Large-Scale Ordered Carbon Nanotube Arrays Initiated from Highly Ordered Catalyst Arrays on Silicon Substrates

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Large-scale fabrication of ordered arrays of carbon nanotubes (CNTs) on silicon substrate has been accomplished using a technique that combines the advantages of the electron-beam lithography (EBL) and template methods. The monodisperse diameters of the fabricated CNTs can be adjusted from about 5 to 100 nm. Using the proposed method, ordered arrays of highly graphitized CNTs can be fabricated economically on most flat and smooth substrates.

Introduction

Aligned carbon nanotubes (CNTs) have attracted considerable interest because of their technological importance for applications such as flat panel displays (FEDs). In some applications of aligned CNTs, well-aligned/patterned CNTs with good regularity and uniformity are highly desirable. For example, in electron source applications, well-aligned/patterned CNTs provide uniform field emission properties throughout the emitter film. In recent years, ordered arrays and patterns of both bundled1–6 and individual CNTs7–23 have been fabricated by chemical vapor deposition (CVD). Ordered arrays of individual CNTs are more desirable in FED application as it is possible to determine the exact geometry of the individual CNT, thereby controlling the field emission properties. It is well-known that in the catalytic CVD growth of CNTs, metal nanoparticles act as catalysts for the growth of CNTs and their size determines the diameter of the CNTs. A key element in achieving uniform ordered arrays of CNTs is the control of the regularity and size of the catalyst particles. To this end, techniques developed include the use of nanoporous5,7–8 and mesoporous substrates2 to confine catalyst particles in the pores, and the use of electron-beam lithography (EBL)19–23 or soft lithography techniques24 to fabricate catalyst nanoparticles regularly on the substrate. Two of the methods that have demonstrated the ability to fabricate ordered arrays of individual CNTs with nearly monodisperse diameters are the EBL method and the template method. With the EBL method,20–23 graphitized CNTs are catalytically grown on silicon (Si) substrates by CVD method from the catalyst arrays formed in the EBL process. Both the diameter and the spacing of the CNTs can be adjusted. However, EBL has its inherent limitations, such as limited pattern area and low throughput. Moreover, the capital cost of high-resolution EBL equip-
ment is very high. Template methods, usually using the pores of an anodic alumina membrane to confine the CNTs, form an alternative and efficient approach to fabricate highly ordered arrays of individual CNTs over large pattern areas with high throughput.7–18 In addition, equipment capital costs are very low. However, it is difficult to fabricate CNT arrays directly on the substrate (such as silicon) by the template method. Most previous works are related to CNTs fabricated directly in anodic alumina membranes with an alumina barrier insulator layer and an aluminum (Al) layer at the backside, thus greatly limiting the application of the CNT arrays in FEDs and silicon-based microelectronics. The low melting point of Al and cracking of the alumina at high temperatures (above 400 °C), caused by the difference in thermal expansion coefficient between Al and the alumina membrane, also greatly degrade the quality of the CNT arrays. Another disadvantage is the poor crystallinity of CNTs7–18 fabricated in the pores of templates. It is believed that 13,15 both the metal nanoparticles (usually at the bottom of the pores) and the pore walls of the membranes act as catalysts in the CNT growth. Hence, there is a competition between the well-graphitized CNTs grown from the metal catalysts and the poorly graphitized (usually amorphous) carbon deposits on the pore walls. Indeed, in the absence of metal catalysts, poorly crystallized CNTs7–13 and even amorphous carbon nanofibers18 were obtained. Poor graphitization of the CNTs degrades their current-carrying capability due to the higher intrinsic resistivity, which will limit the field emission current attainable before catastrophic degradation.

In this paper, we report a novel approach to fabricate ordered arrays of CNTs on Si substrates by combining the advantages of the template and the EBL methods. First, a highly ordered catalyst array is fabricated on the surface of a Si substrate using an ultrathin alumina membrane (UTAM) as an evaporation mask. The mask is subsequently removed and the growth of nanotubes on the catalyst arrays is carried out by plasma-enhanced CVD (PECVD), a process widely used to fabricate vertically aligned CNTs.4,19–23 Using the proposed method, large areas of ordered CNT arrays (up to several tens of square centimeters) can be fabricated without the need for expensive equipment. The monodisperse diameters of the CNTs can be easily adjusted by changing the size of the catalysts, which is in turn determined by the pore size of the UTAMs. Unlike the conventional template method, the ordered CNT arrays are fabricated directly on the substrates, and there is neither the alumina template nor the Al underlayer to affect the CNT growth. The graphitization of the CNTs is much better than the template method because there is no amorphous carbon growth as would be found on the pore walls of alumina membranes. The proposed method provides a new alternative to fabricate large-area ordered arrays of CNTs.

**Experimental Section**

Figure 1 outlines the entire fabrication process of the ordered CNT arrays on Si wafers. First, an UTAM mask was prepared in the following two-step anodization process.25 A high-purity (99.99+% Al) foil was first degreased with acetone, then annealed at 400 °C for 4 h; finally, it was electropolished in a 1:9 solution of perchloric acid and ethanol. After the first anodization (Figure 1a) in 0.3 M oxalic acid solution at 40 V in 17 °C, the oxide layer was removed in a mixture of H3PO4 (6 wt %) and H2CrO4 (1.8 wt %) at 60 °C (Figure 1b). The specimen was anodized again for a very short time resulting in a very thin alumina layer (Figure 1c). Then, a PMMA layer was deposited on the top of the alumina layer from a 6% PMMA/chlorobenzene solution, and baked at 120 °C for about 25 min (Figure 1d). After that, the Al layer was removed in SnCl2 solution. The removal of the barrier layer and the subsequent pore-widening process were carried out in 5 wt % H3PO4 solution, forming an ultrathin alumina mask (UTAM) with a PMMA layer on the top (Figure 1e). Then the UTAM/PMMA was mounted on the Si substrate, followed by the removal of the PMMA (Figure 1f and g). A typical UTAM on Si wafer is shown in Figure 1g. The pore regularity is extremely good as it arises from a long first anodization duration of 10 h. The area of the UTAM can be as large as several tens of square centimeters.

Nickel (Ni) catalyst arrays were subsequently deposited into the pores of the UTAM using thermal evaporation (Figure 1h). After the preparation of the catalyst arrays, the UTAMs were

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removed by simply immersing the samples in acetone for 1–2 min, leaving the highly ordered Ni nanoparticle array on the substrate (Figure 1i). Figure 1h′ shows the ordered Ni array on a Si wafer where part of the UTAM is left behind intentionally, with a Ni layer on the top surface of the UTAM. During the Ni deposition process, the pores of the Ni layer become progressively smaller and finally close (Figure 1h), resulting in cone-like Ni nanoparticles (inset in Figure 1h′).

The CNT growth was carried out by the plasma-enhanced CVD method. The sample was first heated to 700 °C under ammonia flow of 100 sccm at 6 mbar. After the sample temperature reached the growth temperature of 700 °C, acetylene was admitted at a flow rate of 10 sccm. At the same time, a dc plasma was activated, with an anode dc voltage of about 500 V relative to the grounded sample. Chamber pressure was about 7 mbar during growth. Growth time was typically between 5 and 10 min.

All the images in this paper, except Figure 3, were obtained using a scanning electron microscope (Philips XL-30 FEG).

Results and Discussion

Images of as-prepared Ni nanoparticle arrays (Figure 2a), heat-treated Ni nanoparticle arrays (Figure 2b), and ordered CNT arrays grown on the Ni nanoparticle
arrays (Figure 2c) are shown. For comparison, CNTs grown from a continuous Ni film are shown in Figure 2d. The average diameter of the as-prepared Ni nanoparticle is 61 nm and has a quite narrow distribution with a half peak width (HPW), obtained from a Gaussian fit to the diameter histogram, of 8 nm (Figure 2a1). For comparison, Figure 2a3 (and also Figure 2b3 and c3) was obtained at the interface between the Ni particle area and the Ni film area which had no UTAM cover on the Si substrate. The height of the nanoparticles is about 30 nm, which is much smaller than that of the continuous Ni film (which is about 80 nm). The nanoparticle height is limited by pore closure, which also gives rise to cone-like nanoparticles (Figure 2a2). After heat-treatment in ammonia at 700 °C for 5 min (same conditions as that following CNT growth), the size (average diameter of 63 nm and HPW of 10 nm in Figure 2b1) and the regular arrangement of the nanoparticles show no obvious change. On the other hand, the Ni film has transformed to an irregular structure (Figure 2b2). Because of the heat treatment, the particles flattened slightly (Figure 2b2).

Subsequent CNT growth was carried out in acetylene and ammonia gases for 5 min by a dc-PECVD process. Figure 2c2 (top view) and Figure 2c3 (tilted view) show ordered CNT arrays grown on the Ni particle area and disordered CNTs on the adjacent Ni film area. Enlarged views of the ordered CNT area in Figure 2c4 (top view) and Figure 2c5 (tilted view) show that the catalysts on the top of the CNTs have almost identical size and shape, giving rise to the regular CNTs with monodispersed diameters of 47 nm (average diameter) and narrow HPW of 9 nm (Figure 2c5). The height of the CNTs is about 1–2 μm. For comparison, we also grew CNTs on Ni films of the same thickness (30 nm) (Figure 2d) under the same growth conditions. The CNTs from such a process are totally irregular and the diameters have a wide range of distribution from 30 to 180 nm (Figure 2d1). The HPW is 53 nm, which is considerably larger than the 9 nm HPW of the ordered CNTs in Figure 2c. It is obvious that the regularity and the size monodispersity of the CNTs grown on ordered Ni nanoparticles are much better than those of the CNTs typically grown on Ni films.

Figure 2c5 and its inset show that after CNT growth the catalysts changed from flat hemispheroids (base diameter of about 63 nm and height of 25–30 nm in Figure 2b2) to slightly elongated spheroids (diameter of about 47 nm). Because the catalyst volume remains the same, it is clear that each catalyst particle only gives rise to one CNT. This is confirmed by the CNT density of about 107 μm–2 (calculated from the 4 μm2 dashed square area in Figure 2c4), which is almost identical to the density of the Ni nanoparticles of about 105 μm–2 (Figure 2a and b).

Figure 3 shows high-resolution transmission electron microscope (HRTEM; Philips CM300) images of a CNT in the CNT array grown from the Ni nanoparticle array (Figure 2c). It can be clearly seen that the CNT is well graphitized with a diameter of about 47 nm. The thickness of the tube wall lies in the range of 12–14 nm, which suggests that the tube wall is composed of approximately 30–40 graphitic walls. The distance between two neighboring graphitic walls is about 3.45 Å, in agreement with the interplanar distance of graphite (d002 = 3.35 Å).

There is almost no regularity for the arrangement of the CNTs both in the top and tilted views in Figure 2c4 and c5. To study the regularity of the CNT arrangement in the process of CNT growth, very short CNTs with lengths of about 100–200 nm (Figure 4) were grown instead on ordered Ni nanoparticles with larger diameters of about 70 nm. The 45° tilted view (a) and the top view (b) were obtained from the same CNT area; the lengths of the nanotubes are about 100–200 nm. Four representative CNTs, used in registering and identifying similar areas on the two images, are shown circled in white. The insets in (a) and (b) are the enlarged images of the square areas in the figures.
CNTs was also obtained exactly at the same area of the tilted view (Figure 4a). It is clear from Figure 3a that each CNT is grown from a single catalyst nanoparticle. Because the growth time is too short, the catalysts have not changed their shape yet and still remain flat hemispheroids (inset in Figure 4a). Moreover, the two image views, especially from the top, show the regularity of the CNT arrangement. The hexagonal nature of the UTAM pore arrangement transfers directly to the CNT array (inset in Figure 4b).

As the CNT growth progresses, the CNTs can no longer remain perfectly straight and parallel to each other. When the CNTs of ~50 nm diameter grow to about 1–2 μm long (Figure 2c), the ends of the CNTs bunch together (an 8-CNT bunch is shown in the inset of Figure 2c), thereby destroying the regularity of the CNT arrangements at the top of the CNT array while remaining regularly placed at the base.

It is worth noting that the pore diameters of alumina membranes can be adjusted from about 10 to 200 nm to yield Ni nanoparticles of corresponding size. Because the maximum Ni catalyst size to maintain single CNT growth is about 100 nm, the diameters of the ordered-arrayed CNTs in our case can be adjusted from about 5 to 100 nm. Moreover, because the pore size of the UTAMs can be adjusted by the pore-widening process, dense and sparse catalyst dots, and thus the following dense and sparse CNT arrays, can be fabricated.

It should be mentioned that the pore arrangement of anodic porous alumina is usually far from an ideally packed hexagonal columnar array over a sizable region of, say, millimeter dimensions. The defect-free areas of the pore arrays are typically several square micrometers. Thus, the regularity of the catalyst array, and the resultant CNT array, is not entirely perfect as this is dependent on the regularity of the alumina membrane pore array used as the evaporation mask. However, by increasing the anodization time or using a pre-textured process, long-range-ordered pore arrays can be obtained with quite a large defect-free area, even to the order of several square millimeters. Thus, an ideally regular catalyst and CNT array, with a reasonably large defect-free area, could potentially be obtained by using an alumina membrane as the evaporation mask.

Conclusions

In conclusion, ordered arrays of CNTs with monodisperse diameters have been successfully fabricated on Si substrates with large areas. The ordered CNTs are grown from ordered Ni nanoparticles with a one-to-one correspondence. The regularity of the CNT arrays and the uniformity of the CNT diameters arise from the high regularity of the catalyst arrays fabricated using UTAMs as evaporation masks. By changing the diameters of the pores of the UTAMs, the size of the catalyst dots, and thus the diameter of the CNTs, can be adjusted. This approach can be applied to other substrates because the UTAMs can be mounted onto any substrate with a flat and smooth surface. Considering the high uniformity of such aligned arrays of graphitized CNTs, their properties are worthy of further study in the future.

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