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Discharge Capacitance of Electric Double Layer Capacitor with Electrodes Made of Carbon Nanotubes Directly Deposited on SUS304 Plates

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Abstract–Carbon nanotubes were deposited directly on SUS304 plates by PECVD with acetylene and hydrogen as precursors under various deposition conditions. Raman spectroscopy showed that carbon nanotubes were not fully graphitized at the deposition temperatures, 600 to 750 °C, although defects decreased with increase of deposition temperature. SEM microscopy showed that carbon nanotubes were not straight, but their growth followed the tip growth model. Pretreatment of the substrate such as polishing and dipping in HF solution was required for the successful deposition. Using non-aqueous electrolyte we fabricated electrical double layer capacitance (EDLC) with SUS304 plates, on which carbon nanotubes were deposited, without any treatment, and measured charge/discharge characteristics. Discharge capacitance decreased with cycles from initial value of 128 F/g, but stabilized at 58 F/g after 50 cycles.

Key words: Carbon Nanotubes, CVD, EDLC, Raman

INTRODUCTION

Since Iijima discovered carbon nanotubes in 1991, they have been the object of intensive scientific study. Investigators have found that carbon nanotubes have extraordinary properties which could be attributed to their unique structure of graphite sheet rolled into tubes [Collins and Avouris, 2000]. Carbon nanotubes have very high tensile strength and resilience, and their electric current-carrying capacity and heat transmission are extremely high. They are very good for field emission of electrons at low voltage and are found to be able to store a large amount of hydrogen. Many applications are proposed to make use of carbon nanotubes: nano-scale electronic devices, field emission display, electrodes for secondary batteries, storage of gases, tip for STM, high power capacitors, 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: arc discharge, laser vaporization and chemical vapor deposition (CVD). Arc discharge produces relatively defect-free carbon nanotubes, but purification is needed for the removal of carbonaceous particles. Laser vaporization is costly and difficult to scale-up. CVD operates at relatively low temperatures, thus produces carbon nanotubes riddled with defects. On the other hand, it is very versatile and easy to scale up for industrial production. Recently, investigators reported growing of carbon nanotubes directly on solid substrates using various CVD processes: hot filament plasma CVD [Huang et al., 1998; Chen et al., 1997], thermal CVD [Fan et al., 1999; Lee et al., 2000] and microwave plasma CVD [Choi et al., 2000; Bower et al., 2000]. With plasma-enhanced CVD (PECVD) deposition temperature can be significantly lowered enabling the use of substrates which cannot withstand exposure to higher temperatures.

Electric double layer capacitors (EDLC) are attractive energy storage devices particularly for applications involving high power requirements and long cycle life [Conway, 1999]. The key factors determining characteristics of EDLC are the properties of the electrode materials. Carbons with very high specific surface area such as activated carbon powder and activated carbon fiber, of which specific surface area is in the range of 1,500 m^2/g, are used as electrode materials. But they have a wide pore size distribution, thus most of the surface area resides in micropores which are not readily accessible by ions, thereby limiting their usefulness. Recently, investigators reported EDLC made of carbon nanotube electrodes [Niu et al., 1997; Ma et al., 1999; Frackowiak et al., 2000]. However, they prepared carbon electrodes from carbon nanotubes, which were catalytically grown, through several processing steps: purification of powdery carbon nanotubes, forming with or without carbon black and binders, and then attaching to electric collector.

In this study we employed RF PECVD to deposit carbon nanotubes directly on metallic substrates (SUS304) which can be used as current collectors. We studied effects of deposition process variables on the properties of carbon nanotubes deposited. We also fabricated EDLC from them without any treatment and measured discharge capacitance.

EXPERIMENT

The schematic diagram of the PECVD system used for the deposition of carbon nanotubes is shown Fig. 1. SUS304 plates cut into 1×3 cm^2 rectangular pieces were used as substrates. They were polished with sand paper, and then cleaned with acetone and methanol sequentially in an ultrasonic bath. Afterwards, they were dipped in HF solution for 50-120 seconds. After substrates were placed on the heating block, CVD reactor was evacuated to 10^{-3} torr. Then hydrogen gas was introduced and temperature was raised to the pre-

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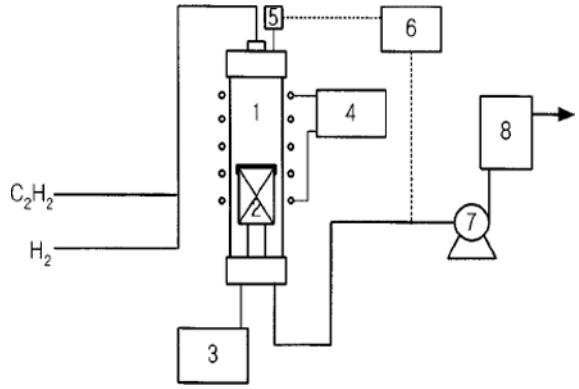

Fig. 1. Schematic diagram of PECVD system.

1. Reactor
2. SiC heater
3. PID temperature controller
4. RF generator
5. Pressure sensor
6. Pressure controller
7. Vacuum pump
8. Incinerator

Table 1. Conditions of carbon nanotubes growth

Temperature	600-750 °C
Pressure	1-10 torr
Plasma power	40 W
C_2H_2 flow rate	7-9 SCCM
H_2 flow rate	21-27 SCCM

determined deposition temperature. Subsequently, plasma was turned on and acetylene was fed into the reactor to deposit carbon nanotubes on the substrates. Flowrates of C_2H_2 and H_2 were 7 to 9 SCCM and 21 to 27 SCCM, respectively. During deposition, plasma power was set to 40 W. Deposition conditions are summarized in Table 1. Weight of substrates was measured before and after deposition to estimate the mass of deposited material. Effluent gases from CVD reactor passed through an electric incinerator and water scrubber before discharge into exhaust duct.

Deposited carbon nanotubes were examined with FE-SEM (Field Emission Scanning Electron Microscopy, Hitachi S-4100) and Raman spectroscopy (light source: Nd: YAG laser). The latter has resolution of 4 cm^{-1} operated in the range of 100-2,000 cm^{-1}.

We fabricated EDLC using carbon nanotubes deposited on SUS304 plates without any treatment. Lithium hexafluorophosphate

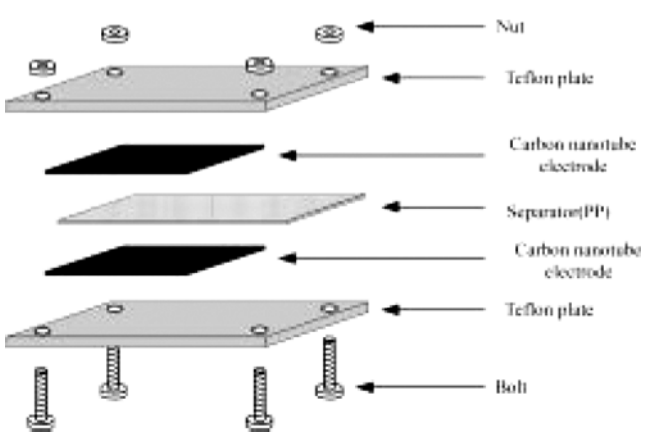

Fig. 2. Capacitor cell assembly.

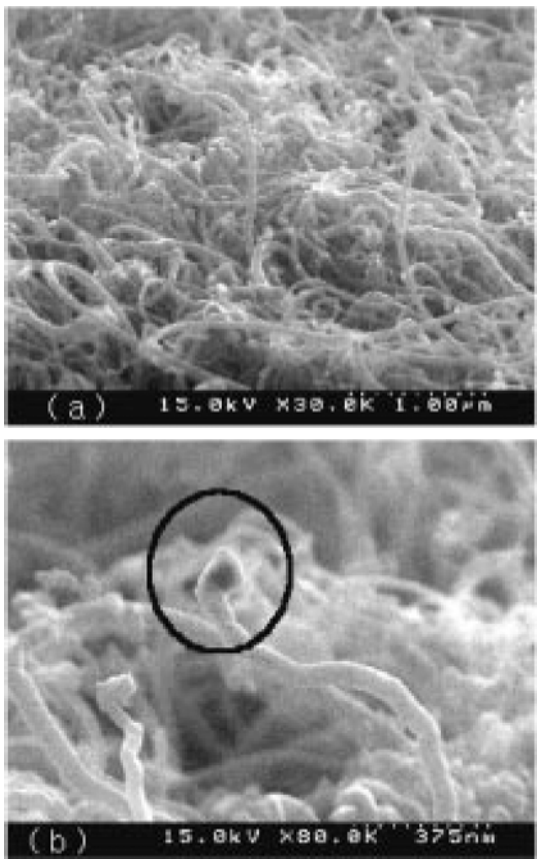

Fig. 3. SEM micrographs carbon nanotubes grown at 10 torr; 750 °C for 20 min (gas flow rate: C_2H_2 7 SCCM, H_2 21 SCCM).

dissolved to 1 M in the 1 : 1 mixture of ethylene carbonate and diethyl carbonate was used as electrolyte. Assembly of the capacitor was carried out in a dry room. The structure of the capacitor is illustrated in Fig. 2. Charge and discharge characteristics of the capacitor was measured by WBCS 3000 (Won A Tech).

RESULTS AND DISCUSSION

Fig. 3 shows typical SEM micrographs of carbon deposition on SUS304 plate. Carbon nanotubes grown were not straight and their diameter was not uniform, but metallic cap was clearly observable on the tip of nanotubes (Fig. 3b). We did not attempt to analyze the composition of the tip, but Ni and Fe in SUS304 plate are suspected to act as catalyst. There are two models for the growth of carbon nanotubes on solid substrates: tip growth model and base growth model [Sinnott et al., 1999]. But growth mechanisms are not clearly understood yet. According to tip growth model, carbon atoms decomposed from precursor come in contact with nano-size metallic catalyst and then transform into carbon nanotubes lifting catalyst particles from the substrate surface as nanotubes grow on the lower part of the catalyst particle. Therefore, catalyst particles remain always at the tip of carbon nanotubes as they grow upward [Chen et al., 1997]. In base growth model, catalyst particles are anchored firmly on the surface of the substrate and carbon nanotubes grow from catalyst particle up. Thus, the tips of base grown carbon nanotubes are free of catalyst particles [Lee and Park, 2000]. The

mechanisms for the formation of nano-sized partcles and detachment of them from solid substrates are not well understood yet. Thin films of metal deposited on substrates (e.g. Ni on glass or silicon wafer) can be transformed into nano-sized islands through thermal treatment. and then diameter of carbon nanotubes grown with the catalysts islands is well correlated with the size of islands [Yudasaka et al., 1997; Bower et al., 2000]. Therefore, one way of growing thin nanotubes is depositing thin films of catalyst on substrates and then transforming thin films into small islands. But if deposited catalyst film is too thin, catalyst islands formed through heat treatment could be too sparse for the growth of nanotubes. Diameter of nanotubes depends on the thickness and properties of deposited catalyst and substrate material together with process of carbon nanotube formation. In the case of solid substrate, the diameter of carbon nanotubes is known to be affected by pretreatment of the substrate and carbon deposition conditions [Huang et al., 1998; Lee et al., 2000; Chen et al., 1997].

The effect of substrate pretreatment was very significant indeed on the formation of carbon nanotubes in this study. Without polishing, the surface formation of carbon nanotubes on SUS304 plate was very poor at best. Dipping time in HF solution also affected growth of carbon nanotubes. Dipping time of 100 seconds was suitable for the growth of carbon nanotubes: either longer, or shorter time resulted in deterioration of deposition.

Growth of well-aligned carbon nanotubes is valued for application in field emission display. For aligned-growth, nanotubes should be close to each other and growth rate should be high as well. However, for the application to EDLC, straight alignment of carbon nanotubes is not necessary. As is evident in Fig. 3, carbon nanotubes grown in this study were not straight. In the tortuous growth of nanotubes there is not enough time available for carbon-deposited atoms to diffuse, and they therefore form pentagonal or heptagonal structures instead of hexagonal structures of graphite that could conduce the tortuous growth of carbon nanotubes. Growth of carbon nanotubes could be terminated when the surface of the catalyst particles is covered by amorphous carbon or the deposition rate of carbon atoms exceeds the rate of nanotube formation.

From Raman spectroscopy we can gather information on the structure of carbons. A peak at 1,597 cm^{-1} indicates graphite sheet, while a peak at 1,286 cm^{-1} corresponds to carbonaceous particles [Rao et al., 1997, 2000]. Rao et al., correlated peak at 190 cm^{-1} with the diameter of carbon nanotubes [Rao et al., 1997]. A peak at 1,720 cm^{-1} is one of the salient features of single-walled nanotubes (SWNT). Fig. 4 shows a typical Raman Spectroscopy for the carbon nanotubes grown on SUS304 plate. While there is no peak at 1,720 cm^{-1}, the peak at 1,286 cm^{-1} is larger than that at 1,286 cm^{-1} indicating multiwalled carbon nanotubes of incomplete graphitization with many carbonaceous particles or defects.

We obtained FWHM (full width half maximum) of peaks and calculated the ratio of FWHM of peak at 1,286 cm^{-1} (corresponding to carbonaceous particles) to that at 1,597 cm^{-1} (corresponding to graphite sheet). We can construe that the smaller the ratio, the more graphitized carbon nanotubes. Fig. 5 shows FWHM ratio increases with deposition time during the initial period of carbon na-

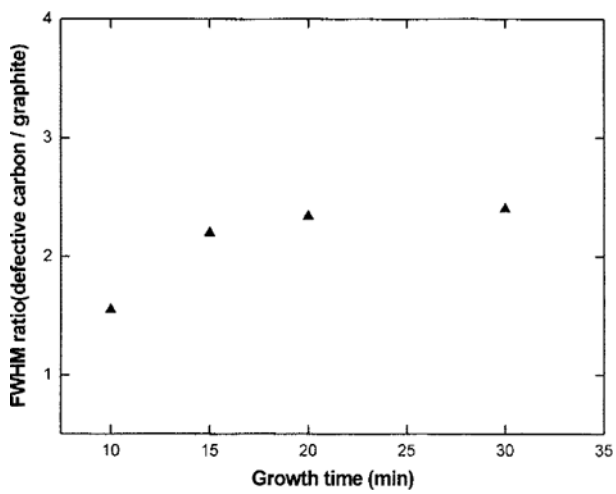

Fig. 5. Change of FWHM ratio with growth time for carbon nanotubes grown at 10 torr, 750 °C (gas flow rate: C_2H_2 7 SCCM, H_2 21 SCCM).

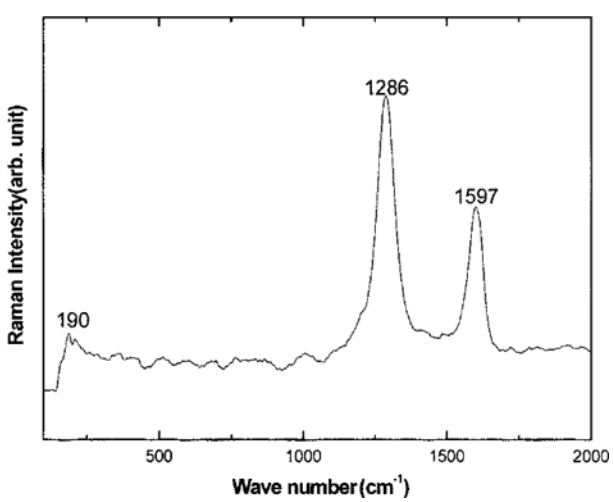

Fig. 4. FT-Raman spectrum for carbon nanotubes grown at 750 °C for 10 min on SUS304 plates (HF dipping 100 sec; gas flow rate: C_2H_2 7 SCCM, H_2 21 SCCM).

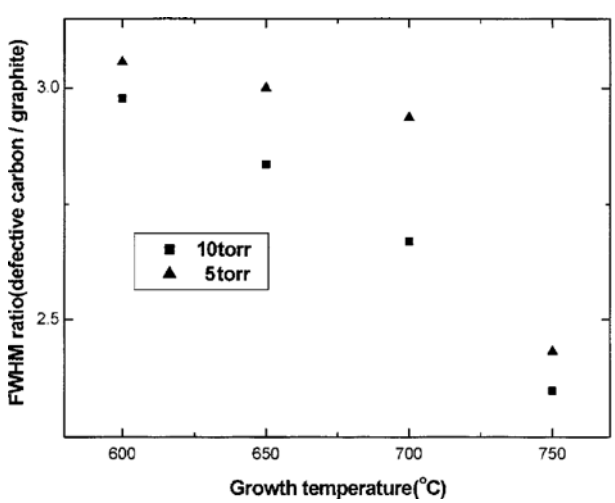

Fig. 6. Variation of FWHM ratio with deposition temperature for carbon nanotubes grown at 5 torr and 10 torr for 20 min (gas flow rate: C_2H_2 7 SCCM, H_2 21 SCCM).

notubes growth. We noticed that growth rate of carbon nanotubes slowed down with deposition time and carbon growth stopped 20 minutes after introduction of acetylene gas probably due to accumulation of carbonaceous deposits on catalyst particles.

Deposition temperature affected FWHM ratio as shown in Fig. 6. Within the range of experiment from 600 °C to 750 °C the ratio decreased with deposition temperature, indicating decrease of defects in nanotubes with increase of deposition temperature. Below 600 °C very little deposition of carbon nanotubes occurred. Above 750 °C, due to deformation of SUS304 plate, a normal deposition experiment could not be performed. Fig. 6 also shows that the FWHM ratio of carbon nanotubes deposited under the reactor pressure of 5 torr was higher than that of 10 torr. The reason for this is not clearly understood.

We fabricated EDLC using carbon nanotubes deposited on SUS304 plates and tested its charge/discharge. The charge was at constant 3.6 V and the discharge at constant 1.2 mA. A typical charge-discharge curve is shown in Fig. 7. A significant IR drop was observed from 3.6 V to 2.2 V. The amount of carbon deposits was too minuscule to apply conventional apparatus for the measurement of specific surface area. Therefore, we estimated the diameter of carbon nanotubes from SEM micrograph and calculated specific surface area from it. Diameter of the nanotubes used for the capacitor was estimated to be about 33 nm and specific surface area 121 m^2/g. Capacity of the first cycle was 129 F/g, but capacity decreased with repeated cycles. However, it stabilized at 58 F/g after 50 cycles (Fig. 8). Discharge efficiency was rather low at 45%. Considering that we employed non-aqueous electrolyte and carbon with relatively small specific surface area (120 versus 1,500 m^2/g), the discharge capacity is promising. There is ample room for improvement in discharge capacity with refinement of carbon deposition and treatment of carbons after deposition.

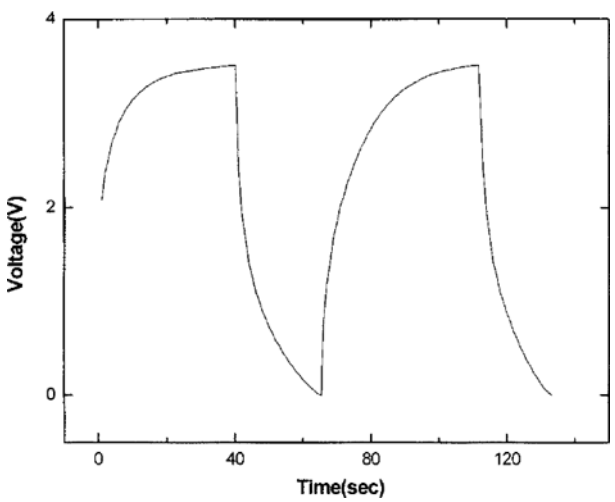

Fig. 7. Charge/discharge curve for a test cell made of carbon nanotubes deposited at 10 torr, 750 °C for 10 min (gas flow rate: C_2H_2 7 SCCM, H_2 21 SCCM).

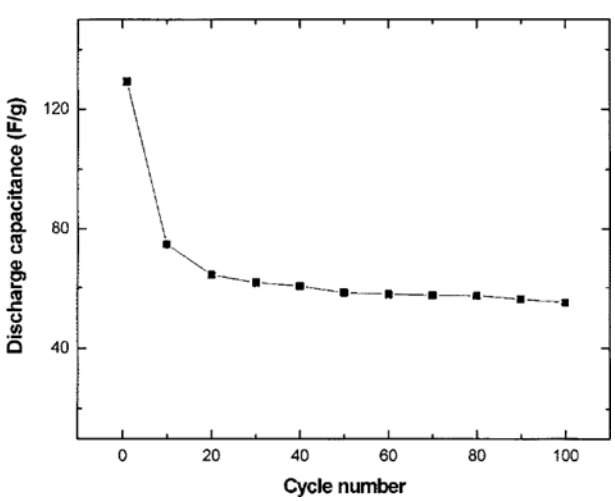

Fig. 8. Discharge capacitance of carbon nanotubes deposited at 10 torr, 750 °C for 10 min (gas flow rate: C_2H_2 7 SCCM, H_2 21 SCCM).

CONCLUSIONS

We deposited carbon nanotubes on SUS304 plates with acetylene and hydrogen in a PECVD reactor. Pretreatment of the substrate such as polishing and dipping in HF solution before deposition was necessary, and without proper pretreatment deposition of nanotube was not possible. Carbon nanotubes grown in this study had many defects as evidenced by Raman spectroscopy, though defects decreased with increase of deposition temperature. We made ELDC with carbon nanotubes deposited on SUS304 plates without any further treatment. A charge/discharge test showed that capacitance decreased from an initial value of 129 F/g with cycles but it stabilized at 58 F/g after 50 cycles. Although this value is lower than that of EDLC made with acivated carbons or powdered carbon nanotubes, we demonstrated that decent capacitance could be obtained for EDLC directly fabricated from carbon nanotubes deposited on metal plates without any other treatment. With further improvement in nanotube deposition and suitable postreatment we believe capacitance can be increased significantly.

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