JOURNAL OF MATERIALS SCIENCE **38** (2003) 4933–4939

Pretreatment of stainless steel substrate surface for the growth of carbon nanotubes by PECVD

DALKEUN PARK*
School of Chemical Engineering, Seoul National University, San 56-1 Shillim-dong, Kwanak-gu, Seoul 151-744, Korea
E-mail: pdk2003@snu.ac.kr

YOUNG HOON KIM, JOONG KEE LEE
Eco-Nano Research Center, Korea Institute of Science & Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

Multiwalled carbon nanotubes were grown from acetylene and hydrogen gas mixture directly on stainless steel plates by rf powered PECVD and then electric double layer capacitors were fabricated from them without any further treatment. It was found that suitable pretreatment of stainless steel substrates was required for the satisfactory growth of carbon nanotubes on them. In this study substrates were polished, etched in HF solution and then treated with hydrogen plasma before the growth of carbon nanotubes. SEM shows that the surface of the substrate became smooth after polishing. It was severely etched to reveal grains of stainless steel after dipping in HF solution. With hydrogen plasma treatment the grains become more rounded in shape and grew in size. When the grains size was tens of nanometers, carbon nanotubes were grown. Exposing substrates to the hydrogen plasma for 10 min or longer caused the grains to grow larger and the growth of carbon nanotubes became poorer. Carbon nanotubes grown in this study were mutiwalled and curly in shape. Capacitors made from the carbon nanotubes showed initial specific capacitance in the range of 80–100 F/g.

1. Introduction

Carbon nanotubes have extraordinary properties that come from their unique structure of graphite sheets rolled into tubes [1]. Carbon nanotubes have very high tensile strength and resilience, and their electric current carrying capacity and heat transmission can be high. They are very good for field emission of electrons at low voltage levels. Many applications are proposed to make use of them: nano-scale electronic devices, field emission display, electrodes for secondary lithium batteries, storage of gases, tips for scanning tunnelling microscopy (STM), supercapacitors, composite material, etc. However, to make use of carbon nanotubes properly some means should be available to grow carbon nanotubes in specific locations, orientations, shapes and sizes. Currently there are three ways to make carbon nanotubes: chemical vapor deposition (CVD), laser ablation and arc discharge. Arc discharge produces relatively defect-free carbon nanotubes, but purification is needed for the removal of carbonaceous particles. Laser ablation is costly and difficult to scale-up for industrial production. CVD operates at relatively low temperatures, thus produces carbon nanotubes riddled with defects. On the other hand CVD is very versatile and amenable to scale-up. Besides it allows carbon nanotubes to grow directly on certain surfaces as demonstrated by many investigators. Direct growth of carbon nanotubes on appropriate substrates has advantages in some applications. The alternative to direct growth on substrates is a sequence of processes consisting of synthesis and purification of carbon nanotubes in bulk, and positioning them on the chosen surface in an appropriate manner. Among others, electrodes of electric double layer capacitor (EDLC) would be a good example that elucidates potential merits of carbon nanotubes synthesized on substrates.

EDLCs are attractive energy storage devices particularly for applications that demand high power and long cycle life [2]. One of the key factors that determine the performance of EDLCs are the properties of the electrodes. Carbons with very high specific surface area such as activated carbon powder and activated carbon fiber are often used as electrode materials. But they usually have a wide pore size distribution, thereby a significant portion of pore surface area resides in micropores which are not readily accessible to ions thus not contributing to capacitance. With carbon nanotubes, in contrast to activated carbons, all surfaces can be available to the access of ions. Recently several research groups studied EDLCs made of carbon nanotube

*Author to whom all correspondence should be addressed.

electrodes [3–5]. However, they prepared carbon electrodes from carbon nanotubes, which were catalytically grown, through processing steps usually adopted for activated carbons: purification of powdery carbon nanotubes, forming with or without carbon black and binders, and then attaching to current collectors. Synthesis of carbon nanotubes directly on metallic substrates, which can act as current collectors, will greatly simplify the preparation of carbon electrodes. However, synthesis of carbon nanotubes on metallic or electrically conducting substrates proved rather difficult compared to that on insulators such as glass or silicon wafers [6].

Investigators employed various kinds of CVD in the synthesis of carbon nanotubes on metal substrates: thermal CVD [7], DC PECVD [8], MPECVD [9, 10]. Emmenegger and coworkers [7] synthesized carbon nanotubes on aluminum substrates with thermal CVD and made EDLCs with them. But they coated the aluminum substrate with $FeNO_3$ by spin coating before CVD in order to provide nuclei for carbon nanotubes synthesis like in CVD on silicon wafer. Huang and coworkers [8] synthesized carbon nanotubes on nickel substrates by hot filament aided DC PECVD, and observed that the diameter of carbon nanotubes varied with plasma power. Kuang and coworkers [10] synthesized carbon nanotubes on nickel and stainless steel with MPECVD. Wang and Yao [9] also employed MPECVD to synthesize carbon nanotubes on stainless steel. They tested them for field emission. In the case of solid substrates, unlike catalyst thin films on insulators or semiconductors, a part of the substrate should be transformed into catalyst particles. The mechanisms for the formation of nano-sized catalyst particles and their detachment form solid substrates are not well understood, although several models were proposed by investigators [10].

In this study we employed rf powered plasma enhanced chemical vapor deposition for the synthesis of carbon nanotubes directly on metallic substrates, which were pretreated in various ways. We also fabricated electric double layer capacitors, EDLCs, with carbon nanotubes synthesized on stainless steel and tested their charge-discharge characteristics.

2. Experimental

Stainless steel (type 304) plates cut into 10×30 mm^2 rectangular pieces were used as substrates for growing carbon nanotubes in this study. Pretreatment of substrates consisted of three steps: polishing, etching with HF solution and hydrogen plasma treatment. Polishing of substrates was done either mechanically with sandpaper or electrochemically (electropolishing) in order to remove contaminants and stains on the surface. Then the substrates were cleaned in an ultrasonic bath with acetone and methanol sequentially. Afterwards they were dipped into HF solution for a few minutes to etch the substrate surface. The concentration of HF and dipping time were varied to test their effects on subsequent PECVD. Following a rinse with distilled water, the substrates were put onto the heating block of the PECVD reactor.

After the reactor was evacuated to 0.13 Pa and the temperature of the heating block was raised to the desired temperature, hydrogen was fed into the reactor and plasma treatment, was carried out for a specified time. The duration of the hydrogen plasma treatment was from 2.5 min to 20 min. After the hydrogen plasma treatment, acetylene gas was fed into the reactor to start the synthesis of carbon nanotubes. Typical conditions of carbon nanotube growth are as follows: pressure 130–1300 Pa, temperature of substrate holder 600–850°C, RF plasma power 60–100 W, acetylene flow rate 7–30 sccm, hydrogen flow rate 20–90 sccm. The reactor volume above the substrate holder was approximately 10^{-3} m^3. Deposited carbon nanotubes were examined with SEM and Raman spectroscopy.

We fabricated EDLCs using carbon nanotubes deposited on stainless steel plates without any further treatment. Stainless steel substrates were used as current collector. We used either organic or aqueous electrolyte to fabricate EDLCs. For an organic electrolyte we used lithium hexafluorophosphate dissolved to 1 M in a 1:1 mixture of ethylene carbonate and diethyl carbonate. For an aqueous electrolyte we used KOH solution. Assembly of the capacitor was carried out in a dry room. Charge and discharge characteristics of capacitors were measured.

3. Results and discussion

Effects of pretreatment on the substrate surface morphology are well illustrated in Fig. 1. Polishing of the substrate made the substrate surface smooth (Fig. 1a). Streaks that appear in Fig. 1a are the result of mechanical polishing. But subsequent etching with HF solution rendered roughening of the substrate surface in nanoscale and baring grains of stainless steel (Fig. 1b). After treatment with hydrogen plasma grains of the substrate surface became more rounded and grew in size to tens of nanometers (Fig. 1c). Through subsequent PECVD with acetylene precursor carbon nanotubes could be synthesized on the stainless steel substrate (Fig. 2).

Carbon nanotubes were densely grown all over the metal substrate. They were not straight, but curly in shape, tens of microns in length and 30 to 100 nm in diameter, roughly the same size of grains on the substrate after hydrogen plasma treatment. Raman spectroscopy showed peaks at 190, 1286, 1,597 cm^{-1} that indicate carbon nanotubes are multiwalled with carbonaceous particles embedded in them.

To elucidate the role of pretreatment of the substrate, conceptual steps of carbon nanotubes growth are schematically compared in Fig. 3 for CVD on catalyst-coated silicon wafer (Fig. 3a) and on stainless steel substrate of this study (Fig. 3b). In the synthesis of carbon nanotubes on insulating or semi-conducting substrates the general practice is to coat a very thin layer of catalyst materials, such as iron or nickel or cobalt on substrate (step (I) of Fig. 3a), and then to transform it to islands of nano-sized catalyst particles either before or during the CVD (step (II) of Fig. 3a).

Carbon nanotubes grow from those catalyst particles by CVD with precursors (step (III) of Fig. 3a). The diameter of carbon nanotubes is correlated to the

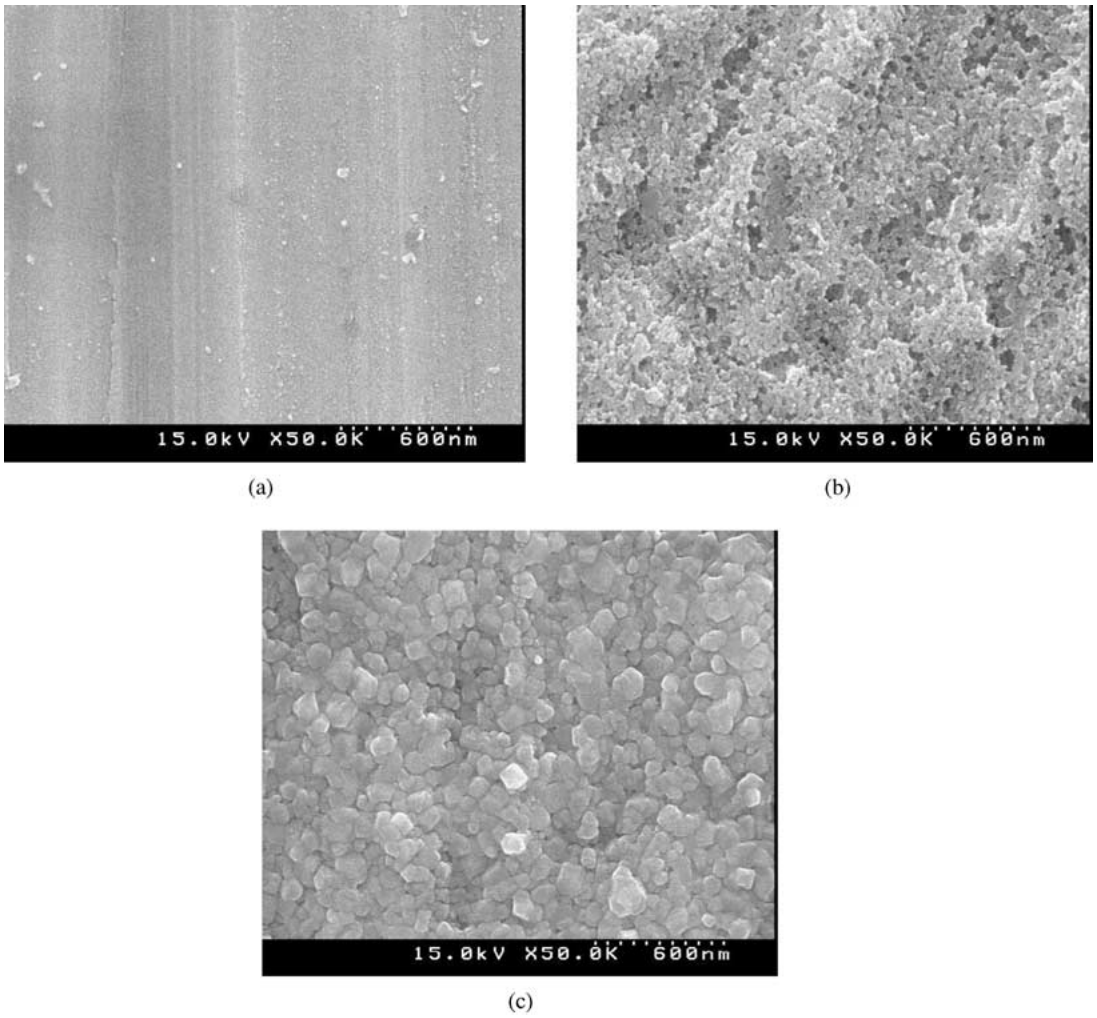


Figure 1 SEM of substrate surface after different pretreatment: (a) after polishing, (b) after polishing and etching with HF solution and (c) after polishing, etching with HF solution and hydrogen plasma treatment.

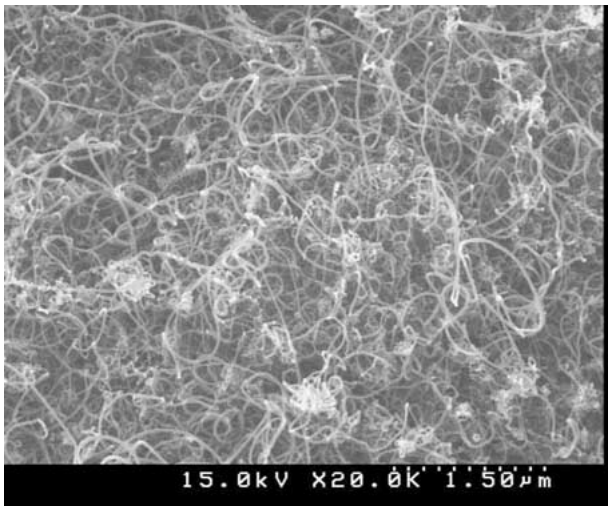


Figure 2 SEM of carbon nanotubes deposited on stainless steel substrate.

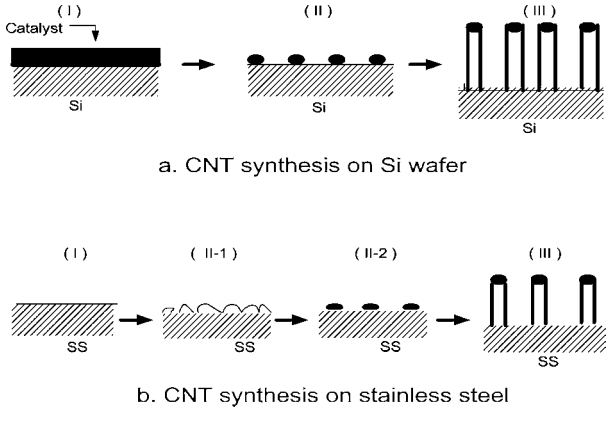


Figure 3 Schematic diagram showing effects of pretreatment.

size of the catalyst islands formed from the deposited thin film. Transformation of catalyst film into particles can be carried out either deliberately before CVD by thermal treatment or during CVD. In the latter case transformation from film to particle occurs under CVD condition. If the catalyst particles or islands are too large, synthesis of carbon nanotubes is not possible [11]. Therefore it is very important to have the right size of catalyst particles. In the case of transforming of thin film into islands on a substrate by thermal treatment the size of islands, and thus the diameter of the carbon nanotubes, is dependent on the thickness of the deposited film [11, 12]. Yudasaka *et al*. reported that round Ni particles with a diameter of 20–30 nm were formed from 5–7 nm thick Ni thin film coated on quartz [11].

The size of catalyst particles or carbon nanotubes also depend on the ammonia treatment conditions before thermal CVD [13] or sputtering conditions for the thin film coating in the case of microwave PECVD [14]. But mechanisms of CVD synthesis of carbon nanotubes on substrates are not clearly understood yet. Basically there are two models, tip growth model and base growth model [15]. According to the tip growth model, carbon atoms decomposed from precursor molecules come into contact with a nano-size metallic catalyst particle which is located on the tip of a carbon nanotube. Then carbon atoms move toward the hidden surface of the catalyst particle and form into a carbon nanotube thereby lifting the catalyst particle from the substrate surface as the carbon nanotube grows in length. Therefore, catalyst particles remain at the tips of the carbon nanotubes as they grow upward. Actually many investigators observed catalyst particles on the tips of carbon nanotubes [16–18].

In the base growth model, catalyst particles are firmly anchored on the surface of the substrate and the addition of carbon atoms to carbon nanotubes, i.e., growth of carbon nanotubes, occurs at the top of the catalyst particle. In this case the tips of carbon nanotubes are free of catalyst particles as was observed by many investigators [19–21]. In either model, the diameter of the synthesized carbon nanometers is closely correlated to the size of catalyst particle. In step III of Fig. 3, the tip growth model is shown as an example only. The base growth model can be applicable as well. In the case of solid substrates, unlike catalyst thin films on insulators or semiconductors, a part of the substrate should be transformed into catalyst particles. The mechanisms for the formation of nano-sized catalyst particles and their detachment from solid substrates are not well understood yet, although some investigators proposed models for them [10]. But observing change of substrate surface morphology we presume that pretreatment of step II-1 (etching with HF solution) and II-2 (hydrogen plasma treatment) of Fig. 3b is conceptually similar to transformation of thin film into particles (step II of Fig. 3a).

Proper pretreatment of the substrate was very important for the successful synthesis of carbon nanotubes in our PECVD system. It was possible to render the substrate surface covered with grains of a certain size with polishing and hydrogen plasma only, that is bypassing the HF etching step. Fig. 4 shows the substrate surface which underwent polishing and hydrogen plasma treatment, but without etching with HF solution. As far as the range of grain size is concerned, the substrate surface looked roughly the same as that pretreated through polishing, etching and hydrogen plasma (Fig. 1c). However, in the PECVD system of this study, synthesis of carbon nanotubes did not occur on the substrate of Fig. 4. In order to search for other clues we analyzed the composition of substrate surface after each step of pretreatment by EPMA (Electron Probe Micro Analysis, JEOL JXA-8600). Chemical analysis of the substrate surface showed that etching with HF solution caused preferential removal of iron. Neither polishing nor hydrogen plasma changes the composition of the surface

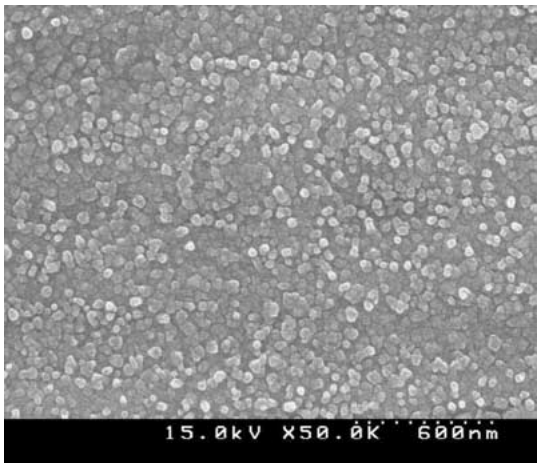


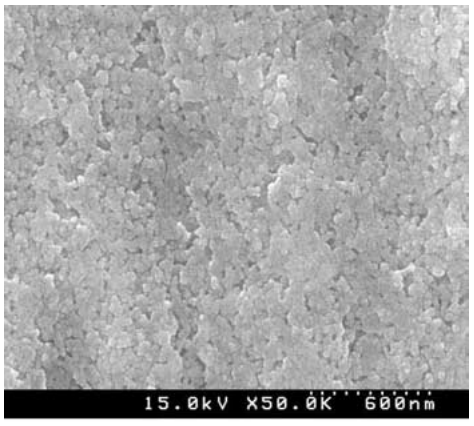
Figure 4 SEM of substrate surface after hydrogen plasma treatment for 10 min without etching with HF solution.

to any significant extent. Thus etching with HF solution made the surface of the substrate of Fig. 1c relatively Fe deficient compared to that of Fig. 4. But the role of HF etching is not clear at the present time and we cannot conclude that less Fe on the substrate surface is conducive to the formation of carbon nanotubes. We found that dipping in 25% HF solution for 200 s was most appropriate condition. Wang and Yao reported growth of carbon nanotubes on stainless steel without pretreatment with their microwave PECVD system [9]. This is believed to be due to different processing conditions such as plasma environment.

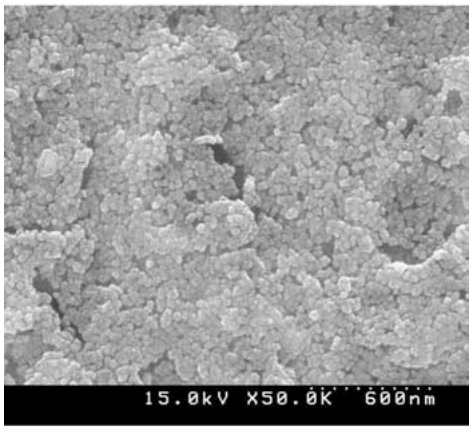
As was discussed above, the size of the grains is closely related to the diameter of the nanotubes synthesized. Therefore, just like catalyst islands, which are transformed from a thin film on silicon wafers in the case of thermal CVD as shown in stage (II) of Fig. 3a, the size of grains should be within an appropriate range for the synthesis of carbon nanotubes on stainless steel substrates. Then the pretreatment condition of the substrate should be favorable to the formation of the right morphology of the substrate surface. We observed that the morphology of the substrate surface differed depending on the duration of the hydrogen plasma treatment. Fig. 5 shows the surface morphology after 2.5, 5 and 20 min of plasma treatment. Note that Fig. 1c is for 10 min of hydrogen plasma treatment. After 2.5 min of hydrogen plasma treatment, sharp edges of grains, that were visible for the substrate surface fresh after etching with HF solution (as shown in Fig. 1b), became smoother (Fig. 5a).

After 5 min of plasma treatment, individual grains became more rounded in shape (Fig. 5b). Then after 10 min of hydrogen plasma treatment grains became larger and even more rounded in shape (Fig. 1c). After 20 min of plasma treatment, grains became even bigger (Fig. 5c). Therefore we can see that under the hydrogen plasma environment at high temperature, the surface morphology of the substrate changes with time and grains grow in size.

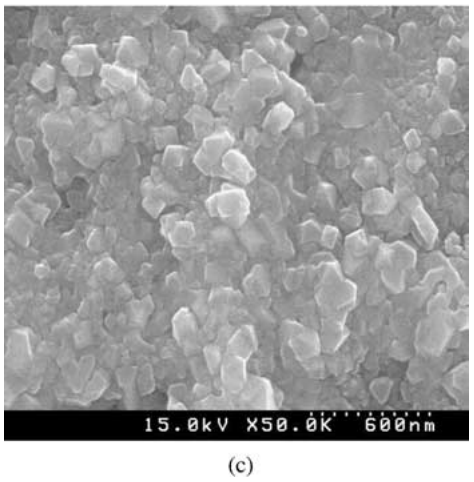
Fig. 6 shows carbon nanotubes grown on the substrates that had been treated with hydrogen plasma for 2.5 (Fig. 6a), 10 (Fig. 6b) and 20 min (Fig. 6c),



(a)

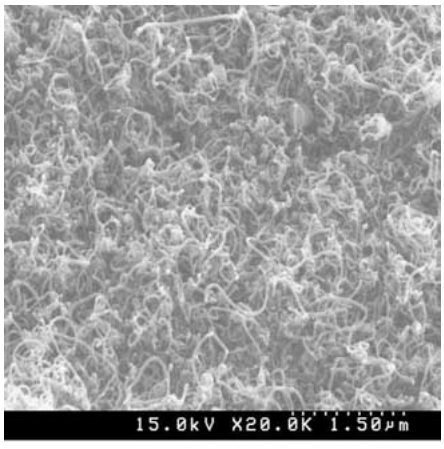


(b)

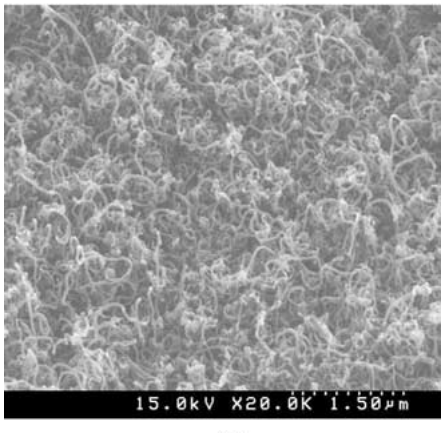


(c)

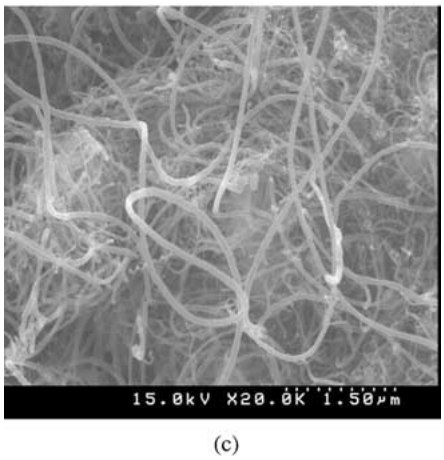
Figure 5 SEM of stainless steel substrate surface after HF etching and hydrogen plasma treatment: (a) 2.5 min hydrogen plasma treatment, (b) 5 min hydrogen plasma treatment and (c) 20 min hydrogen plasma treatment.



(a)



(b)



(c)

Figure 6 SEM of carbon nanotubes grown after HF etching and hydrogen plasma treatment of substrate: (a) 2.5 min hydrogen plasma treatment, (b) 5 min hydrogen plasma treatment and (c) 20 min hydrogen plasma treatment.

respectively. From SEM micrographs we can estimate a representative diameter of the carbon nanotubes of Fig 6a, Fig. 2, Fig. 6b and Fig. 6c as 30, 30, 45, and 30–75 nm, respectively. Thus we can observe that there is correlation between the diameter of the carbon nanotubes and the size of the grains on the substrate surface similar to carbon nanotube growth on nano-sized catalyst particles on silicon wafer.

The carbon nanotubes synthesized in this study were curly and not well aligned. One of the reasons for this is that the substrate surface became rough after etching with HF solution and the growth direction was not uniform. One other reason is that the carbon nanotubes were not crowded enough to have van der Waals effects that some investigators believe make aligned growth of nanotubes possible in the absence of a strong electrical field [22]. In the PECVD system of this study, the bias voltage exerting on the growth of the nanotubes is probably not sufficient for the aligned growth of carbon nanotubes.

EDLCs made from carbon nanotubes deposited on stainless steel in this study showed initial specific

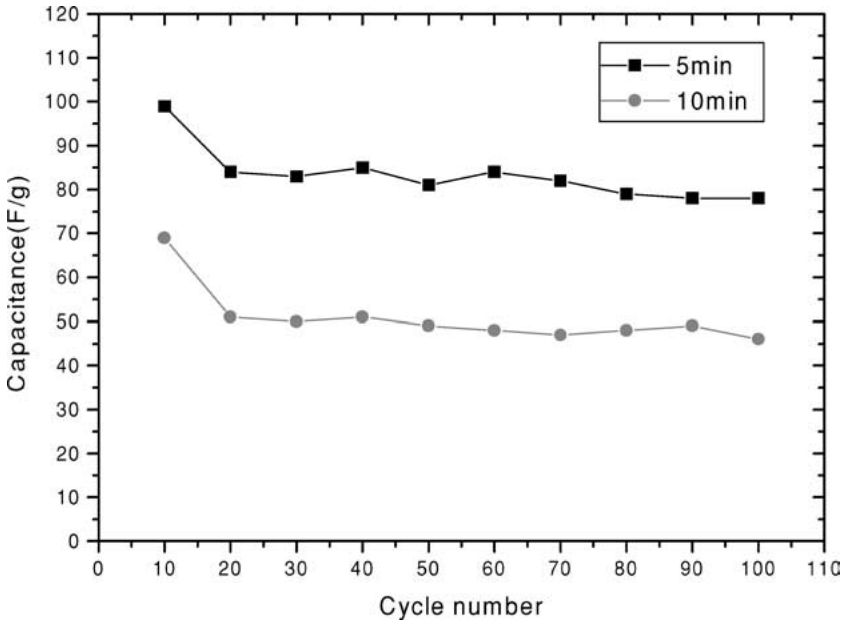


Figure 7 Capacitance of EDLC made from carbon nanotubes synthesized on stainless substrates treated with hydrogen plasma for 5 and 10 min, respectively.

capacity in the range of 80–100 F/g based on deposited carbon (Fig. 7).

The specific capacity decreased initially with charge/discharge cycle but then stabilized to 60–80 F/g after a few tens of charge discharge cycles. It also shows that the capacitor made from carbon nanotubes deposited on the substrate that was treated with hydrogen plasma for 5 min had higher capacitance than that for the sample formed with a substrate treated with hydrogen plasma for 10 min. This is due to the fact that the diameter of carbon nanotubes of the former is smaller than that of the latter, thereby providing more specific surface area available for formation of an electrical double layer. The IR drop was rather high, probably due to high electrical resistance between the stainless steel substrate and the carbon. Although further improvements are needed, this study shows that carbon nanotubes can be grown directly on metallic substrate and then can be fabricated, without any further treatment, into EDLC.

4. Conclusions

Carbon nanotubes were synthesized from acetylene and hydrogen directly on stainless steel substrate by PECVD. It was found that pretreatment of the substrate surface was very important for successful synthesis. Etching with HF solution rendered the substrate surface rough, baring nano-sized grains, and Fe was etched more than Ni or Cr. Subsequent treatment with hydrogen plasma made grains more spherical and larger in size. With increase of hydrogen plasma treatment time, the size of the grains on the substrate surface increased resulting in an increase of carbon nanotubes grown from them. EDLCs were successfully fabricated from carbon nanotubes synthesized on stainless steel substrates without any post-treatment.

References

1. P. G. COLLINS and P. AVOURIS, *Sci. Amer.* Dec. (2000) 38.
2. B. E. CONWAY, in "Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications" (Kluwer Academic, New York, 2000) p. 611.
3. C. NIU, E. K. SICHEL, D. MOY and H. TENNENT, *Appl. Phys. Lett.* **70** (1997) 1480.
4. R. MA, J. LIANG, B. WEI, B. ZHANG, C. XU and D. WU, *Bull. Chem. Soc. Jpn.* **72** (1999) 2564.
5. E. FRACKOWIAK, K. JUREWICZ, S. DELPEUX and F. BEGUIN, *J. Power Sourc.* **97/98** (2001) 822.
6. A. M. RAO, D. JACQUES, R. C. HADDON, W. ZHU, C. BOWER and S. JIN, *Appl. Phys. Lett.* **76** (2000) 3813.
7. C. EMMENEGGER, P. MAURON, A. ZUETTEL, C. NUETZENADEL, A. SCHNEUWLY, R. GALLAY and L. SCHLAPBACH, *Appl. Surf. Sci.* **162/163** (2000) 452.
8. Z. P. HUANG, J. W. XU, Z. F. REN, J. H. WANG, M. P. SIEGAL and P. N. PROVENCIO, *Appl. Phys. Lett.* **73** (1998) 3845.
9. N. WANG and B. D. YAO, *ibid.* **78** (2001) 4028.
10. M. H. KUANG, Z. L. WANG, X. D. BAI, J. D. GUO and E. G. WANG, *ibid.* **76** (2000) 1255.
11. M. YUDASAKA, R. KIKUCHI, Y. OHKI, E. OTA and S. YOSHIMURA, *ibid.* **70** (1997) 1817.
12. Y. Y. WEI, G. ERES, V. I. MERKULOV and D. H. LOWNDES, *ibid.* **78** (2001) 1394.
13. C. J. LEE, J. H. PARK and J. PARK, *Chem. Phys. Lett.* **323** (2000) 560.
14. Y. C. CHOI, Y. N. SHIN, Y. H. LEE, B. S. LEE, G. S. PARK, W. B. CHOI, N. S. LEE and J. M. KIM, *Appl. Phys. Lett.* **76** (2000) 2367.
15. S. B. SINNOTT, R. ANDREW, D. QIAN, A. M. RAO, Z. MAO, E. C. DICKEY and F. DERBYSHIRE, *Chem. Phys. Lett.* **315** (2000) 25.
16. Z. F. REN, Z. P. HUANG, J. W. XU, J. H. WANG, P. BUSH, M. P. SIEGAL and P. N. PROVENCIO, *Science* **282** (1998) 1105.
17. M. OKAI, T. MUNEYOSHI, T. YAAGUCHI and S. SASAKI, *Appl. Phys. Lett.* **77** (2000) 3468.
18. H. MURAKAMI, M. HIRAKAWA, C. TANAKA and H. YAMAKAWA, *ibid.* **76** (2000) 1776.

19. S. FAN, M. G. CHAPLINE, N. R. FRANKLIN, T. W. TOMBLER, A. M. CASSEL and H. DAI, *Science* **283** (1999) 512.
20. C. BOWER, O. ZHOU, W. ZHU, D. J. WERDER and S. JIN, *Appl. Phys. Lett.* **77** (2000) 2467.
21. C. J. LEE and J. PARK, *ibid.* **77** (2000) 3397.
22. M. I. MERKULOV, A. V. MELECHKO, M. A. GUILLORN, D. H. LOWNDES and M. L. SIMPSON, *ibid.* **79** (2001) 2970.

Received 22 October 2002
and accepted 14 August 2003