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Hydrogen plasma treatment on catalytic layer and effect of oxygen additions on plasma enhanced chemical vapor deposition of carbon nanotube

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Abstract

Multi-wall carbon nanotubes have been synthesized by plasma enhanced chemical vapor deposition (CVD) on Co-coated silicon substrates. Prior to the deposition of carbon nanotubes, dense and uniform nanosized catalytic seeds were formed by hydrogen plasma treatment on Co thin film. The size and morphology of Co catalytic seeds varied with hydrogen plasma treatment time. In the carbon nanotube growing process, a mixture of CH_4 and H_2 was used as gas source. Small O_2 additions to the CH_4–H_2 gas mixture (0~12% of mixture gas) improved the purity of carbon nanotubes and surprisingly led to high quality even at low growth temperature (610°C) as observed in high-resolution transmission electron microscopy (HRTEM). In order to understand the growth process by CH_4–H_2–O_2 plasma CVD in detail, optical emission spectroscopy (OES) was introduced. The results of OES analysis showed that, with the increase of oxygen amount, the intensity of C_2 decreased gradually, but the intensity of the OH radical increased sharply. It probably leads to increasing the etching effect on defective structure by affluent OH radical and suppressing super-saturation of carbon molecules at growing edges.

Keywords: Chemical vapor deposition; Hydrogen plasma treatment; Oxygen additions; Carbon nanotubes; Optical emission spectroscopy

1. Introduction

Since the first observation of carbon nanotubes (CNTs), numerous papers have reported studies on the yield of well-graphitized nanotubes [1], their growth mechanism [2], controlling diameter and chirality [3–5], theoretical predictions [6] and potential applications [6]. Different diameter and chirality of nanotubes give rise to diverse chemical, physical and mechanical properties. In particular, the growth of carbon nanotubes with high purity and high quality is of importance for good electronic conductivity along tube axis and chemical stability [7,8]. A chemical vapor deposition (CVD) method has several advantages in controlling the structures with various growth parameters and in obtaining pure CNTs at relatively low temperature. Recently, aligned CNTs have been grown by hot-filament plasma-enhanced CVD on Ni-coated glass substrates pretreated with NH_3 gas at temperatures below 666°C [3]. The control of the CNT diameters has been attempted using different transition metals deposited on Si substrate followed by the HF treatment [9]. Despite such breakthroughs in growth, the carbon nanotubes grown at relatively low temperature contained other carbonaceous material like amorphous carbon as well as the curled structure induced by defective graphitic layer. In addition, the method to systematically control the diameter of CNTs has not been clearly suggested.

Here we have grown the high quality aligned carbon nanotubes by oxygen addition as reactive gas in microwave plasma-enhanced CVD and the influence on the assembly of carbon nanotube has been discussed. It was also found that the uniform carbon nanotubes could be obtained by hydrogen plasma treatment on Co catalytic layer and the diameters was controlled with respect to the plasma treatment time.

2. Experimental

Cobalt layer with a thickness of 50 nm was deposited on Si substrate by radio frequency (RF) magnetron sputtering at 100 W RF power and the pressure was adjusted to 30 mTorr by feeding Ar gas (1 Torr=133.322 Pa). Prior to the

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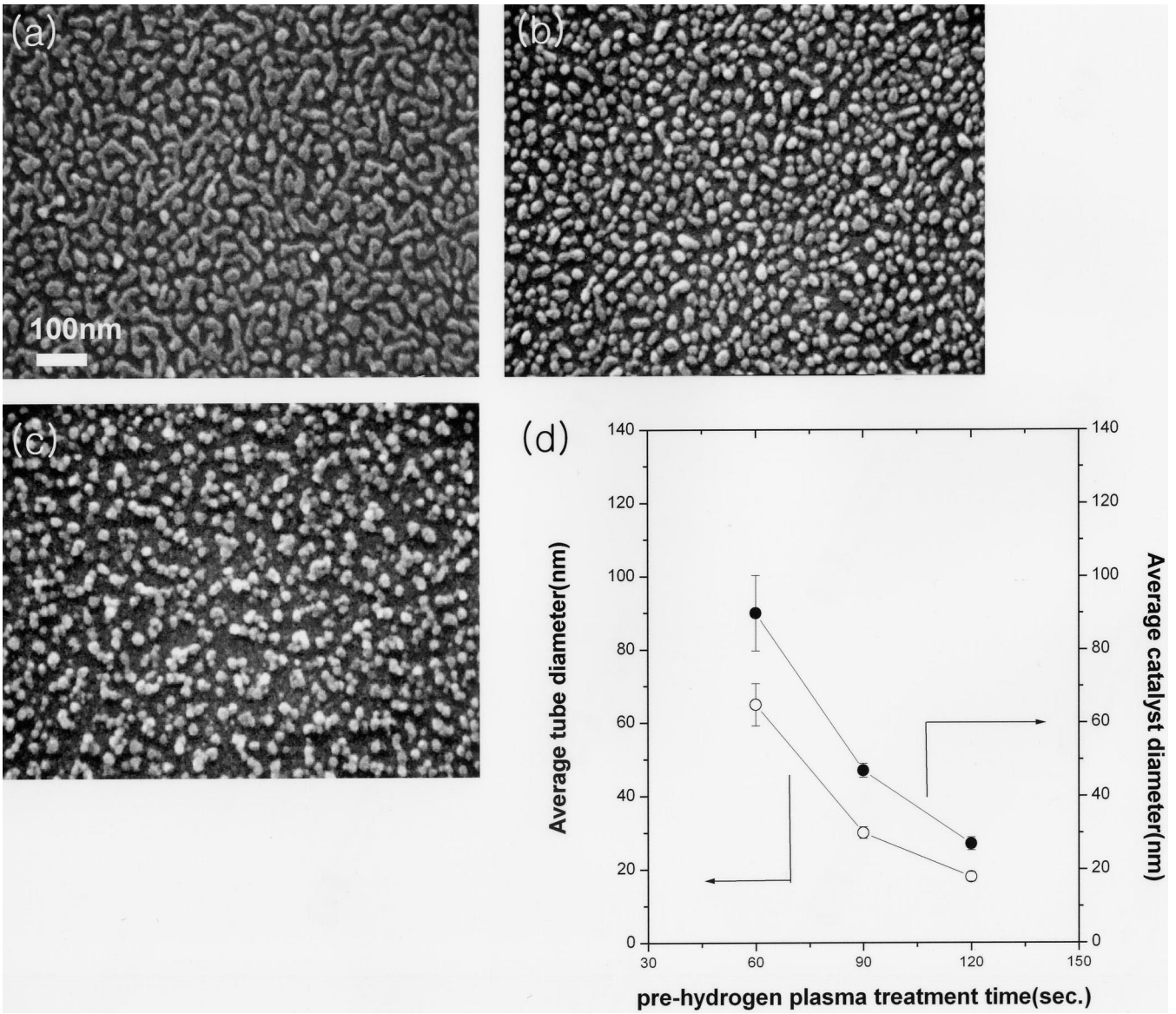

Fig. 1. SEM images of Co catalytic layer treated by hydrogen plasma at a microwave power of 1100 W for (a) 60 s, (b) 90 s, and (c) 120 s, and (d) the average catalytic size and the diameter of multiwall carbon nanotube as a function of pre-hydrogen plasma treatment time.

growth of the carbon nanotubes by microwave plasma-enhanced CVD, hydrogen was introduced and plasma treatment was conducted at 1100 W microwave power for various treatment times. A mixture of H_2 (99.9%) and CH_4 (0.1%) was used as a gas source and 0~10% oxygen of the mixed gas was added. The microwave power and the working pressure during the growth of CNTs were 700 W and 30 Torr, respectively. The substrate pretreated by hydrogen plasma was maintained at 610°C by halogen lamp heating. The surface morphology of Co catalytic seeds and CNTs were investigated with scanning electron microscopy (SEM). The CNTs were characterized by Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM) in detail. Optical emission spectroscopy (OES) was performed with the addition of oxygen to investigate the different intensity of species in plasma.

3. Results and discussion

Fig. 1a–c shows the SEM pictures of the surface morphology of the Co catalytic layer treated by microwave hydrogen plasma for 60, 90 and 120 s. The layer was transformed into catalytic seeds and the size decreased with the increase of treatment time. In case of the plasma treatment for 60 s, the size of catalytic seeds is widely distributed as shown in Fig. 1a but the uniformity of the size was improved with the increase of treatment time. However, Co catalytic seeds treated for 120 s shows a lower density because the Co surface is probably etched away by the microwave plasma for long time. Fig. 1d represents the average diameter of grown nanotubes and the average seeds size as a function of plasma treatment time, where the error bar implies the uniformity of the diameter and size. The distribution of diameter of carbon nanotubes was closely related with the size of catalytic seeds. Fig. 2 shows the Raman spectra of the multiwall carbon nanotubes grown by microwave plasma-enhanced CVD in CH_4–H_2–O_2. The Renishaw System was used with an excitation wavelength of 632.8 nm of a He–Ne laser. The G line (1580 cm^{-1}) can be assigned to the tangential C–C stretching mode and broad D line (1360 cm^{-1}) is related to either defective graphitic layers or carbonaceous particles [10]. When over 8% oxygen of the mixed gas was added, the I_G/I_D relative intensity ratio increased drastically. The results implied the amounts of amorphous carbonaceous by product adhered to wall and defective structure in multiwall layer decreased. In previous reports by other groups, multiwall carbon nanotubes grown as low as 700°C were not straight and contained incomplete structure as well as carbonaceous particles [11]. However, the multiwall carbon nanotubes grown by CH_4–H_2–O_2 (more than 8% of the mixed gas) plasma CVD at 610°C had straight structures and were aligned from the root of Co nano-particles as shown in Fig. 3a, b. Fig. 3c is a HRTEM image of the stem of CNT and represents the perfect graphitic layers without amorphous particles at outer wall surface, which implies the defective structures containing the amorphous carbonaceous particles was effectively removed during growth. OES was introduced to understand the detailed growth process by CH_4–H_2–O_2 plasma CVD. Emissive species observed in the CH_4–H_2–O_2 plasmas in the wavelength range of 300~800 nm were OH, CH, H_a and C_2. Fig. 4a shows the emission intensity of each species normalized by the intensity of the plasma without oxygen. As oxygen was added up to 12% of the mixed gas, the relative intensity ratio of C_2, CH and H_a decreased gradually, but the intensity of OH radical showed a sharp rise as shown in Fig. 4b. It leads probably to an increase of the etching effect by affluent OH radical which has been known as a strong etchant and suppress supersaturation of carbon molecules at growing edges. As a result, co-deposited amorphous carbonaceous particles and defective structures (i.e. pentagonal and heptagonal rings) with lower binding energy [12] than perfect hexagons were removed away selectively, then stable perfect hexagons were reassembled at the growing edges. The pentagons and heptagons in graphite sheet would allow the structure to curl up. Therefore, the concentration changes of each species in plasma leads to the changes in structure.

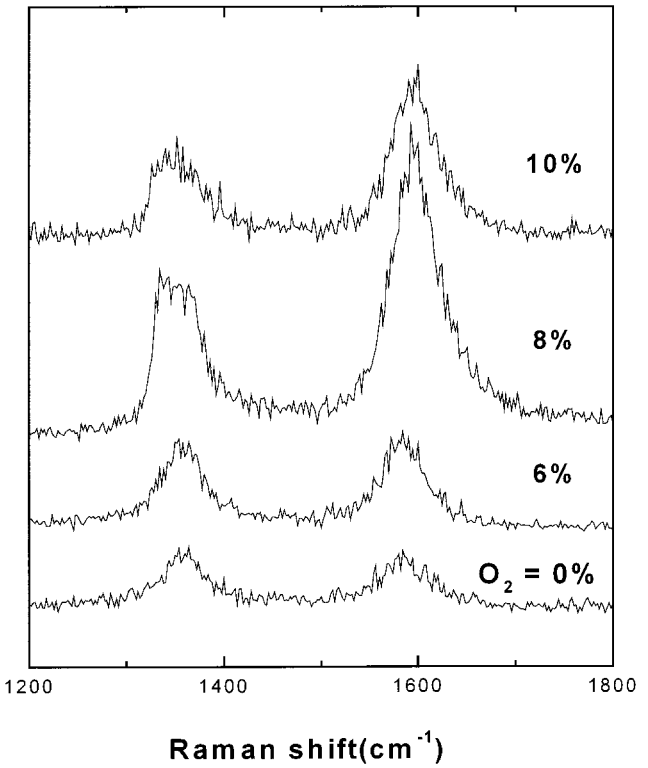

Fig. 2. Raman spectra of carbon nanotubes synthesized by microwave plasma enhanced CVD in CH_4–H_2–O_2.

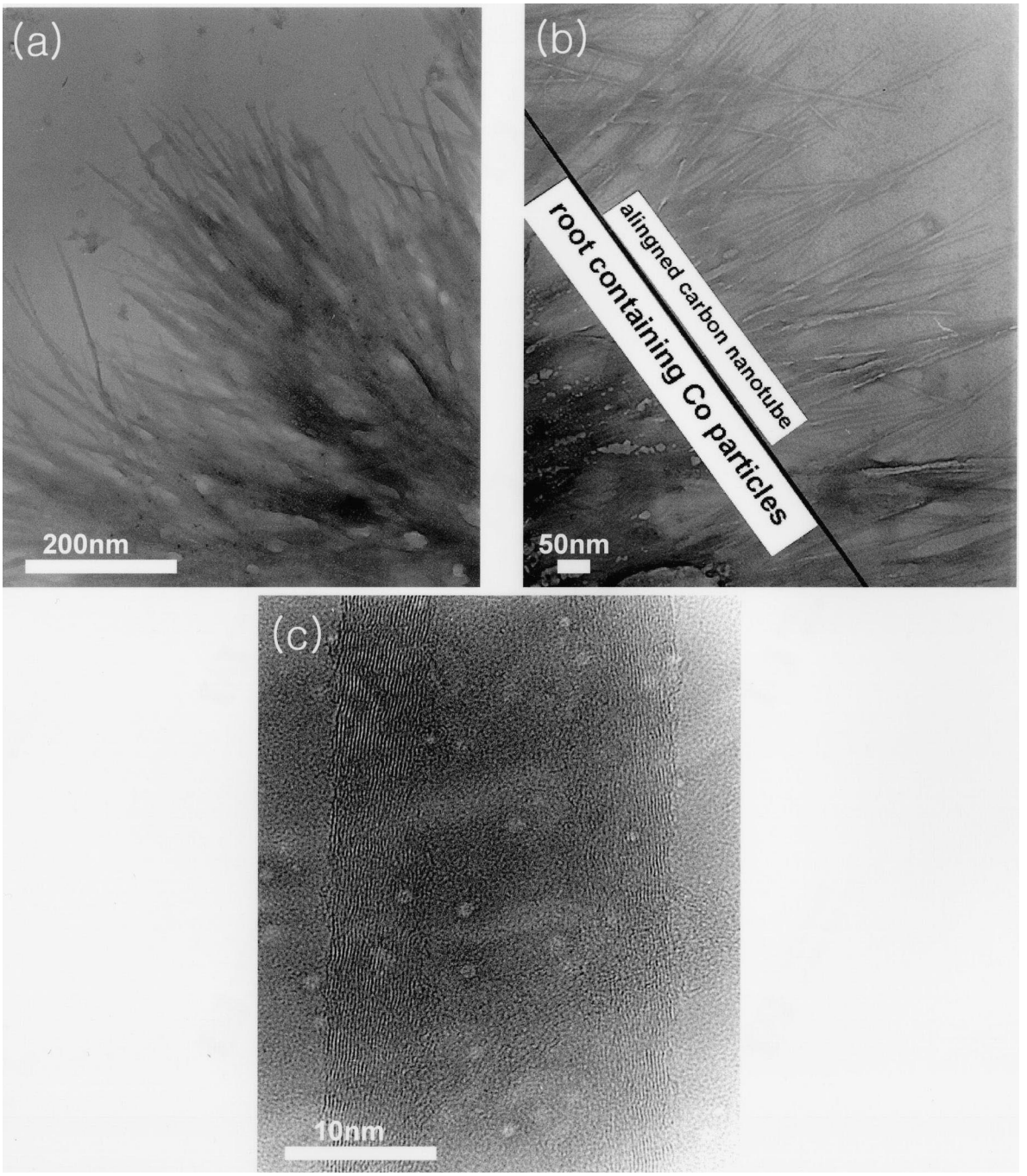

Fig. 3. TEM images of carbon nanotubes synthesized by CH_4–H_2–O_2 (8% of the mixed gas) plasma CVD at 610°C. The scale bars indicate (a) 200 nm, (b) 50 nm, and (c) 10 nm, respectively.

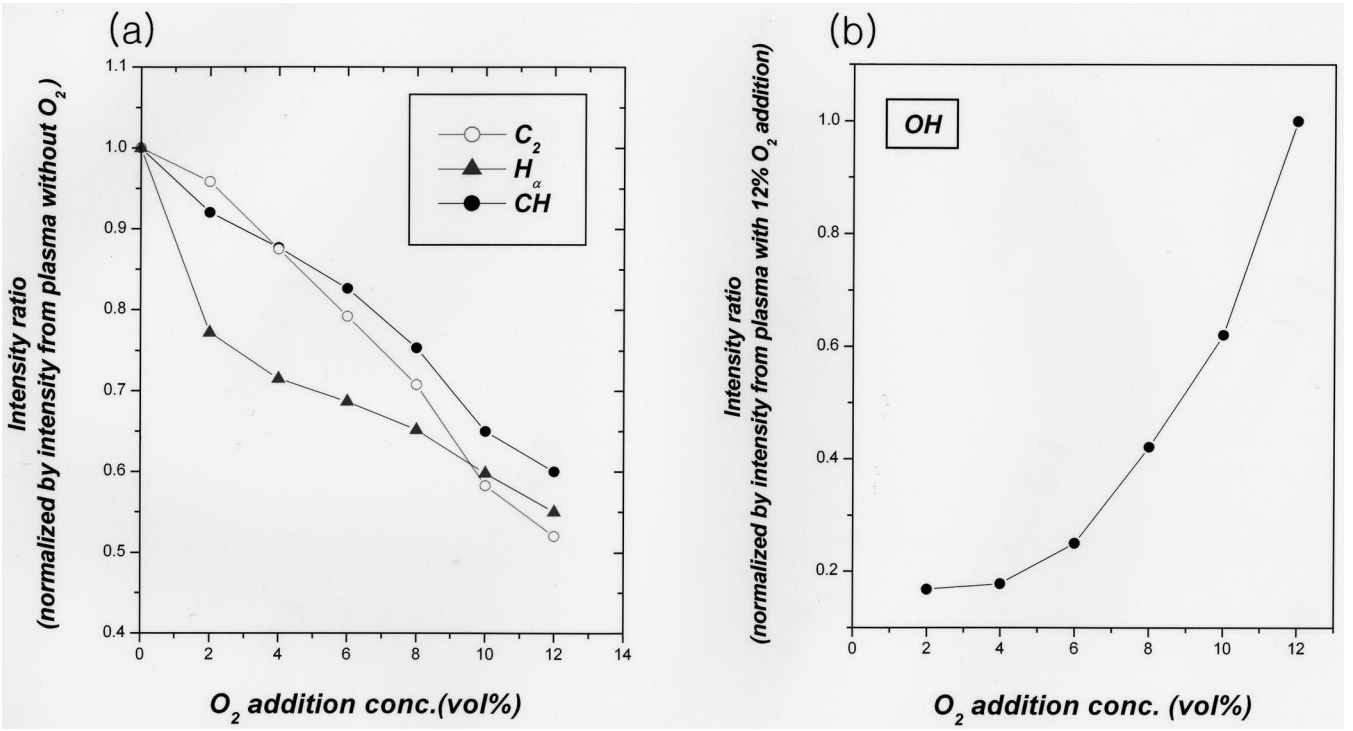

Fig. 4. Optical emission intensities from CH_4–H_2–O_2 plasma at various oxygen concentrations. (a) The relative intensity ratio of C_2, CH and H_a normalized by the intensity from plasma without oxygen, (b) OH radical intensity ratio normalized by intensity from plasma with 12% oxygen.

4. Conclusions

We synthesized dense and uniform metal catalytic seeds by hydrogen plasma treatment on metal layer and controlled the size of catalytic seeds by changing the plasma treatment time. O_2 addition in CH_4 and H_2 gas mixture improved the quality of CNTs grown even at 610°C by plasma enhanced chemical vapor deposition, which is caused by etching effect of affluent OH radical and suppressing the supersaturation of carbon molecules in plasma. This results open up the possibility of the low temperature growth of multiwall carbon nanotubes with enhanced quality.

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