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ABSTRACT OF THE THESIS

FABRICATION OF VERTICALLY ALIGNED CARBON NANOTUBES AND HORIZONTAL NANO-STRUCTURES

Fabrication of ordered anodic alumina nanopore arrays and anodization parameters including electrolyte, concentration, voltage, temperature and time have been investigated. Cobalt nanoparticles were electrodeposited at the bottom of the pores. Vertically aligned, open-tipped multi-walled 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. The diameter and length of the nanotubes are controlled by the geometry of the aluminum oxide template. It is the cobalt catalyst particles, not the porous aluminum templates, help the growth of carbon nanotubes through graphitization and bonding of carbon nanotubes to the silicon substrates.

Fabrication of nano-structures has been demonstrated. Nano-trenches of 20 nm have been achieved using single-walled nanotube bundles as shadow masks, which were aligned across electrodes under high frequency AC voltage.

KEYWORDS: Carbon Nanotube, Porous Alumina Film, Flame Synthesis, Silicon Substrate, Shadow Mask

WENCHONG HU

12/10/2002

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FABRICATION OF VERTICALLY ALIGNED CARBON NANOTUBES AND HORIZONTAL NANO-STRUCTURES

By

Wenchong Hu

Zhi Chen Director of Thesis

William Smith Director of Graduate Studies 12/10/2002

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THESIS

Wenchong Hu

The Graduate School

University of Kentucky

2002

FABRICATION OF VERTICALLY ALIGNED CARBON NANOTUBES AND HORIZONTAL NANO-STRUCTURES

THESIS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Electrical Engineering in the College of Engineering at the University of Kentucky

By

Wenchong Hu

Lexington, Kentucky

Director: Dr. Zhi Chen, Professor of Electrical Engineering

Lexington, Kentucky

2002

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Chapter One Introduction

1.1 Backgrounds

Carbon is an element with unique properties in column IV of the periodic table. It can form the most ordered allotropes: diamond, a three-dimensional (3D) material with almost isotropic properties; graphite, a highly anisotropic two-dimensional (2D) semimetal; carbon nanotube, a one-dimensional (1D) tiny hollow carbon pipe and fullerene, a zero-dimensional (0D) form. Diamond and graphite have been known to the world for several decades and have been widely used in many fields. However, fullerene and carbon nanotube (CNT), have become intense research fields after their discoveries. C60 (one group of fullerenes, Figure 1.1 (a)), a carbon molecule shaped like a soccer ball, was discovered in 1985 by Harry Kroto of the University of Sussex in England and a team at Rice University, Texas, led by Richard Smalley [1]. The new perspectives that it opened up were acknowledged by the award of the 1996 Nobel Prize in chemistry to Smalley, Kroto and colleague Robert Curl. CNT (shown in Figure 1.1 (b)) was discovered in 1991 by an electron microscopist, Sumio Iijima at NEC, when studying materials deposited on the cathode during the arc-evaporation synthesis of fullerenes. These CNTs were multi walled nanotubes. After the report of this discovery in Nature [2], many people working on fullerenes quickly switched their focus to these tiny filaments instead. The simple reason was that, as theorists predicted, the properties that nanotubes should possess would let them do more interesting things besides fullerenes.

1.2 CNT Definition and Classification

Carbon nanotube can be considered as a hexagonal network of carbon atoms that has been rolled up to make a seamless hollow cylinder whose ends are each capped with half a fullerene molecule [3]. These cylinders can be tens of micrometers long. CNTs form in two categories: multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). The diameter for MWCNTs can be from several up to tens of nanometers across, while the typical diameter of a SWCNT is just one to two nanometers. SWCNT has only one layer and MWCNT has two to more than twenty layers. Figure 1.2 shows images of a SWCNT and MWCNTs with different layers under High Resolution Transmission Electron Microscopy (HRTEM).

1.3 CNT Synthesis Methods

1.3.1 Arc Discharge Method

This is the most common and perhaps easiest way to produce carbon nanotubes. The principle of this method is based on an electric arc discharge generated between the two graphite electrodes under an inert atmosphere of helium or argon. The high temperature (>3000°C) between the two rods during the process causes the sublimation of carbon to form nanotubes. This technique has been used for the synthesis of SWCNTs and MWCNTs, synthesis of gram quantities of nanotubes has also been reported [4].

1.3.2 Laser Ablation Method

This method involves shooting a laser at a graphite target in the presence of metal catalyst. In contrast to arc discharge method, direct laser vaporization allows far greater control over growth conditions thus can produce high quality of SWCNTs with high yield [5]. SWCNT bundles are catalyzed by Co/Ni (0.6/0.6 at wt%) with an oven temperature of 1200°C.

1.3.3 Chemical Vapor Deposition (CVD)

CVD offers the best chance of obtaining a controllable process for the selective production of nanotubes with defined properties. It is possible to produce well-aligned MWCNTs by this method [6, 7]. Large scale synthesis of SWCNTs has also been reported [8].

This technology involves a tube (CVD reactor) that can be heated to high temperature, catalysts such as Fe, Co, Ni are prepared on a substrate or are introduced into the CVD reactor *in-situ* as a form of a floating catalyst. Carbon sources include various hydrocarbon such as methane, acetylene, ethylene or CO. The synthesis is carried out in Ar, N_2 or H_2 to prevent oxidation of catalyst.

1.3.4 Other Synthesis Methods

Flame Synthesis of CNTs. Flame has been used for commercial synthesis of a wide range of materials such as carbon black, also for the study of combustion and soot. Although Howard et al. [9] reported the presence of CNTs in the soot formed in acetylene and benzene; Vander Wal, et al. [10] observed SWCNTs in the acetylene diffusion flames, flame synthesis of CNTs met

with little success. Dr. Saito's group reported growth of MWCNTs from a methane flame [11] and well aligned MWCNTs by an ethylene flame [12] with high yield. Besides, Electrolysis method [13], Solar energy synthesis [14] have been reported recently.

1.3.5 Comparison of Methods

Arc discharge and laser ablation are principal methods to synthesize carbon nanotubes before CVD method is available. Although Arc discharge and laser ablation can provide higher quality MWCNTs and SWCNTs, the higher synthesis temperature (> 3000°C) and relatively low throughput with poor selectivity prevent their further development. On the contrary, CVD synthesis is a promising method for its large-scale potential. CVD can yield high pure, well-aligned CNTs with good control of diameter and length through catalyst preparation and synthesis time. It is easy to pattern CNTs with different areas to meet various requirements. Furthermore, the lower temperature (<1100 °C) makes this method possible to incorporate CNTs into electronics fabrication in future.

The advantage of flame method lies in its efficient source of energy and simple operation, besides its widely commercial usage. This method was used in our experiments through a cooperation with Dr. Saito's group at Mechanical Engineering Department, University of Kentucky.

1.4 CNT Properties and Applications

What makes CNT such an intense research field is its exceptional structure and properties that may lead to commercial applications.

1.4.1 Electrical Properties

One aspect of nanotubes that interests researchers is that their properties can be changed simply by varying the way the sheets are rolled. A single graphite sheet (also known as graphene) is a semimetal, which means that it has properties intermediate between semiconductors and metals. When a graphite sheet is formed into a nanotube, the properties must also match up. Depending on how the tube is rolled up (chirality) and its diameter, nanotube can be either a semiconductor, a semimetal, or a metal [15]. The band gap of CNTs has been predicted to decrease with the increasing of tube diameter. Therefore, MWCNTs with diameters of 10 nm or more are expected to show metallic rather than semiconducting behavior at room temperature, while structurally deformed MWCNTs may well be employed in NT-FETs [16]. However, for SWCNTs, theoretical calculations shows that all armchair tubes (n, n) are metallic, but only one third of the zigzag (n, 0) and chiral (n, m) tubes are metallic and the remaining 2/3 are semiconducting, depending on the tubule diameter and chiral angle. Besides, SWCNTs, which normally exhibit p-type behavior, can exhibit n-type conduction after under-going treatment at elevated temperature [17].

Frank *et al.* [18] in Georgia Tech. reported an interesting results on MWCNTs. They measured the conductance of MWCNTs using a liquid metal contact (mercury), and found quantized conductance. The measured conductance appeared to be independent of the length, implying that electronic transport occurs ballistically in nanotubes, which means there is no heat dissipation and a single MWCNT can carry very high current density, which in the tube was greater than 10^7 A/cm^2 . Relatively early in the research of nanotubes, Thess *et al.* [19] reported the resistivity of ropes of metallic SWCNTs to be in the order of $10^{-4} \Omega$ -cm at 300 K. One of their values they measured was 0.34×10^{-4} , which they noted would indicate that the ropes were the most highly conductive carbon fibers known.

1.4.2 Mechanical Properties

One of the most important applications of carbon nanotubes is the use of their mechanical properties or, their high strength-to-weight ratio. CNT is the strongest and most flexible molecular material because of C-C covalent bonding and seamless hexagonal network architecture. Theory and experiments show that the Young's modulus of CNTs is at least as high as graphite and can be even higher for small SWCNTs, which can be over 1 TPa (10¹² Pa). CNTs seems to behave as ideal carbon fibres that can be stiff yet flexible, associating very high modulus with very high strength [20].

1.4.3 Other properties [21]

Based on CNTs' special structures, their chemical, thermal and optical properties have been widely explored. Nanotube functionalization is an intense research field, the caps of CNTs can be removed and the open ends can be functionalized. CNT walls can also be chemically

functionalized to increase their adhesion in composite materials, to solubilize them or increase their sensing capabilities. CNTs can be filled with hydrogen as energy storage, filled with liquids and solids such as HNO₃, S, Cu, Cr to meet specific requirements. CNTs have a thermal conductivity up to 37,000 W/m.K in the axial direction with small values in the radial direction, which is similar to that of an isolated grapheme layer and varies with temperature.

1.5 CNT Applications

CNT's excellent properties have stimulated explosive research around its future applications based on the special structural, mechanical and electrical advantages. Because they are very strong and elastic, nanotubes can be used to enhance mechanical properties of carbon such as diamond, or polymer composite materials [22]. In electronics, promising applications have been demonstrated in the fabrication of transistors [23, 24], advanced scanning probes [25,26], chemical sensors [27,28], field emission sources [29] and other nano-electronic components including capacitors, diodes and basic logic gates [30,31], quantum wires [32] and interconnects between nano-electronic components [33]. Researchers from high-tech companies and universities all over the world are thriving to work on CNTs towards the molecular electronics.

1.6 Challenges

Though carbon nanotubes are promising in many aspects, enormous challenge still exists. There are several fundamental unsolved issues. *First*, how to fabricate atomically high quality CNTs with very high purity? Many synthesis methods have been developed in the past years, however, the quality can hardly meet with commercial requirements. For a SWCNT, a single molecular, it can be a semi-metal, semiconductor or a metal depending on the diameter and chirality, and a subtle change will shift its properties sharply. But before a SWCNT is used as an electronic component, at least its electrical properties should be determined, which requires exact control the synthesis conditions at atomic level. Unfortunately, currently there is no way to achieve this, different batches under the 'same' conditions yield different CNTs, and quite often, one can expect a mixture of the three types of CNTs from the same batch. Although the synthesis of MWCNTs is much easier than SWCNTs, defect free nanotubes still remain big problems. *Second*, regarding the potential applications in microelectronics, it is necessary to control the diameter, length and orientation of CNTs. Under commonly used methods, especially for

SWCNTs, nanotubes are entangled together, which is unacceptable in the applications. Hongjie Dai's group in Stanford University has made great efforts at controlling the orientation of the SWCNTs by an electric-field-directed growth [34] or by a selective catalyst pattern design [35, 36], the diameter and length still remain uncontrollable. Even for the orientation purpose, there is no exact control. *Third*, how to manipulate nanotubes? Theories and experiments on CNTs have shown their fantastic properties, however, how can we manipulate those CNTs? In laboratories, researchers can at least use some fine probes such as Atomic Force Microscopy (AFM) or Scanning Tunneling Microscopy (STM) to manipulate these single molecules at the expense of time and cost. In large-scale fabrication, this method is impractical. How to put a desired CNT at an exact nano-scale spot remains a big challenge towards its application. A possible way is to use self - assembly technology to grow CNTs at desired nano-spot with desired orientation.

1.7 Motivations

Although CNT has emerged as a promising electronic material with many potential applications since its discovery, in the early stage of research and development towards industrial applications, most of nanotubes are grown as random and entangled strings on substrates, which have little interests to engineers. For electronic device research, the majority of research have been focused on manipulation of carbon nanotubes using STM or AFM to study the electrical transport effect [37, 38, 39]. Recently, several groups [6,7, 40, 41, 42] reported growth of aligned carbon nanotubes. Li et al. [6] reported the first aligned CNTs directly on Silica substrate. This type of aligned CNTs has little applications for electronic devices because the nanotubes can not be isolated from each other. Recently, successful growth of vertically aligned MWCNTs through the anodized aluminum oxide (AAO) nano-porous template has attracted the engineers' interest [40]. The nanotubes grown from the AAO templates duplicate the order, orientation, pore diameter and length of the template, besides, the AAO template provides a perfect insulating media for isolation of conductive nanotubes from each other. Suh et al. [41] also fabricated the similar nanotube array structure. However, the above highly ordered CNT arrays were successfully fabricated on aluminum substrates. Growth of CNTs on silicon rather than on aluminum substrates 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. One group, Iwasaki et al. [42], only achieved sparsely distributed CNTs on silicon substrate and the nano-template has no control of CNT growth. It is vital to fabricate CNT arrays directly on silicon substrates with controllability for electronic device applications.

In this thesis, major efforts have been made to the fabrication of vertically aligned MWCNTs on silicon substrate using porous alumina nano-templates with full controllability of the diameter, length, and orientation. It covers the following topics:

- a) AAO template fabrication with different key parameters
- b) Catalyst deposition in AAO template
- c) Flame synthesis (ethylene) of CNTs (through the cooperation with Dr. Saito's group, Mechanical Engineering, University of Kentucky),

d) Structural characterization and growth mechanism of CNTs.

Besides, horizontal nano-structure has been demonstrated using SWCNTs as shadow masks, which were aligned by high frequency AC electrical field.

1.8 General Processes for Fabrication of Vertically Aligned CNTs

Fabrication of vertically aligned CNTs follows the procedures shown in Figure 1.3. Step One (Figure 1.3 (a)): Deposition of aluminum thin film using thermal evaporation, e-beam evaporation or sputtering method under high vacuum. Thickness and quality of the film layer will affect the uniformity of pore structures. Step Two (Figure 1.3 (b)): Fabrication of highly ordered porous AAO template by anodization. Under a DC electrical field, aluminum film mounted on anode is transferred to AAO, and at the same time, porous structure with fully controllable pore size and length is achieved. Step Three (Figure 1.3 (c)): Co catalyst is then electro - deposited at the bottom of the pores to facilitate synthesis of CNTs. Catalyst is found to be necessary to fabricate CNTs with high quality. An AC electrical field is built up between anode and cathode, and catalyst is deposited on both electrodes in a short time. Step Four (Figure 1.3 (d)): Synthesis of CNTs. A newly developed flame synthesis is used in this thesis with easy operation and high efficiency. Using ethylene as a carbon source, uniformly distributed CNTs attached to the substrate are obtained.

1.9 Summary of Chapters

Major parts of this thesis concern with fabrication of vertically aligned carbon nanotubes on silicon substrate, which covers Chapter Two, Three and Four. One application - carbon nanotubes as shadow masks is presented in Chapter Five.

Chapter One provides a general introduction. Background of carbon nanotube including its definition, synthesis methods, properties, potential applications, challenges and motivations are presented. Besides, the general process for fabrication of vertically aligned CNTs is discussed.

Chapter Two presents the preparation of AAO template. Principle of electrochemistry and anodization are first discussed. Anodization parameters such as electrolyte, solution concentration, temperature, voltage and anodization time are studied in details. Mechanism of AAO pore structure is also discussed.

In chapter Three, deposition of catalyst nanopaticles at the bottom of pores is covered.

Chapter Four presents the synthesis and characterization of carbon nanotubes. An ethylene flame method is adopted in the experiments. CNTs from AAO templates with catalyst and without catalyst are compared. Field Emission Scanning Electron Microscopy (FE-SEM), Transmission Electron Microscopy (TEM), TEM-EDS (Energy-Dispersive Spectrometry) and High-Resolution Transmission Electron Microscopy (HRTEM) are used in the characterization. Growth mechanism including functions of deposited catalyst particles and AAO are given in the final part.

Fabrication of horizontal nano-structure is studied in Chapter Five. Electrodes with a smallest gap of around 1 micron by photolithography are obtained. SWCNT alignment is carried out with high frequency under an AC electric field. SWCNTs across the electrodes after trench definition is removed by a thermal oxidation. A better strategy is suggested to fabricate nano-trenches of sub 10 nm.





Figure 1.1: (a) Schematic model of a fullerene molecule, (b) simulated structure of a carbon nanotube made primarily of graphite (http://wwwup hexagons. g.eng.cam.ac.uk/nano/nanotube.htm).



Figure 1.2: HRTEM images of carbon nanotubules with increasing numbers of concentric tubes – one to five layers seen in (a) to (e), correspondingly. (From Ebbesen et al. 1996)



Figure 1.3: Schematic for general processes, a) Al thin film deposited on Si substrate, b) Cross section of AAO porous template, c) Co catalyst deposited at the bottom of pores, and d) MWCNTs grown in the pores.

Chapter Two

Preparation of Highly Ordered Porous Alumina Template

2.1 Introduction

Electrochemistry is a component part of physical chemistry, and plays an important role today in many areas of science and technology. Plated copper is playing a major role in the change from aluminum to copper in semiconductor interconnect technology, which signals one of the most important changes in materials that the semiconductor industry has experienced since its creation. Electrochemistry is primarily concerned with charge transfer at the boundary between an electronically conducting or semiconducting phase and an ionically conducting phase, such as a liquid, molten or solid electrolyte. The electrode at which negative charge enters the electrolyte solution is termed the *cathode*, and electrons leave the system through the *anode*. In the presence of current flow, reduction always occurs at the cathode and oxidation occurs at the anode. Electrochemical cell can be classified into two categories: one in which the electrode reactions take place spontaneously, producing an electrical current, is referred to *galvanic cell*, and is capable of conversion of chemical to electrical energy; the other in which a material is decomposed through the passage of an electrical energy. Figure 2.1 shows a schematic for galvanic cell and electrolytic cell.

Anodization falls into the electrolysis. During the electrolysis, reduction occurs at the cathode. If there are several anions in the solution and there exists the possibility that more than two reductions can occur, the anion with higher electrode potential has the priority to liberate. On the contrary, the oxidation with lower electrode potential should have priority at the anode. Electrode potential E is also called electromotive force (EMF). E^0 is usually reported under *standard conditions* (1 mol/L, 25°C, 1 atm), relative to a reference electrode – the standard hydrogen electrode (SHE). Electrode potential under non standard conditions can be calculated using Nerst equation. Assume there is a reaction occur at an electrode as: $M^{Z^+} + ze \Leftrightarrow M$. Where z is the number of electrons involved in the reaction. Reaction from left to right is a reduction, and reaction from right to left is called oxidation. The potential E of the M^{Z^+}/M electrode is a function of the activity of metal ions in the solution according to the Nerst equation.

$$E = E^o + \frac{RT}{zF} \ln a(M^{z+})$$

Where R, T, z and F are gas constant (8.3145 J·mol⁻¹ ·K⁻¹), absolute temperature (K), number of electrons involved in the reaction (mol), and Faraday's constant (96,500 Coulombs) respectively. A is the activity of the ion, defined as : $a(M^{Z^+}) = \gamma^* c(M^{Z^+})$, where $c(M^{Z^+})$ is the concentration of M^{Z^+} in moles per liter and γ is the activity coefficient of M^{Z^+} , when the concentration of a solution is low, such as 0.001 molar or lower, the activity may be replaced by concentration in moles per liter.

If a piece of aluminum is connected to the anode and a piece of platinum is connected as cathode, when a DC voltage is applied, the reactions are as follows:

Al
$$\Leftrightarrow$$
 Al³⁺ + 3e
 $O_2 \Leftrightarrow 2O^{2-} - 4e$
+
4Al + 3O₂ \Leftrightarrow 2Al₂O₃ (Anode)
2H⁺ + 2e \Leftrightarrow H₂ (Cathode)

The aluminum is oxidized to Al₂O₃. If the electrolyte is acidic solution, the Al₂O₃ will be etched away by the solution. Amazingly enough, this process is not a flat etching step, instead, under the electrical field, a porous anodic aluminum oxide (AAO) may occur. Early in forties of last century, Edwards et al. [43,44] has found this phenomenon, Keller et al. [45], Hunter et al. [46], Wood et al. [47] and Thompson et al. [48] have reported on the structural features, factors affecting the formation of AAO, the direct observation of barrier layers, and direct observation of nucleation and growth. However, the pore structure was not ordered, researchers at that time might not focus on the regularity. In 1995, Hideki Masuda et al. [49,50] obtained a highly ordered porous AAO, which is characterized by a long anodizing period. This naturally occurring self-ordered structure has attracted increasing attention as a key material for fabrication of devices on a nano-meter scale, such as electronic and photonic devices [51-54]. The structure has no confinement for large-scale fabrication, in addition, the pore depth and size can be fully controlled. Researchers have explored the different parameters such as electrolyte, concentration, temperature, applied voltage, anodization time and proposed possible mechanisms for this novel structure [55-59]. Those researches, however, are basically studied on thick aluminum substrates to facilitate the long anodization time, which is undesirable in electronic

applications. A better way is to fabricate AAO thin film on silicon substrate. In this chapter, An attempt has been achieved to fabricate AAO thin film on silicon substrate. Parameters including different electrolytes (H_2SO_4 , $H_2C_2O_4$, H_3PO_4), solution concentration, temperature, voltage and time are studied in details.

2.2 Experimental Procedures

Fabrication of porous AAO began with the thermal evaporation of an aluminum layer on a silicon wafer. N⁺- Si (100) with a resistivity of less than 0.005 Ω – cm, test grade was used to ensure an ohmic contact between the silicon substrate and the thin film. Ohmic contact is a necessary condition for anodization and later process. Before evaporation, wafer was chemically etched in HF (20%) solution for 5 min to remove the native oxide layer on the surface. Thermal evaporation was operated under a high vacuum of 5 x 10⁻⁷ Torr. After several cycles, a clean and shiny uniform aluminum thin film with a thickness of about 3 µm was obtained.

The aluminum thin film was then anodized in an acidic solution. The sample was partially rinsed in the electrolyte as anode, and the cathode was a platinum plate. Constant voltage was used through the anodization. To make the porous structures more regular and uniform, the so-called "two-step" method was adopted [50]. The first anodization was operated for several minutes followed by an etching 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 ordered indented hole arrays upon it, due to the barrier layer structure formed at the bottom of the alumina pores in the first step. Anodization of the remaining aluminum layer, under the same conditions, yielded AAO nanoporous arrays with better uniformity and straightness. The current at the final stage was dropped and the color of the film layer was changed indicating complete transformation of Al to AAO. A Field Emission Scanning Electron Microcopy (FE-SEM) – Hitachi S900 was used to characterize top view and cross view images.

2.3 Results and Discussion

2.3.1 Effect of Film Cleanness

Film cleanness is critical to achieve ordered porous structure. Researchers often use chemical electro-polishing method, a similar process for anodization except for a much larger current flow [50, 55,56], leading to a shiny, flat, and clean surface. Sample not clean enough may result in a

dense and rough surface as shown in Figure 2.2. The sample was anodized in 15.0 wt% sulfuric solution 20 V DC at room temperature for 5 min. There are many particles on the surface which block the development of ordered pore structure. A typical cleaning process in the experiments includes spraying acetone to degrease the sample, followed by isopropyl alcohol (IPA) to remove the residual acetone and then rinsing sample in deionized water.

2.3.2 Effect of Electrolytes

Three electrolytes were used for comparison. Table 2.1 shows all the parameters in the anodization process. Samples of 2 μ m thick were anodized with two steps, the first step lasted 5 min, followed by an etching in a mixture of H₃PO₄:CrO₃ (6.0:1.8 wt %), a second anodization was operated at the given conditions in Table 2.1. Because oxidation rate and pore structures are affected by electrolytes, concentration, voltage and temperature, in addition, there is an optimal parameter window for each electrolyte which is described in next sections, we can not show electrolytic effect here while setting other parameters the same value. However, even under different conditions, distinguishable results can be expected.

Porous structures from different electrolytes are shown in Figure 2.3 (a) and (d) H_2SO_4 , (b) and (e) $H_2C_2O_4$, and (c) and (f) H_3PO_4 . Images (a), (b) and (c) are top-view and (d), (e), (f) are cross-sectional view. The pore size sequence is (a), (d) \leq (b), (e) \leq (c), (f). At room temperature, regularity of pore structures in H_2SO_4 solution is better than that in $H_2C_2O_4$ which is better than that in H_3PO_4 . Regularity can be seen in two different aspects: the shape of a single pore structure and the pore uniformity across the surface. It is shown in (b) that some of the pores cease at the initial stage and individual pore has different shape from each other, round or irregular. While in (c), the regularity is even worse, the wall structure on the surface is collapsed and a net-like structure is formed, no regular ordered pores are visible. The cross-sectional view in Figure 2.3 (d), (e) and (f) further reveals different electrolyte properties. For the internal structures, samples anodized in H₂SO₄ solution is better than those in H₂C₂O₄, which is better than those in H_3PO_4 , this coincides with the surface images in Figure 2.3 (a), (b) and (c). Oxide in H_2SO_4 solution is thicker than that in $H_2C_2O_4$, which is again thicker than that in H_3PO_4 , even though the anodization voltage is in an opposite sequence. In general, the pore formation process is concerned with an initially random oxidation at higher electric field density spots, which are the aluminum peaks or the foreign compounds, followed by locally centered anodization where

pores are developed under the surface layer, together with field-assisted dissolving of AAO into solution [55]. Both anodization (oxidation) process and oxide dissolution process partially depend on electrolyte. Stronger electrolyte can dissolve the oxide faster, resulting in a higher anodization rate. It can be seen from the thickness of the AAO in Figure 2.3 that electrolyte of H_2SO_4 is stronger than $H_2C_2O_4$ and $H_2C_2O_4$ stronger than H_3PO_4 under the given conditions. It is also noticed in experiments that even for one step anodization, i.e. without the intermediate oxide layer etching by other chemicals in the two–step method, samples anodized in H_3PO_4 do not. However, pores can still be developed under the surface. Since H_3PO_4 is the weakest electrolyte among the three, even at higher voltage, the rate of initial pore development is much lower in H_3PO_4 , and electrical field has not centered at the bottom of the pores before the total surface oxide layer is uniformly etched away, thus leading to a pore structure on the surface. In the case of $H_2C_2O_4$ or H_2SO_4 , the initial process is fast enough to develop the pore structure before the surface layer is etched away, yielding a dense and rough surface as shown in Figure 2.4.

2.3.3 Effect of Solution Concentration

Solution concentration affects the pore structure regularity, pore straightness and surface flatness. A sulfuric acid solution was used to examine the effect. Three different concentrations, 15.0 wt%, 3.0 wt% and 1.5 wt% were examined at room temperature. Samples of 2.5 μ m thick were anodized with two steps, the first step lasted 5 min at 20 V, followed by an etching in a mixture of H₃PO₄ : CrO₃ (6.0:1.8 wt %) at 60°C, a second anodization was operated with the same conditions as first step for a longer time of 20 min, samples were finally etched in H₃PO₄:CrO₃ for 60 s at 60°C to explore clear pore structures. Figures 2.5 and 2.6 show the surface images and cross-sectional views respectively. It is shown in Figure 2.5 that concentration has almost no effect on the pore size, however, it affects regularity and surface flatness. Concentration of 3 % provides with a better result, while 1.5 % yields a rough surface with many small bumpers. Concentration up to 15 % produces a flat surface with some pores stopping growing after the initial pore developing stage. Figure 2.6 shows cross-sectional views with 3 % and 1.5 % concentration. It is obvious that 3 % produces much more straight pore channels, and there is almost no ramification on the wall. Samples with 1.5 % concentration have a lot of ramifications and the channels are not very straight. Generally, the dissolving rate

depends partially on the concentration at the same voltage and temperature. A higher concentration (>15%) can yield a higher dissolving rate thus the current density (mA per unit area) during anodization is higher, which leads to a flat surface at the cost of the regularity. For a very low concentration (<1.5%), the dissolving process is not strong enough to etch away oxide layer on the surface and exactly at the bottom of pores, leading to surface roughness and ramifications.

2.3.4 Effect of Voltage

Sulfuric acid solution was used to show this effect. Samples of 2.0 μ m thick were anodized at 20 V, 10 V and 5 V with concentration of 3 %, 3%, and 10% respectively at room temperature. Higher concentration of 10 % was used for 5 V anodization because of the much lower dissolving rate with lower voltage, which can be partially enhanced with higher concentration. First step lasted for 5 min, 5 min, and 30 min, second step stayed for 20 min for all samples, followed by an etching in H₃PO₄: CrO₃ for 1 min.

Figure 2.7 represent surface images and cross-sectional views. It is noted in Figure (c) that cobalt particles are electro-deposited at the bottom of the pores without effects on the pore structure. To show the surface change with anodization, an original aluminum film is presented in (a). The original film is very flat with some small non-continuous cracks spreading over the surface, which may be due to the tensile stress on the film surface. Interestingly, with appropriate anodization conditions, for example, a voltage of 20 V or 10 V, these tiny cracks can be totally healed (Figure 2.7 (b) and (d)). Anodization process is accompanied by a voltage-related volume expansion. With further anodization and volume expansion, cracks may be replaced with pores with the release of locally distributed stress. For the sample anodized at 10 V (Figure 2.7 (d)), surface are very rough and lots of bumpers spreads across it. Considering the original flat surface, the bumpers may be caused by the non-uniform volume expansion at this voltage, at which stress is concentrated at some spots to form bumpers. For samples anodized at 5 V, the surface becomes a little rougher without too much change from the original ones, and pore structures of less than 10 nm can be barely seen at 40,000 magnification, with cracks on the surface (Figure 2.7 (f)). Due to the much lower voltage, the smaller volume expansion is not enough to "heal" the original cracks. Cross-sectional views in Figure 2.7 (c), (e) and (g), corresponding to the top images on left side, may further reveal the voltage effect. It is shown

that 20 V-anodization yields straight and uniform pore walls. However, 10 V or 5 V leads to curved, non-uniform and non-continuous pore walls. In addition, alumina thickness decreases with voltage. This may imply that the dissolving process is a field-assisted process, i.e. the higher voltage, the faster the dissolving rate is. A moderate dissolving rate, together with a moderate oxidization rate, is suitable for ordered pore structures.

2.3.5 Effect of Temperature

Temperature is one of the key factors to determine the pore structures, because temperature is an important factor in chemical reactions. A 2.7 % $H_2C_2O_4$ was used to examine this effect. Samples were anodized at 40 V. In the first step, anodization was processed for 5 min, and in the second step, for 20 min, followed by an etching in H_3PO_4 6% 30 min at 30°C. Figure 2.8 is the cross-sectional images for different temperatures of (a) 0°C and (b) 20°C. It should note that the sample shown in (a) has carbon nanotubes in some pores, which do not affect the pore structure.

It is clear that lower temperature at a fixed voltage and concentration yields much lower oxidizing and dissolving rate, which may benefit the pore structure, since pore formation is a natural process with volume expansion. As shown in (a), the wall is straight and uniform with no ramifications. However, the sample anodized at room temperature shown in (b), has some ramifications on the wall and the wall is not very smooth.

2.3.6 Effect of Time

Highly ordered pore structure features a very long (more than 20 hours or even longer) anodization time on highly pure aluminum bulk [50]. For thin film, unfortunately, it is impossible to anodize so long. However, we can still briefly observe the time effect. A 2.7 % $H_2C_2O_4$ was used in the experiments. Al films with different thickness were anodized at 40 V, and the anodization time was carefully controlled so as not to over-anodize the samples. In the first step, anodization was carried out for 5 min, followed by etching in H_3PO_4 (6%) + CrO₃ (1.8%) at 60°C. In the second step, anodization lasted for different times indicated in Figure 2.9. It is noted that samples in (a) and (b) have carbon nanotubes in some pores, which does not affect the pore structure. Figure (d) is the top view image with anodization time of 40 min (first step) + 15 min (second step), producing an ordered pore structure. It shows in Figure 2.9 that long anodization time can yield better pore quality. With 90 min-anodiztion, the walls are

approaching to perfect structure, especially at the bottom of the pores, as shown in Figure 2.9 (c). Figure 2.9 also reveals the evolution of ordered pore structure. Pores near the surface experience disturbance with some ramifications on the walls. With longer anodization time, this disturbance becomes less and less, and at the same time, the oxidization and dissolution processes reach a dynamic equilibrium so that a steady anodization proceeds.

2.3.7 Etching Effect

Before the second anodization, oxide layer from the first step has to be chemically removed with H_3PO_4 (6 wt %) + CrO₃ (wt 1.8%). Should there be no pore structure, the etching process would be a layer by layer process from the surface. However, with pore structure, this process changes as shown in Figure 2.10. The sample was prepared on a 3.6 µm thick film, anodized in 3 % oxalic acid at 40 V, 0 °C for 60 min. The etching process lasted for 5 min at 60 °C, yielding a blurring surface. Second anodization lasted for 10 min. Ordered pore structures are clear under roots of aligned "rice straws". During etching, solution can fill up the pores, which leads to isotropic etching on the surface and in the pores. Since the standard pore structure is hexagonal [50], the conjunction among three adjacent cells is thicker than other areas, at the final stage of the etching, only triangle-shaped pillars are left, which appear in Figure 2.10.

2.4 The Anodization Mechanism

Many researcher have contributed to anodization mechanisms [45,47,50,55-59], and the formation has also been directly observed by Thompson et al.[48]. A brief summary is given below.

The anodization process includes two steps: pore initiation and steady-state pore growth, as shown in Figure 2.11. At the very beginning of the anodization, there is a uniform growth stage and thus a barrier layer (Figure 2.11 (a) and a of (b)) is formed. After the initial stage, the current is the greatest at the regions above metal ridges, which consequently develop locally thicker film and tend to flatten the metal/film interface (Figure 2.11 b of (b)). Preferential growth of locally thicker film and thickening of the barrier layer generally continue until current becomes concentrated into the film regions between the protuberances, i.e., the lower resistance pathways, as a consequence of pore development, where the electric field and ionic current become concentrated in the barrier layer beneath the major pores (Figure 2.11 c, d of (b)). As shown in

Figure 2.11 c)), the oxidation process is associated with the ingress of O^{2-}/OH^{-} ions to form solid film at the metal-oxide interface, and the dissolution process is associated with the field-assisted ejection of Al^{3+} at the oxide-electrolyte interface, a steady-state pore growth is determined by the dynamic equilibrium of two processes. The formation process is accompanied by a high starting current during formation of the initial barrier oxide, a current reduction when the oxide becomes insulating against ion migration, followed by a current rise due to the formation of pores, and a constant current in the regime of steady-state pore growth.

2.5 Summary of Chapter Two

A brief background of electrochemistry and aluminum anodization are introduced. Factors including surface cleanness, electrolyte, concentration, voltage, temperature, anodization time and etching effect are studied, finally, a brief summary of anodization mechanism is presented.

Sample cleanness is important for pore growth, especially, for the initial stage. Different electrolyte yields different anodization properties. Anodization rate of phosphoric acid is lower than that of oxalic acid, which is lower than that of the sulfuric acid under the given conditions, phosphoric acid may yield a very rough surface after anodization and a lot of ramifications. Concentration has an important effect on the regularity and straightness of the pores. Voltage affects pore structure and surface flatness. It is found that lower temperature and longer anodization time benefit pore formation and growth. In summary, electrolyte, concentration, voltage and temperature can vary anodization rate and there is an optimal window for these parameters. Etching process with pore structure is isotropic in the pores and on the surface. Anodization mechanisms, by other researchers and also confirmed in our experiments, include pore initiation and steady-state pore growth, accompanying by a current drop at the very initial stage, a rise within several minutes, followed by a steady current indicating the steady-state pore growth.

Electrolyte	Concentration	Voltage(V)	Temperature	Time
	(wt%)		(°C)	(min)
H_2SO_4	3	20	20	20
$H_2C_2O_4$	2.7	30	20	20
H ₃ PO ₄	4	40	20	20

Table 2.1: Parameters for different electrolytes



Figure 2.1: Electrolytic cell Vs. Galvanic cell, a) an electrolytic cell, where charges leave the system at the anode and enter the system at the cathode, b) a galvanic cell.



Figure 2.2: A sample without pore structure on the surface, anodization conditions: 15.0 wt% H_2SO_4 , 20 V, 5 min at room temperature.






(c)

(d)



(e)



Figure 2.3: Pore structures from different electrolytes, (a) and (d) H_2SO_4 , (b) and (e) $H_2C_2O_4$, (c) and (f) H_3PO_4 , with anodization conditions given in table 2.1.



Figure 2.4: Top view showing non-porous structure. Sample is anodized in $H_2C_2O_4$ 2.7% for 5 min, 30 V at room temperature.



Figure 2.5: Top-view images in different concentration H_2SO_4 solutions at room temperature, (a) 15.0%, (b) 3.0%, and (c) 1.5%.





Figure 2.6: Cross – sectional views for samples anodized in different concentration H_2SO_4 solutions at room temperature, (a) 3.0%, and (b) 1.5%.





(d)

(e)



(g)

Figure 2.7: Top- view and cross-sectional view images of pores anodized in H_2SO_4 with different voltage at room temperature, (a) original Al film, (b) top view, 20V, (c) cross view, 20V, (d) top view, 10V, (e) cross view, 10V, (f) top view, 5V, (g) cross view, 5V.





(b)

Figure 2.8: Cross-sectional images of samples anodized in 2.7 % $H_2C_2O_4$ at 40 V, (a) 0°C, (b) room temperature.



Figure 2.9: Images for samples anodized in 2.7 % $H_2C_2O_4$ at 40 V, 0°C for (a) 20 min, (b) 30 min, (c) 90 min, and (d) 55 min.











(b) [58]



Figure 2.11: An anodization process, (a) pore structure with barrier layer, (b) pore initiation, (c) steady-state pore growth.

Chapter Three

Catalytic Cobalt Nanoparticle Deposition

3.1 Introduction

Catalyst plays a very important role in synthesizing aligned carbon nanotubes in large scale. Catalyst is substance that causes change in the rate of chemical reactions where the catalyst itself is not consumed. Substances that increase the rate of reaction are called positive catalysts, or, simply, catalysts, while substances that decrease the rate of reaction are called negative catalysts or inhibitors [60]. We will focus on positive catalysts, in brief, catalysts in this chapter. Catalysts work by changing the activation energy in a reaction, i.e., the minimum energy needed for the reaction to occur.

There are several ways to prepare catalyst particles including precipitation, impregnation, deposition and so on [61]. Deposition yields catalysts with smaller particle size, better dispersion and larger surface area. Electro-deposition (ED) has been proved to be a useful technique widely used in chemistry and semiconductor industries. ED is often non-homogeneous, both on macroscale and nanoscale, leading to nanocrystalline deposits rather than coherent coverage. Besides, it is usually a low-temperature technique which is not favorable for crystal growth, resulting in a very small grain size. In general, material for ED is located at cathode, when a current flow through the cell full of electrolyte solution, particles, metal or semiconductor, are deposited onto substrate at cathode.

In this chapter, deposition of cobalt catalysts in porous AAO is studied.

3.2 Cobalt Nanoparticle Deposition in AAO Template

AAO template preparation was discussed in Chapter Two, where oxalic and sulfuric acids were used in the experiments. Electric field is necessary to enable cobalt to be deposited into pores. As discussed in Chapter Two, there is an insulating barrier layer after anodization, which tends to reduce the electric field during deposition, thus has to be thinned. Since thickness of the barrier layer is related to applied voltage: the higher voltage, the thicker the barrier layer is. One way to thin this layer is to slowly decrease voltage at the final stage of anodization and maintain the

reduced voltage for some time to allow barrier layer to be thinned. The other way is to chemically thin this layer after anodization, at the same time, to widen the pores which is called "pore-widening". In our experiments, voltage was slowly decreased to less than 5 V and kept for about 15 min. The solution to thin barrier layer was H_3PO_4 or a mixture of H_3PO_4 and CrO_3 , the latter one has a much faster etching rate while the former one is easier to control.

AAO has a rectifying property, acting like a diode [62], accordingly, an AC voltage can be applied to deposit cobalt into the bottom of the pores. Although the applied voltage is sinusoidal and symmetrical, the current is greater during the cathodic half-cycles, making deposition possible without subsequent stripping during the anodic half-cycles. This results in catalyst to be mainly deposited into the bottom of the pores, not on the wall or on the surface.

Figure 3.1 shows the samples with cobalt particles at the bottom. Samples were anodized in oxalic acid at 30V, and at the final stage of second anodization, voltage was slowly decreased to 5 V and maintained for 15 min. A H_3PO_4 of 5 wt% was used to do pore widening for 20~30 min at 30°C to further thin the barrier layers. Electro-deposition was carried out in $CoSO_4:H_3BO_3:ascorbic acid:H_2O$ (24 : 4 : 0.1 : 100 wt), 14 Vrms for 1 min [68,69]. Figure 3.1 (a) shows a sample with over-widened pores, and (b) a better one, both of which have nanoparticles at the bottom of pores. One advantage of the nano-particles is that the size can be fully controlled by the pore structure. For longer time deposition, nanowires with high aspect ratio of metal or semiconductor can be achieved.

Figure 3.2 shows samples with cobalt particles at the bottom anodized in sulfuric acid at 20 V. At the final stage of second anodization, voltage was slowly decreased to 3 V and maintained for 15 min. The pore-widening lasted for 30 min at 30°C. Samples in Figure 3.2 follows the same electro-deposition process for samples in Figure 3.1. Figure 3.2 (a) shows a sample anodized at 20 V in 3 wt %, and (b) in 1.5 wt% H₂SO₄ solution. The pore structure obtained in 3 % sulfuric acid is better. Despite of this, uniformly distributed cobalt particles can be found in the images. Compare nano-particles in Figure 3.1 with those in Figure 3.2, different particle sizes are observed. Lower voltage produces smaller pores, yielding smaller particles after electro-deposition. This suggests a good pathway for preparation nanoparticles. Once particles are deposited, AAO template can be etched away by a base solution, leaving free nanoparticles on the surface.

3.3 Summary of Chapter Three

Cobalt nanoparticles are electro-deposited into the bottom of AAO pores with AC voltage on samples anodized in sulfuric and oxalic acids. Barrier-layer-thinning is a key factor in the experiments, since barrier layer is an insulator. Using AAO template, the particle size can be fully controlled at nano-scale, which provides a better way to prepare narrowly distributed nanoparticles.





(b)

Figure 3.1: Samples with cobalt at the bottom of the AAO pores anodized in oxalic acid at 30 V, (a) a sample with over-widened pores, (b) a better sample.





Figure 3.2: Samples with cobalt at the bottom of the AAO pores anodized in sulfuric acid at 20 V, (a) 3 wt% H_2SO_4 , 20 min, (b) 1.5 wt% H_2SO_4 , 30 min.

Chapter Four

Synthesis and Characterization of Vertically Aligned Carbon Nanotubes on Silicon Substrates

4.1 Introduction

Carbon nanotubes (CNTs) can be classified into two types: single-walled tubes and multi-walled tubes, depending on the number of graphite layers. Because of the diameter and helicity of the graphite layers, nanotubes can be metallic or semiconducting. With their excellent electrical and mechanical properties, CNTs have a very wide range of applications, especially in sensing and molecular electronic devices. Several methods including CVD, arc discharge and laser ablation have been developed to synthesize CNTs,

In this chapter, a method is described to grow vertically aligned CNTs on silicon substrates through porous AAO templates using an ethylene flame synthesis. CNTs were characterized by field emission scanning microscopy (FE-SEM), transmission electron microscopy (TEM), TEM-EDS (energy-dispersive spectrometry), and high-resolution transmission electron microscopy (HRTEM). The CNT growth mechanism, role of catalyst and role of pore structure are studied.

4.2 Experimental Procedures

AAO templates with cobalt particles at the bottom of the pores have been discussed in Chapter Two and Chapter Three. Sulfuric (1.5 wt%) and oxalic acid (1.8 %) solutions were used for anodization. Based on the AAO template, Cobalt particles were electro-deposited at the bottom of pores. To examine catalytic effects of AAO and cobalt particles, an AAO template from the same process as sulfuric anodization *without cobalt deposition was* also prepared for CNT growth, which thereinafter is called Sample II, and the template anodized in sulfuric acid solution *with cobalt deposition* is labeled as Sample I, the template anodized in oxalic solution as Sample III.

The CNTs were grown from a laminar ethylene-air co-flow diffusion flame [66]. 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 [66, 67]. The setup for the same synthesis, similar to the one used previously [58], is shown in Figure 4.1. 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 cm3/s, and air flows through the annular space between the inner and outer tubes at a rate of 1176 cm3/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 mm x 5 mm) was inserted into the flame perpendicular to the gas flow direction and kept in place for 20 min. The pyrolysized gaseous products were impinged on the template. With the heat generated at flame sheet, the gas environment near the template is suitable for CNT synthesis with a temperature of 1200–1500 °C. Visual inspections show a layer of smooth and shiny black material on Sample I and III; most of the thin film layer on Sample II has been peeled off, and the remaining parts appear 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, I etched the AAO overnight in aqueous NaOH (0.1M). Because CNTs in Sample I with cobalt deposition are bonded tightly to the silicon substrate, the substrate has to be broken into pieces to release CNTs. After rinse for several times using ethanol alcohol and dispersion by ultrasonic cleaning for 10 min, drops of CNTs were placed on the copper TEM grids and dried.

4.3 Results and Discussion

In our experimental observation, the nano-pore structure of the AAO template is still in good shape after growth of the CNTs in flame. Since the temperature of flame is $1200^{\circ}C \sim 1500^{\circ}C$ [68], the substrate temperature changes dramatically during growth. The above fact suggests that the porous structures are able to withstand thermal shock. In our structures, the stability is simply achieved using a thin aluminum film, left after second anodization, as the buffer layer. In previous report [42], AAO films on silicon wafers cracked during high temperature processes.

4.3.1 CNT Morphologies under SEM

Morphologies of CNTs from different samples (Sample I, II, III) were studied using SEM, Sample I and II were anodized in sulfuric acid with electro-deposition of cobalt in Sample I, Sample III was anodized in oxalic acid. Sample I and II were synthesized for 20 min, and Sample III was synthesized for 5 min. One sample with a process same as Sample I was also prepared except for a shorter synthesis time of 5 min. Figure 4.2 show the FE-SEM images of the resulted CNT array in Sample III, ethylene synthesis for 5 min, with different magnifications. The images in (a) and (b) were taken from some cracks that were deliberately created by ultrasonics for SEM observation. Figure 4.2 (c) shows a bottom view image in which the AAO thin film with bunches of CNTs inside is peeled off from the silicon substrate. Well-aligned CNTs are seen grown inside the template pores with high density. Due to the confinement of the pore channels, these nanotubes have mono-dispersed diameter which is identical to that of the AAO template pores, approximately 60 nm. The nanotube growth stops at the surface of the aluminum oxide film. Thus the nanotube length can be readily controlled through film thickness. Moreover, the open-tipped feature of the nanotubes is similar to those observed by other authors using bulk aluminum sheets as the substrate [40, 41]. Figure 4.3 shows the side-view images of In-situ CNTs, of which the template is processed at the same condition as for Sample I, except for synthesis for 5 min. It is shown that CNTs are grown from each pore. However, surface of each CNT looks spongy and is covered by some amorphous carbon. The CNT quality is comparable to that in Figure 4.2, which is also synthesized for 5 min.

Figure 4.4 is the images of CNTs in Sample I, grown for 20 min. The FE-SEM top-views of CNTs are shown in (a), (b) and, and cross-sectional views are shown in (c), (d), (e). After partially removal of the surface layer, it is shown in Figure 4.4 (a) that clean CNTs are grown from most of the pores with one CNT in one pore, separated from each other. It should be noted here that some CNTs have been pulled away from the pores, leaving hollow holes in the template. Figure 4.4 (b) shows CNTs after totally removing the surface layer. 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. It can be seen in Figure 4.2 and Figure 4.3. This may imply that longer synthesis time benefits CNTs' growth. Because the flame temperature is

around 1200~1500°C, longer time can also anneal the formed CNTs, thus improving CNTs' quality. The growth of CNT is stopped at the pore openings, indicating that AAO has some catalytic effect on the growth of CNTs. To study the interaction between CNTs and the substrate in Sample I, the AAO template was dissolved in 0.1M NaOH overnight, resulting in CNT bundles on the silicon substrate, as shown in Figure 4.4 (f) and (g). Although there is a very thin AAO barrier layer after the electro-deposition, 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 not clear.

Figure 4.5 shows the top view of Sample II, grown for 20 min. 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 have a weak bond to the substrate; accordingly, after etching overnight in 0.1M NaOH, all of the CNTs are separated from the substrate. This indicates that cobalt particles help CNTs bond to the substrate.

4.3.2 CNT Morphologies under TEM and TEM-EDS

TEM characterization was carried out with a JEM-2000FX at 200 kV to explore the internal structures of Sample I. Figure 4.6 (a) and (b) show typical CNT bundles in Sample I, which have not been fully dispersed by ultrasonics. These CNTs attached to the silicon substrate are open at the tips. The wall thickness is about 10 nm. TEM-EDS in Figure 4.6 (c) shows that there are cobalt particles with a K α 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 4.6 (c) are introduced by the use of the copper grid and the sample holder.

4.3.3 CNT Morphologies under HRTEM

HRTEM (JEM-2010F, 200 kV) may reveal the fine structures of CNTs, as shown in Figure 4.7. CNT in image (a) has been grown at the same processing conditions as in Sample I, but for shorter time (5 min). It is non-well-graphitized and the wall structure is not clear. In Sample I, we find two types of CNTs, but only one type in Sample II. Figure 4.7 (b) shows one type of CNT with a multi-walled structure in Sample I. 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 non-well-graphitized. 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 [40]. 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 4.7 (c) shows a better quality CNT grown out of the pores in Sample I, with a fine and clear wall structure. Figure 4.7 (d) shows the other type of CNTs that are found in Sample I. The CNTs are non-well-graphitized without clear distinction between the inner shells and outer shells. Figure 4.7 (e) is the tip-ended structure of a CNT in Sample II. Even without catalyst particle deposition, CNTs may be grown because of the catalytic effect of AAO itself. This is also supported by the SEM image of Sample II shown in Figure 4.5 (d). The quality of CNTs from Sample I (Figure 4.7 (e), exhibit almost the same structure (non-well-graphitized) as those from Sample I (Figure 4.7 (d)). The quality of CNTs from Sample II is lower than that of the well-graphitized counterparts in Sample I (Figure 4.7 (e)).

4.3.4 Nanotube Growth Mechanisms

4.3.4.1 Effect of Synthesizing Temperature

Temperature plays a very important role in synthesis of CNTs, which decomposes carbon sources, normally organic carbonhydrate, and provides energy to form CNTs. Thus, higher temperature may benefit the synthesis. In our experiments, high temperature of the flame, around $1200~1500^{\circ}$ C, decomposes ethylene more efficiently and activates the catalytic functions of cobalt and AAO. Thus we can get better CNTs in Sample I than CNTs by CVD method [40, 41, 69]. In addition, the bonding force between the substrate and the CVD-produced CNTs is weak. The temperature used in CVD synthesis 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, which can withstand higher temperature. Because of the much higher temperature of the C₂H₄ flame, CNTs with the help of cobalt particles may be able to firmly adhere to the substrate.

4.3.4.2 Effect of AAO Templates

In the case of growth of CNTs from AAO template, carbon nanotubes are supposed to be grown from the cobalt catalyst particles and the AAO pore channels only offer physical confinement to CNTs' diameter and position. However, it is found that the AAO pores may serve as an effective catalyst media during CVD growth [40, 41]. When using flame method, we also observe several phenomena possibly related to the catalytic function of AAO pores. Firstly, growth of nanotubes stops at the openings of the pores, implying that the ethylene may not decompose so effectively in the absence of the catalytic AAO pores. Secondly, it is 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 alumina template, as reported before [69]. Further, in some areas, the catalytic function of AAO pores is observed being enhanced, leading to the coating of an amorphous carbon layer outside the nanotubes. To achieve well-graphitized nanotubes from the AAO pores, overwhelmingly catalytic function of AAO pores is undesirable and needs to be suppressed with optimal growth condition.

High surface aluminum oxide is a good support for catalyst particles in synthesizing CNTs. Hongjie Dai's group [8, 70] used aluminum oxide powder in growth of SWCNTs. The decomposed carbon source is easier to diffuse through the high surface support to facilitate CNT synthesis in root mode. Porous AAO is also an effective, if not a better support for catalyst. Figure 4.8 (a) shows CNTs with AAO support. The sample was anodized in H₂SO₄ 10 wt%, 5 V, as discussed in Chapter Two 2.3.4 and in Figure 2.7 (f) and (g). After anodization in the second step for 5 min, the sample was etched in phosphoric and chromic acid mixture for 10 s, followed by a brief electro-deposition of cobalt. The porous template was then etched in NaOH 0.1M to remove the AAO layer till only the barrier layer was left. Cobalt particles were then exposed directly to the air but the lower part of the particle was still embedded in the shallow pore structures. CNTs are found to spread uniformly across the sample surface. High density CNTs support each other, making them stand up vertically to the substrate. Figure 4.8 (b) shows the CNT bundles grown from the substrate surface, its small magnification image is shown in Figure 4.8 (c). The sample was prepared in 2.7 wt% oxalic solution, followed by electro-deposition for 40s. Some cobalt particles were found to aggregate into small "cobalt islands" on the surface. Aligned CNTs are observed around the edge of the aggregation areas, as shown in Figure 4.8 (c). Unlike CNTs in Figure 4.8 (a), where vertically aligned CNTs cover the whole sample surface, cobalt particles in Figure 4.8 (c) are separated from each other only at the edge of the "islands", thus have catalytic functions during synthesis. Inner parts of the "islands" produce no aligned

CNTs. The confinement and support properties of AAO provide a better choice for growth of CNT bundles with full control of CNTs' diameter.

4.3.4.3 Effect of Cobalt Catalyst

There are studies [40, 71] that suggest, in agreement with our study, 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, we recall the difference between Samples I and II, where two types of CNTs were found in Sample I, and only one type of CNTs, non-well-graphitized, was found in Sample II. The structural differences of CNTs from Sample I are not likely due to the temperature difference in substrate surface (because it is very small). Then I consider the effect of preheating the sample to the steady temperature level (1200-1500°C). The transition time is estimated to be 2 s, so two different samples were prepared: one with cobalt particles and the other without cobalt particles. I repeated the synthesis experiments under the same conditions as before, except for a short growth time of 2 s, and found no CNTs on either sample. The study suggests the dependence of CNT structure on types of catalyst: AAO resulting in non-well-graphitized CNTs and cobalt yielding well-graphitized CNTs. However, cobalt particles in sample I do not have the same catalytic effect, which remains unclear, leading to both well-graphitized and non-wellgraphitized CNTs in Sample I. While in Sample II, since there are no catalytic particles, only non-graphitized CNTs were observed. The electrodeposited cobalt particles have at least two positive effects: they help the growth and graphitization of CNTs and bind CNTs to silicon substrate. This is an interesting result that suggests the need for further studies to test different types of catalysts on the growth of CNTs.

Catalyst is found to be necessary in synthesizing high quality CNTs in large-scale. Transition elements of Fe, Ni, and Co are effective catalysts. To some sense, synthesizing CNTs is to prepare appropriate catalyst particles in nano-scale dimensions. Dense catalyst layer or bulk catalyst has no effect on growth of CNTs. Furthermore, it seems that tips of catalyst particles, if in a needle-like shape, are the most active parts for growth of CNTs. Control of the orientation of catalyst needles might lead to control the orientation of CNTs. Figure 4.9 shows parallel CNTs grown from the side wall of pores. The template was anodized in oxalic acid and cobalt needle-like particles were deposited in the pores. AAO in some areas has been torn away somehow, thus

Catalyst particles along the edge of the broken area were exposed directly to the air, that is, no confinement from the AAO. Although no image showing the orientation of particles, it is reasonable to assume that the needle-like particles fell down from a vertical position in the pores to a parallel position to silicon surface, leading to parallel-oriented CNTs. The sample after synthesis was further plasma etched in a simple plasma oven at 40 W with an argon flow rate of 5 SCCM (standard cubic centimeter per minute). Parallel CNTs without too much entanglement are shown in Figure 4.9 (a). Figure 4.9 (b) shows the original part of CNTs with clear demonstration of CNT growth from the edge of AAO structure.

4.3.5 Plasma Etching Effect

Nanotubes can be etched away in plasma. Figure 4.10 shows CNTs' image before and after plasma etching. The sample was anodized in oxalic acid, followed by an electro-deposition of cobalt on the surface, after synthesis, the sample is etched in a simple plasma oven at 40 W with an argon flow rate of 5 SCCM. The original sample, shown in Figure 4.10 (a), has many curved CNTs, which can be easily etched away by plasma, leaving straight CNTs as in Figure 4.10 (b). As discussed in Chapter One, properties of CNTs are related to their chirality. Curved CNTs might have poor mechanical properties so as to be easily attacked by plasma. Straight nanotubes should be more desirable for future applications.

4.4 Summary of Chapter Four

Flame synthesis is briefly discussed, followed by CNTs characterizations with SEM, TEM, TEM-EDS and HRTEM. Nanotube growth mechanisms including the effect of temperature, AAO's catalytic, confinement, and support functions, effect of cobalt and finally the plasma etching effect are studied in this chapter. Vertically aligned multiwalled carbon nanotubes were successfully fabricated on silicon substrates by the ethylene flame synthesis, 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. It is found that the AAO template has some catalytic effect, but the cobalt catalytic particles deposited at the bottom of pores are necessary for the growth of well-graphitized CNTs with strong bonding to the substrate. It is possible to grow well-graphitized CNTs and control their diameters and orientations with AAO template. Straight CNTs have better mechanical properties than curved CNTs.



Figure 4.1: A schematic diagram of flame-synthesis experiment to produce carbon nanotubes





(b)





Figure 4.2: CNT arrays of Sample III (anodized in H_2CO_4 , 40 V) at (a) low magnification, (b) high magnification, (c) bottom-view. Cracks in (a) and (b) are deliberately created in order to observe the nanotubes. The original surface is free of cracks (synthesis for 5 min).



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(b)

Figure 4.3: Side-view images of *In-situ* CNTs (synthesis for 5 min, anodized in H₂SO₄, 20V), (a) high magnification, (b) low magnification.





(b)



(c)



(d)



(e)



Figure 4.4: CNT images of Sample I (anodized in H_2SO_4 20 V, and electro-deposited with cobalt particles), (a) CNTs in the pores after removal of the surface layer, (b) top-view CNT image after totally removing template surface, (c) original cross-sectional image, (d) cross-sectional image of CNT bundles with removal of most AAO template, (e) cross-sectional image after removing template surface, (f) collapsed CNT bundles after removing AAO template, (g) a close-up of the collapsed CNT bundles.



Figure 4.5: CNTs image for Sample II, synthesis for 20 min, without cobalt deposition.





(b)



Figure 4.6: TEM images showing the CNT bundles (a) and (b), TEM-EDS showing cobalt elements in CNT roots (c).





(b)


(d)



Figure 4.7: HRTEM images of CNTs, (a) CNT with same processing conditions as Sample I for shorter synthesis time (5 min), (b) Well-graphitized CNT in the pores in Sample I, (c) Well-graphitized CNT out of the pores in Sample I, (d) Not well graphitized CNT in Sample I, (e) CNT in Sample II, without cobalt catalyst deposition.



Figure 4.8: Aligned CNTs, (a) from AAO shallow pores, (b) from AAO surface, (c) low magnification for CNTs in (b), CNTs are located at the edge of cobalt "island".



(b)

Figure 4.9: Parallel CNTs on silicon surface, (a) middle part of CNTs, (b) original part of CNTs



(b)

Figure 4.10: Etching effect of plasma for CNTs, (a) original CNTs, with many curves, (b) plasma-etched CNTs.

Chapter Five

Fabrication of Horizontal Nano-Trenches using Nanotubes as Shadow Masks

5.1 Introduction

Carbon nanotube is a very important material with great potentials. However, several challenges remain before commercial applications as discussed in Chapter One. One of them is how to manipulate CNTs? Dai's group in Stanford University has made great efforts in achieving long and oriented SWCNTs [36, 72]. External electrical field has also been applied to direct the growth of MWCNTs and SWCNTs [73, 74]. The process is complicated and the throughput, especially for SWCNTs, is very low. Another way for manipulation and assembly of CNTs is to use mass-produced CNTs. Alignment by electric field is a simple and efficient method [75, 76, 77].

The continuing shrinkage of chips in semiconductor industry is limited by the inefficiency of defining very small patterns (less than 10 nm) in large scale. Lithography, including photolithography, e-beam lithography or x-ray lithography is the main method. However, with sub-10 nm pattern, lithography can barely meet the requirements for the resolution. CNTs, especially SWCNTs with an individual diameter of less than 5 nm may have potential to solve this problem, that is, using CNTs as shadow masks to realize lithography. Lefebvre et al. [78] has demonstrated nanometer size gaps using CNTs as shadow masks. Yun et al.[79] has also reported metal nanowire using CNTs. In this chapter, the nano-trench fabrication processes are discussed in details. A better strategy is also suggested.

5.2 Experimental Procedures

Schematic of fabrication process flow is shown in Figure 5.1.

a) Solution Preparation:

SWCNT bundles with an average outer diameter of 25~30 nm and length of 2~5 μ m were obtained from Carbolex, Lexington. 100 mg original SWCNT bundles were roughly purified by removing remaining catalyst particles in a mixture of HNO₃ (70%): EtOH (2:1) for 30 min with stirring, rigorous reaction was observed accompanied by a lot of bubbles. A common filer paper

was used to filter out the solution, after several times filtering, SWCNT bundles on the paper were transferred into 30ml alcohol, followed by ultrasonic dispersion for 10 min. A transparent water-like solution with many SWCNT bundles was obtained.

b) Electrode Preparation:

A thermal oxide layer of 200 nm thick was grown on a n^+ -silicon (100) substrate to isolate electrodes. Electrode patterns were made by photolithography with positive photoresist (PR) of S1813 from Shipley, followed by thermal deposition of a 50nm-thick aluminum layer. After a lift-off process, the electrodes with a feature gap of about 1 µm were obtained.

c) SWCNT Alignment:

Alignment of SWCNTs was carried out by applying a 2 MHz, 20 Vp-p alternating electric field to the electrodes for 10 min. The solution was sonicated for 10 min right before alignment to disperse CNT bundles. Electrodes with a gap of 1 µm then had some separated SWCNT bundles lying across.

d) Aluminum/Titanium Evaporation:

A 20 nm thick aluminum was thermally evaporated at 2 x 10^{-6} Torr. The shadow areas under the aligned SWCNTs were free of aluminum deposition.

e) SWCNT Removal:

To show trenches shadowed by SWCNTs, SWCNT bundles were burned out at 600°C/700°C with an oxygen flow rate of 80 SCCM for 30 min, leaving the fabricated trenches uncovered.

5.3 Results and Discussion

A FE-SEM (S900) was used to characterize the results. The density of aligned SWCNT bundles depends on the solution concentration, applied voltage and the alignment time, while the alignment degree depends on frequency [75]. AC alignment is possible with the electronic polarization induced in SWCNT bundles by the electric field.

Figure 5.2 shows CNTs aligned across electrodes. Figure 5.2 (a) is CNTs aligned in a solution without any purification, many particles, including catalytic metallic particles and amorphous

carbon produced in the synthesis, are aligned simultaneously at both electrodes. As discussed in Chapter One, synthesis of highly pure SWCNTs is a hard job, post-purification is necessary for further applications and purification methods have been reported by Eklund et al. [80, 81, 82]. Cleaner CNTs across the electrodes are shown in Figure 5.2 (b), (c) and (d). The outer diameter of SWCNT bundle is about 27 nm, and the gaps between the electrodes are 1.2 μ m (Figure 5.2 (b) and (c), and 3 μ m (Figure 5.2 (d)). Figure 5.3 is the image of CNT covered by a thin titanium layer of 20 nm. This layer is deposited in an e-beam evaporator under a vacuum of 1 x 10⁻⁵ torr. CNTs across the electrodes function as shadow masks and block the area underneath.

To expose the nano-trenches, CNTs have to be removed. Thermal oxidation was used in the experiments at different temperature. For temperature below 600°C, there is almost no effect, which is not in agreement with the data from other sources, where the burning temperature for SWCNTs is around 500°C [83, 84]. However, in our experiments, as also shown in Figure 5.3, CNTs are covered by a thin metal layer, which may increase the burning temperature. Temperature over 600°C works effectively. Figure 5.4 shows nano-trenches after successful removal CNTs. Figure 5.4 (a) was burned at 600°C 30 min and a trench of 20 nm was obtained. The much smaller trench (compared to the aligned SWCNTs) is partially due to the diameter difference between the evaporation source (2.5 cm) and SWCNT (~27nm). Thermal expansion of the metal film may also contribute to it. Figure 5.4 (b) shows a nano-trench burned at 700 °C. Due to thermal expansion, the trench is even smaller than in Figure 5.4 (a), cost of which is the oxidation of metal thin film, resulting a very rough surface.

5.4 A Better Strategy to Fabricate Electrodes

Nano-trenches have been demonstrated in section 5.3 and the results are shown in Figure 5.4 (a) and (b). However, high temperature was applied to burn SWCNTs across electrodes and metal surface might be corrupted at the same time. A better strategy is suggested in this section.

Schematic of modified fabrication process flow is shown in Figure 5.5. A double PR layer structure sandwiched by a metal film is first fabricated (Figure 5.5 a), the electrodes on a PR layer are obtained by definition of electrode pattern, removal of undesired metal and PR underneath (in Figure 5.5 b, c and d). SWCNT bundles are aligned across the suspended electrodes (Figure 5.5 e), followed by nano-trench formation with the use of SWCNT bundles as shadow masks (Figure 5.5 f). Size of nano-trenches may be partially determined by the height of

PR under the metal layer. In addition, this structure should benefit easier removal of bundles by lift-off in the final step (Figure 5.5 g).

5.5 Summary of Chapter Five

CNTs as shadow masks are demonstrated in this chapter. Nano-trench of 20 nm has been obtained in the experiments. The purification of SWCNTs is found to be very important and so is the removal of SWCNTs after defining the nano-trench by metal deposition. Thermal oxidation was used to burn SWCNTs above 600°C. A better strategy is also proposed.











Figure 5.1: Schematic of fabrication process



Figure 5.2: CNTs aligned across electrodes, (a) without purification, (b), (c) and (d) with purification.



(a)



(b)

Figure 5.3: Images after titanium deposition



(a)



(b)

Figure 5.4: Nano-trenches after thermal removal of CNTs at (a) 600°C, 30 min, (b) 700°C, 30 min.









(d)



(e)



(f)



Figure 5.5: Schematic of modified fabrication process, (a) Double PR layer structure, (b) photolithography patterning, (c) chemical removal of uncovered metal, (d) PR removal by RIE, (e) CNTs alignment, (f) metal deposition, (g) nano-trench after lift-off.

Chapter Six Conclusions and Future Work

6.1 Conclusions

Fabrication of vertically aligned carbon nanotube arrays on silicon substrates using porous alumina film as nano-template has been studied in this thesis and horizontal nano-structure using carbon nanotubes as shadow masks has also been demonstrated.

I. In the preparation of highly ordered porous alumina template, a two-step anodization was carried out with short anodization for the first step and long time for the second step. Ohmic contact between silicon and aluminum thin film is a necessary condition for anodization and later electro-deposition. Sample cleanness is important for pore growth, especially, for the initial stage. It is found that lower temperature and longer anodization properties. Anodization rate of phosphoric acid is lower than that of oxalic acid, which is lower than that of sulfuric acid under the given conditions, phosphoric acid may yield a very rough surface after anodization. Concentration has an important effect on the regularity and straightness of the pores. In summary, there is an optimal window for concentration, voltage and temperature in a given electrolyte. The etching process, also called pore widening, is isotropic in the pores and on the surface. Anodization mechanisms includes pore initiation and steady-state pore growth, accompanying by a current drop at the very initial stage, a rise in several minutes, followed by a steady current indicating the steady-state pore growth.

II. Cobalt nanoparticles were electro-deposited into the bottom of AAO pores with AC voltage on both samples anodized in sulfuric and oxalic acids. Barrier-layer-thinning is a key factor in the experiments, since barrier layer is an insulator. Voltage was decreased slowly to below 5 V to thin the barrier layer followed by a pore widening in H_3PO_4 or H_3PO_4 +CrO₃. Using AAO template, the particle size may be fully controlled at nano-scale. Based on this, a better way to prepare narrowly distributed nanoparticles might be achieved.

III. Vertically aligned multiwalled carbon nanotubes were successfully fabricated on silicon substrates using an ethylene flame synthesis. The flame synthesis has been proved to be effective in the synthesis of CNTs because of its energy efficiency, low cost, and high energy density. The

diameter and length of the open-tipped CNTs may be controlled by the AAO nanotemplate. AAO is a very good support for growth of CNTs. It is found that AAO template has some catalytic effect, but the cobalt catalyst particles deposited at the bottom of pores are necessary for growth of well-graphitized CNTs with strong bonding to the substrate. Using AAO template, it is possible to grow well graphitized CNTs and control their diameters and orientations. It is found that straight CNTs have better mechanical properties than curved CNTs.

IV Fabrication of horizontal nano-structure using SWCNTs as shadow masks has been demonstrated. Nano-trenches of 20 nm have been obtained in the experiments. Highly pure SWCNTs can benefit the cleanness of samples after alignment. High frequency (up to MHz) AC voltage is necessary to align SWCNTs across electrodes. Thermal oxidation was used to burn SWCNTs after definition of the nano-trench by metal deposition. To suspend SWCNTs across the electrodes is a better strategy, which may be achieved by the design of a double PR layer structure sandwiched by a metal film. Size of nano-trenches may be partially determined by the height of PR under the metal layer. In addition, this structure should benefit removal of bundles in the final step.

6.2 Future Work

Highly ordered AAO nano-pores in large-scale are interesting templates in various applications. However, there is always a barrier layer under the pores which in most cases is undesirable for further applications, how to remove this layer without sacrificing the pore structure needs further study.

Vertically aligned carbon nanotubes grown in ordered pore structures have been proved in this thesis. However, the growth mechanism, complicated with AAO catalytic function, is not very clear. Many nanotubes, grown in the pores, are non-well-graphitized, which hinders further applications. Improving the quality of CNTs based on a better understanding of the growth mechanism is necessary.

Principle of nano-trench fabrication has been demonstrated and an improvement has been suggested. To fabricate useful nano-electrodes and to put them into applications need further consideration.

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Vita

Name: Wenchong Hu Date of Birth: November 18, 1972 Place of Birth: Renshou, Sichuna, P. R. China

Educational Background:

August, 2001 – December, 2002: Research Assistant Department of Electrical and Computer Engineering University of Kentucky, Lexington, KY

August, 2000 – August, 2001 Research Assistant Department of Chemical and Materials Engineering

September, 1991 – July, 1995: B.E., Metallic Materials and Heat-treatment Department of Materials Engineering Southwest Jiaotong University, Chengdu, P. R. China

March, 1993 – July, 1994: Minor, Computer Applications College of Computer Science and Communication Engineering Southwest Jiaotong University, Chengdu, P. R. China

Working Experience:

April, 1999 – June, 2002: Software Engineer Chengdu Zongwang Information Industrial Co. Ltd., Chengdu, P. R. China

February, 1997 - April, 1999: Division of Export and Import Sichuan Construction Machinery Works, Chengdu, P. R. China

February, 1997 - April, 1999: Division of Export and Import Sichuan Construction Machinery Works, Chengdu, P. R. China

July, 1995 – February, 1997: Processing Institute Sichuan Construction Machinery Works, Chengdu, P. R. China

Publications:

Four journal papers and two conference proceedings.

Honors:

- a) Reviewer for Electron Device Letters, IEEE (2002).
- b) Excellent Graduate in 1995, Southwest Jiaotong University, P.R. China.
- c) Excellent Graduation thesis in 1995, Southwest Jiaotong University, P. R. China.