

## Periodicity and alignment of large-scale carbon nanotubes arrays

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Intensive studies have been carried out on controlling the periodicity and alignment of large-scale periodic arrays of carbon nanotubes (CNTs) using plasma-enhanced chemical vapor deposition. Catalytic dots are first prepared by self-assembly of polystyrene spheres on chromium-coated silicon substrates. Preparation parameters for CNTs growth including temperature, thickness of catalytic dots, plasma current intensity, and pregrowth plasma etching time are fine tuned and analyzed to achieve optimal combinations. High-quality aligned CNTs arrays with long-range periodicity and controlled diameters have been achieved. The good periodicity and alignment are critical for their applications such as photonic crystals, negative index of refraction, etc. © 2004 American Institute of Physics. [DOI: 10.1063/1.1819992]

Aligned carbon nanotubes (CNTs) have drawn considerable attention for many potential applications such as field emitters,<sup>1–5</sup> chemical and biological sensors,<sup>6–9</sup> nanostructure building blocks,<sup>10,11</sup> etc. Because of the difficulty in manipulating individual CNTs and the high cost of patterning catalytic particles over a large area by electron beam lithography, synthesizing large-scale prepatterned low cost CNT arrays with high quality remained a challenge. Kempa *et al.* first reported an easy and inexpensive way to prepare large-scale periodic honeycomb CNT arrays by utilizing self-assembly nanosphere lithography.<sup>11</sup> However, the CNTs reported there were not very straight in shape and the detailed growth conditions for the nickel (Ni) dots prepared from different sized polystyrene spheres (PSs) were not reported. To synthesize more satisfactory samples using this method for photonic crystals as well as other applications, better growth parameters control is necessary. In this letter, we demonstrate a detailed study of growth parameters for controlling the quality of these periodic CNT arrays.

Self-assembled PSs with diameters of 540, 980, and 1710 nm have been used as a mask to deposit periodic Ni dots on chromium-coated silicon (Cr-coated Si) substrates. Plasma enhanced chemical vapor deposition (PE-CVD) as reported previously<sup>12,13</sup> was used to grow the CNTs on the Ni dots. The catalytic dots and growth conditions: dot size, temperature, plasma current intensity, and pregrowth plasma etching time (time of substrates under plasma before introduction of carbon sources), are found to be critical for satisfactory quality control of the final CNTs. Briefly, a self-assembled monolayer of PSs on an aqueous surface<sup>14</sup> was first transferred onto Cr-coated Si wafers. This assembly was used as a mask for deposition of Ni dots by electron beam evaporation. All the PSs were then completely removed by ultrasonication in toluene or water. Finally, quasitriangular shaped catalytic Ni dots in a honeycomb lattice pattern were

formed. In this work, the size of the Cr-coated Si substrates covered with PSs is typically  $1 \times 1 \text{ cm}^2$ , but up to 7.5 cm in diameter have also been accomplished. These substrates were then placed on a bottom-heated sample stage acting as the cathode, directly below the rod-shaped anode in the PE-CVD system. The separation, cathode to anode is about 1.5 cm. The system was first pumped down to  $10^{-2}$  Torr while the heater was set to heat up the stage to 450–600 °C continuously.  $\text{NH}_3$  (160 sccm) was introduced into the system during the heating. As soon as the desired temperature was reached, a dc plasma was generated. After exposing the substrate under plasma for a certain time (pregrowth plasma etching time),  $\text{C}_2\text{H}_2$  (80 sccm) was introduced to trigger the CNT growth at 5–10 Torr. The  $\text{NH}_3$  plasma plays two roles: (a) etch the triangular Ni dots into round dots, (2) enhance the decomposition of  $\text{C}_2\text{H}_2$ . All the results reported here are from a growth time of 3 min. Scanning electron microscope (SEM) was used to examine the quality.

The effect of growth temperature on sample quality was first studied. Experiments were carried out on Ni dots made from all three PSs already mentioned. For the 980 nm spheres, other preparation parameters were fixed at: 40 nm thick Ni, 0.35 A plasma current intensity and 80 s pregrowth plasma etching time. Figure 1 shows the quality of the CNTs obtained at growth temperatures of 500, 550, and 600 °C, respectively. Figures 1(a), 1(c), and 1(e) are the SEM top view to show the periodicity, whereas Figs. 1(b), 1(d), and 1(f) are the inclined view to show the straightness of each CNT. At 600 °C [see Figs. 1(e) and 1(f)], location and straightness disorders appeared mainly due to the high mobility of Ni dots and high growth rate of CNTs, respectively. The high mobility could cause the Ni dots (before CNTs growth) and CNTs (at the beginning of their growth) to move around and end up at a position away from the original spot of Ni dots. The high growth rate due to fast supply of carbon source resulted from high temperature could possibly be the reason for nonideal straightness. At a lower temperature of 500 °C [see Figs. 1(a) and 1(b)], Ni dots were less mobile

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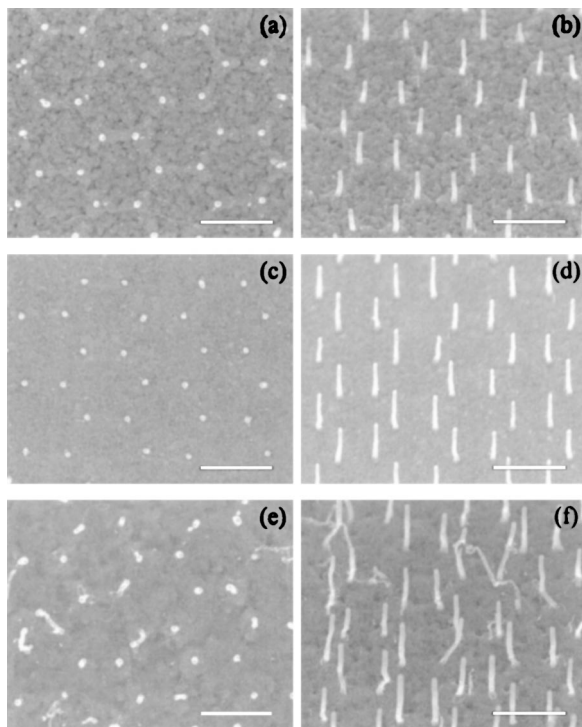


FIG. 1. Effect of temperature on periodicity and alignment of CNTs grown on Ni dots prepared from 980 nm PSs: (a) and (b) are the SEM top- and side-views of CNTs grown at temperature 500 °C; (c) and (d) are from 550 °C; and (e) and (f) are from 600 °C. Scale bars, 1  $\mu$ m.

and certainly stayed where they were, and the decomposition of  $C_2H_2$  was also slower, leading to much better alignment and certainly slower growth rate [can be seen from the shorter length compared with those in Figs. 1(d) and 1(f)]. Therefore an intermediate temperature of 550 °C [see Figs. 1(c) and 1(d)] appeared to be the most desirable choice for spheres of 980 nm. In the case of Ni dots made from spheres 540 nm (60 nm thick Ni, 0.3 A plasma current intensity, and 60 s plasma etching time) and 1710 nm (30 nm thick Ni, 0.4 A plasma current intensity, and 120 s plasma etching time), a similar trend was observed and the optimal temperatures were found to be 500 and 600 °C, respectively. The reason that thicker Ni dots are required for smaller sphere is that a certain amount of Ni volume is needed to survive the pregrowth plasma etching. It is worth pointing out that temperature is much more sensitive for the Ni dots made from spheres 540 nm than 1710 nm due to the difference in Ni dot sizes.

With the optimal heating temperatures established for Ni dots made from different spheres, all substrates were subjected to different plasma current intensities in independent experiments. Figure 2 shows the SEM top- [Figs. 2(a), 2(c), and 2(e)] and side-views [Figs. 2(b), 2(d), and 2(f)] of the CNTs grown from Ni dots made from spheres 540 nm with temperature of 500 °C and Ni dot thickness of 60 nm as established above. It was found that plasma current intensity is more effective than voltage or total power on controlling the final quality of CNTs. Clearly, plasma current intensity has to be high enough ( $\geq 0.3$  A) to align the CNTs all straight up as shown in Figs. 2(c)–2(f), but low enough for the Ni dots to survive the plasma etching. When the plasma current intensity is too low, the alignment was clearly not good as shown in Fig. 2(b). The effect of plasma current intensity on the CNT straightness may be related to the

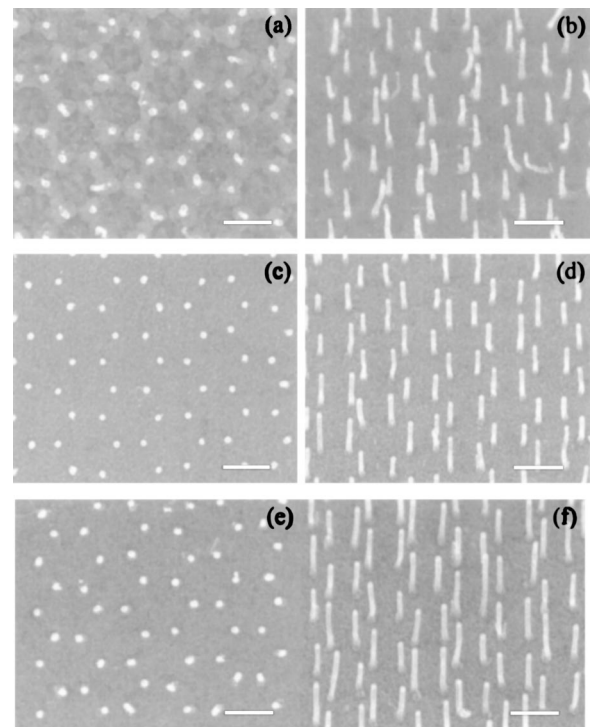


FIG. 2. Effect of plasma current intensity on periodicity and alignment of CNTs grown on Ni dots prepared from 540 nm spheres: (a) and (b) are the SEM top- and side-view of CNTs grown at 0.25 A plasma current intensity and 70 s pregrowth plasma etching; (c) and (d) are from 0.3 A plasma current intensity and 60 s pregrowth plasma etching; (e) and (f) are from 0.35 A plasma current and 40 s pregrowth plasma etching. Scale bars, 500 nm.

strength of local electric field and the decomposition rate of  $C_2H_2$ . It is necessary to point out that a different pregrowth plasma etching time (70 s for 0.25 A, 60 s for 0.3 A, and 40 s for 0.35 A) was used to compensate the different etching rate due to different plasma current intensity in order to grow CNTs of similar diameters. Even though Ni dots made from spheres 540 nm can sustain a higher current intensity of 0.35 A for a shorter time of 40 s [see Figs. 2(e) and 2(f)], a lower current intensity of 0.3 A and a longer plasma etching of 60 s were normally preferred [see Figs. 2(c) and 2(d)]. For Ni dots made from spheres of 980 and 1710 nm, the optimal plasma current intensity was found to be 0.35 and 0.4 A, respectively.

After optimizing both the temperature and plasma current intensity, pregrowth plasma etching time was studied since it plays a very important role not only in determining the number of CNTs grown from each original catalytic Ni spot but also the CNT diameters for a given thickness of Ni dots. As introduced earlier, honeycomb lattices of quasitriangular particles form after sphere mask removal, but some Ni dots are still connected to each other due to the minor variation in diameter of the spheres in the mask, which introduces difficulty in separating them completely during CNT growth without leaving small catalyst dots in between. Since the horizontal spread of each Ni dot is usually much larger than its vertical height, the particle is very likely to break into smaller pieces as the growth begins and gives multigrowth on a single Ni dot. These problems can be simply overcome by exposing the Ni dots to the  $NH_3$  plasma for a proper pregrowth plasma etching. This pregrowth plasma etching plays two roles: (1) breaking the connections between Ni

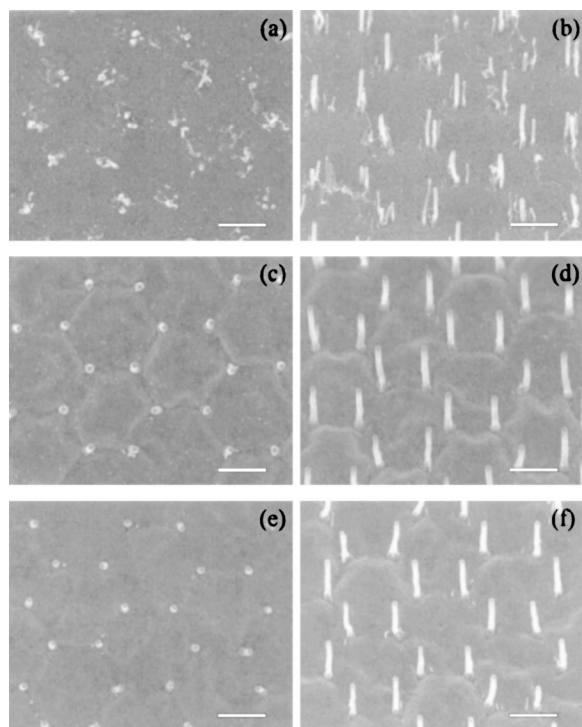


FIG. 3. Effect of plasma etching time on periodicity and alignment of CNTs grown on Ni dots prepared from 1710 nm spheres: (a) and (b) are the SEM top- and side-view of CNTs grown with 100 s pregrowth plasma etching, (c) and (d) are from 120 s pregrowth plasma etching, and (e) and (f) are from 140 s pregrowth plasma etching. Scale bars, 1  $\mu\text{m}$ .

dots so that a single dot at the original Ni spot can be formed, and (2) reducing the Ni dot size to result in smaller CNT diameters and shorter CNTs. Certainly when the pregrowth plasma etching time is too short (100 s for 1710 nm spheres), the original triangular Ni dots break into multiple smaller Ni dots leading to multiple growth of CNTs as shown in Figs. 3(a) (top view) and 3(b) (side view). Obviously, when the etching time is sufficient (120 s), a single Ni dot on each original spot was formed, leading to nice single growth of CNTs as shown in Figs. 3(c) and 3(d). However, the Ni dots become smaller when etching is too long (140 s), leading to shorter and smaller (in diameter) CNTs as seen in Figs. 3(e) and 3(f). This procedure hence offers an opportunity to control the CNT diameters in a certain range. Table I lists the results of the optimal pregrowth plasma etching time along with all the other optimal parameters for Ni dots made from all the three types of spheres of 540, 980, and 1710 nm.

It should be evident now that all growth parameters are sensitive to the Ni dot dimensions and therefore choosing a

TABLE I. Optimal parameters for Ni dots preparation and CNTs growth to achieve almost perfectly aligned periodical CNTs arrays.

Sphere diameter (nm)	Ni thickness (nm)	Heating temperature ( $^{\circ}\text{C}$ )	Plasma current intensity (A)	Pregrowth plasma etching time (s)
1710	30	600	0.4	120–160
980	40	550	0.35	80–100
540	60	500	0.3	40–60

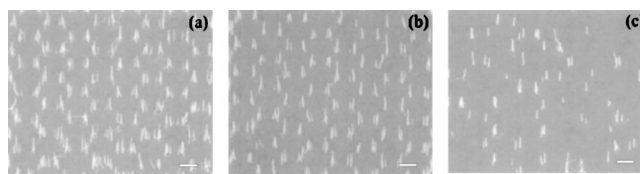


FIG. 4. SEM side-view of multigrowth of CNTs on Ni dots prepared from 1710 nm spheres: (a), (b), and (c) are for 80, 100, and 120 s plasma etching, respectively. Scale bars, 1  $\mu\text{m}$ .

proper deposition thickness of Ni is a prerequisite. For example, 20 nm thick Ni dots made from spheres 1710 nm could only sustain a 0.4 A plasma current intensity (optimal) pregrowth plasma etching for about 100 s that is not long enough to get its horizontal width reduced to be as small as what the single-growth requires, so multiple growths on each Ni spot have been observed as shown in Figs. 4(a)–4(c) for etching time 80, 100, and 120 s, respectively. Clearly some of the Ni spots have been completely etched away [see Fig. 4(c)] due to too long etching time at this Ni thickness. Thicker Ni will be easier for single growth but the increased particle volumes will generally lead to enlarged diameters and more structural complexities of the CNTs.

In conclusion, high quality aligned CNTs arrays with different lattice constants and controllable diameters have been experimentally achieved in large scale by manipulating preparation parameters in a PE-CVD system. The optimization of each individual parameter can be generally utilized for controlling growth of aligned CNTs from catalytic dots predefined by other various techniques in the PE-CVD system.

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