Synthesis of Carbon Nanotubes by Using Inductively Coupled Plasma Chemical Vapor Deposition at Low Temperature

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Abstract

Carbon nanotubes (CNTs) were synthesized by inductively coupled plasma CVD at 450 ℃. CNTs were grown on the 1-nm-thick Fe-Ni-Co with C_2H_2 and H_2 at different pressures and plasma powers. CNTs were grown longer in height as the H_α/CH ratios became lower by decreasing plasma powers and increasing growth pressures.

1. Introduction

Since the CNTs were discovered by Iijima[1], they have attracted much attention as one of the representative nanomaterials due to their versatile potential to a wide range of applications. In particular, CNTs have been considered very promising for field emitter materials as they exhibit peculiar morphologies of extremely large aspect ratios (nm-scale diameters and μm-range length) and extraordinary properties in terms of electrical conductivity, mechanical strength, chemical inertness, etc. [2]. The application of CNTs to large-area field emitters puts several stringent requirements, most importantly, the growth of CNTs at temperature low enough to adopt glass substrates. In our early-stage study, we met difficulties in growing CNTs at low temperatures, as Meyyappan reported that the growth of CNTs did not occur below 550°C [3]. We attempted to synthesize the CNTs at low temperatures of 450 ℃ by using inductively coupled plasma chemical vapor deposition (ICP-CVD) since the plasma could decompose more easily hydrocarbon gases at low temperatures than conventional thermal CVD. In this study, a substrate was located remote from the plasma to suppress the ion bombardment, otherwise, stubby CNTs were produced[4]. We successfully synthesized thin multi-walled CNTs at low temperatures of 450°C by optimizing pressures and rf plasma powers.

2. Experimental

Fig. 1 shows a schematic of an ICP-CVD system used in this study, where the ICP antennas are located at the top of the chamber while the substrate is located on a resistive electric heater, generating the plasma remote from the substrate. The process gas would be decomposed by the plasma and then be supplied to the substrate located at a distance so that CNTs could be grown without ion bombardment onto the substrate.
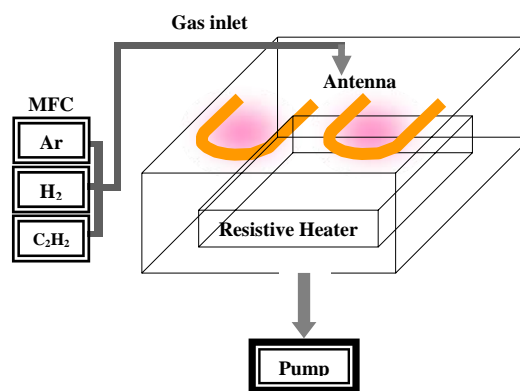
**Fig. 1. Schematic of ICP-CVD system used in this study**

The catalyst layer of the 1-nm-thick Fe-Ni-Co ternary alloy was thermally evaporated onto the Si

wafer, following the coating of a Ti diffusion barrier and an Al underlayer. The catalyst film was agglomerated into island-like particles by thermal annealing, providing the sites for the nucleation and growth of CNTs. The initial thickness of the catalyst film is considered important, because the sizes of island-like catalyst particles increase with larger initial film thickness. The particle sizes also become larger by annealing at higher temperatures [5,6].

The substrate was annealed in H_2 at 450°C by resistive heating and was thereafter fed for 5 min with a feedstock of C_2H_2 and a carrier gas of H_2 for the CNT growth. CNTs increased in height linearly with time, but were stopped to grow at 10~15 min probably due to the deactivation of catalyst particles. Here we synthesized CNTs for 5 min. The CNT growth was investigated at different pressures and plasma powers of 0.5~1.2 torr and 20~100 W, respectively. The plasma was diagnosed *in situ* by using optical emission spectroscopy (OES, Mikropack PlasCalc-2000) during the CNT growth. As-grown CNTs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy.

3. Results and discussion

Fig. 2 gives SEM images of CNTs grown at different plasma powers of 20~100 W under the pressure of 0.5 torr. With higher plasma powers, the CNT lengths decreased. We changed the pressures in the range of 0.5~1.2 torr, which is presented in Fig. 3. As expected, the CNT length increased at higher pressures. The CNT growth could not be carried out over 1.2 torr since the plasma became unstable. Here we performed the OES analysis of our plasmas at the growth conditions in order to correlate the CNT growth and the experimental parameters. The OES spectra produced many peaks of gas species existing in the plasma such as H_α, H_β, CH, C_2, etc. It is considered that CH and H radicals would have a great effect on the growth of CNTs.
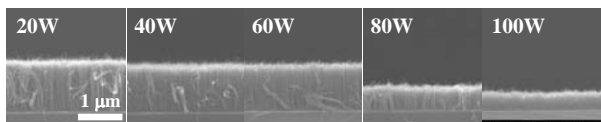
Fig. 2. SEM images of CNTs grown at different plasma powers under the pressure of 0.5 torr.
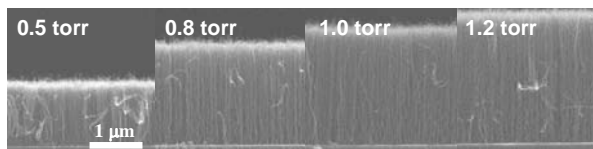

Fig. 3. SEM images of CNTs grown at different pressures under the plasma power of 20W.

As shown in Fig. 4, therefore, the relative intensity ratio of H_α/CH is presented here as a factor which should be considered to monitor the growth rate of CNTs. The H_α/CH ratios decreased at lower plasma powers and higher gas pressures, which in turn seems to result in longer CNTs as seen in Figs. 2 and 3. Conclusively, the CNT length increases with lower H_α/CH ratios, which is in good agreement with previous studies [7,8]. CH seems to work as precursors for the CNT growth, because CH can be easily dissociated to supply C into the catalyst. Atomic H can act as an etching agent of amorphous C (a-C) and simultaneously can lead to sp^3 hybridization of surface C atoms on the growth front of CNTs [8].

With higher plasma powers, the H_α intensity increased more rapidly than the CH intensity, resulting in the larger ratios of H_α/CH. The CNTs grew shorter with higher plasma powers. The growth rate would be determined by integrating the incorporation rate of C atoms supplied from CH radicals and the etching rate of CNT lattices by atomic H. As increasing the powers, the etching rate of atomic H seems to be greater than the incorporation rate of C atoms, totally decreasing the CNT lengths [9]. In this study, the growth rate of CNTs was greater at higher pressures, as reported previously [10]. As the pressure was increased, in the OES spectra, the H_α intensity was lowered more rapidly and the CH intensity, giving rise to lower H_α/CH ratios. At higher pressures, the incorporation rate of C atoms would be decreased but the etching rate would be reduced faster, overall increasing the growth rate of CNTs. When the OES analysis was made at different gas compositions, the H_α intensity sensitively changed with the C_2H_2 flow rates, but not with the H_2 flow rates. It can be easily understood by the fact that the bonding energies of C-H and H-H are 244 and 435 kJ/mol, respectively. Thus, atomic H is mainly supplied by the decomposition of C_2H_2 rather than H_2.

Fig. 5 shows the Raman spectra of CNTs grown at different pressures. The spectra are composed of two main peaks at 1326 and 1580 cm^{-1}, which are called as D-band and G-band, respectively.
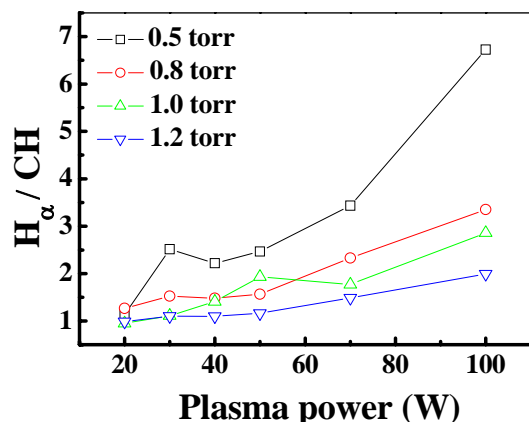
**Fig. 4. Intensity ratios of H_α/CH peaks with plasma powers and pressures**.

In general, the D-band occurs at 1346~1350 cm^{-1} and the G-band at 1580 cm^{-1} [11]. The G band is originated from the tangential vibration mode of C atoms in the graphite structure, while the D band is attributed to the lattice defects in the CNTs and the presence of a-C. The quality of CNTs can be evaluated by the perfection of their lattice structure and the amount of other carbonaceous impurities exiting together with the CNTs. Thus high quality CNTs would show low I_D/I_G ratios. A variation of the I_D/I_G ratios as a function of pressures is given in Fig. 6.
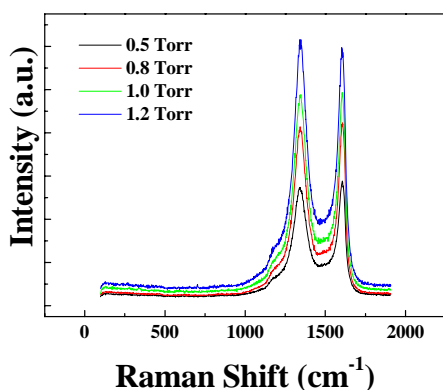
**Fig. 5. Raman spectra of CNTs grown at different pressures.**

The ratios increase with higher pressures, indicating the presence of more lattice defects and more a-C impurities. This result is in good agreement with the higher growth rate of CNTs at higher pressures. Here greater growth rates at higher pressures were attributed to the lower etching rate of atomic H. Defective sites in the lattice would be preferentially etched out by atomic H, but if the atomic H concentration is low enough, the defects would survive and remain in the CNTs, which would increase the intensity of D band.
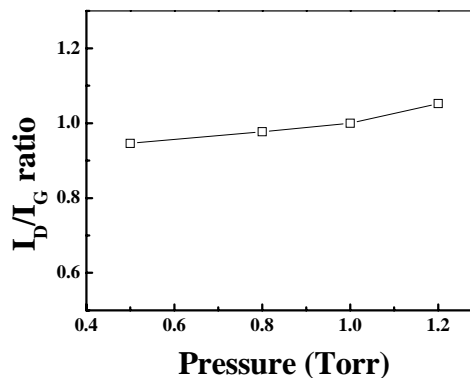
Fig. 6. Intensity ratios of D and G bands, I_D/I_G, of CNTs grown at different pressures.

TEM images of CNTs grown at 1.2 torr, as presented in Fig. 7, reveal that they are composed of well graphitized graphene layers of 4~7 and an outer diameter of 7~8 nm. There is little a-C at the side walls of CNTs.
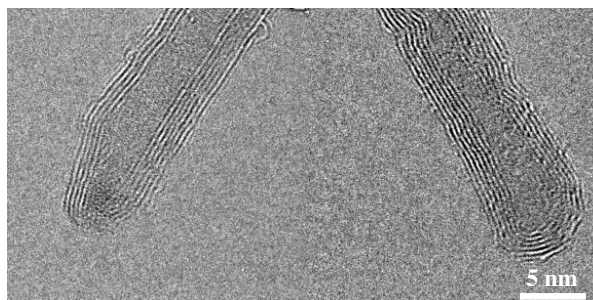
Fig. 7. HRTEM images of CNTs grown at 1.2 torr

4. Summary

CNTs were grown at low temperatures of 450°C using ICP-CVD. The CNT growth strongly depended on the plasma powers and pressures. We have discussed the growth mechanism of CNTs in terms of the H_α/CH ratios measured *in situ* during the CNT synthesis.

5. References

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