

Growth of well-aligned carbon nanotube arrays on silicon substrates using porous alumina film as a nanotemplate

Wenchong Hu, Dawei Gong, and Zhi Chen^{a)}

Department of Electrical and Computer Engineering and Center for Micro-Magnetic and Electronic Devices, University of Kentucky, Lexington, Kentucky 40506

Liming Yuan and Kozo Saito

Department of Mechanical Engineering, University of Kentucky, Lexington, Kentucky 40506

Craig A. Grimes

Department of Electrical Engineering and Materials Research Institute, 208 Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16803

Padmakar Kichambare

Department of Electrical and Computer Engineering and Center for Micro-Magnetic and Electronic Devices, University of Kentucky, Lexington, Kentucky 40506

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Aligned, open-tipped carbon nanotube arrays of high density and uniformity were synthesized via a flame method on silicon substrates using a nanoporous template of anodized aluminum oxide from which the nanotubes were grown. The diameter and length of the nanotubes are controlled by the geometry of the aluminum oxide template. These results show the feasibility of integration between carbon nanotube arrays and silicon microelectronics. © 2001 American Institute of Physics.

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Carbon nanotubes (CNTs) are promising candidates for use in field-emission (FE) devices and nanoelectronics.^{1,2} Recently, researchers have been trying to grow nanotube arrays of controlled geometry and electrical properties on various substrates. Earlier work reported the use of an anodized aluminum oxide (AAO) film, having highly ordered pore arrays, as a nanotemplate to control the geometry of subsequently grown carbon nanotubes.^{3,4} The nanotubes grown from the AAO templates duplicate the order and pore size diameter of the template, which is determined via the applied voltage during the anodization process. The earlier results^{3,4} were achieved using an aluminum sheet as the substrate, which is not favorable for integration with silicon-based microelectronics. Attempts to grow carbon nanotubes from AAO thin-film templates deposited on silicon substrates have met with little success, only sparsely distributed CNTs were observed grown from some pores.^{5,6}

In this letter, we report on the fabrication of well-aligned, carbon nanotube arrays of high density and uniformity upon silicon substrates. A flame method⁷ is used to grow carbon nanotubes from pore channels of a thin nanoporous AAO film template on a silicon wafer. The geometric parameters of the resulting nanotubes, such as diameter and length, are controllable with the template structure. These results should help facilitate the integration of carbon nanotubes with silicon solid-state circuits.

Fabrication of the CNT array began with the thermal evaporation of an aluminum layer on an n^+ -Si(100) substrate. Uniform Al layer thickness of 0.5 μm was used in this study. Anodic oxidation of the aluminum layer was then performed in 0.2 M oxalic solution at 0 °C. The Al-coated sili-

con substrate was partially dipped into the solution as the anode, and the cathode was a platinum plate. Constant anodizing voltages were used through anodization and the value was 40 V in the case of oxalic acid solution. To make the porous structures more regular and uniform, the so-called "two-step" method was used.⁸ The anodization was stopped when approximately half of the aluminum layer was consumed. Then, the sample was immersed in a mixture of chromic and phosphoric acid at 60 °C to remove the porous alumina layer formed in the first anodization. The surface of the remaining aluminum film had a highly ordered indented hole array upon it, due to the barrier layer structure formed at the bottom of the alumina pores in the first anodization. Anodization of the remaining aluminum layer, under the same conditions, resulted in AAO nanoporous arrays of better uniformity and more straight pore channels, as shown in Fig. 1(a). Straight pores are desirable for the electrodeposition of cobalt catalyst particles at the bottom of every pore. However, at the end of the anodization process there is a residual alumina layer at the bottom of the pore, which makes electrodeposition of the Co particles into the pore channel difficult due to the low-field intensity. Hence, to make the electrodeposition process easier, the AAO template was immersed in a 3 wt% phosphoric acid solution at 35 °C for 20 min; this treatment reduced the thickness of the alumina layer at the bottom of the pore, and increased the diameter of the pores from approximately 45 to 60 nm. It should also be noticed that there was a thin aluminum layer left even after the second anodization. This thin aluminum layer served as a buffer layer to alleviate the thermal shock to the AAO film during flame growth.

Using ac electrodeposition⁹ with an aqueous solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$: boric acid:ascorbic acid (240:40:1 g/l), cobalt catalyst nanoparticles were electrodeposited onto the bottom

^{a)}Electronic mail: zhichen@engr.uky.edu

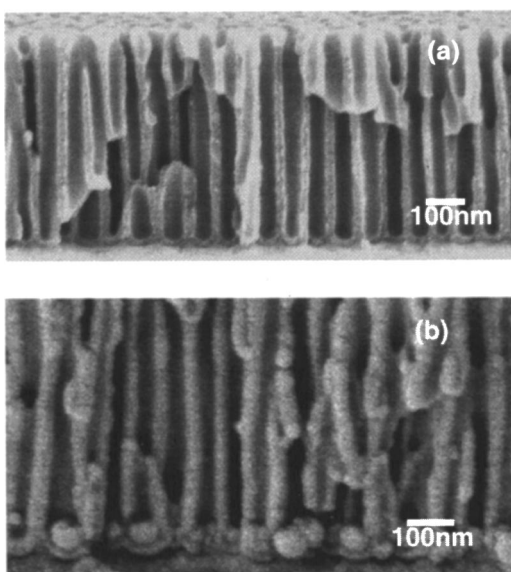


FIG. 1. Cross-sectional SEM images of AAO nanopore arrays with a pore depth of about 500 nm: (a) before Co electroplating and (b) after Co electroplating.

of the AAO pores. The FE scanning electron microscopy (SEM) image, see Fig. 1(b), shows uniform deposition of Co nanoparticles inside the pores; most of the catalyst particles are at the bottom of the pores and tend to be grained into big clusters, filling the bottom of the pore.

The CNTs were grown using a laminar ethylene–air co-flow diffusion flame, with which graphitized multiwall carbon nanotubes had been grown without the presence of graphite particles.¹⁰ The detailed description of the experimental apparatus is provided elsewhere,¹⁰ and briefly summarized here. Ethylene (99.5% purity) was issued from a 1.1-cm-diam stainless-steel tube, which was surrounded by a 5-cm-diam tube through which air flowed. With the average linear fuel flow rate of 4.7 cm/s and the average linear air flow rate of 63 cm/s, a steady and stable laminar flame with a visible flame height of 33 mm was established on the burner port. The flame diameter at the sampling location is about 10 mm. In our experiment, the basal plane of the AAO template (10 mm×5 mm) was placed perpendicular to the gas flow direction and kept in place for 5 min. Visual inspections showed a layer of smooth and shiny black material deposited on the template. The sample was then dipped into the chromic and phosphoric acid mixture to partially remove the AAO template, making it possible to observe the resulting CNT array that grew inside the AAO pores.

The Figs. 2(a) and 2(b) show the FE-SEM images of the resulted CNT array with different magnifications. The images were taken from some cracks that were deliberately created by ultrasonic bath for SEM observation. Well-aligned CNTs were seen grown inside the template pores with high density. Due to the confinement of the pore channels, these nanotubes have a monodispersed diameter which is identical to that of the AAO template pores, approximately 60 nm. The nanotubes are found to stop growing at the surface of the aluminum oxide film, hence, the nanotube length can be readily controlled through film thickness. Moreover, the open-tipped feature of the nanotubes is similar to those ob-

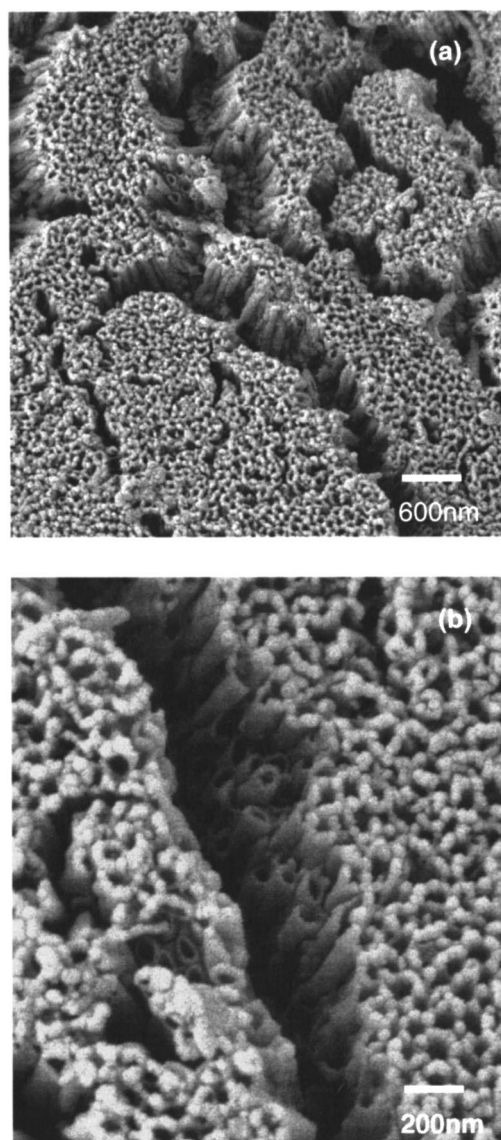


FIG. 2. Cross-sectional SEM images of CNT arrays (about 500 nm long) on silicon substrates for (a) low magnification and (b) high magnification. The cracks were deliberately created in order to observe the nanotubes. The original surface was free from cracks.

served by other authors using bulk aluminum sheets as the substrate.^{3,4}

In our experimental observation, the nanopore structure of the AAO template is still complete after the flame growth of the CNTs. Since the temperature of the flame is 1200–1500 °C,¹¹ with the substrate temperature changing dramatically during the growth process, the AAO porous structures obtained here are certainly stable to thermal shock. In our structures, this stability is simply achieved using a thin aluminum film, left after the second anodization, as the buffer layer. In a previous report, AAO films on silicon wafers cracked during high-temperature processes, thus requiring a Nb layer between the Al film and silicon substrate to prevent the AAO porous structure from collapsing.⁵

In the case of growing CNTs from the AAO template, the carbon nanotubes were supposed to grow from the cobalt catalyst particles, and AAO pore channels only offer physical confinement to the CNTs' diameter and position. However, it was found that the AAO pores can serve as an effective

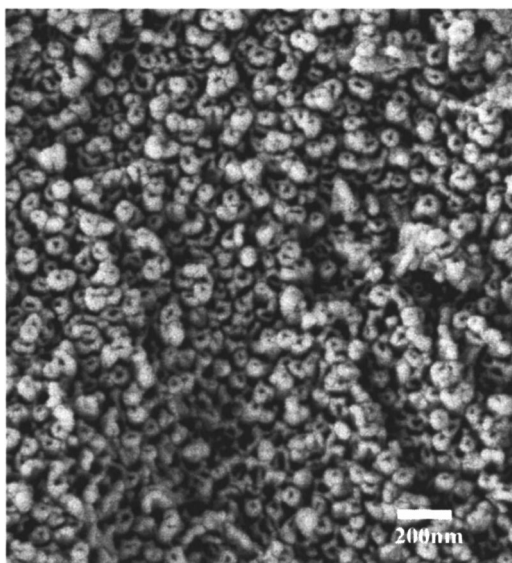


FIG. 3. Top view of CNT arrays growing from a template prepared in sulfuric acid solution (1.5 wt %), 20 V.

catalyst media during chemical-vapor deposition growth.^{3,4} When using the flame method, we also observed several phenomena possibly related to the catalytic function of AAO pores. First, the growth of nanotubes stopped at the openings of the pores, implying that the ethylene may not decompose so effectively in the absence of the catalytic AAO pores. Second, it was found that the topologies of CNTs match the shape of their hosting pore channels so well that CNTs should strongly interact with the pore channels. As an illustrative example of this, “Y” shaped carbon nanotubes have been obtained in our experiments using “Y” shaped channels of the alumina template, as reported before.¹² Further, in some areas, the catalytic function of AAO pores was observed being enhanced, leading to the coating of an amorphous carbon layer outside the nanotubes. This might attribute to higher temperature in the areas. To achieve well-graphitized nanotubes from the AAO pores, the overwhelmingly catalytic function of the AAO pores is undesirable and needs to be suppressed with optimum growth condition.

AAO templates with smaller pore size were also used for

nanotube growth. Figure 3 shows the top-view SEM image of nanotubes grown from the AAO template anodized in sulfuric acid solution (1.5 wt %) at 20 V. Because of the thinner barrier layer, the cobalt catalyst particles were easily electrodeposited at the bottom of the pores, even with brief pore widening. The average diameter of the CNTs grown from these pores was around 35 nm and these CNTs were also open tipped.

It should be noted that small catalyst particles deposited on the pore sidewalls resulted in nanotubes with a diameter of a few nanometers growing beyond the surface of the pore opening; these nanotubes were much like those observed in Ref. 5. These randomly grown nanotubes can be removed with the AAO template.

In conclusion, open-tipped CNTs grown using a flame method were synthesized in array form upon a silicon wafer using an anodized aluminum oxide template. The resultant nanotube arrays exhibit high density and uniformity, with the diameter and length of the carbon nanotubes determined, respectively, by the pore diameter and depth of the AAO layer. The open-tipped structure of the nanotubes should facilitate their use in sensing applications, while the ability to integrate nanotube arrays with silicon substrates offers the promise of building smart sensor arrays and molecular electronic devices.

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