Growth of carbon nanotubes by microwave plasma-enhanced chemical vapor deposition at low temperature

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Carbon nanotubes have been grown on Ni-coated Si substrates by microwave plasma-enhanced chemical vapor deposition with a mixture of methane and hydrogen gases at temperatures ranging from 520 to 700 °C. The density and the length of the carbon nanotubes increased with increasing growth temperature. At a growth temperature of 520 °C, the carbon nanotubes were curly, whereas the nanotubes were straight and self-aligned upward at temperatures above 600 °C. Images from high-resolution transmission electron microscopy showed that the nanotubes were multiwalled, with a few wall structures. The graphitized structures were also confirmed by Raman spectra. We show that the size of Ni grains on Si substrates is correlated to the diameters of the grown carbon nanotubes. © 2000 American Vacuum Society. [S0734-2101(00)10004-1]

I. INTRODUCTION

Because of their unique and superb properties, carbon nanotubes are considered to be a promising material in various applications such as field-emission displays,1–3 hydrogen storage vehicles,4,5 atomic force microscope/scanning tunneling microscope tips,6 and terabit memory devices.7 Preparation of highly purified carbon nanotubes in large quantity, well-aligned nanotubes, and low-temperature synthesis are prerequisites for such applications. An arc discharge method has been used to synthesize a large amount of carbon nanotubes.8,9 Laser vaporization of a graphite powder mixed with a small amount of transition metals was suggested as a tool for mass production of single-walled carbon nanotubes with high yield.10,11 These processes, however, involve very high temperature (arc discharge: 5000–20 000 °C, laser vaporization: 4000–5000 °C),12 which prohibits easy control of diameters and chiralities of nanotubes during growth. In addition, a subsequent purification process is required for practical application of carbon nanotubes. Therefore, a systematic in situ on-chip synthesis of nanotubes at low temperature is always desirable for controllable integration production of field-emission displays. For this reason, chemical vapor deposition (CVD) has received a great deal of attention since carbon nanotubes with few carbonaceous particles can be synthesized at significantly lower temperatures (below 1000 °C).13,14 To use glasses for field-emission displays, it is necessary to reduce the growth temperature to below 600 °C.

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Microwave plasma-enhanced CVD (MPECVD) has been used to grow nanocrystalline diamond thin films on Si substrates. However, different experimental parameters, for example, a higher methane-to-hydrogen gas ratio and higher growing temperature, resulted in the growth of carbon nanotubes on transition-metal-coated Si substrates.12,15 Therefore, no pretreatment was necessary, in contrast to other CVD methods. Nonetheless, the reported growth temperature of MPECVD is still higher than the desired value.

In this article, we report the synthesis of carbon nanotubes by MPECVD at temperatures below 700 °C. The nanotubes were aligned upward at temperatures above 600 °C, where multiwalled carbon nanotubes with a few graphitized walls were uniformly grown on Ni-coated Si substrates. The density and the length of carbon nanotubes increased with increasing growth temperature.

II. EXPERIMENT

Ni thin films with a thickness of 70 nm were deposited using rf magnetron sputtering on Si substrates on which titanium nitride (TiN) films had been coated to enhance adhesion of the Ni films. The chamber was evacuated to a base pressure of 1.0 × 10−6 Torr before the deposition. The deposition of Ni films was carried out under a chamber pressure of 3.7 mTorr at a substrate temperature of 350 °C. The rf power density during the sputter deposition was 1.97 W/cm2. Carbon nanotubes were synthesized by MPECVD using gas mixtures of methane (CH4) and hydrogen (H2) gases. Figure 1 shows a schematic diagram of the MPECVD apparatus employed for the growth of carbon nanotubes. During growth, the substrate surface was in contact with the lower edge of the glow generated by a microwave plasma. As
shown in Fig. 1, the growth temperature was detected by two thermometers, i.e., a pyrometer and a thermocouple. The temperature measured by the pyrometer was about 100 °C higher than that detected by the thermocouple. We used the pyrometer-read value as a growth temperature. Details of the experimental conditions are listed in Table I.

The diameters, lengths, and nucleation densities of carbon nanotubes were investigated by scanning electron microscopy (SEM) (JEOL JSM-6400). The wall structures of the nanotubes were evaluated by high-resolution transmission electron microscopy (HRTEM) (Hitachi H-9000NA). Fourier transform (FT) Raman spectroscopy (Bruker RFS 100/S) using a Nd:YAG laser (1064 nm) was used to confirm the formation of graphitized structures.

### III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the x-ray diffraction (XRD) pattern and the atomic force microscopy (AFM) image, respectively, of a Ni thin film (70 nm) deposited on TiN/Si (A/B stands for A on B) substrate by rf magnetron sputtering. In the XRD pattern, in addition to TiN (111) and Si (400) peaks, sharp Ni (111) and Ni (200) peaks were detected, indicating that the deposited film is polycrystalline Ni with good crystallinity. It has been suggested that the grain size of the transition metal is closely related to the diameter of the nanotubes when carbon nanotubes are synthesized on transition-metal-coated substrates by the thermal CVD method. To investigate this relationship, the surface morphology of Ni thin film was investigated by AFM, as shown in Fig. 2(b). Ni grains, with sizes ranging from 50 to 100 nm, were uniformly distributed over the entire surface.

Figures 3(a)–3(d) are SEM images of carbon nanotubes formed on Ni-coated Si substrates by MPECVD at temperatures ranging from 520° to 700 °C. Figures 3(b)–3(d) are shown at a viewing angle of 45°. The methane content in a methane/hydrogen gas mixture was 20%, and the growth time was 10 min. Figure 3(a) shows the SEM image of nanotubes grown at 520 °C. We did not use any heating source in this case. Therefore, the temperature of 520 °C was achieved only by microwave plasma power of 400 W. Figure 3(a) shows a large amount of carbonaceous particles together with a small amount of carbon nanotubes embedded in the particles, indicating that this temperature is not high enough for carbon atoms to have sufficient diffusion length to form nanotubes. However, at temperatures above 600 °C, a relatively small amount of the particles was observed. Furthermore, nanotubes are rather straight and grown upward. Figure 3(b) shows that the carbon nanotubes grown at 600 °C

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<th>Table I. Growth conditions of carbon nanotubes by MPECVD.</th>
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were self-aligned upward with a relatively small amount of carbonaceous particles compared to Fig. 3(a), although the density of nanotubes was low. The growth rate was about 0.3 μm/min. The number of carbon nanotubes increased with increasing growth temperature, as shown in Figs. 3(c) and 3(d). The growth rate of nanotubes also increased with increasing growth time. Nanotubes grown at 700 °C are about 15 μm in length. Such long nanotubes may be useful for an application such as a storage vehicle for hydrogen and other gases. A growth rate of 1.5 μm/min was observed at 700 °C. However, some carbonaceous particles still remained on the top of the nanotubes. It is well known that some transition metal particles are at the top of aligned carbon nanotubes, which is also related the cap growth mechanism. Energy dispersive x-ray (EDX) spectra carried out during TEM measurements confirmed that Ni-carbon complexes are present at the top of nanotubes but contain only a small amount of Ni. In general, there are two approaches to remove carbonaceous particles. One is to purify samples after the growth, and the other is to find experimental conditions that produce only nanotubes. We first tried thermal annealing in a furnace at 700 °C in order to remove carbonaceous particles. However, careful control is required for the annealing temperature and annealing time, and in addition the yield after the annealing was quite low. We also tried different experimental conditions of hydrogen content and microwave power; however, this approach was not efficient for removing the particles. The etching effect due to hydrogen plasma should be effective for removing the carbonaceous particles and, hence, the growth time should also be an important factor. To confirm this, carbon nanotubes were grown at 520 °C for growth times of 10, 30, and 50 min, respectively, as shown in Figs. 4(a)–4(c). As clearly seen, the amount of carbonaceous particles decreased markedly with increasing growth time. As a result, very pure carbon nanotubes were obtained for 50 min. This phenomenon could be explained by the etching effect induced by hydrogen plasma. It is well known that atomic hydrogen in the hydrogen plasma has a strong etching effect on the growing film in MPECVD. At the early stage of nanotube growth, reactants (CH₄ radicals formed in plasma) are decomposed by the catalytic assistance of Ni, resulting in the formation of carbon nanotubes and nanoparticles, as shown in Fig. 4(a). This eventually leaves the surface of the Ni films covered with carbon nanotubes and nanoparticles. Once the Ni surface is covered with carbon nanomaterials, the etching effect caused by hydrogen plasma will be dominant, instead of growth. Because carbon nanotubes are more stable than carbonaceous particles, they are not easily etched by hydrogen plasma. In contrast, the plasma readily etches the particles preferentially. This resulted in pure carbon nanotubes when sufficient growth time was allowed, as shown in Fig. 4(c). Carbon nanotubes are curly in this case, suggesting that the nanotubes are highly defective. This is due to low growth temperature (520 °C).

We investigated the dependence of nanotube growth on methane content in gas mixtures. Figures 5(a)–5(c) are SEM images of carbon nanotubes grown with methane contents of 10%, 15%, and 20%, respectively. The growth temperature and time were 650 °C and 10 min, respectively. It is rather unusual that the density of nanotubes increased with decreasing methane (CH₄) content. Gas phase reactive species needed for the growth of carbon nanotubes such as methyl radicals are generated by hydrogen abstraction reactions. These reactants will eventually initiate the formation of nanotubes by the catalytic assistance of Ni. A large portion of atomic hydrogen effectively decomposes the methane gases, resulting in many reactive species, which in turn causes a high density of nanotubes. It is, therefore, believed that for methane content from 10% to 20%, the number of reactive species increased with increasing hydrogen content.

To investigate the wall structures of carbon nanotubes, TEM images were obtained for nanotubes. Figure 6(a) shows a TEM image of carbon nanotubes grown at 700 °C with a
methane content of 20% for 10 min. The diameters are in the range of 10–50 nm, which is smaller than the grain size of Ni thin films (50–100 nm), observed by AFM measurement [Fig. 2(b)]. This result differs from our previous report that the diameter of carbon nanotubes is almost the same as the grain size of the transition metal when thermal CVD is used. Because MPECVD is employed in this study, it is believed that the Ni surface can be etched away by microwave plasma at the early stage of growth, resulting in a smaller grain size than that of the as-prepared Ni surface and a correspondingly smaller size of nucleation seeds. Therefore, the diameters of carbon nanotubes grown on such nucleation seeds are presumably smaller than the grain size of as-prepared Ni thin films. A TEM image also shows carbonaceous particles in the middle of the left side in Fig. 6(a). The observed particle is relatively large in size. Figure 6(b) shows a HRTEM image of carbon nanotubes grown at 700 °C with a methane content of 20% for 10 min. The HR-TEM image clearly shows that the nanotubes are well graphitized, with outside diameters of 10–15 nm. These nanotubes are multiwalled, with hollow insides having about six graphitized carbon layers. Note that no amorphous layer was observed on the outer surface of the walls, despite the relatively low growth temperature. Multiwalled carbon nanotubes with a relatively small number of walls were uniformly synthesized on Ni-coated Si substrates by MPECVD.

Figure 7 shows FT-Raman spectra of carbon nanotubes grown at temperatures ranging from 520 to 700 °C with a methane content of 20% for 10 min. In all spectra, a well-graphitized structure was confirmed from the G-band peak located around 1600 cm$^{-1}$. The intensity of the G-band peak increased with increasing growth temperature, indicating that a complete hexagonal nanotube structure can be easily formed at high temperature. The absence of a second-order
peak at around 1740 cm$^{-1}$ suggests that this nanotube is not single walled. However, in the spectra of nanotubes grown at 650 and 700 °C, a few shoulder peaks on the lower energy side (marked by arrows) are shown, which is characteristic of the Raman spectra of single-walled carbon nanotubes. This may be because the nanotube obtained is composed of only a few walls, as confirmed from the HRTEM image. A relatively large D-band peak located at around 1300 cm$^{-1}$ was also observed, meaning that some carbonaceous particles are included, as was verified in SEM images. The D-band peaks at 650 and 700 °C are larger than those at lower temperatures. This is because carbonaceous particles are placed on the top of carbon nanotubes when nanotubes are grown at high temperatures, as shown in Fig. 3.

**IV. CONCLUSION**

Carbon nanotubes were grown on Ni-coated Si substrates using microwave plasma-enhanced chemical vapor deposition at temperatures ranging from 520 to 700 °C. Carbon nanotubes were formed throughout this temperature range. The density and growth rate of the nanotubes increased with increasing growth temperature. At a growth temperature of 520 °C, the carbon nanotubes were curly, whereas the carbon nanotubes were straight and aligned upward at temperatures above 600 °C. The nanotubes grown were multiwalled with hollow insides. Well-graphitized structures with a few walls were observed from TEM images and Raman spectra.

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