

Fabrication and Characterization of Vertically Aligned Carbon Nanotubes on Silicon Substrates Using Porous Alumina Nanotemplates

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An ethylene-air laminar diffusion flame successfully provided silicon substrates of anodic aluminum oxide (AAO) template with vertically oriented well-aligned carbon nanotubes. Field emission scanning electron microscopy (SEM) showed that open-tipped carbon nanotubes consisting of tube elements with the same length and diameter uniformly coated the template. High-resolution transmission electron microscopy (TEM) analyses revealed these nanotubes to be multiwalled carbon nanotubes, some well graphitized. It was found that cobalt catalyst particles, but not the porous aluminum templates, helped the growth of carbon nanotubes through graphitization and bonding of carbon nanotubes to the silicon substrates.

Keywords: Carbon Nanotube, Porous Alumina Film, Flame Synthesis, Silicon Substrate.

1. INTRODUCTION

Carbon nanotubes (CNTs) can be classified into two types: single-walled tubes and multiwalled tubes, depending on the number of graphite layers. Because of the diameter and helicity of the graphite layers, nanotubes can be metallic or semiconducting.¹ With their excellent electrical and mechanical properties, CNTs have a very wide range of applications, especially in sensing and molecular electronic devices. Promising applications have been demonstrated in the fabrication of transistors,^{2,3} scanning probes,^{4,5} and field emission sources.⁶ Several methods have been developed to synthesize CNTs, including chemical vapor deposition (CVD),⁷ arc discharge,⁸ and laser ablation.⁹ Regarding the potential applications in microelectronics, it is necessary to control the diameter, length, and orientation of CNTs. Li et al.¹⁰ have grown large-scale aligned CNTs on silica substrates. Using porous anodic aluminum oxide (AAO) as a template, Xu's group⁷ and Suh and Lee¹¹ reported synthesis of highly ordered CNTs by CVD. The templates were fabricated by anodization of aluminum sheets in aqueous oxalic acid under a constant voltage for a long time. AAO can function as a good template through which the diameter, length, and orientation of CNTs can be fully

controlled; meanwhile, the CNTs are separated from each other by the oxide.

Growth of CNTs on silicon substrates rather than on aluminum substrates, however, is more favorable for potential applications in microelectronics, which provides the possibility of incorporating CNT growth into modern semiconductor processing technologies. Attempts have been made to grow CNTs on silicon substrates with the use of AAO thin films as templates with little success; only sparsely distributed CNTs were observed to be grown from some pores.¹² Recently, we reported the first evidence of the synthesis of well-aligned large-scale CNTs from AAO thin film on silicon substrates.¹³ No details of the fabrication and characterization were reported. In this paper, we report the role of catalyst particles in the synthesis and growth of CNTs on silicon substrates. CNTs are characterized by field emission scanning microscopy (FE-SEM), transmission electron microscopy (TEM), TEM-EDS (energy-dispersive spectrometry), and high-resolution transmission electron microscopy (HRTEM). An electrolyte of aqueous sulfuric acid was used in this study to prepare AAO thin films on silicon substrates, and oxalic acid was previously used for anodization.¹³ Because the diameter of nanopores made by sulfuric acid solution is smaller than those made by oxalic acid, it may be possible to grow smaller diameter CNTs with sulfuric acid.

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2. EXPERIMENTAL DETAILS

Fabrication of vertically aligned CNTs was started with thermal deposition of an aluminum thin film with a thickness of $2\ \mu\text{m}$ on an $n^+\text{-Si}(100)$ wafer with a resistivity of $0.005\ \Omega\text{-cm}$ under a pressure of 2.0×10^{-6} torr. A porous AAO template was then obtained by anodization of the aluminum thin film. To make the pores of AAO as straight and uniform as possible, a two-step anodization was adopted in an aqueous solution of sulfuric acid (1.5 wt%) under constant voltage (20 V) at $20\ ^\circ\text{C}$.^{7, 11, 14} In the first step, the sample was anodized for 5 min followed by etching for 5 min in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%) at $60\ ^\circ\text{C}$ to remove the anodized surface layer. In the second step, anodization was carried out for 30 min under the same conditions as in the first step. At the final stage, the voltage was decreased to about 3 V for 15 min to reduce the oxide barrier layer at the bottom of the pores. Note that the second anodization left a thin layer of aluminum, which can act as a buffer layer to alleviate the thermal shock to AAO film during flame synthesis. The sample was then etched in a mixture of chromic acid (1.8 wt%) and phosphoric acid (6.0 wt%) at $60\ ^\circ\text{C}$ for 90 s for to further thin the barrier layer and widen the pore size. Catalyst particles were then electrodeposited in the bottom of pores in an aqueous solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$:boric acid:ascorbic acid (240:40:1 g/L) under $14\ \text{V}_{\text{rms}}$ AC voltage. Within 1 min, cobalt particles filled up the bottoms of pores and the film color changed. To find catalytic effects of AAO and cobalt particles, an AAO template from the same process *without cobalt deposition* was also prepared for growth, which thereafter was called Sample II, and the template *with cobalt deposition* was labeled as Sample I.

The CNTs were grown from a laminar ethylene-air co-flow diffusion flame.¹⁵ The flame method has been proved to be effective in the synthesis of CNTs because of its energy efficiency, low cost, and high energy density.^{15, 16} The setup for the flame synthesis, similar to the one used previously,¹⁷ is shown in Figure 1. The apparatus consists of two concentric tubes. The inner tube, made of stainless steel, is 1.1 cm in diameter. The outer tube is made of copper and has a diameter of 5 cm. Fuel flows through the inner tube at a rate of $4.46\ \text{cm}^3/\text{s}$, and air flows through the annular space between the inner and outer tubes at a rate of $1176\ \text{cm}^3/\text{s}$. The fuel used is a chemically pure (CP) grade ethylene of 99.5% purity. A steady and stable laminar diffusion flame with a visible flame height of 33 mm is established on the burner port.

The experimental results show that the position in the flame suitable for synthesis of CNTs is about 4 mm above the burner exit. The flame diameter at this location is about 10 mm. The AAO template ($10\ \text{mm} \times 5\ \text{mm}$) was inserted into the flame perpendicular to the gas flow direction and kept in place for 20 min. The pyrolyzed gaseous products were impinged on the template. With the heat

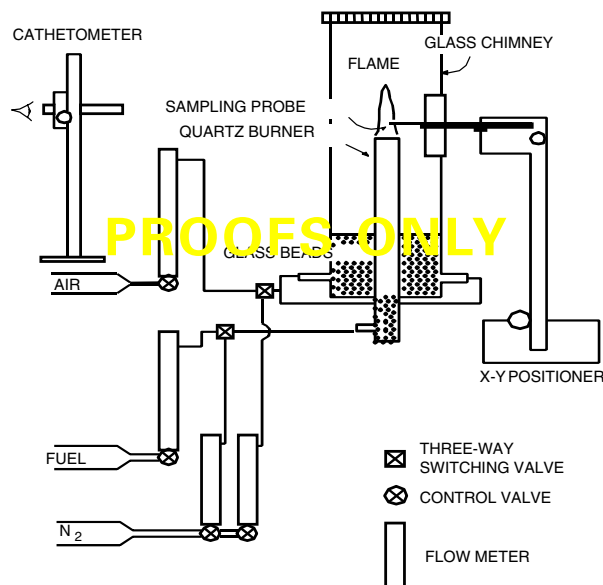


Fig. 1. A schematic of a flame-synthesis experimental apparatus.

generated at flame sheet, the gas environment near the template was suitable for CNT synthesis with a temperature of $1200\text{--}1500\ ^\circ\text{C}$. Visual inspections showed a layer of smooth and shiny black material on Sample I; most of the thin film layer on Sample II was peeled off, and the remaining parts appeared spongy. This shows that without cobalt catalyst (Sample II), CNTs do not adhere well to the substrate. To observe the CNT arrays inside the AAO pores under SEM, the samples were dipped in the chromic and phosphoric acid mixture to partially remove AAO templates. To prepare samples for TEM analysis, we etched the AAO overnight with aqueous NaOH (0.1 M). Because CNTs in Sample I with cobalt deposition were bonded tightly to the silicon substrate, the substrate had to be broken into pieces to release CNTs. After several washes by ethanol alcohol and dispersion by ultrasonic cleaning for 10 min, drops of CNTs were placed on the copper TEM grids and dried.

3. RESULTS AND DISCUSSION

Figure 2a is a cross-sectional image of the nanopores taken by FE-SEM (Hitachi S900, 3 kV), showing a $1.8\text{-}\mu\text{m}$ -thick film layer with straight and uniform pores. To find optimal conditions for producing a straight and highly ordered pore structure, further parameter studies are required. For example, an increase in anodization time will make both the pore diameter and the pore distribution uniform. The AAO pore diameter after anodization has a linear relationship with applied voltage.¹⁴ With a lower voltage, one can expect a smaller pore diameter and thus a higher pore density per unit area. The average pore diameter in our samples is about 30 nm, half the diameter in our previous report,¹³ and the pore density is about $3 \times 10^{10}/\text{cm}^2$. Figure 2b is a cross-sectional image taken after

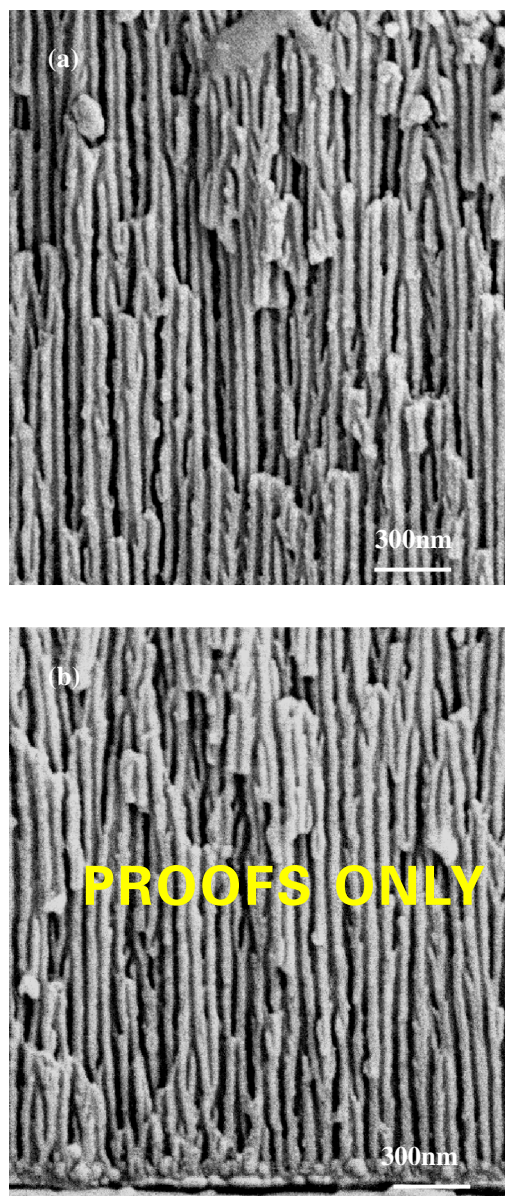


Fig. 2. SEM cross-sectional images of AAO nanopores in Sample I. (a) Before Co electrodeposition. (b) After Co electrodeposition.

electrodeposition, showing the catalyst particles deposited uniformly at the bottom of pores, with one particle in each pore. The diameter of particles is limited by pores to the nanometer scale, which is critical for its catalytic effect.

The FE-SEM top views of CNTs are shown in Figure 3, a and d, and cross-sectional views are shown in Figure 3b. Figure 3a (top view of Sample I) shows CNTs grown from most of the pores with one CNT in one pore, separated from each other. These open-tipped CNTs have the same outer diameter, which is limited by the pore size. However, the diameter of CNTs released from pores is slightly larger than that trapped in the pore, probably because of the absence of confinement and the adsorption of water. The growth of CNT was stopped at the

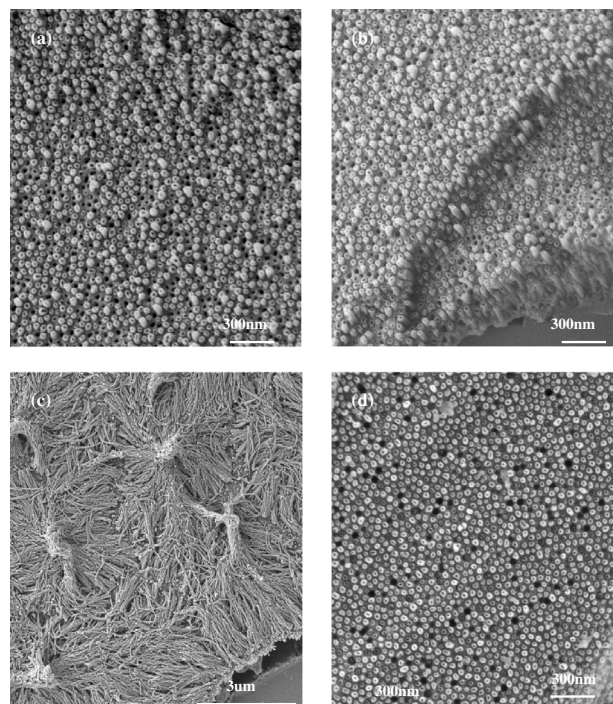


Fig. 3. SEM images of CNT arrays on silicon substrates. (a) Top view of Sample I. (b) Cross-sectional view of Sample I. (c) CNT bundles in Sample I after the AAO template is dissolved. (d) Top view of Sample II.

pore openings, indicating that AAO has some catalytic effect on the growth of CNTs. Figure 3b shows the cross-sectional image of Sample I CNTs, which were grown from the bottom of the pores. To study an interaction between CNTs and the substrate, the Sample I AAO template was dissolved with 0.1 M NaOH overnight, resulting in CNT bundles on the silicon substrate, as shown in Figure 3c. Although there is a very thin AAO barrier layer after the electrodeposition, the bundles are firmly attached to the substrate, indicating that CNTs in our case are directly bonded to the silicon substrate or via a thin media layer composed of silicon, aluminum, and cobalt elements. However, the exact structure of the alloy is unclear.

Contrary to the above, the bonding force between the substrate and CVD-produced CNTs is weak. The temperature for the CVD method is normally less than 800 °C because of the low melting point of aluminum. However, in our case there is no temperature limit when a silicon substrate is used, because of the high melting point of Si. Because of the much higher temperature of a C₂H₄ flame (1200–1500 °C), CNTs with the help of cobalt particles may be able to firmly adhere to the substrate, together with the alumina template separating CNTs from each other. It may be possible to operate on single CNT or to etch away the template to yield CNT bundles. Figure 3d shows the top view of Sample II. Although there are no CNTs in many areas because the thin film has been peeled off, the morphology in some areas of Sample II

is almost the same as that of Sample I. Note that CNTs in Sample II had a weak bond to the substrate; accordingly, after etching overnight in 0.1 M NaOH, all of the CNTs were separated from the substrate. This indicates that cobalt particles help CNTs bond to the substrate.

TEM characterization was carried out with a JEM-2000FX at 200 kV to explore the internal structures of Sample I. Figure 4a shows typical CNT bundles in Sample I, which have not been fully dispersed by ultrasonic cleaning. These CNTs attached to the silicon substrate are open at the tips. The wall thickness is about 10 nm. TEM-EDS in Figure 4b shows that there are cobalt particles with a $K\alpha$ of 6.9254 keV in the root of CNT bundles. The weight percentage of cobalt elements is about 9.66% among Co, Fe, Cr, Cu, and Si. Copper, iron, and chromium elements shown in Figure 4b are caused by the use of the copper grid and the sample holder.

Some researchers might question whether true carbon nanotubes are synthesized with the flame synthesis

method. HRTEM can be used to answer this question, as has been done by other researchers. HRTEM (JEM-2010F, 200 kV) can reveal the fine structures of CNTs, as shown in Figure 5. We found two types of CNTs in Sample I, but only one type in Sample II. Figure 5a shows one type of CNT with a multiwalled structure in Sample I. The wall thickness is about 8 nm, and the maximum hollow width is 7 nm. These CNTs are well graphitized compared with the CNTs grown by CVD on an aluminum sheet substrate.¹⁸ Because the flame temperature is much higher than that in CVD, the high temperature may benefit the catalytic effect of AAO and cobalt particles in the bottom of the pores. Figure 5a shows that there is a clear distinction between the inner shells and the outer shells of the CNT. The inner shells are multiwalled structures with about 11 layers, whereas outer shells are not well graphitized. Figure 5b shows the other type of CNTs that were found in Sample I. These not well graphitized CNTs have a ~ 30 -nm diameter and no clear distinction between the inner shells and outer shells. Figure 5c shows the tip-ended structure of a CNT in Sample II. Even without catalyst particle deposition, CNTs can grow because of the catalytic effect of AAO itself, which is also supported by the SEM image of Sample II shown in Figure 3d. CNTs from Sample II, shown in Figure 5c, have almost the same structure (not well graphitized) as those from Sample I (Fig. 5b). The quality of CNTs from Sample II is lower than that of the well-graphitized counterparts in Sample I (Fig. 5a).

There are studies^{7,19} that suggest, in agreement with our previous study,¹³ the AAO's positive effects on the growth of CNTs. These studies raise an interesting question: whether or not cobalt particles are needed as a catalyst for the growth of CNTs. To answer this question, first we looked at the difference between Samples I and II. The structural difference in CNTs from Sample I is not likely due to the temperature difference in the substrate surface (because it is very small). Then we considered the effect of preheating the sample to the steady temperature level (1200–1500 °C). The transition time was estimated to be 2 s, so we prepared two different samples: one with cobalt particles and the other without cobalt particles. We repeated the growth experiments under the same conditions as before, except for a short growth time of 2 s, and found no CNTs on either sample. Our study suggests the dependence of CNT structure on types of catalyst: AAO makes nongraphitized CNTs, whereas cobalt can make well-graphitized CNTs. The electrodeposited cobalt particles have at least two positive effects: they help the growth and graphitization of CNTs and produce pores that can function better. This is an interesting result that suggests the need for further studies to test different types of catalysts on the growth of CNTs.

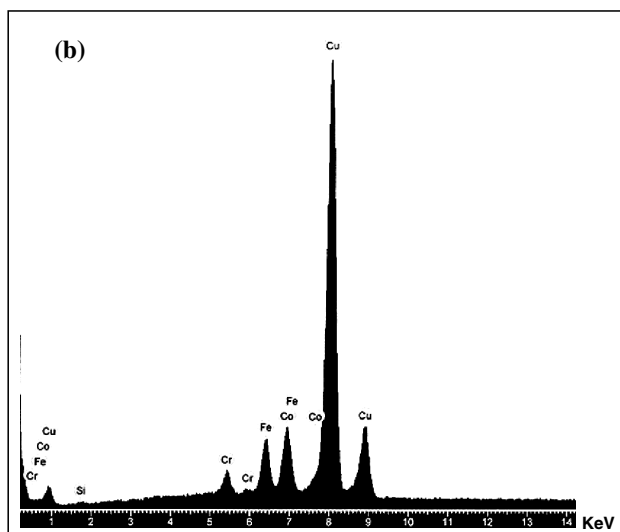
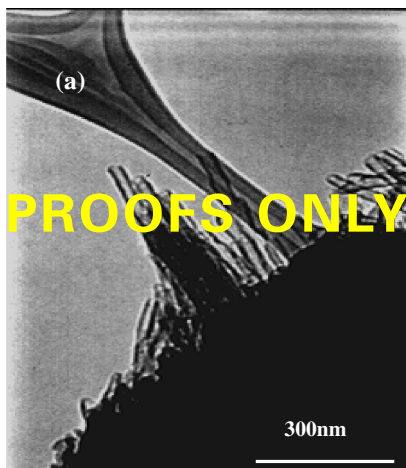


Fig. 4. (a) TEM images of CNT bundles in Sample I. (b) TEM-EDS, showing that catalyst particles exist in Sample I after CNT growth.

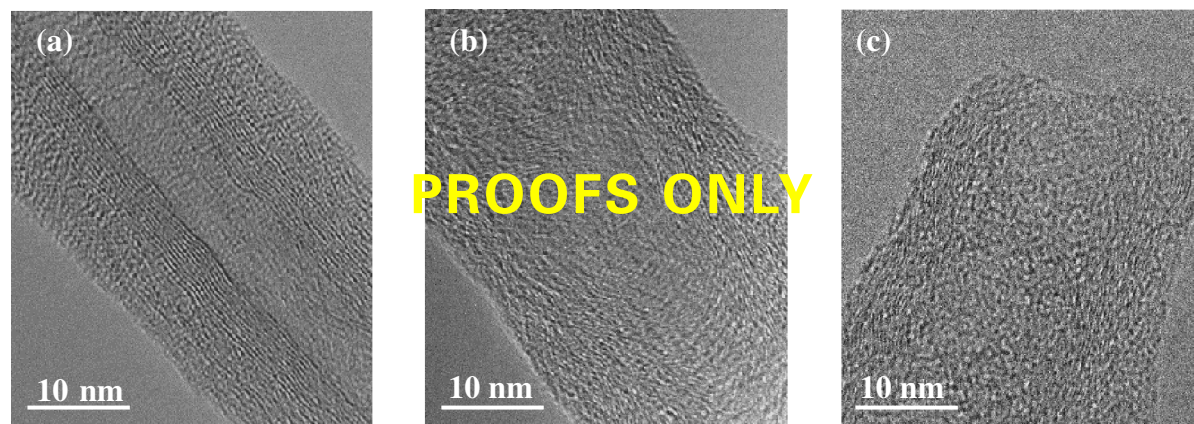


Fig. 5. TEM images of CNTs. (a) Well-graphitized CNTs from Sample I. (b) Not well graphitized CNTs from Sample I. (c) CNTs from Sample II.

4. CONCLUSIONS

Vertically aligned multiwalled carbon nanotubes were successfully fabricated *on silicon substrates* by the ethylene flame method, with thin-film anodic aluminum oxide (AAO) as the template. The diameter and length of the open-tipped CNTs can be controlled by the AAO nanotemplate. We also found that the AAO template has some catalytic effect, but the cobalt catalyst particles deposited at the bottom of pores are necessary for the growth of well-graphitized CNTs with strong bonding to the substrate.

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