each was dissolved into ethanol at a concentration of 0.01 wt%. SiO₂/Si substrate was submerged into the metallic solution for 10 min and then drawn up from the solution at a constant speed of 4 cm/min. Immediately after this process, the substrate was dried in a furnace maintained at 400°C for 5 min in air.

The CNFs grown were observed with scanning electron microscopes (SEM, Hitachi High-Technologies Corp., S-4300 and S-4800: acceleration voltage = 5 kV) and transmission electron microscope (TEM: JEOL Ltd., JEM-2000FX: acceleration voltage = 200 kV). The TEM is equipped with an energy dispersive X-ray analyzer (EDX) for analysis of the chemical composition of the CNFs.

3. Results and discussion

3.1. Dependence of catalysts on CNF growth

SEM micrographs of the CNFs grown from the different catalysts, (a) PdNi, (b) NiCo, (c) Pd, (d) Ni at T = 1100°C are shown in figure 1. CNFs grew from all the catalysts, but there was a big difference in the number density of CNFs. The diameter and number density of CNFs were evaluated from SEM micrographs of the CNFs at a magnification of ×30,000 and are listed in table 1. PdNi and NiCo yielded a higher number density of CNFs than Ni and Pd. A synergy effect on the CNFs grown was shown by bimetallic catalysts. The diameters of the CNFs grown from PdNi and Pd were larger than those from NiCo and Ni. A lot of short CNFs of ≤ 500 nm grew from Pd.

Figure 2 shows a TEM micrograph of CNFs grown from the PdNi catalyst. A CNF with a diameter of ~37 nm is seen to grow straight. EDX analyses of the CNF at the edge (#1) and body (#2) were performed; their chemical compositions are listed in table 2. At the edge of the CNF, 0.13%-Pd and 0.01%-Ni were detected, but the body was confirmed to be composed of mostly carbon. The result is similar to a tip growth mode of CNTs [9] and indicates that the CNF separated out from a carbon-dissolved PdNi bimetallic catalyst. In this TEM observation, we could not see the layer structures of crystalline graphite. This is discussed in subsection 3.3.
Figure 1. SEM micrographs of CNFs grown on (a) PdNi, (b) NiCo, (c) Pd and (d) Ni catalysts placed at +30 mm from the target. Oven temperature, $T$ was 1100$^\circ$C. Scale bar, 1 $\mu$m.

Table 1. Diameter and number density of CNFs grown from catalysts.

| Catalyst | Number density ($\mu$m$^{-2}$) | Diameter (nm)  |
|----------|--------------------------------|----------------|
| PdNi     | 36.3                           | 33.7±9.2       |
| NiCo     | 26.3                           | 20.1±5.3       |
| Pd       | 4.5                            | 35.2±12.2      |
| Ni       | 2.6                            | 19.4±4.1       |

3.2. Dependence of temperature
Figure 3 shows the diameter and number density of CNFs grown on Ni/SiO$_2$/Si substrates at $T$ between 1000 and 1100$^\circ$C. In this experiment, Ni films with a thickness of 5 nm were prepared by DC sputtering. SEM micrographs of CNFs at $T = (a)$ 1100 and (b) 1000$^\circ$C are shown in figure 4. The diameter increases with $T$; although the number density at $T$ between 1000 and 1040$^\circ$C does not seem to change with $T$; however, a lot of CNFs were grown on substrate at $T = 1100^\circ$C. Almost all the CNFs at $T = 1100^\circ$C were more than 3 $\mu$m in length, but those at $T = 1000^\circ$C were less than 500 nm. At $T < 1000^\circ$C, CNFs did not grow, but amorphous carbon particles grew instead.

3.3. Growth mechanism of CNFs by LTCVD
From the results shown above, we speculated that Pd and temperature promoted the separation of more carbons from the carbon-dissolved catalysts, and then lead to the growth of longer and thicker CNFs with higher number densities. Pd is well known to have good catalytic activity to decompose methane (CH$_4$) into hydrogen and carbon. Also, the diffusion coefficient of carbon in Pd ($D_{Pd} = 1.76 \times 10^{-10}$
Figure 2. TEM micrograph of the CNFs grown from PdNi. Scale bar, 50 nm.

Table 2. EDX analyses of CNFs grown from PdNi.

| Element | #1 (at.%) | #2 (at.%) |
|---------|-----------|-----------|
| C       | 99.85     | 99.98     |
| Ni      | 0.01      | 0.00      |
| Pd      | 0.13      | 0.02      |

Figure 3. Dependence of the diameter (●) and number density (□) of CNFs on the oven temperature.

m$^3$s$^{-1}$ at 1100°C), which is believed to correlate with the growth rate and number density of CNTs [10], is higher than those in Ni ($D_{Ni} = 6.42 \times 10^{-11}$ m$^3$s$^{-1}$ at 1100°C) and Co ($D_{Co} = 3.99 \times 10^{-11}$ m$^3$s$^{-1}$ at 1100°C) [11]. Takenaka et al showed that when Pd was added to Ni (PdNi), PdNi had a higher catalytic activity and longer life for decomposition of CH$_4$ even at a high temperature (800°C) than Pd and Ni did individually [12]. Consequently, it seems reasonable to determine that the catalysts containing Pd grew thicker CNFs than those with NiCo and Ni, and that PdNi grew longer CNFs than Pd.

In CNT syntheses, temperature is essential to control CNT diameter [13, 14]. Li et al performed CNT growth by CVD using an acetylene (C$_2$H$_2$)/ammonia (NH$_3$)/N$_2$ gas mixture at temperatures from 600 to 1050°C and showed that the diameter of CNTs increased with temperature [15]. In the CVD of
Figure 4. SEM micrographs of CNFs grown at $T =$ (a) 1100 and (b) 1000°C. Scale bar, 500 nm.

CNTs, it is accepted that CNTs are formed by carbon atoms dissolving, diffusing, and precipitating through the catalyst particles. Li et al. mentioned that the dependence of temperature on CNT diameter is probably attributable to an increase of the surface area of catalyst particles due to coalescence and an increase of carbon atom concentration in the catalyst particles due to the promotion of the decomposition of C$_2$H$_2$ gas [15].

We would like to stress that the difference between CVDs and LTCVD is the carbon source: pure carbon clusters by LTCVD and hydrocarbons (e.g., CH$_4$ and C$_2$H$_2$) by CVDs. In the LTCVD experiment, the threshold temperature (~1000°C) for CNF growth was much higher than that for the growth of multi-walled CNTs by CVD (~500°C). The reason for this difference is still not clear; however, it seems reasonable that catalyst particles should be heated at a high temperature to dissolve carbon because the diffusion coefficients and solubilities of carbon in Ni, Co and Pd increase with temperature [11]. Though Pd effectively enhanced the growth of CNFs, the layer structure of crystal graphite was not seen in the CNFs; which correlates with the ineffectiveness of Pd as a graphitization catalyst, as mentioned by Yudasaka et al [16]. They examined the difference in the catalytic activities of catalyst metals for single-walled CNT growth using PLA, and concluded that the yield of single-walled CNTs from Pd was much lower than that from NiCo [16].

To understand the correlation between carbon clusters generated from a laser ablation plume of graphite and CNFs, the dependence on the substrate position from the target was examined. Figure 5 shows SEM micrographs of CNFs deposited on PdNi/SiO$_2$/Si substrates at (a) +30 mm ($T_{\text{sub}}$~1060°C), (b) +80 mm ($T_{\text{sub}}$~1020°C) and (c) +130 mm ($T_{\text{sub}}$~818°C). It shows that the number density of CNFs drastically decreased with an increase of the distance. Two reasons to explain the suppression of CNF growth are considered: (1) $T_{\text{sub}}$ decreases with the distance; (2) carbon clusters get larger as the distance increases due to the increase of collisions between the clusters and ambient Ar gas atoms. Further investigation of this issue is needed.

Figure 5. SEM micrographs of CNFs deposited on PdNi/SiO$_2$/Si substrates at different positions from the target. Scale bar, 500 nm.
4. Conclusions
CNFs were grown on metal-catalyzed Si substrates by LTCVD. The enhancement of CNF diameter and number density by Pd was revealed through experiments, and we discussed the high diffusion coefficient of carbon in Pd. As well, temperature has the same role in increasing the diffusion coefficient and CNF diameter. Further investigation is needed into the correlation between the carbon clusters ablated from the graphite target and grown CNFs.

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