

GROWTH OF SINGLE-WALLED CARBON NANOTUBES AT LOW TEMPERATURE AND LOW PRESSURE CVD CONDITIONS

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ABSTRACT

Controlling the detailed structures of single-walled carbon nanotubes (SWNTs) is imperative for realizing many SWNT applications, and understanding the SWNT growth mechanism is important to improve the growth techniques. In the present study, we performed SWNT growth by a catalytic chemical vapor deposition (CVD) method in wide temperature and pressure ranges, using a high-vacuum CVD chamber. We focused on low CVD gas pressure and low temperature conditions and investigated the SWNT growth mechanism.

SWNTs were synthesized by using ethanol gas as the carbon source. As the catalyst, Co and Mo metal nano-particles deposited onto silicon substrates were used. SWNTs were grown via the reaction between ethanol gas and the catalytic metal nano-particles at high temperature. The ethanol gas pressure ranged from 10^{-3} Pa to 10^2 Pa, and the CVD temperature ranged from 400 to 900 °C. The yield of SWNTs was assumed to be proportional to the G-band intensity, which was measured by Raman scattering spectroscopy. SWNT samples were observed by scanning electron microscopy and transmission electron microscopy.

An optimum CVD temperature existed for each ethanol gas pressure, and decreased with decreasing ethanol gas pressure. Moreover, SWNTs were grown even at 500 °C, when the ethanol gas pressure was low (less than 10^{-2} Pa). In this study, the minimum temperature and pressure at which SWNTs could be grown were 450 °C and 10^{-3} Pa. At low temperature and low CVD gas pressure, the activity of the catalyst and the growth rate of SWNTs were low, while the catalyst lifetime was long.

INTRODUCTION

Single-walled carbon nanotube (SWNT) is a rolled up graphene sheet, which was discovered by S. Iijima et al., in 1993 [1]. The diameter of an SWNT is a few nm, whereas the length can be several millimeters. Owing to this one-dimensional structure, SWNTs have various exceptional properties, which motivate much research in many related fields.

Some of the SWNT properties strongly depend on the chiral structure, which is described by the chiral vector C_h . Chirality-controlled synthesis of SWNTs remains one of the most challenging topics in SWNT growth research. Understanding of the growth mechanism of SWNTs is critical for the development of a chirality control synthesis technique.

Chemical vapor deposition (CVD) is one of the most widely used generation techniques of SWNTs. In CVD methods, SWNTs grow from nano-particles, which are called the catalyst. SWNTs form via the high-temperature reaction between the catalyst particles and carbon-containing gas molecules. Methane or acetylene is generally used as the carbon source. The hydrocarbon molecules are decomposed thermally in the gas phase or decomposed on the catalyst, and carbon atoms are supplied to the catalyst particles. The carbon atoms are re-crystallized by the catalyst and SWNTs are synthesized.

When alcohol, such as ethanol or methanol, was used as the carbon source, high-quality SWNTs were generated [2]. When Fe/Co metal particles, which were supported on zeolite particles, were used as catalyst, high-quality SWNTs were

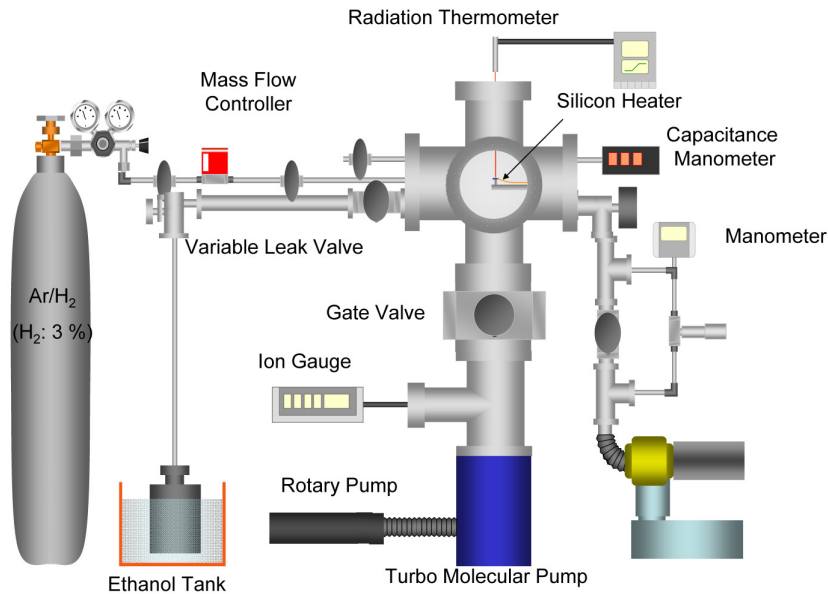


Fig. 1 Schematic image of a high-vacuum chamber CVD apparatus.

generated at relatively low temperature (550 °C) and at low pressure (a few Torr). Because ethanol is comparably safe and inexpensive material, it is an appealing carbon source for SWNT growth. Moreover, vertically-aligned SWNTs were obtained from Co/Mo particles supported on a silicon wafer or a quartz substrate [3]. The Co/Mo particles were prepared by a simple dip-coating method.

The alcohol catalytic CVD (ACCVD) method became one of the distinguished SWNT generation techniques and it was important to investigate and analyze the growth conditions of the ACCVD method. In this paper, we focused on the ACCVD condition dependence of grown SWNTs and discussed the growth mechanism.

EXPERIMENT

SWNTs were generated by the ACCVD method. Ethanol was the carbon source and Co/Mo metal particles were used as the catalyst. A silicon substrate was immersed into Co and Mo acetate solutions (metal content 0.01 wt% each) and drawn up at 4 cm/min. The dip-coated substrate was then heated in air at 400 °C, which oxidized the Co and Mo acetates. CVD was performed in a high-vacuum chamber, which was evacuated by a turbo-molecular pump, as shown in Fig. 1. The sample was heated by Joule-heating. The substrate was connected to a pair of electrodes, which applied an AC voltage, and the substrate was heated by Joule heating. The temperature of the substrate was measured by a radiation thermometer.

The CVD temperature and CVD gas pressure were investigated in a wide range. The temperature and ethanol gas pressure ranged from 400 to 800 °C and from 10^{-3} to 10^2 Pa, respectively. For comparison, dimethyl ether (DME) was also

used as the carbon source. DME has the same compositional formula (C_2H_6O) as ethanol.

Raman scattering spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed for SWNT sample analysis.

RESULTS AND DISCUSSION

An electric furnace is typically used for sample heating in CVD methods, which increases the temperature of both the sample and CVD gas. This is known as “hot-wall” CVD. On the other hand, when only the sample is heated, this is known as “cold-wall” CVD. In cold-wall CVD, the CVD gas is thermally decomposed only near the sample surface, which simplifies the CVD process. The efficiency of the CVD process, however, is

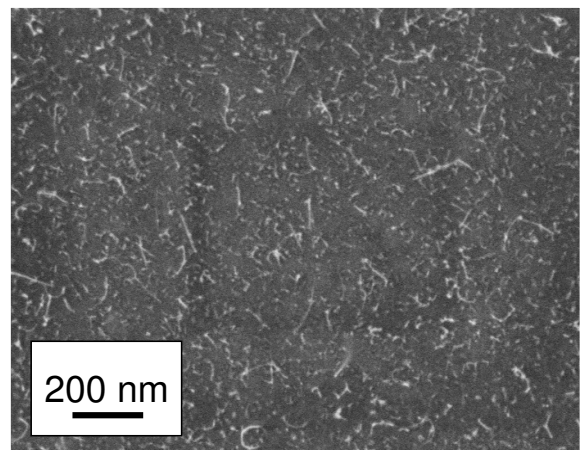


Fig. 2 SEM image of SWNTs grown on a silicon substrate in the high-vacuum CVD chamber.

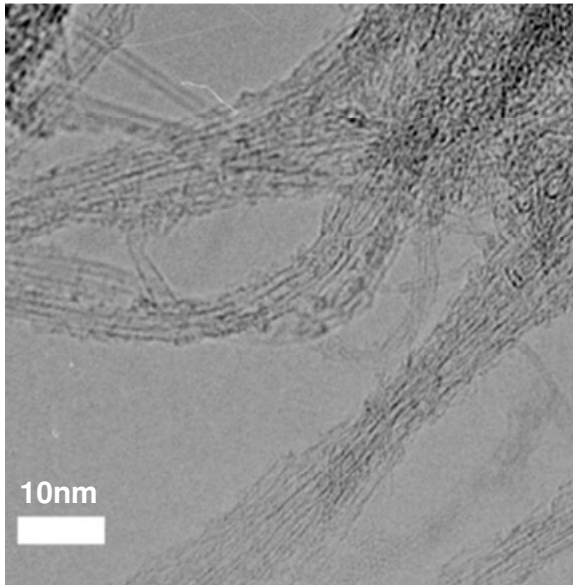


Fig. 3 TEM image of SWNTs generate in the high-vacuum CVD apparatus.

generally lower than hot-wall CVD.

Figure 2 shows an SEM image of SWNTs grown on a silicon substrate. The CVD temperature and ethanol gas pressure were 600 °C and 10 Pa, respectively. SWNTs were uniformly generated. Although the CVD was cold-wall type, SWNTs were sufficiently obtained.

Although SEM is useful for observation of the sample surface morphology, it is impossible to analyze the inner structure of the SWNTs. Figure 3 shows a TEM image of this sample. The cylindrical structure of SWNTs was clearly observed and the TEM images revealed that the tube diameter ranged from 0.7 to 1.8 nm. The average diameter was 1.2 nm.

Next we investigated the CVD condition dependence of SWNT growth by using the high-vacuum CVD apparatus. Figure 4 shows the CVD temperature and ethanol gas pressure dependence of the Raman scattering spectra from SWNTs. These spectra showed SWNT characteristic peaks, such as the G-band, D-band and radial breathing mode peaks. The G-band peak corresponds to the honeycomb structure of carbon atoms common to graphite, graphene and SWNTs. The G-band from SWNTs is composed of multiple peaks and is a good signature for analysis of the SWNT sample. The D-band comes from defects in the carbon honeycomb structure. Therefore the intensity ratio between the G-band and D-band (G/D) indicate the quality or crystallinity of the graphitic structure. Figure 4 shows that SWNTs were synthesized in a wide range of temperatures and ethanol gas pressures. At low ethanol gas pressure (10^{-3} Pa) we succeeded in synthesizing of SWNTs even at 450 °C, although the quality was not so high. Low temperature CVD growth is important for the fabrication of SWNT devices.

Figure 5(A, B) shows the CVD temperature and ethanol gas pressure dependence of the normalized G-band intensity. Since the Raman peak from silicon always appears at 520 cm^{-1} , the relative intensity between the G-band from SWNTs and silicon peak corresponds to the amount of grown SWNTs. The CVD temperature dependence of the normalized G-band intensity is shown in Fig. 5(A). An optimum temperature existed for each pressure, and the temperature range over which SWNTs could be grown strongly depended on the ethanol gas pressure. Decreasing of ethanol gas pressure caused the optimum temperature to decrease, and the growth temperature range narrowed.

The ethanol gas pressure dependence also clearly appeared, as shown in Fig. 5(B). At high temperature, SWNTs were synthesized only for high ethanol gas pressures (from 1 to 100

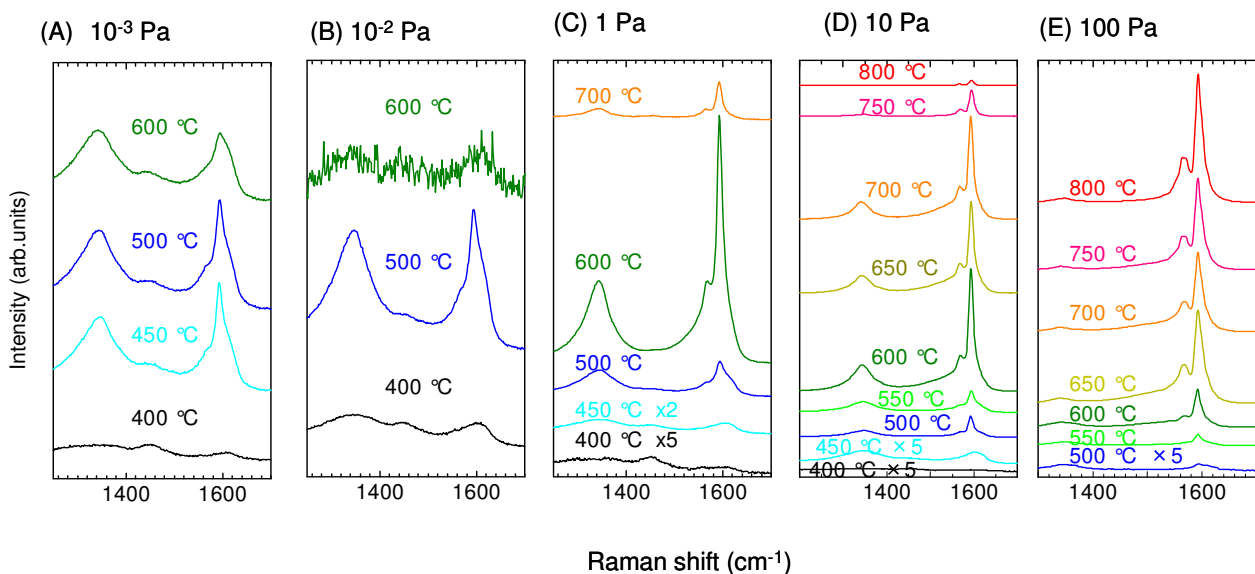


Fig. 4 CVD temperature and ethanol gas pressure dependence of Raman scattering from SWNTs.

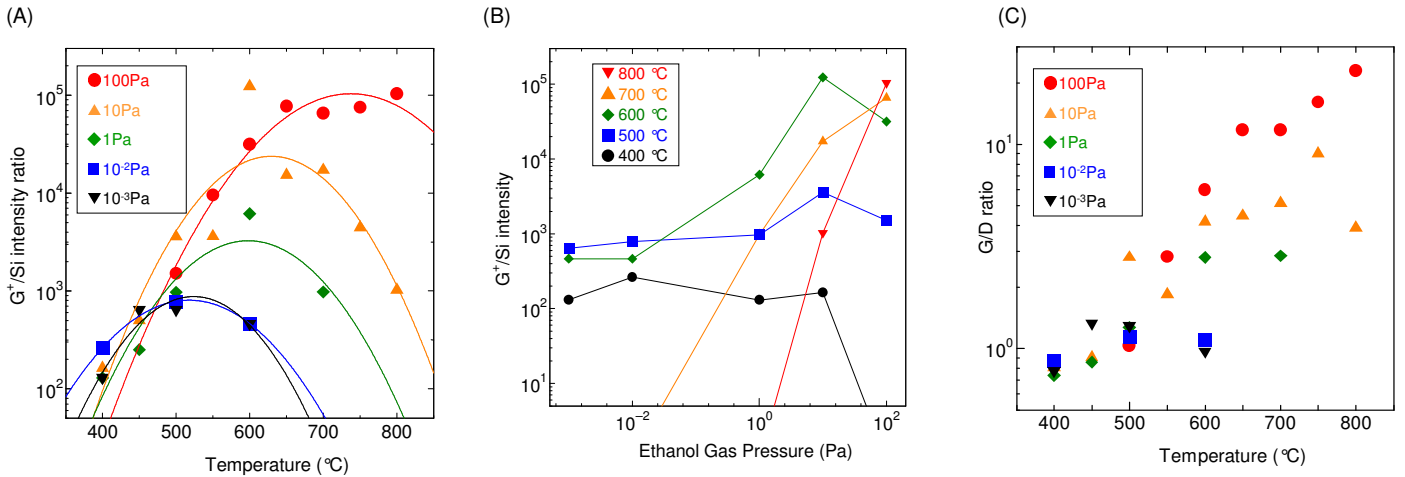


Fig. 5 CVD temperature and ethanol gas pressure dependence of (A, B) normalized G-band intensity and (C) the G/D intensity ratio.

Pa). On the other hand, when the CVD temperature was low (from 400 to 600 °C), SWNTs were generated over a wide pressure range.

The CVD condition dependence of the G/D intensity ratio is shown in Fig. 5(C). The G/D intensity ratio, which corresponds to the quality of SWNTs, simply increased with increasing CVD temperature. An increased CVD temperature increases the activity of the catalyst and the diffusion and recrystallization rates of carbon, which promotes high-quality SWNT growth. However, high temperature also increases the carbon supply to the catalyst. If the supply rate of carbon atoms is larger than the growth rate of SWNTs, by-products (amorphous carbon, graphite flake) can be generated on the catalyst surface, which reduced the SWNT growth. In CVD growth, the balance between the carbon supply and SWNT growth rate is critical.

The growth rate of SWNTs was measured by in-situ observation during the CVD process [4, 5]. In-situ optical absorption spectroscopy is a powerful tool for analysis of the SWNT growth mechanism. It revealed that the growing SWNT length $L(t)$ was represented by the equation,

$$L(t) = (\gamma_0 \tau) [1 - \exp(-t/\tau)], \quad (1)$$

where τ is the catalyst lifetime, γ_0 is the initial growth rate [5]. The final amount of grown SWNTs ($\gamma_0 \tau$) corresponds to the normalized G-band intensity, as shown in Fig. 5(A, B). The catalyst lifetime τ slightly increased with decreasing temperature, while the initial growth rate γ decreased.

Figure 6 shows the SWNT yield at different CVD temperatures and gas pressures of (A) ethanol gas and (B) DME gas. The diameter of the circles indicates the yield of SWNTs, while the cross indicates no SWNT growth. In the case of ethanol gas (Fig. 6(A)), SWNTs were grown over a wide range of CVD temperature and ethanol gas pressure.

When using DME gas as the carbon source, SWNTs were also synthesized, as shown in Fig. 6(B). Both DME and ethanol have the same compositional formula and they contain one oxygen atom. The oxygen atom was thought to remove by-

products (amorphous carbon and graphite flakes) and promote SWNT growth. Therefore, the growth mechanism of DME is expected to be similar to that of ethanol. Although the SWNT quality from DME was as high as that from ethanol, its growth temperature and the pressure ranges were narrower than that of ethanol, as shown in Fig. 6(B). Since DME thermally decomposes more rapidly ethanol at a given temperature, the

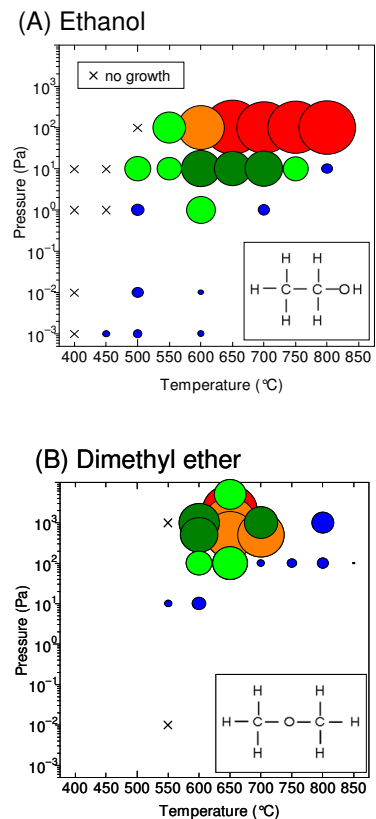


Fig. 6 Yield of SWNTs at different CVD temperature and gas pressure for (A) ethanol and (B) DME.

supply rate of carbon to the catalyst is faster for DME than for ethanol. Thus the high thermal decomposition rate of DME was suitable only for the higher temperature range. Since the growth rate was also dependent on temperature, it was difficult to balance the carbon supply with SWNT growth, and we could not synthesize SWNTs at low temperature range with DME.

CONCLUSION

SWNTs were synthesized by the ACCVD method over wide temperature and pressure ranges in the high-vacuum chamber. The optimum temperature for the ethanol gas pressure increased with ethanol gas pressure, and a high CVD temperature increased the crystallinity of SWNTs. Although SWNTs were also synthesized from DME gas by using a similar CVD method as ethanol, the CVD conditions were more limited for DME. DME showed the maximum yield at 650 °C, and the difference between ethanol and DME came from the thermal decomposition at the catalyst.

ACKNOWLEDGEMENTS

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