Role of oxygen in the growth of carbon nanotubes on metal alloy fibers by plasma-enhanced chemical vapor deposition

Young Kyun Moon and Chang Goo Jung
Department of Nanosystem and Nanoprocess Engineering, Pusan National University, Miryang-si, Gyeongnam 627-706, Republic of Korea

Seok Joo Park
Clean Energy System Research Center, Korea Institute of Energy Research, Yuseong-gu, Daejeon 305-343, Republic of Korea

Tae Gyu Kim and Soo H. Kim[a]
Department of Nanosystem and Nanoprocess Engineering, Pusan National University, Miryang-si, Gyeongnam 627-706, Republic of Korea

A method allowing for the stable growth of carbon nanotubes (CNTs) on the surface of a fibrous metal mesh substrate (SUS304) was developed with the assistance of the microwave plasma-enhanced chemical vapor deposition process. The controlled addition of up to $\sim$13% of O_2 to the CH_4 plasma reacting gas flow was found to promote the growth of the CNTs by oxidizing the amorphous carbon and removing the active H_2 radicals. However, excessive amounts of O_2 (i.e., fraction of $O_2 > \sim$13%) and H_2 were found to play a negative role in the growth of the CNTs. The control of the density and length of the CNTs was also achieved by varying the H_2 plasma reduction time and CH_4 plasma reacting time, respectively. Longer H_2 reduction pretreatment of the catalytic metal islands resulted in the formation of a less dense CNT forest with craters. When the growth time of the CNTs was increased to $\sim$20 min, their length was increased to $\sim$10 µm. However, when the growth time of the CNTs exceeded 20 min, their length was significantly decreased, indicating that the continuous presence of O_2 in the CH_4 plasma destroys the preformed CNTs due to the oxidation reaction.

I. INTRODUCTION

Thermal chemical vapor deposition (CVD) processes have been used by numerous researchers to grow carbon nanotubes (CNTs) on a catalytic metal medium because of their simplicity.[1–3] However, the repeatability of the stable growth of CNTs in thermal CVD processes is not easy to achieve. This is because the relatively high-temperature environment in thermal CVD processes (e.g., tube furnace) causes the hydrocarbon sources to be directly decomposed into amorphous carbon, which results in the coking of the catalytic particles. Unlike thermal CVD processes, plasma-enhanced CVD (PECVD) processes have the advantage of maintaining a precisely controlled local temperature condition on the heating stage and vacuum operating conditions, which minimize the coking of the catalytic particles due to amorphous carbon contamination in the plasma reactor.

Given the advantages of PECVD processes, we used a microwave plasma-enhanced chemical vapor deposition (MPECVD) process to grow CNTs directly on a commercially available metal (SUS304) substrate without preformed catalytic metal particles, which can be easily adapted to industrial applications. On the basis of guidelines suggested by numerous researchers,[4–7] we performed a series of MPECVD experiments to grow CNTs. However, the growth of CNTs on the surface of a catalytic metal substrate was rarely achieved in our MPECVD-based approach. Instead, we repeatedly observed that amorphous carbon-made particle islands were formed over the entire surface of the metal substrate, indicating that the stable growth conditions of CNTs, in general PECVD processes, exist in a very narrow window.

In this work, we conduct a systematic investigation to find the stable formation conditions of CNTs grown on the as-received metal alloy substrates (i.e., SUS304) without depositing additional transition metal catalysts (e.g., Ni, Fe, Mo, or Co) in an MPECVD process. We also suggest possible strategies to control the length and density of CNTs grown directly on a metal alloy substrate.

II. EXPERIMENTAL

The growth of the CNTs was performed in an MPECVD reactor (150 mm in diameter $\times$ 330 mm in height). The micron-sized fibrous stainless steel (SUS304) metal mesh substrate (25 mm in diameter $\times$ 1mm in thickness) was placed on a graphite heating stage at ~720 °C. Here, a ring-type substrate holder design was used to press the circumference of the metal alloy substrate so that it prevented the thermal expansion-induced bending of the thin metal alloy substrate after PECVD. H_2 reduction treatment (i.e., H_2 plasma) was then performed to activate the metal islands on the surface of the metal substrate. The flow rates of the reacting gases in the microwave plasma reactor used to grow the CNTs via 2 GHz microwave-based CH_4 plasma were controlled by mass flow controllers. The mixed reacting gases were injected into the MPECVD reactor with flow rates of methane (~10 sccm), hydrogen (up to ~50 sccm), and oxygen (up to ~5 sccm) with a total pressure of ~15 Torr. The microwave plasma input power was maintained at 500 W during the growth of the CNTs. The elemental analysis of the metal substrate was performed by energy dispersive x-ray (EDX) analysis, and it was found that the SUS304 metal substrate used in this study was composed of Fe (~70 wt%), Cr (~20 wt%), Ni (~7 wt%), C (~2 wt%), and S (~1 wt%). The physical properties of the as-grown carbon nanostructures were characterized by field-emission scanning electron microscopy (FE-SEM; Hitachi Ltd., Tokyo, Japan, Model S-4200) operated at ~15 kV, transmission electron microscopy (TEM; JEOL Corp., Japan, Model JEM 2011) operated at ~100 kV, and a Raman spectrometry (Renishaw Co., Gloucestershire, UK).

III. RESULTS AND DISCUSSION

It is important to know the effect of the H_2 reduction time on the surface of a metal substrate, because the growth of CNTs takes place on the catalytic metal islands formed on the metal substrate after the H_2 reduction process. It is known that the surface diffusion of transition metal atoms enhanced by hydrogen plasma ion bombardment results in the formation of metal islands. Figure 1 shows the SEM images of the evolution of the SUS304 metal substrate surface as a function of the H_2 plasma reduction time. As one can see, the average size of the metal particle islands increased with increasing H_2 reduction time. Simultaneously, the density of the metal islands was observed to decrease with increasing H_2 reduction time. These results imply that the size and density of the as-grown CNTs can be controlled by varying the H_2 reduction time, because the diameter of the CNTs is known to be very similar to that of the seeded catalytic metal particles.[8,9]

After the H_2 reduction process (i.e., H_2 plasma treatment), a controlled amount of CH_4 as a carbon source and H_2 as an etching agent were added to the MPECVD reactor to grow CNTs on the surface of the fibrous metal substrate. Figure 2 shows the mixture of amorphous carbon islands and some CNT networks formed on the fibrous metal surface. It turns out that the addition of hydrogen was unfavorable for the growth of the CNTs, and that it even etched out the preformed CNTs.

At this point, we turned our attention to the role of oxygen in the MPECVD-based growth of the CNTs. Medium oxidizers (e.g., water or acetone) are known to act as an effective promoter of the growth of the CNTs by (i) oxidizing the amorphous carbon, which otherwise results in the coking of the catalytic metal particles and (ii) removing active hydrogen radicals, which play a negative role in the growth of the CNTs.[10,11] To verify the role of oxygen, we added a controlled amount of O_2 to the CH_4 plasma reactor without the addition of H_2. Figure 3 presents the morphological change of the CNTs as a function of the amount of oxygen added. One can clearly observe in Figs. 3(a) and 3(b) that the growth of the CNTs was enhanced with an increasing amount of oxygen up to a fraction of ~13% in the total reacting gas flow. However, the addition of too much oxygen (i.e., fraction of O_2 > ~13%) induced the oxidation of the preformed CNTs, as shown in Fig. 3(c). To observe the combined effect of H_2 and O_2 on the growth of the CNTs, we then added various mixture ratios of H_2 (up to ~50%) and O_2 (fixed at ~13%) to the CH_4 plasma. When the amount of H_2 was increased, the CNTs were significantly destroyed, confirming that an H_2-rich environment is unfavorable for the homogeneous growth of the CNTs.

The surface of the metal substrate before and after the MPECVD process is shown in Fig. 4(a). After the MPECVD process, the gray SUS304 metal substrate was covered with a black thin film. The SEM image in Fig. 4(b) shows that the black thin film formed was composed of CNTs grown in the radial direction of the fibrous metal substrates. The TEM image of the sampled CNTs shown in Fig. 4(c) presents the mixture of polydisperse multiwalled CNTs (MWCNTs). In addition, Raman spectrum in Fig. 4(d) corroborates the presence of MWCNTs by showing the strong peaks at 1350 cm^{-1} [i.e., D mode, disorder-induced band originating from carbon (or metal) impurities or defects] and 1576 cm^{-1} (i.e., G mode, stretching mode in the graphite plane) without significant spectrum at the low frequency (i.e., radial breathing mode). The full width at half-maximum (FWHM)-based D/G ratio at 1350 and 1576 cm^{-1} (i.e., I_{1350}/I_{1576}) is ~0.9, indicating that the as-prepared CNTs in this approach had a relatively high degree of graphitization.

Here, to find the relation between the diameters of the as-grown CNTs and metal islands, we grew CNTs on the
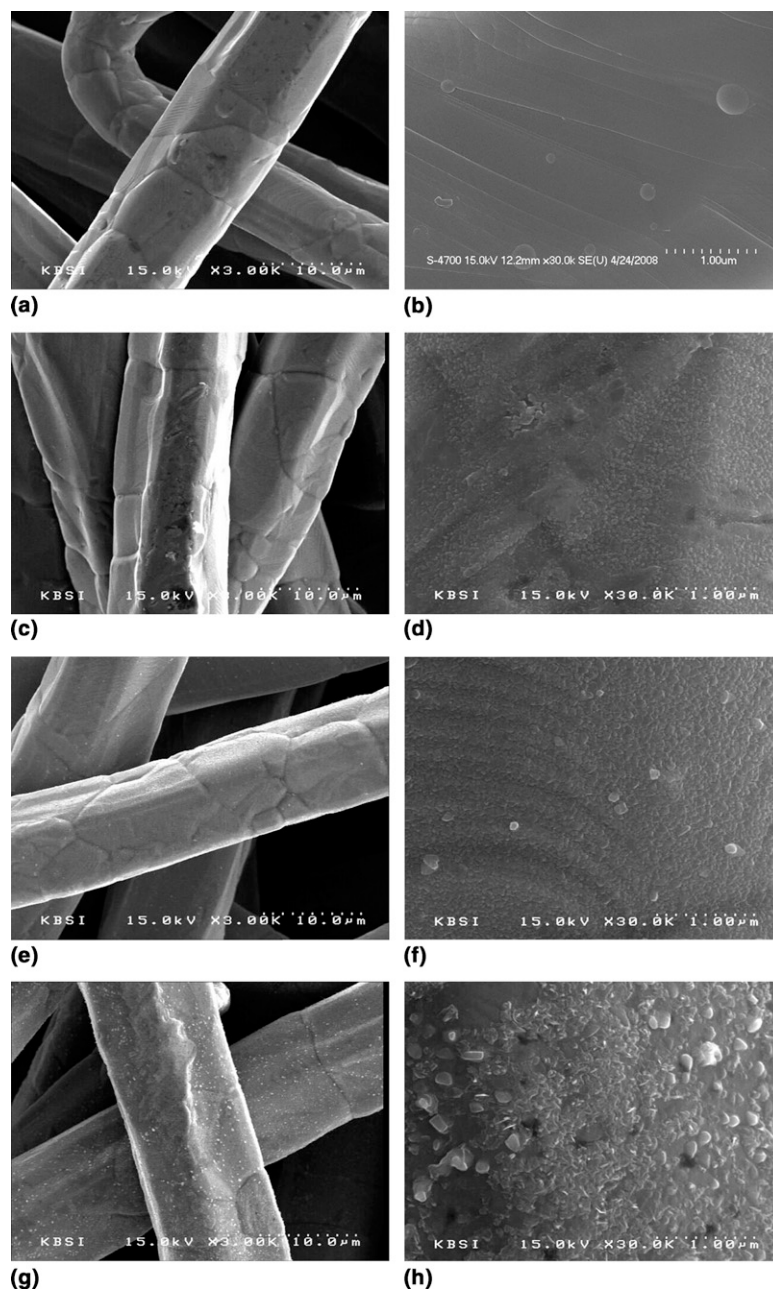
FIG. 1. SEM images of the surface of the metal mesh substrate treated by hydrogen reduction for (a, b) 0 min, (c, d) 1 min, (e, f) 5 min, and (g, h) 10 min.

metal substrates treated by various H_2 reduction times, namely 1 min, 5 min, and 10 min. The results of the TEM image analysis indicated that the diameter of the resulting CNTs was $\sim16 \pm 2$ nm for all three H_2 reduction times, implying that the catalytic particle islands with diameters of $\sim$several tens to $\sim$several hundred nanometers, as shown in Figs. 1(f) and 1(h), were not effectively seeded to grow CNTs in our MPECVD process. This result also implies that the range of diameters of the CNTs, which can be achieved in this study, is limited (i.e., average CNT's diameter $< \sim20$ nm). Simultaneously, it opens up the possibility of controlling the density of the CNT forests, meaning that the surface

of particle islands with larger than 20 nm can be served as a CNT-free zone.

Because the H_2 reduction time strongly affected the density and size distribution of the metal particle islands, we believed that it would be possible to control the density of the CNTs by varying the H_2 reduction time. To do so, we first pretreated the fibrous metal substrate with various H_2 reduction times before the growth of the CNTs. Then, the optimum growth conditions of the CNTs (i.e., $CH_4 = 10$ sccm, $O_2 = 1.5$ sccm) found previously were applied. The resulting CNTs were then analyzed by an FE-SEM. As shown in Fig. 5(a), densely packed CNTs were formed at an H_2 reduction
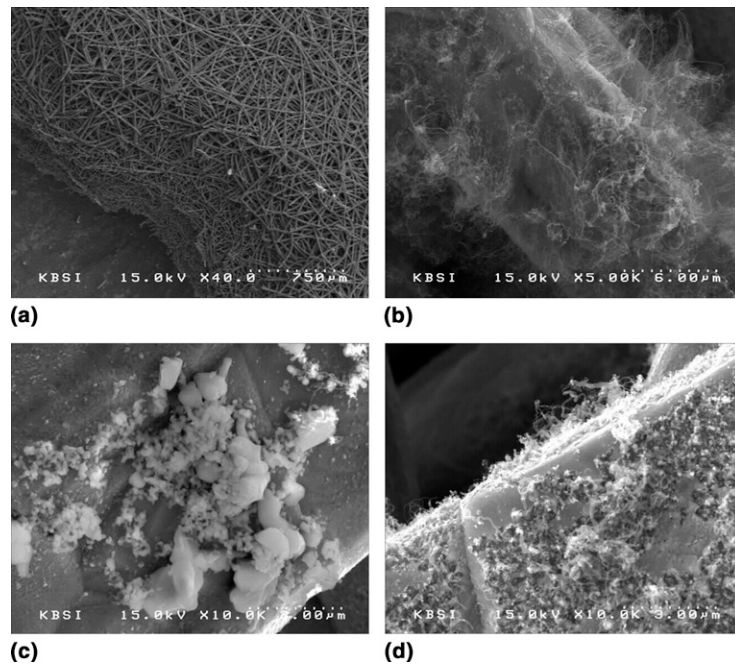
FIG. 2. SEM images of (a) surface of the fibrous metal substrate, (b) CNT networks, (c) amorphous carbon islands, and (d) mixture of CNTs and amorphous carbon grown on the surface of the fibrous metal substrate treated by CH_4–H_2 plasma. Experimental conditions: H_2 reduction time = 1 min, CH_4 = 5 sccm, H_2 = 100 sccm, CNT growth time = 15 min, power = 500 W, total pressure = 15 Torr, T = 720 °C.
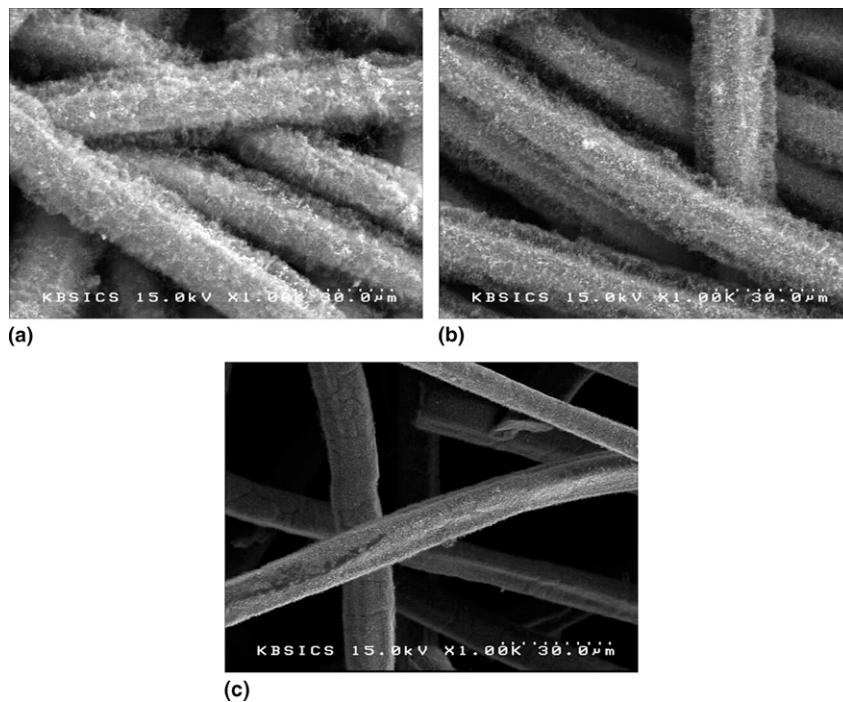

FIG. 3. Effect of O_2 addition on the growth of CNTs. Experimental conditions: H_2 reduction time = 1 min, power = 500 W, total pressure = 15 Torr, T = 720 °C, CNT growth time = 10 min, CH_4 = 10 sccm, H_2 = 0 sccm with (a) O_2 = 0.15 sccm, (b) O_2 = 1.5 sccm, and (c) O_2 = 5 sccm.

time of ∼1 min, which generated metal islands with an average primary size of ∼20 nm [see Fig. 1(d)]. However, when the H_2 reduction time was increased to ∼5 min, the density of the CNTs was clearly decreased, as shown in Fig. 5(b), due to the formation of less dense metal

islands with an average diameter of ∼100 nm [see Fig. 1(f)]. After 10 min of H_2 reduction, the distribution of the CNTs was inhomogeneous, due to the polydispersed size distribution of the metal islands with an average size of ∼200 nm [see Fig. 1(h)], so that a CNT
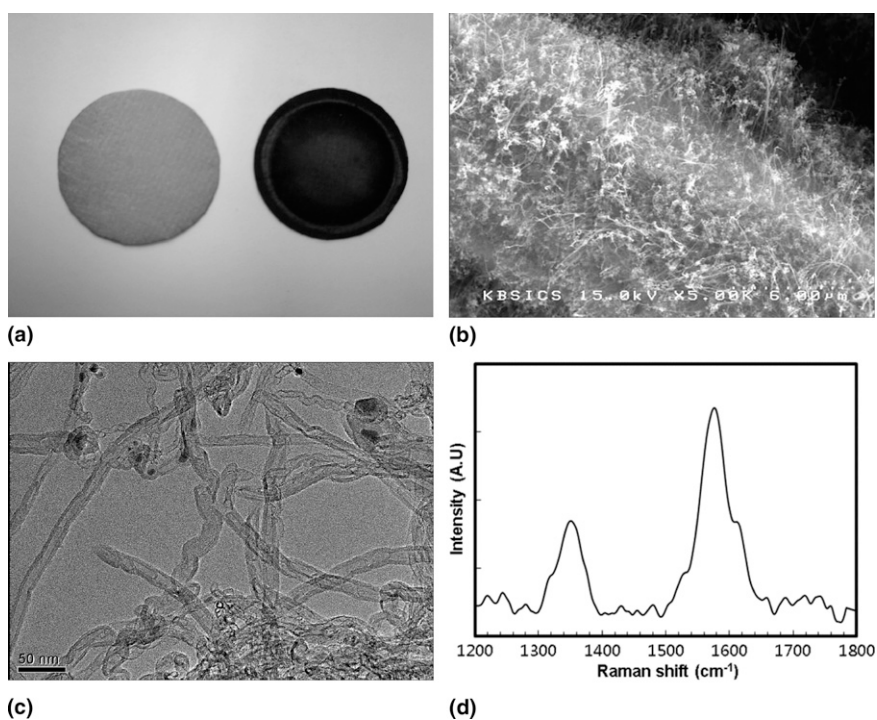
FIG. 4. MPECVD-assisted synthesis of CNTs. (a) Image of raw metal mesh substrate (left) and black carbon nanostructures grown on the metal mesh substrate (right), (b) SEM image of CNTs grown in radial direction of fibrous metal mesh substrate, (c) TEM image, and (d) Raman spectrum of the mixture of polydisperse MWCNTs sampled from the black thin film formed on the metal mesh substrate.
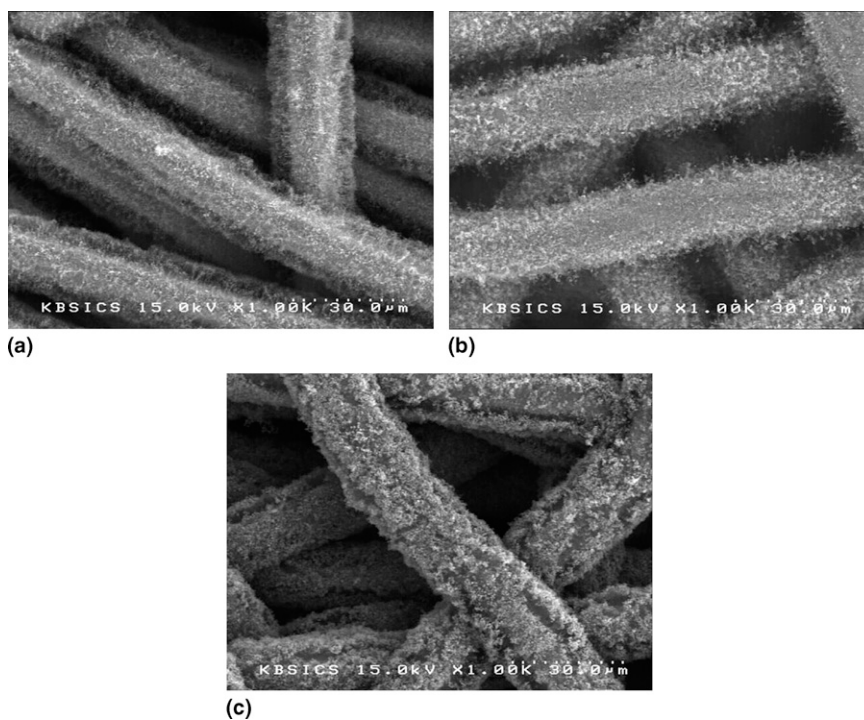

FIG. 5. Density control of CNTs. Experimental conditions: power = 500 W, total pressure = 15 Torr, T = 720 °C, CNT growth time = 10 min, CH_4 = 10 sccm and O_2 = 1.5 sccm with H_2 reduction time of (a) 1 min, (b) 5 min, and (c) 10 min.
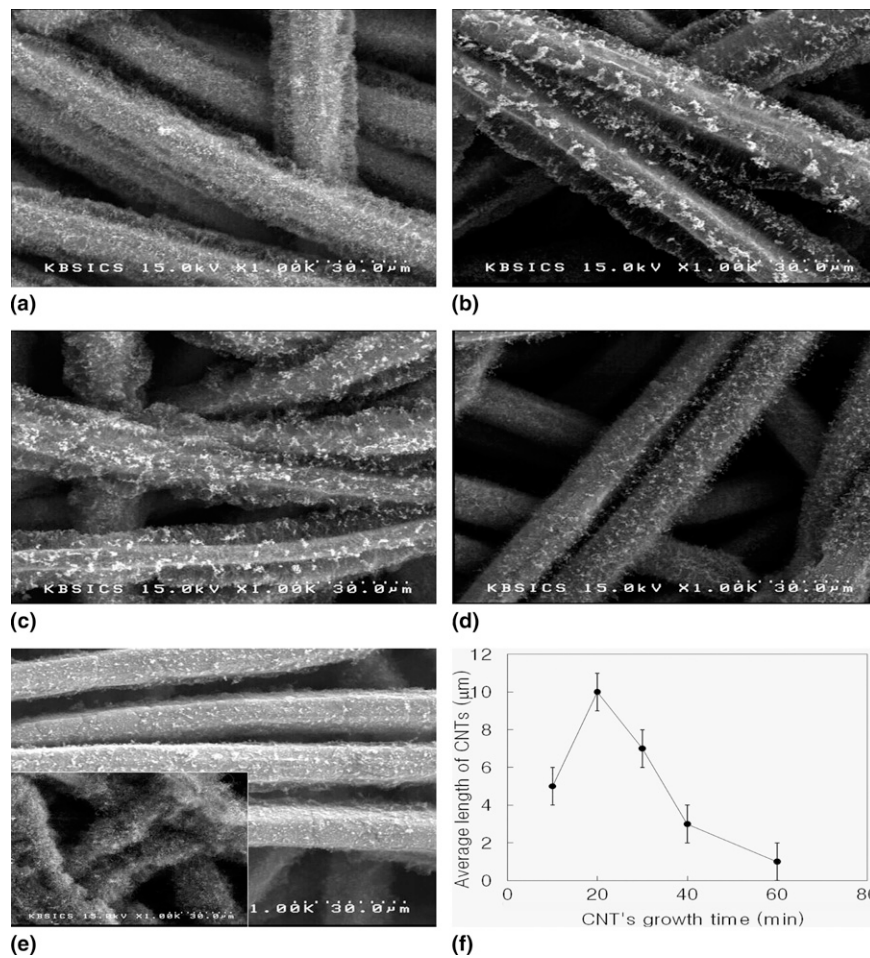
FIG. 6. Control of the length of the CNTs. Experimental conditions: H_2 reduction time = 1 min, power = 500 W, total pressure = 15 Torr, T = 720 °C, CH_4 = 10 sccm, H_2 = 0 sccm, and O_2 = 1.5 sccm with CNT growth time of (a) 10 min, (b) 20 min, (c) 30 min, (d) 40 min, (e) 60 min: the center area of the metal substrate (where the inset shows the edge of the metal filter), and (f) the evolution of the length of the CNTs as a function of the CNT growth time in the MPECVD plasma process.

forest with craters (i.e., CNT-free zone) was clearly observed, as shown in Fig. 5(c).

To determine the controllability of the length of the CNTs on the fibrous metal substrates, we varied their growth time (i.e., CH_4 plasma reacting time). Highly dense and straight CNTs oriented in the radial direction of the fibrous metal substrates were grown for CNT growth times (t_G) of up to ∼20 min, as shown in Figs. 6(a) and 6(b). The average length of the CNTs reached around ∼10 μm at t_G = 20 min [see Fig. 6(b)]. However, once the growth time exceeded ∼20 min, the average length and density of the CNTs began to be significantly decreased, as shown in Figs. 6(c) and 6(d). After a CH_4 plasma reacting time of 60 min, we observed that the center of the metal substrate turned a brownish color, indicating that the preformed CNTs and metal islands were strongly oxidized by the relatively long-term presence of O_2 [see Fig. 6(e)]. However, some of the CNTs in the edge area of the metal substrate survived the severe oxidation, and were observed to have long and

curled nanostructures, as shown in the inset in Fig. 6(e). Figure 6(f) summarizes the evolution of the average length of the CNTs as a function of the CNT growth time. It is clearly observed that the presence of O_2 promotes the growth of the CNTs in the early stage of the plasma reaction, whereas it eventually leads to the destruction of the preformed CNTs by the strong oxidation process in the later stages of the plasma reaction.

IV. CONCLUSIONS

In this work, we described the stable growth of CNTs on the surface of as-received fibrous metal alloy mesh substrates (i.e., SUS304) without adding any pure transition metal particles (e.g., Ni, Fe, or Mo) by varying the amount of oxygen and hydrogen in the MPECVD process. To reproduce the stable growth of the CNTs, the addition of a controlled amount of oxygen (i.e., fraction of O_2 up to ∼13%) to the CH_4 plasma was required. However, the addition of an excessive amount of O_2

exceeding $\sim$13% caused the preformed CNTs to be destroyed by the strong oxidation process. Unlike the role of O_2 in the MPECVD process, the addition of H_2 resulted in the formation of a mixture of amorphous carbon islands and some loose CNT networks on the surface of the metal substrates, implying that the excessive hydrogen radicals in the CH_4 plasma play a negative role in the growth of the CNTs. The control of the density and length of the CNTs was also achieved by varying the H_2 reduction time before the CNT growth reaction and the reaction time for the growth of the CNTs, respectively. The precise control of (i) the amount of oxygen and hydrogen added, (ii) the H_2 reduction time for the metal substrate, and (iii) the hydrocarbon plasma reacting time in the MPECVD processes make it possible to reproduce the stable growth of CNT forests with controlled length and density.

ACKNOWLEDGMENT

REFERENCES

1. O.A. Nerushev, M. Sveningsson, L.K.L. Falk, and F. Rohmund: Carbon nanotube films obtained by thermal chemical vapour deposition. *J. Mater. Chem.* **11,** 1122 (2001).
2. L. Delzeit, C.V. Nguyen, R.M. Stevens, J. Han, and M. Meyyappan: Growth of carbon nanotubes by thermal and plasma chemical vapour deposition processes and applications in microscopy. *Nanotechnology* **13,** 280 (2002).
3. L. Ci, S.M. Manikoth, X. Li, R. Vajtai, and P.M. Ajayan: Ultrathick freestanding aligned carbon nanotube films. *Adv. Mater.* **19** (20), 3300 (2007).
4. Y. Chen, Z.L. Wang, J.S. Yin, D.J. Johnson, and R.H. Prince: Well-aligned graphitic nanofibers synthesized by plasma-assisted chemical vapor deposition. *Chem. Phys. Lett.* **272,** 178 (1997).
5. V.I. Merkulov, D.H. Lowndes, Y.Y. Wei, G. Eres, and E. Voelkl: Patterned growth of individual and multiple vertically aligned carbon nanotubes. *Appl. Phys. Lett.* **76,** 3555 (2000).
6. G.W. Ho, A.T.S. Wee, J. Lin, and W.C. Tjiu: Synthesis of well-aligned multiwalled carbon nanotubes on Ni catalyst using radio frequency plasma-enhanced chemical vapor deposition. *Thin Solid Films* **388,** 73 (2001).
7. M. Meyyappan, L. Delzeit, A. Cassell, and D. Hash: Carbon nanotube growth by PECVD: A review. *Plasma Sources Sci. Technol.* **12,** 205 (2003).
8. R. Andrews, D. Jacques, A.M. Rao, T. Rantell, F. Derbyshire, Y. Chen, J. Chen, and R.C. Haddon: Nanotube composite carbon fibers. *Appl. Phys. Lett.* **75,** 1329 (1999).
9. H. Ago, S. Ohshima, K. Uchida, and M. Yumura: Gas-phase synthesis of single-wall carbon nanotubes from colloidal solution of metal nanoparticles. *J. Phys. Chem. B* **105,** 10453 (2001).
10. K. Hata, D.N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima: Water-assisted highly efficient synthesis of impurity-free single-walled carbon nanotubes. *Science* **306,** 1362 (2004).
11. S.H. Kim and M.R. Zachariah: In-flight kinetic measurements of the aerosol growth of carbon nanotubes by electrical mobility classification. *J. Phys. Chem. B* **110,** 4555 (2006).