Growth of aligned carbon nanotubes with controlled site density

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Pulse-current electrochemical deposition has been used to prepare Ni nanoparticles that are used as the catalysts for the growth of aligned carbon nanotubes. The nucleation site density of the Ni nanoparticles was controlled by changing the magnitude and duration of the pulse current. The aligned carbon nanotubes from the nickel nanoparticles were grown by plasma enhanced hot filament chemical vapor deposition. The site density of the aligned carbon nanotubes varied from $10^5$ to $10^8$ cm$^{-2}$. The achievement of controlling the site density is significant for applications of carbon nanotubes as field emitters, nanoelectrodes array, etc. © 2002 American Institute of Physics. [DOI: 10.1063/1.1482790]

Carbon nanotubes (CNTs) have attracted great attention because of their unique physical properties such as high mechanical strength and light weight, good heat conductance, large surface area, high aspect ratio, and varying electronic properties depending on their chirality.1–3 Both random4,5 and aligned CNTs6–8 can be synthesized easily right now. For the well-aligned CNTs, tuning of the diameter, length, and site density is very important for certain applications, such as field emission,9,10 nanoelectrode array,11 etc. because of the shielding effect of the dense array. Although the diameter and the length of aligned CNTs can be easily controlled by changing the catalyst particle size and the growth time, respectively,12 control on the site density is challenging. The current methods used to reduce the site density of CNTs array are to reduce the catalyst site density by electron-beam lithography,13 photolithography,14 micro contact printing,15 shadow mask,15 etc. However, all these methods either require expensive equipment and intensive labor or can not control the site density in large area.

Fortunately, electrochemical deposition has been used to prepare Ni,16 Ag,17,18 Au,19 Pt,20 etc. nanoparticles with different nucleation densities and different particle diameters for their applications in catalysis, electronics, and sensors. In this letter, we reported the preparation of Ni nanoparticles with varying site densities by pulse-current electrochemical deposition. By adjusting the amplitude of the pulse current, and duration and electrolyte concentration, the nucleation site density and the size of the Ni nanoparticles could be controlled in a wide range from $10^5$ to $10^8$ cm$^{-2}$. These Ni nanoparticles were used as the catalyst for growth of aligned CNTs by plasma enhanced hot filament chemical vapor deposition (PE-HF-CVD) method. The site density of the CNTs was defined by the site density of the Ni nanoparticles. The pulse-current electrochemical deposition is a cheap, effective technique, and scalable to tens of inches in linear dimension.

Previously, electrochemical deposition was used to synthesize metal nanoparticles with high density, small size, and uniform diameter for their unique catalytic, magnetic, and spectroscopic properties. In contrast, we are interested in reducing the site density of the Ni nanoparticles so that we can grow aligned CNTs with low site density. In order for the Ni nanoparticles to survive the plasma during CNT growth, the Ni nanoparticles should have a relative large size. So our goal was to make low density and big particles on a fairly large area.

In order to achieve the goal, we used the pulse-current electrochemical deposition technique. The experiment was carried out on a two-electrode system. The constant current pulse was applied by using a current source and a voltage source, both were controlled by the computer program. The working electrode was prepared by sputtering a layer of Cr on a silicon wafer in order to get a flat, conductive, and defect free surface. Gold plate was used as counter electrode. About 1 cm$^2$ of the working electrode surface was exposed to the solution. The distance between the two electrodes was kept at about 1 cm. The composition of the solution is 0.01 M NiSO$_4$ and 0.01 M H$_3$BO$_3$ in water. The solution was weakly acidic. All chemicals are reagent grade from Aldrich and used as received. Double distilled water was used to prepare the bath solution. All experiments were performed at room temperature.

After electrochemical deposition, the substrates with Ni nanoparticles were loaded into a PE-HF-CVD system described previously.7,12,13 The system was pumped down to $2 \times 10^{-6}$ Torr, then 160 standard cubic centimeter per minute (sccm) ammonia gas was introduced into the chamber and the temperature was increased by applying current on the tungsten filament. 100 W dc plasma was applied for 10 to 20 s first to pre-etch the Ni nanoparticles, then 40 sccm acetylene gas was introduced and the plasma intensity was increased to 170 W for the aligned CNTs growth. The pressure during growth was about 15 Torr. Both acetylene and ammonia had minimum purity of 99.99%. The growth time was 5 min, and the sample temperature during growth was below 660 °C.7

Scanning electron microscopy (JEOL JSM-6340F) was...
employed to examine the morphology. Transmission electron microscopy [(TEM) JEOL 2010] was used to characterize the structure of the CNTs.

In the pulse-current electrochemical deposition experiments, many factors could affect the deposited nanoparticles, including the composition of the electrolyte solution, the surface morphology of the substrate, the magnitude of the applied pulse current density, and the duration time. Lowering the concentration of Ni ions will decrease both the nucleation site density and the size of the deposited Ni nanoparticles. 0.01 M Ni$^{2+}$ was used in our experiments. Different boric acid concentration had been used to change the pH value, and the solution with support electrolyte (potassium chloride) added also had been tested. It was found only when the concentration of boric acid was very low and no other support electrolyte was added, the Ni nanoparticles with low site density and large size (larger than 100 nm in diameter) could be achieved. When the boric acid concentration increased or some other support electrolyte was added, the conductivity of the solution increased, and the electrodeposited Ni nanoparticles had higher density and smaller size. The surface morphology of the substrate also affected the distribution of the deposited Ni nanoparticles. The nanoparticles formed easily on the defect site of the substrate with high site density. In order to eliminate the aggregation of the nanoparticles, we used sputtering method to coat a thin layer of Cr on the Si wafer to get the conductive and defect free surface.

When the solution composition and the substrate were fixed, the site density and the size of the Ni nanoparticles were determined by the combined effect of applied pulse current density and duration time. High current density and long duration time resulted in high site density and big particles. In this experiment, the size distribution of the electrochemical deposited Ni nanoparticles was quite large. Both big particles (>100 nm) and small particles (<50 nm) were deposited on the substrate. Those small particles were removed by plasma etching before the growth of CNTs. Figure 1 shows the different nucleation site densities of the Ni nanoparticles from about $7.5 \times 10^5$ to $3 \times 10^8$ cm$^{-2}$. The white dots shown in Fig. 1 were the Ni nanoparticles that had been confirmed by energy dispersive x-ray spectroscopy. Most

particles had a diameter from 100 to 200 nm with some nanoparticles smaller than 50 nm. The Ni nanoparticles were randomly located on the surface of the substrate.

After the nanoparticles were deposited on the substrate by pulse-current electrochemical deposition, CNTs were grown from the Ni nanoparticles by PE-HF-CVD method. In the PE-HF-CVD method, the Ni nanoparticles were subjected to the plasma that directed the CNTs growth direction. The plasma etched the catalyst and at the same time assisted the CNTs growth. The morphology of the CNTs was related to the size of the Ni nanoparticles. When the diameter of the Ni nanoparticles is smaller than 50 nm, either no CNTs or only short and curved CNTs were grown. When the size of the Ni nanoparticles is large, well-aligned CNTs with uniform length distribution were grown. As stated, both small and large Ni nanoparticles were presented on the substrate after electrochemical deposition. In order to completely eliminate the small particles, the pre-etching was employed by applying low intensity plasma to the substrate for a short time before the introduction of acetylene gas. After the pre-etching, those small particles were removed and the other big particles became smaller. The final samples consisted of mostly well-aligned CNTs with uniform length.

Figures 2(a) to 2(e) show the different site densities of CNTs grown from the electrodeposited Ni nanoparticles. The CNTs site densities of the samples were about $7.5 \times 10^3$ cm$^{-2}$, $2.0 \times 10^4$ cm$^{-2}$, $6.0 \times 10^6$ cm$^{-2}$, $2.0 \times 10^7$ cm$^{-2}$, and $3 \times 10^8$ cm$^{-2}$, respectively. Figure 2(f) provides a closer look at one of the well-aligned CNTs. Figure 3 shows the typical TEM image of the CNTs. It shows that CNTs have bamboo structure, which is similar with that of the CNTs grown from the Ni thin films prepared by sputtering using the same PE-HF-CVD method.
the microstructure does not depend on the way the Ni catalyst was prepared.

Figure 4 shows the CNTs site density dependence of electrochemical deposition current density and deposition time. At current density 1.0 mA/cm², the CNTs site density increased about eight times when the deposition time increased from 1.0 to 2.0 s, whereas at 2.0 mA/cm², the CNTs site density increased more than 100 times when the deposition time increased from 0.8 to 1.8 s. By adjusting the current density and the deposition time, aligned CNTs with site density from $10^5$ to $10^8$ cm⁻² had been achieved.

These well-aligned CNTs with different site densities are very promising for the study of shielding effect between each nanotubes. The studies using these low site density CNTs arrays for field emission and nano electrode are under way and will be reported subsequently.

In conclusion, pulse-current electrochemical deposition is an effective technique to prepare Ni nanoparticles with different nucleation site densities. Well-aligned CNTs with site densities from $10^5$ to $10^8$ cm⁻² had been grown using these Ni nanoparticles as a catalyst.

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