Growth of large periodic arrays of carbon nanotubes

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Large periodic arrays of carbon nanotubes have been grown by plasma-enhanced hot filamen chemical vapor deposition on periodic arrays of nickel dots that were prepared by polystyrene nanosphere lithography. A single layer of self-assembled polystyrene spheres was firs uniformly deposited on a silicon wafer as a mask, and then electron beam vaporization was used to deposit a nickel layer through the mask. The size of and spacing between the nickel dots are tunable by varying the diameter of the polystyrene spheres, which consequently determines the diameter and site density of carbon nanotubes. The technique can be scaled up at much lower cost than electron beam lithography. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1539299]

The site-density control of carbon nanotubes is a critical issue in many potential applications, such as optical antennas,[1] biosensors and bioprobes,[2–7] fiel emission devices, etc.[8] In order to grow a single freestanding carbon nanotube from each patterned catalyst dot, the dot size has to be below 300 nm.[9,10] Although electron beam, x ray, and scanning tunneling microscope lithography can yield such submicron dots with perfect edge definition they are limited by the low processing speed and high cost. Electrochemical deposition was demonstrated to be able to yield dots of 30–200 nm with controlled site density,[11] but the dot position is random and the size is nonuniform. Recently, nanosphere lithography has been proposed, which is capable of yielding periodic arrays of dots of 20–200 nm.[12] In this technique, a self-assembled single or double layer of nanospheres is used as a mask for subsequent metal deposition. The metal vapor passes through the nanosphere interspacings to form nanodots on the substrate and consequently the dot size and spacing between the dots are controlled by the diameter of the nanospheres. Using double layers of nanospheres, nickel dots as small as 30 nm have been achieved. Since nanosphere lithography can yield large-scale periodic arrays of metal nanodots at low cost, the ability to grow carbon nanotubes on these arrays is of great importance to commercialization.

The experiment described in this letter explores the growth of carbon nanotubes in periodic arrays on the periodic Ni dots made by nanosphere lithography. A single layer of polystyrene spheres was formed as a lithography mask. Using hot filamen plasma-enhanced chemical vapor deposition (PECVD), well-aligned carbon nanotubes grew on the periodic arrays of nickel dots. Atomic force microscope (AFM), scanning electron microscope (SEM), and transmission electron microscope (TEM) were utilized to characterize the distribution of nickel dots, the morphology, and structure of carbon nanotubes, respectively. Based on the geometrical location of carbon nanotubes, their site density was also calculated.

The preparation of nickel dots in a periodic array starts with the mask formation of self-assembled nanosphere layers. A 10 wt % solution of monodisperse polystyrene nanospheres was purchased from Microparticles GmbH (Germany). Commercially available (111) 10 Ω cm n-type silicon wafer was used as a substrate. The silicon surface was kept hydrophilic and the surface roughness was around 1 nm. The solution containing 496 or 1040 nm diameter polystyrene nanospheres was applied dropwise on a 10×10 mm^2 cleaned surface of silicon and then distributed using an Eppendorf pipette tip. Once the polystyrene coated silicon wafer was dipped into deionized water, polystyrene lifted off from the silicon and formed an unordered single layer on the water surface. After a droplet of 2% dodecylsodiumsulfate solution

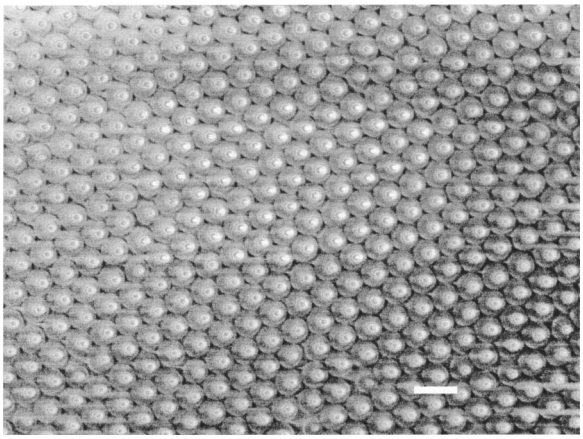

FIG. 1. SEM image of monolayer self-assembled polystyrene nanospheres on silicon (scale bar: 1 μm).

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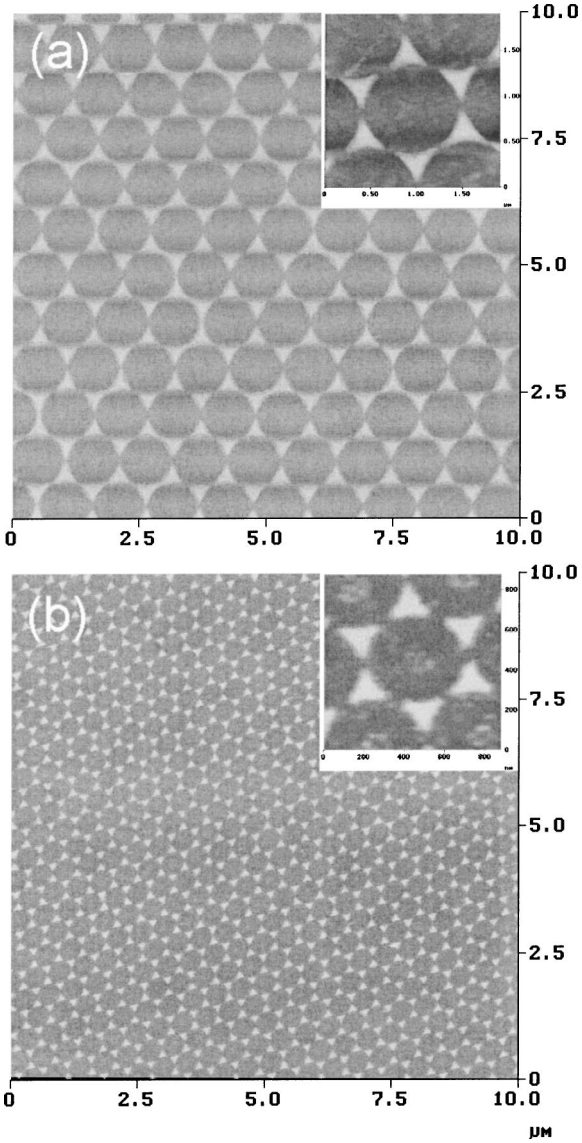

FIG. 2. AFM images of Ni dots with a thickness of 30 nm evaporated through 1040 (a) and 496 nm (b) polystyrene nanosphere masks. Higher magnificatio images are shown as the inserts of each image.

was added, all polystyrene spheres immediately assembled into an ordered single layer, as shown in Fig. 1. This ordered layer of polystyrene nanospheres was put back on the silicon when it was lifted off from water surface by the original silicon wafer. Nickel deposition was executed in an electron beam evaporation system and 30 nm thickness of nickel went through the interspacing of polystyrene spheres to form nanoscale nickel dots in a honeycomb (hexagonal) array. After nickel deposition, the polystyrene nanospheres were thoroughly removed from silicon in an ultrasonic bath of tetrahydrofuran. On these nickel dots, well-aligned carbon nanotubes were grown in a hot filamen PECVD system.[13,14] A base pressure of 10^{-6} Torr was obtained prior to the introduction of high purity of acetylene and ammonia (40:160 sccm). The growth pressure was maintained at 10–20 Torr during the PECVD process and the growth time was set at 1–2 min for proper length control of carbon nanotubes. The substrate temperature was kept below 660 °C.

AFM images of the periodic arrays of nickel dots from 1040 and 496 nm single layer nanospheres are presented in Figs. 2(a) and 2(b), respectively. The dots have a quasitriangular shape as shown in the inset and form a honeycomb lattice. The maximum dimension of the as-deposited Ni dot is about 400 nm for 1040 nm sphere mask and 200 nm for 496 nm sphere mask. It is worth pointing out that the dots become much smaller under the growth conditions. Figures 3(a) and 3(b) show the corresponding as-grown carbon nanotube arrays from 1040 and 496 nm polystyrene spheres, respectively. As reported in our previous studies, carbon nanotubes are always capped with metallic catalyst particles regardless of the catalyst preparation technique (continuous nickel film by sputtering or nickel nanodot arrays by electron beam lithography and electrochemical deposition)[9,11,13] which indicates the top growth model. It is also true for the catalyst made by the current nanosphere lithography. The nanotube length for both arrays [Figs. 3(a) and 3(b)] is around 1 μm, but the nanotube diameter is different. In Fig. 3(a), the nanotubes are about 100 nm in diameter and just 50 nm in Fig. 3(b). These results are also in agreement with the previous reports,[13–18] that is, the carbon nanotube diameter is directly proportional to the catalyst particle size.

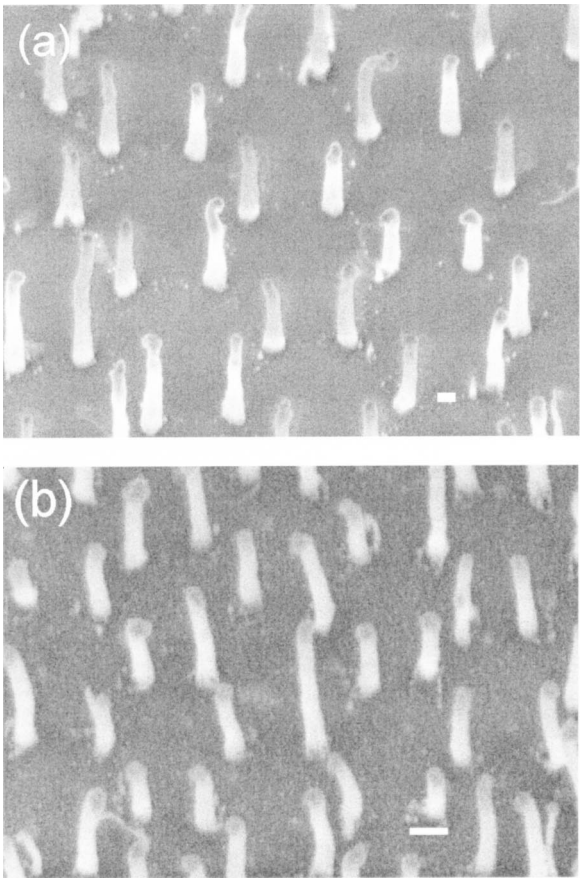

FIG. 3. As-grown periodic carbon nanotubes arrays (a) from 1040 nm polystyrene sphere mask (scale bar: 100 nm), (b) from 496 nm polystyrene sphere mask (scale bar: 100 nm).

Figure 4 shows TEM images of the carbon nanotubes from the periodic array. The inset is a high magnificatio image showing wall graphitization and the bamboo structures of the interior. It also has been found that many carbon nanotubes are encircled by amorphous carbon and carbon nanoparticles that result in a rough surface. This observation may be explained as carbon oversupply during the carbon nanotube growth. In the catalytic growth mechanism, the difference of carbon concentrations across the catalyst surface

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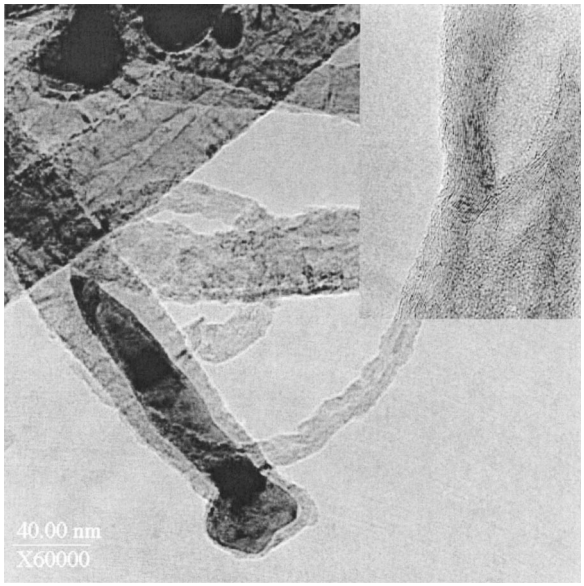

FIG. 4. TEM images of carbon nanotubes from the periodic arrays.

makes carbon diffuse in and segregates from catalyst particles. However, it is well known that the carbon concentration inside the catalyst, for any certain temperature, is limited by carbon solid solubility. Once the maximum concentration of carbon has been reached in the catalyst particle, it is supposed that the extra carbon will directly deposit on carbon nanotube surface. Therefore, a decrease in the gas ratio of acetylene to ammonia should reduce or remove amorphous carbon and carbon particles on carbon nanotubes, which is the subject of further studies.

To calculate the carbon nanotube density in our arrays, we take six nanotubes in a honeycomb as a unit and each single nanotube in the honeycomb belongs to three units. As a result, each unit totally possesses two nanotubes. Consequently the site density is given by

$$D=2/(3RDip)=(3^{1/2}R^2)^{-1}, \quad (1)$$

where R is nanosphere radius; Dip is interdot spacing; $Dip=2R/(3^{1/2})$ (see Fig. 5). For the mask assembled by a single layer of 496 nm polystyrene spheres, carbon nanotube density $D=9.40\times10^8/\mathrm{cm}^2$. For a single layer of 1040 nm polystyrene spheres, $D=2.14\times10^8/\mathrm{cm}^2$. If a single layer of 5000 nm polystyrene spheres were applied, the site density of carbon nanotubes would further decrease to be $9.40\times10^6/\mathrm{cm}^2$ (100 times lower than the site density of carbon nanotubes grown on a continuous nickel fil). Such a control of the nanotube density is of great importance to the fiel emission devices. However, when the polystyrene spheres are 5000 nm, the Ni dots are about 2000 nm. As pointed out earlier that single nanotube will grow out of one Ni dot only if the dot is not larger than 300 nm. Therefore, multinanotubes would be expected from 2000 nm Ni dot. In order to insure single nanotube out of each Ni dot, the Ni dot has to be reduced to be about 300 nm by either acid etching or in-situ plasma etching. Work on this aspect is in progress.

In conclusion, we have developed large periodic arrays of Ni dots by the inexpensive self-assembly technique: polystyrene nanosphere lithography. In a hot filamen PECVD system, large periodic arrays of carbon nanotubes have been grown on the Ni dots. The nanotubes site density and diameter can be easily controlled by the size of the polystyrene spheres.

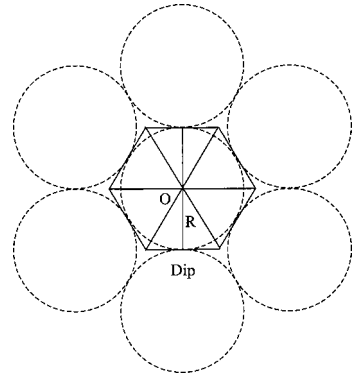

FIG. 5. A schematic diagram of hexagon area S_{unit}, interdot spacing Dip, and nanosphere radius R.

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