RICE UNIVERSITY

Continued Growth of Single-Walled Carbon Nanotubes from Open-Ended SWNT Substrates

By

Myung Jong Kim

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

Jason H. Hafner, Assistant Professor of Physics & Astronomy and Chemistry, Chair

Deceased
Richard E. Smalley, University Professor, Gene and Norman Hackerman Professor of Chemistry, and Professor of Physics & Astronomy, Co-Chair

Robert H. Hauge, Distinguished Faculty Fellow of Chemistry, Thesis Director

James M. Tour, Chao Professor of Chemistry, Professor of Computer Science, and Professor of Mechanical Engineering & Materials Science

Douglas Natelson, Assistant Professor of Physics & Astronomy and Electrical & Computer Engineering

HOUSTON, TEXAS

MAY 2006
INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.
ABSTRACT

Continued Growth of Single-Walled Carbon Nanotubes from Open-Ended SWNT Substrates

By

Myung Jong Kim

We prepared nanoscopically flat open-ended SWNT substrates from SWNT spun fibers by using the microtome cutting technique or the focused ion beam cutting technique followed by various etching and cleaning schemes or alternatively from vertically aligned SWNT film by flipping-over. Deposited catalyst was docked to the open ends of SWNTs, and carbon feedstocks were catalyzed into continued single-walled carbon nanotube growth resembling 1D molecular epitaxy. The data obtained from Raman spectroscopy indicates that the \((n, m)\) structure of the newly grown SWNT was cloned from that of the pre-existing SWNT substrate. Such results lead us to believe that this method will provide us with a means of chirality-controlled SWNTs growth on a macroscopic scale using a fairy general and scalable setup in the future.
ACKNOWLEDGEMENTS

I am grateful to my adviser, Dr. Richard E. Smalley for leading me to pursue the challenging and exciting project. He passed away Oct. 28th, 2005, but he is remembered as the greatest scientist and teacher. I am proud that I learned from him for 4.5 years.

I would like to thank my committee members, Dr. Robert H. Hauge, Dr. Jason H. Hafner, Dr. James M. Tour, and Dr. Douglas Natelson for careful proofreading of my thesis and advices.

I have been honored to work with my team members, Carter Kittrell, Dr. Yuhuang Wang, Erik Haroz, Hongwei Shan, Nolan Nicholas, and Dr. Howard Schmidt.

I would like to thank my family, especially my wife, Youngran. Her love, devotion, and faith in me have helped keep me moving toward my research goals.

I would like to give final thanks to my parents (Joodal Kim and Heesoon Lee) who pray for me all the time and God.
# TABLE OF CONTENTS

Title Page ........................................................................................................... i  
Abstract............................................................................................................... ii  
Acknowledgements ............................................................................................ iii  
Table of Contents ............................................................................................... iv  
List of Figures ..................................................................................................... vii  

1. Introduction .................................................................................................... 1  
2. Background ................................................................................................... 4  
   2.1 The Terawatt challenge and the armchair quantum wire project .......... 4  
   2.2 Why Armchair Tubes? (SWNT structure and energy band) ................. 6  
      2.2.1 SWNT Structure ............................................................................ 6  
      2.2.2 SWNT Energy Band Theory .......................................................... 7  
2.3 SWNT Synthesis ......................................................................................... 15  
   2.3.1 Arc Discharge .................................................................................... 15  
   2.3.2 Laser Ablation .................................................................................. 15  
   2.3.3 Chemical Vapor Deposition ............................................................. 17  
2.4 Raman Spectroscopy of SWNT ................................................................ 20  
   2.4.1 Resonant Raman Scattering ............................................................. 20  
   2.4.2 Chirality Assignment from the RBM (Radial Breathing Mode) ....... 21  
   2.4.3 The G Peak ....................................................................................... 22  
   2.4.4 The D Peak and The G’ Peak ........................................................... 23
3. Flat SWNT Substrates Preparation

3.1 The Hypothesis of Continued Growth

3.2 Cutting Technique

3.2.1 The Microtome Cutting Technique

3.2.2 The Focused Ion Beam Cutting Technique

3.3 Planarization

3.3.1 Overall Scheme of Planarization

3.3.2 Instrumentation of Planarizer

3.3.3 Catalyzed Etching Chemistry and Results

3.4 Electrochemical Method

4. Continued Growth from Microtome Cut Fiber

4.1 Oxygen Plasma Etching

4.2 UV Ozone

4.3 Hydrogen Cleaning

4.4 Continued Growth

4.4.1 The Continued Growth Apparatus

4.4.2 Continued Growth Procedure and Results

5. Continued Growth from Focused Ion Beam Cut Fiber

5.1 Cleaning Process of FIB Cut Surface

5.2 End Opening and Characterizing Open Ends

5.3 Catalyst Docking and Growth
6. Continued Growth from Flipped-Over Vertically Aligned SWNT Film......85

6.1 Vertically Aligned SWNT Film Growth...........................................85

6.2 The Flip-Over Technique and Continued Growth..............................89

7. Conclusion ..............................................................................................94

Appendix A. Laser Heating and Temperature Measurement System.........97

Bibliography..................................................................................................102
LIST OF FIGURES

Figure 2.1. Crystal structure of SWNT.......................................................6

Figure 2.2. Three types of tubes specified by chiral angle.........................7

Figure 2.3. The energy dispersion relation of graphite..............................9

Figure 2.4. The one dimensional Brillouin zone of SWNT.........................10

Figure 2.5. The DOS of (10, 10) tube.....................................................11

Figure 2.6. A contour plot of the 2D energy of graphite............................13

Figure 2.7. The calculated inter-band energy.........................................14

Figure 2.8. Schematic design of laser ablation method, closely packed
individual nanotubes in bundle..........................................................16

Figure 2.9. HiPco reactor, with reaction zone enlarged,
SEM image of raw HiPco material......................................................18

Figure 2.10. Overall Scheme of the HiPco process..................................18

Figure 2.11. Schematic setup for CVD..................................................19

Figure 2.12. Raman spectrum from 780nm laser....................................21

Figure 2.13. The D peak processes and The G’ peak process.....................23

Figure 3.1. Overall scheme of continued growth.....................................25

Figure 3.2. SWNT fiber spinning apparatus, SEM image of the spun fiber.....26

Figure 3.3. Schematic illustration of microtoming of the spun fiber.............27

Figure 3.4. Overall microtome cut surface............................................28

Figure 3.5. Side view of FIB cut surface...............................................30

Figure 3.6. A “bed-of-nails” membrane before lifted out from the trench.....31
Figure 3.7. Magnified TEM image at normal angle of a “bed-of-nails”........32

Figure 3.8. Raman spectra using 780 nm excitation of a “bed of nails” membrane........................................................................................................33

Figure 3.9. Overall scheme of planarization.............................................34

Figure 3.10. A picture of inchworm motor IW-810.................................36

Figure 3.11. Cross sectional view of the main chamber of planarizer........37

Figure 3.12. A picture of the main chamber of the planarizer...............38

Figure 3.13. Methanation of a steam-activated granular carbon
with respect to temperature.................................................................40

Figure 3.14. SEM images and Raman data from planarized sample with \( \text{H}_2 \).......41

Figure 3.15. SEM images from planarization with oxygen.......................42

Figure 3.16. SEM images taken after planarization with \( \text{CO}_2 \)..................43

Figure 3.17. Basic scheme of electrochemistry with concept of double layer..44

Figure 3.18. Scheme of electrochemical polishing..................................45

Figure 3.19. Electrochemistry setup......................................................46

Figure 3.20. Linear sweeping voltammetry and bulk electrolysis.............47

Figure 3.21. Electrochemical etching with water and acid.......................48

Figure 3.22. Electrochemical etching with \( \text{NaOH} \)..............................50

Figure 4.1. Proposed mechanism for side wall etching with atomic oxygen.....52

Figure 4.2. Plasma chamber assembly.....................................................53

Figure 4.3. SEM image taken after oxygen plasma etching, SEM
image taken after HCl dipping............................................................54

Figure 4.4. SEM image taken from the side of the fiber after
Figure 4.5. A picture of the overall UV ozone setup........................................65
Figure 4.6. SEM images taken after UV ozone etching and
subsequent cleaning process.................................................................69
Figure 4.7. SEM images taken after oxygen plasma and
subsequent hydrogen cleaning process..................................................70
Figure 4.8. The scheme of spill-over mechanism......................................72
Figure 4.9. Schematic drawing of the continued growth apparatus..............73
Figure 4.10. A picture of the continued growth apparatus..........................74
Figure 4.11. Laser heating and temperature measurement..........................75
Figure 4.12. SEM images taken from each step for preparing an
open-ended SWNT substrate.................................................................78
Figure 4.13. Continued growth from an open-ended substrate......................79
Figure 4.14. Polarized Raman spectra. an open-ended SWNT
substrate and a continued growth sample.............................................80
Figure 4.15. RBM data of continued growth............................................82
Figure 4.16. Side views of another continued growth example.....................83
Figure 5.1. EDX data of FIB cut surface..................................................84
Figure 5.2. Residual catalysts cleaning scheme........................................85
Figure 5.3. SEM images after cleaning process........................................86
Figure 5.4. AFM images of CO$_2$ etching for open end characterization........87
Figure 5.5. End opening scheme with short exposure to oxygen plasma..........88
Figure 5.6. End opening scheme with sputtering.....................................90
Figure 5.7. SEM images taken before and after growth experiment.............82

Figure 5.8. Raman data taken before and after growth experiment
with three different lasers..............................................................83

Figure 6.1. AFM image and diameter analysis of the catalyst
on the surface..............................................................................86

Figure 6.2. SEM and TEM image taken from the grown V-SWNT film.........87

Figure 6.3. One example of Raman data from V-SWNT film.....................87

Figure 6.4. SEM images of V-SWNT film. (Produced with
Acetone and grown form 1.8 nm diameter sized Fe$_3$O$_4$ particles.)........88

Figure 6.4. SEM images of entangled bundles at the top of
the SWNT film, Scheme for flip-over technique.................................89

Figure 6.5. SEM images from flipped-over V-SWNT film.....................90

Figure 6.6. Scheme of flip-over technique using evaporated
gold and a picture of result............................................................91

Figure 6.7. SEM images after growth experiment..................................92
1. Introduction

Since the Nobel Prize winning discovery of the fullerenes[1] in 1985, carbon nanomaterials such as fullerenes, multi-walled carbon nanotubes[2], and single-walled nanotubes[3, 4] have been playing a pivotal role in nanotechnology because of their remarkable physical and chemical properties. Specially, single-walled carbon nanotubes, whose nickname is “bucky tubes”, have versatile properties such as molecular perfection, superlative thermal conductivity[5], an unrivaled tensile strength[6, 7]. The most important aspects of single-walled carbon nanotubes (SWNTs) are their electronic properties. Each single-walled carbon nanotube is uniquely specified by two integers, n and m, which correspond to the “chirality” of the tube[8]. If n and m are the same, then n-m=0 and those tubes are called “armchair tubes”, and they conduct electricity better than copper [9-11]. Electrons move down this tube as a coherent quantum particle in a manner similar to that of a photon of light traveling down a single-mode optical fiber[12]. If n-m is an exact multiple of 3 (but n-m ≠ 0), the corresponding tube has a tiny band gap of a few meV, and it is called a semi-metallic tube. All other tubes are semi-conducting tubes and have higher carrier mobility than silicon with a similar band gap[13-15], so they are useful to fabricate nano-sized field effect transistors.

Highly conducting armchair nanotubes open the possibility of ultra-efficient energy transport. The “Armchair Quantum Wire” may play a crucial role in solving future energy problems, “Terawatt Challenge”[16] that we will face within 50 years. However, controlling chirality remains the most challenging part of SWNT growth, because none of
the current SWNT synthesis methods- arc discharge[4, 17], laser ablation[18], chemical vapor deposition(CVD)[19-23]- has the capability of producing chirality selected material, and even the use of identically sized catalyst particles in CVD does not allow us to grow uniform diameter SWNTs[22].

Smalley’s group has proposed two ways to achieve the “Armchair Quantum Wire”. The first way to achieve the goal is by amplification of SWNTs from a small amount of chirality selected SWNT seeds through cloning process in CVD reactor. The seeds have catalyst particles in the open ends of the tubes, and the amplified SWNT materials can be spun into continuous fibers[24]. The second way is by continued growth of SWNTs[25] from a nano-scopically flat, well aligned and open ended SWNT substrate. This type of growth will not only clone the structure of substrate SWNTs but also follow the tip growth mechanism by lifting off catalysts. Thus, we would expect the growth to not be terminated by a diffusion process of carbon feed gas as base growth would. In the ideal case of continued growth, individual nanotubes would run the whole length of the long product materials. Hence, they would exhibit super strong mechanical strength, and, if they start from open-ended armchair SWNT substrates, they should also exhibit true metallic conductance.

This thesis describes our continued growth of single walled carbon nanotubes from an open-ended SWNT substrates prepared either from spun fiber or vertically aligned SWNT film. From the perspective of individual nanotubes, continued growth follows one dimensional epitaxy with assistance from nano-sized catalyst particles.

The procedures for continued growth can be divided into three parts; preparing an open ended substrate, catalyst docking, and growth. The most challenging steps were
nano scale fabrication, such as preparing a flat substrate on the nano scale, ends opening, characterizing open ended tubes, and docking the right size of catalyst to the open ends. To crack those challenges, we have tried various chemical methods including HCl dipping, Piranha etching, gas phase etching with and without catalyst, UV ozone, and even electrochemistry as well as physical methods such as Focused Ion Beam technique, argon ion sputtering, and e-beam evaporation. Additionally, we constructed a HV (high vacuum) type CVD reactor system including laser heating, temperature measurement optics setup, and UHV (ultra high vacuum) type e-beam evaporator as well as the planarizer with an angstrom precision inch worm motor and a quartz tube CVD furnace. These scientific efforts have allowed us to solve the challenges of continued growth step by step and finally demonstrate continued growth from open-ended SWNT substrate in a way analogous to epitaxy.

This thesis details the scientific ideas and technological tools behind preparing open-ended SWNT substrates and continued growth. It is our hope that our research will contribute to development of nanotechnological solutions to the energy problems inevitably facing human kind.
2. Background

2.1 The Terawatt challenge and the armchair quantum wire project [16]

Dr. Smalley gave the following prioritized list of the top ten problems mankind will face in the near future. 1. Energy 2. Water 3. Food 4. Environment 5. Poverty 6. Terrorism and war 7. Disease 8. Education 9. Democracy 10. Population. The reason energy is located at the top of the list is that none of the other problems can be solved without an abundant source of energy. For example, we will need to find a vast new source of clean water. Luckily, we have a huge amount of water in the sea, but it is not useful without removing the salt and delivering it to homes, both of which requires energy. The challenge of food production is similar. We cannot provide food without fertilizing, harvesting, packaging, and delivering the products, all of which require energy. Likewise, energy plays an important role in determining the quality of environment, the prevention of disease, and so on. In conclusion, energy is the single most important problem we face.

In 2004, we consumed 220 million barrels of oil, the equivalent of up to 14.5 terawatts. To provide all 10 billion people on the planet with the level of energy of an advanced country, we would need 60 terawatts of energy, the so-called “Terawatts Challenge”. We need to acquire the ability to produce energy at this magnitude in a sustainable, continual way with sufficiently low expense: pennies per kilowatt-hour.

For supplying energy, three major parts have to be integrated: energy generation, an energy grid for transportation, and energy storage. Solar energy might be a good solution
for the aspect of energy generation since 165,000 terawatts of solar power hits the earth
every moment of every day. Although there is plenty of solar energy, we do not have the
technology to inexpensively convert it into a useful form of energy such as heat and
electricity. Wind might be another solution, but solar or wind energy requires a local
energy storage system to supply energy to homes 24 hours a day, so the role of energy
storage is very important for developing a sustainable and continual supply of energy.
The last part involves developing on energy grid for transportation of energy. What is the
cheapest way to transport energy? The best answer would be to transport energy as
energy, not mass. For example, oil, which is currently the preferred form of energy, is
transported by truck or ship at substantial cost. By comparison, a high-voltage
transmission line for transporting energy as electricity would be a very efficient way to
carry energy more than 1500 miles with fairly low loss.

We expect that nanotechnologies, new materials, and possibly new physics will
enable us to create new sources of energy, an effective energy grid, and large scale
energy storage. Especially for the energy grid, Dr. Smalley proposed an ambitious
“armchair quantum wire” project motivated by the remarkable electric property of
armchair nanotubes. Armchair nanotubes conduct electricity ten times better than copper,
and each of them can carry 20 μA of current. A wire, one-half inch in diameter, which is
made of these tubes aligned parallel to each other along the fiber axis, would have over
100 trillion conductors packed side by side, so current carried by this wire will be 100
million amps even in the case where each nanotube carries only 2 % of its full capability.
Fabricating such a wire is a prime objective of our work.
2.2 Why Armchair Tubes? (SWNT structure and energy band)

2.2.1 SWNT Structure

Single-walled carbon nanotubes present a new form of carbon possessing one-dimensional cylindrical geometry formed by rolling up a graphene sheet. The structures of SWNTs are represented by the chiral vector \((n, m)\) and formed by bringing together the start and end point of the chiral vector. Hence, the diameter of SWNT can be expressed by the length of the chiral vector via, 

\[
d = \frac{C_h}{\pi} = \frac{\sqrt{3}a}{\pi} \sqrt{n^2 + nm + m^2},
\]

where \(C_h\) is the chiral vector and \(a_{CC}\) is the C-C bond length.

![Figure 2.1. Crystal structure of SWNT.](image)
When \( n = m \), the open end of a nanotube has an armchair shape, so it is called "armchair" tube. When \( m = 0 \), the tube edge has a zigzag shape and it is therefore called a "zigzag" tube. All other nanotubes are called "chiral" tubes, and have carbon hexagons helically spiraling along the tube axis at a chiral angle between 0° and 30°.

![figure](image)

**Figure 2.2.** Three types of tubes specified by chiral angle[8].

2.2.2 SWNT Energy Band Theory

(1) Band structure of graphite

The 1-D electronic band structure is given by zone folding of the 2-D energy band structure of graphite. The 2-D energy bands are calculated by finding the eigenvalues of the \( 2 \times 2 \) matrix Hamiltonian and \( 2 \times 2 \) overlap integral matrix \( S \) associated with the A and B (nearest neighbor) atom sites in 2D graphite through the tight binding method. In the tight binding method, only nearest neighbor hopping allowed by orbital overlap is considered.
$$H = \begin{pmatrix} \varepsilon_{2p} & -tf(k) \\ -tf(k)^* & \varepsilon_{2p} \end{pmatrix} \quad \text{and} \quad S = \begin{pmatrix} 1 & sf(k) \\ sf(k)^* & 1 \end{pmatrix}$$ (1)

Where $\varepsilon_{2p}$ is the site energy of the 2p atomic orbital, $t$ is absolute value of the transfer integral and

$$f(k) = e^{i\rho a/\sqrt{3}} + 2e^{-i\rho a/2\sqrt{3}} \cos \frac{k_x a}{2}$$ (2)

Here, $a = \sqrt{3}a_c = 2.46 \text{Å}$. From the secular equation,

$$\det(H - ES) = 0$$ (3)

we are able to get eigen state energy values of graphite.

$$E_{g2D}^{\pm}(\vec{k}) = \frac{\varepsilon_p \pm tw(\vec{k})}{1 \mp sw(\vec{k})}$$ (4)

For $t>0$, $E^+$ and $E^-$ correspond to the valence $\pi$ and the conduction $\pi^*$ bands. The function $w(\vec{k})$ in Eq. (4) is given by

$$w(\vec{k}) = \sqrt{|f(\vec{k})|^2} = \sqrt{1 + 4\cos \frac{\sqrt{3}k_x a}{2} \cos \frac{k_x a}{2} + 4\cos^2 \frac{k_x a}{2}}$$ (5)

In Figure 2.3, the energy band for 2D graphite is plotted as a function of the two dimensional $k$ values in the hexagonal Brillouin zone.
Figure 2.3. The energy dispersion relation of graphite[26].

At the K point, there is no band gap, so graphite is a zero band gap semi-conductor at $0^\circ$K and is metallic at room temperature.

(2) Band structure of SWNTs

The 1-D energy band structure of SWNT is given by

$$E_\mu(k) = E_{g2D} \left( k \frac{\bar{K}_2}{|\bar{K}_2|} + \mu \bar{K}_1 \right)$$

$$\mu = 1, 2, ..., N \quad \text{and} \quad -\frac{\pi}{T} \langle \frac{\pi}{T} \rangle$$ (6)

where T is the magnitude of the unit cell vector along the nanotube axis, k is a wave vector along the nanotube axis and N is the number of hexagons of the graphite honeycomb lattice that lie within the nanotube unit cell.

The periodic boundary condition (i.e. the wave function has to be the same after turning one circle) for a carbon nanotube gives N discrete k vectors in the circumferential direction, and $\bar{K}_1$ gives the separation between two adjacent k vectors.
Figure 2.4. The one dimensional Brillouin zone of SWNT is shown in the two dimensional Brillouin zone of graphite. (A) Metallic tube (B) Semi-conducting tube[26].

From Figure 2.4, we can understand that the SWNT is metallic if the one dimensional Brillouin zone of the SWNT touches the K point of the Brillouin zone of graphite. Otherwise, the SWNT will be semi-conducting. The distance $D$ between the K point and the 1D SWNT Brillouin zone is mathematically given by

$$D = \frac{2n + m}{3} \bar{K}_1 \quad . \quad (7)$$

Therefore, the condition for metallic nanotubes is that $(2n+m)$ or, equivalently, $(n-m)$ is a multiple of 3. (Since $3n$ is a multiple of 3, the remainders of $(2n+m)/3$ and $(n-m)/3$ are identical.)

(3) Density of state and van Hove singularities

The 1D density of states (DOS) in the units of states/C atom/eV can be calculated by
\[ D(E) = \frac{2}{N} \sum_{\mu} \frac{1}{dE_{\mu,k}(k)} \delta(E_{\mu,k}(k) - E) dE. \] (8)

From the Eq. (8), we see that the density of states becomes very large when the energy band becomes flat as a function of \( k \). We call the peaks where the DOS is infinite van Hove singularities.

![Figure 2.5](image)

Figure 2.5. The DOS of (10, 10) tube. The peaks are singularities on the conduction band[26].

We can define the energy difference between the van Hove singularities of the conduction band and valence band as a \( E_{ii} \), which is the allowed transition by selection rules when the polarization of the incident light is parallel to nanotube axis. \( E_{ii} \) can be calculated near to the \( K \) point by approximation.

Near the \( K \) point at the corner of the hexagonal Brillouin zone of graphite, \( w(\vec{k}) \) has a linear dependence on \( k = \vert \vec{k} \vert \), which is measured from the \( K \) point as

\[ w(\vec{k}) = \frac{\sqrt{3}}{2} ka + \ldots \ldots \ for \ ka \ll 1. \] (9)

From Eq.(9), we get the linear dispersion relation for graphite given by

\[ E(k) = \pm \frac{\sqrt{3}}{2} tka = \pm \frac{3}{2} tka_{cc} \] (10)
The energy minimum of each sub-band near the K point corresponds to a van Hove singularity because van Hove singularities appear when \( \frac{dE}{dk} = 0 \). Since the energy has linear dispersion with respect to \( k \) (Eq. (10)), the smallest \( k \) value from the K point gives van Hove singularity. From the Figure 2.4., we see that the smallest \( k \) value from the K point could be given with respect to \( K_i \) and \( |K_i| = 2/d_i \). For metallic tubes, the first van Hove singularity energy occurs at \( k = |\vec{K}_i| = 2/d_i \), so \( E(k) = \pm 3 \frac{ta_{c-c}}{d_i} \) from Eq. (10) and

\[
E_{11}^M(d_i) = 6a_{c-c} t / d_i .
\]

For semi-conducting tubes, the first van Hove singularity energy is given by \( k = \frac{1}{3} |\vec{K}_i| \) and

\[
E_{11}^S = 2a_{c-c} t / d_i .
\]

With these approximations for a semiconducting tube, the energy difference betweens van Hove singularities occurs at \( E_{11}^S(d_i), 2 E_{11}^S(d_i), 4 E_{11}^S(d_i), 5 E_{11}^S(d_i), 7 E_{11}^S(d_i), \ldots \), and for metallic nanotubes, the energy difference will be \( E_{11}^M(d_i), 2 E_{11}^M(d_i), \ldots \).

(4) Trigonal warping effect

When \( |K_i| = 2/d_i \) is large, which corresponds to smaller values of \( d_i \), the linear dispersion approximation is no longer correct. As we see from Figure 2.6, the equi-energy contour becomes triangular, which connects three M points around the K point for a large \( k \) value. This distortion of the equi-potential line from a circular contour in materials with a three-fold symmetry axis is known as the “trigonal warping effect”.
Near the Fermi energy, the trigonal warping effect acts on the energy dispersion relation to split the peaks of density of state, and the magnitude of the splitting depends on the chiral angle of nanotubes. The width of splitting is maximal for metallic zigzag nanotubes, while no splitting occurs for armchair nanotubes. The density of state splits in all metallic nanotubes but armchair tubes because two Brillouin zones symmetrically positioned from the K point have same van Hove singularity energy but they are not symmetric with respect to trigonal zone of the three M points.

This trigonal warping effect consequently causes a spread of the $E_u(d_i)$, so each nanotube $(n,m)$ has a unique set of inter-band energies $E_u$ denoting the energy differences between the i-th van Hove singularities in the conduction and valence bands (Figure 2.7.).
(5) Curvature effect

Metallic nanotubes (n-m= an exact multiple of 3) have been proposed to be good one dimensional conductors from the tight binding calculation. However, the finite curvature of the graphene sheet can modify their electronic properties of nanotubes. Briefly, finite curvature reduces the overlap of nearest-neighbor $\pi$ orbitals depending on chiral angle and diameter. The band gap induced by the curvature effect is maximum at zigzag tubes ($\alpha =0$), zero at armchair tubes ($\alpha =30$), and is inversely proportional to the square of the diameter. In summary, only armchair tubes (n=m) are truely metallic [27], and all other metallic tubes are semi-metallic with a band gap of a few meV. The rest of tubes are semi-conducting tubes with roughly 1 eV direct band gap.
2.3 SWNT Synthesis

So far, three major methods of SWNT synthesis have been developed. They are arc discharge, laser ablation, and chemical vapor deposition. I will briefly review these methods. Until now, no method has the capability of producing chirality selected SWNTs that will be very useful for semiconductor industry or armchair quantum wire. That remains as great challenge.

2.3.1 Arc Discharge

Iijima and Ichihashi at NEC in Japan[3], and Bethune and coworkers at IBM in the US[4] discovered that SWNTs could be produced if certain metals such as Co/Ni, or Ni were imbedded in the anode of a DC carbon arc operated in a fashion expected to synthesize C_{60}. The carbon nanotubes they found were all SWNTs and largely free of defects over their entire length, but were also typically coated with amorphous carbon. Interestingly, the sizes of the diameters were narrowly distributed around 1.2 nm even though the two groups used different catalysts. Since there is no way to control the size of metal clusters condensing from the vapor of the arc, the appropriate explanation for the narrow distribution in diameter is that the diameter of tubes are decided by the energy balance between a decreasing strain energy and an increasing number of energetically costly dangling bonds at open ends as the diameter of the tube increases.

2.3.2 Laser Ablation

The first growth of high quality of SWNTs at a 1-10 g scale was achieved by Smalley and coworkers using a laser ablation method[18]. In this process, a laser vaporizes a
composite graphite/transition metal target inside a heated quartz flow tube. The condensed materials are collected downstream by cold finger (Figure 2.8.A). Using a target rod of 98.8% C, 0.6% Ni, and 0.6% Co resulted in over 50% of the vaporized carbon forming SWNTs. These SWNTs were found bundled together in ropes 5-10 nm in diameter, containing roughly 10-100 individual nanotubes in cross section, and all close-packed into hexagonal crystals via van der Waals interactions (Figure 2.8.B).

Interestingly, no open-ended SWNTs have been observed, and no metal catalysts have been found clearly associated with nanotubes. This growth process could be explained by a scooper mechanism[18] in which one or a few metal atoms sit at open end of a tube and prevent carbon pentagons from forming by scooting around the growing edge. The metal cluster ultimately leaves the ends of the SWNTs either by evaporation, or by slowly catalyzing the closure of the ends in the case that the cluster is sufficiently large. These nanotubes were distributed as “tubes@Rice”, and many properties of this material have been measured.

**Figure 2.8.** (A) Schematic design of laser ablation method, (B) Closely packed individual nanotubes in a bundle[18].
2.3.3 Chemical Vapor Deposition

(1) HiPco Process

The carbon arc discharge and laser ablation methods are not economically favorable for mass production due to the excessive energy required to evaporating graphite, the cost of the feedstock, and the limited scale. The clear direction for scale up and mass production appears to be finding an all gas phase process. The most difficult problem in conventional chemical vapor deposition (CVD) is amorphous carbon generated by self-pyrolysis of carbon feed gas such as ethylene, acetylene, and even methane. Fortunately, carbon monoxide is perfectly stable, as it does not decompose into amorphous carbon without the presence of catalyst.

The HiPco process was first developed by Smalley and coworkers, and the basic idea of the process is quite simple[28, 29]. A cool and high pressure stream of CO feed gas containing Fe(CO)$_3$ catalyst precursor is heated to 1000°C in less than a millisecond by mixing it with preheated CO gas at 1200°C (Figure 2.9.A). When suddenly heated to 1000°C, Fe(CO)$_3$ begins to be decomposed, and nucleates a tiny nanoparticle of iron for catalyzing the Boudard reaction where two CO molecules produce one CO$_2$ molecule and graphite. The most favorable form of graphite in that environment is a perfect single wall carbon nanotube, but C$_{60}$ and larger spheroidal fullerenes are also produced as side products. This process runs continuously and produces 25 g of SWNTs per day at Rice, and was recently scaled up in industry to produce 50 lbs per day (Figure 2.10.).
Figure 2.9. (A) Hipco reactor, with reaction zone enlarged[28]. (B) SEM image of raw Hipco material.

Typically, the Hipco process produces SWNTs in tangled ropes of 10-30 nm in diameter forming endless spaghetti structures (Figure 2.9.B). The diameters of each tube varies from 0.7 nm to 1.4 nm. From the fluorescence measurement, over 33 semi-conducting tubes were identified by obtaining $E_{11}$ and $E_{22}$ inter-band transition energy values from absorption and emission spectroscopic data[30].

Figure 2.10. Overall Scheme of the Hipco process (Courtesy of Steven Ho)
(2) Conventional CVD

Chemical vapor deposition methods have been successfully used to grow carbon fibers, filaments, and nanotubes for more than 10-20 years. The growth process of SWNTs involves depositing catalysts on the substrate and heating them to high temperatures while hydrocarbon gas flow through a quartz tube furnace (Figure 2.11.) The key factors are the hydrocarbons, catalysts and growth temperature. In a CVD growth process, introduced hydrocarbon is decomposed at the surface of nano-sized catalyst particles, and carbon atoms diffuse around the catalyst particles. At some point, the carbon atoms become supersaturated within catalyst particles and precipitate into nanotubes. The formation of nanotubes is energetically favored over graphite due to the elimination of dangling bonds.

![Figure 2.11. Schematic setup for CVD](image)

Growth of SWNTs with structural perfection was enabled by CVD methods. Hongjie Dai and coworkers found that high quality SWNT materials were produced using methane as carbon feedstock, reaction temperatures of 850-1000°C, and suitable catalyst materials[31-34]. High temperatures were required to form SWNTs with small diameter
and few defects. Methane was the key to producing high quality material without forming amorphous carbon because methane is very stable and thus not easily self-decomposed.

Recently, millimeter long vertically aligned SWNT growth was developed by Hata et al.[35]. A controlled amount of water was introduced with the hydrogen/argon carrying gas, which enhanced the activity and lifetime of the catalysts and resulted in massive growth of dense and vertically aligned SWNTs. Hata et al. claimed that the water cleaned the amorphous carbon that cause a poisoning of the catalyst surface while leaving the nanotubes undamaged[35, 36].

2.4 Raman Spectroscopy of SWNT

There are 2N carbon atoms in a unit cell, and they have 6N degrees of freedom, where N is the number of hexagons in a unit cell. For example, a (10,10) nanotube has 40 atoms in the unit cell and 120 degrees of freedom, but it only has 66 distinct phonon branches because of mode degeneracy. Some SWNT phonon modes observed in Raman spectroscopy can reveal properties of the corresponding nanotubes such as diameter, defects and electrical properties.

2.4.1 Resonant Raman Scattering

The observation of Raman spectra from just one nanotube is possible because of the very large density of electronic states close to the van Hove singularities in the 1D structure. When incident or scattered light is in resonance with the inter-band energy $E_{\mu}$,
the Raman scattering cross section becomes very large, because strong coupling occurs between the electrons and phonons at resonance.

Resonant Raman scattering opens the door to observe Raman scattering at a single nanotube level and allows us to assign chirality and obtain information about the intensity, line width, defects and polarization.

The generic spectrum of a SWNT is shown in Figure 2.12.

![Raman spectrum](image)

**Figure 2.12.** Raman spectrum from 780nm laser. * are from Si or SiO₂.[37]

2.4.2 Chirality Assignment from the RBM (Radial Breathing Mode)

The RBM is the phonon mode from in phase displacement, and its symmetry is $A_{1g}$. The frequency of the RBM varies as $1/d_i$.

$$\omega_{RBM} = \alpha / d_i$$  \hspace{1cm} (13)

For the Si/SiO₂ substrate, $\alpha$ is experimentally found to be 248 cm⁻¹.
The determination of \((n,m)\) by resonance Raman scattering depends on the determination of \(E_{ii}\) using the unique relationship between \(E_{ii}\) and \((n,m)\), as given by the trigonal warping effect in Figure 2.7. First, using a tunable laser, we need to find the resonance energy of light which gives the maximum peak intensity. Second, we find the RBM frequency from the resonant Raman spectrum and calculate the diameter of the nanotubes by Eq. (13). Now, we have two unknowns, \(n\) and \(m\), and two known conditions which are the diameter and inter-band energy. If we refer to the table of \(E_{ii}\) value as a function of \((n,m)\), we find only a few nanotubes with different diameters are resonantly scattered by the same laser light. Since we already know the diameter of nanotubes, we can uniquely determine \(n\) and \(m\).

2.4.3 The G Peak

The G-peak for carbon nanotubes occurs between 1500 to 1600 cm\(^{-1}\). This range basically arises from the optical mode \(E_{2g}\) of graphite, but it is different in that the 2D graphite Brillouin zone is folded into a 1D Brillouin zone and \(A, E_{1}\) and \(E_{2}\) symmetry mode including the tangential and circumferential modes are Raman active. The G-band is thus an intrinsic feature of carbon nanotubes that is closely related to vibrations in all \(sp^2\) carbon material. The most important feature of the G peak is that its shape is different between metallic and semi-conducting nanotubes. The G peak shows overlap of two peaks: \(\omega^-\) (at about 1550 cm\(^{-1}\)) from the circumferential direction and \(\omega^+\) (at about 1590 cm\(^{-1}\)) from the tangential direction. Metallic tubes show a very broad Breit-Wigner-Fano line at \(\omega^-\) by a strong coupling to surface plasmons, so this Breit-Wigner-Fano line is a strong indication of metallic nanotubes.
2.4.4 The D Peak and The G’ Peak

The frequency of the disorder-induced D peak (at about 1350 cm\(^{-1}\)) and its overtone G’ peak (at about 2700 cm\(^{-1}\)) has strong dependence on laser excitation energy whereas the RBM and G peak are independent of laser excitation energy. The physical origin of the D peak and G’ is a double resonance mechanism which is operative for graphite, but is modified by the 1D van Hove singularities. The double resonance effect in SWNT occurs when both the initial (or final) state and the scattered intermediate state are van Hove singularity states. In this way, it is possible to gain a sufficiently high Raman intensity to produce strong D and G’ peaks in the Raman spectrum.

![Diagram of D and G' peaks](image)

**Figure 2.13.** (a), (b), (c), (d) are D peak processes and the dotted line indicates elastic scattering with defects. (e), (f) are G’ peak process[37].

As we see from Figure 2.13, the D peak is generated by the one phonon and one defect process, and the G’ peak is generated by a two phonon process. Both processes take place around the K point of the graphite Brillouin zone. From the mechanism of the
D and G' peak, we can conclude that the D peak could be a indication of defects or any symmetry breaking factors in nanotubes, and the G' peak could be a indication of clean and defect free tubes, because the G' peak shows up when a van Hove singularity induces double resonance and two phonon process are uninterrupted by interfering circumstances.
3. Flat SWNT Substrates Preparation

3.1 The Hypothesis of Continued Growth

Continued growth of single-walled carbon nanotubes starts by preparing a nanoscopically flat, well-aligned and open-ended SWNT substrate. Then, we deposit catalyst onto the open ends of SWNTs, activate the catalyst, and introduce carbon feedstock to produce continued growth of SWNTs by adding carbon atoms directly to the pre-existing nanotube structure.

![Diagram of continued growth]

**Figure 3.1.** Overall scheme of continued growth.

If we can achieve a high growth efficiency from a high density open-ended SWNT substrate, growing nanotubes will support each other with neighbors such that continuously grown tubes will be aligned along the one direction. Also, we expect that the growth will not be terminated by the diffusion limit of carbon feedstock due to a proposed tip growth mechanism. Once we start from the armchair substrate, this might be a means to produce armchair quantum wire.
3.2 Cutting Technique

3.2.1 The Microtome Cutting Technique

Our strategy for preparing an open-ended substrate is using SWNT spun fiber and cutting the fiber perpendicular to the fiber axis. Since most of individual nanotubes are aligned parallel to the fiber axis in the spun fiber, this strategy will provide us with flat, well-aligned, and open-ended SWNT substrate.

Ericson et al. developed a means to spin SWNTs of 1 µm length into a continuous, aligned, neat fiber[24] with about 70% of ideal packing density.

![Image](image_url)

**Figure 3.2.** (A), (C) SWNT fiber spinning apparatus, (B) SEM image of the spun fiber[24].

We have developed a microtome technique for cutting the spun fiber. We dropped one droplet of 2.3M sucrose solution onto an aluminum stub, picked up a 1 cm length of
fiber and inserted it into a hole in the stub, leaving one end slightly protruding out of the droplet. Then, the sample was mounted in a cryo-ultramicrotome stage (Leica Ultracut 125) and frozen to -100°C to make the sucrose solution hard enough to slice. First, we roughly trimmed the sample with a stainless steel knife to prepare a small trapezoid shape end with the fiber in the center. Second, we switched to a 35° diamond knife (DiATOME) and sliced the sample with 50 nm steps consecutively with 1.0mm/s speed until the complete cross section of the fiber was cut off. After microtoming, the remaining fiber was transferred to a 26 Gauge hypodermic needle and glued using a conductive silver paint (Leitsilber 200, Ted Pella) to secure the fiber to the needle and avoid charging problems while taking SEM. The fiber protruded 3-4mm from the end of needle and was rinsed with de-ionized water to remove the sucrose solution. The sample was stored in a Forensic sample holder (Ted Pella) using a luer lock (Cole-Parmer) fitting.

**Figure 3.3.** Schematic illustration of microtoming of the spun fiber (A) 1 cm long fiber was mounted through sucrose droplet and a hole of stub. (B) trimming sample into a trapezoid shape (C) mounting the fiber to the hypodermic needle by silver paint (D) Forensic sample holder (E) the image of the fiber glued into the needle
Figure 3.4. (A) Overall microtome cut surface, (B) Starting part of cutting, (C) Middle of cutting, (D) End part of cutting.

The SEM images taken from the microtomed surface of the fiber are presented in Figure 3.4. The microtome reveals the entire cross section of the fiber, so this technique enables us to measure physical properties of the SWNT spun fiber accurately. Tensile strength, Young’s modulus, density, thermal conductivity, and electrical conductivity were measured based upon the cross sectional area measured after microtome cutting[24].

The SEM image at high magnification (figure 3.4.C) shows that the diamond knife did not cut the tubes, but generated a 10-50nm thick combed layer where the sidewalls of nanotubes are exposed.

To remove a combed layer, we need a highly aggressive etching species because carbon is bound to three other carbon atoms with 12 eV at the sidewall of nanotubes.
3.2.2 The Focused Ion Beam Cutting Technique

In the last section, we found that microtome cutting produced a flat surface, but generated a combed layer with the exposed sidewalls of nanotubes. The focused ion beam technique was employed to really cut SWNT spun fiber and prepare a nanoscopically flat surface of the substrate.

The focused ion beam technique was developed for lithography, ion beam milling, doping (implantation), and deposition[38]. Broad beam ion milling, where ions of a few hundred eV energy hit on a surface, is a widely used method of material removal. In focused ion beam cutting, an ion beam is scanned in a line on a surface producing a trench with an inverse Gaussian shape as expected from the beam profile. However, when the dose is increased, the trench becomes very sharp, narrow, and unexpectedly deep.

Our collaborators in AFB, UPenn, and FEI performed focused ion beam cutting on the SWNT spun fiber by using FEI Strata DB235 Focused Ion Beam. Gallium ion (Ga\(^+\)) was used as an ion source and focused down to 10-20 nm sized spot. Accelerated gallium ions transfer huge momentum, sputtering carbon atoms from their hexagonal lattices so that real cutting of tubes can be achieved. The procedure is comprised of two parts, cutting and cleaning. An acceleration voltage of 10 kV and current of 500-1000 pA were used for rough cutting, and voltage and current of 10 kV and 100-500 pA were used for cleaning. The cleaning cycle was repeated until most of artifacts generated by cutting were removed. Finally, a nanoscopically flat surface was revealed after two processes (Figure 3.5.).
Even though the surface looks very smooth and clean, it is covered by amorphous carbon and implanted gallium. The amorphous carbon layer is produced by ion damage resulting from the displacement of atoms from their lattice sites due to collisions with the ions or by re-deposition of carbon atoms caused by back scattering. Also, the ends of each tube might be closed by generated heat or by carbon deposition. Thus, we need a cleaning process to remove Ga and amorphous carbon as well as an end opening step.

Using focused ion beam technique, a “bed-of-nails” SWNT membrane was successfully prepared[39]. Taking advantage of the good alignment along the fiber axis, we milled perpendicular to the fiber axis and prepared slices of membrane with a thickness 75nm or so. The membrane was able to be lifted out with a hydraulic micromanipulator and placed on a holey TEM grid without any damage to reveal the inner structure of the fiber.
Figure 3.6. (A) A “bed-of-nails” membrane before lifting out from the trench (B) Bright field TEM image of a section of membrane (C) Magnified TEM image at normal angle, and (D) at 10° tilt.

TEM observation was carried out in a JEOL JSM 2010 TEM operating at an acceleration voltage 100kV. High magnification images (Figure 3.6. C and D) show dark circles and dark lines. The dark circles are recognized as the tube aligned along to the direction of e-beam, and dark lines are the tubes off from the e-beam axis. At 10 degrees tilt from the normal direction, most of dark circles disappeared. This indicates that most of tubes in the fiber are aligned parallel to the normal direction.
Figure 3.7. (A) Magnified TEM image at normal angle, (B) Fourier transformation of (A), (C) magnitude of (B) with respect to distance.

Fourier transform of the TEM image is plotted in Figure 3.7.B, and that is transformed again into real space in Figure 3.7.C. There are three distinct peaks at 1.53nm, 0.76nm, and 0.52nm corresponding to the lattice constant $a$ of hexagonal packing of SWNTs, $a/2$, and $a/3$. Considering a van der Waals spacing of 0.34 nm, we can derive the average diameter of tubes. The estimated diameter was 1.19nm, which is slightly larger than the diameter estimated from fluorescence data obtained from
semiconducting tubes [30]. This discrepancy might be attributed to deviation of van der Waals spacing caused by loose packing during the process of fiber spinning.

![Raman Spectra Graph](image)

**Figure 3.8.** Raman spectra using 780 nm excitation of a “bed of nails” membrane in comparison with a “bucky-paper” prepared from as-grown HiPco material.

In Figure 3.8, Raman spectra taken from a “bed of nails” membrane is compared to a bucky paper made up of HiPco tubes. The absolute intensity of G peak of the membrane is 1/16 of that of a bucky paper due to limited thickness of the membrane. The D peak of the membrane is almost double of a bucky paper, indicating that amorphous carbon might be generated by ion damage or re-deposition from back scattering.

In conclusion, the focused ion beam technique provide us with means of preparing a nanoscopically flat substrate for continued growth by cutting the SWNT spun fiber as
well as a method for cutting nanotubes with a desired and precise length compared to other cutting techniques that produces a broad distribution of lengths[40-42].

3.3 Planarization

3.3.1 Overall Scheme of Planarization

As an alternative approach to nano-scopically flat SWNT substrate, planarization was tested. The idea of planarization began as a catalyzed etching scheme.

![Figure 3.9. Overall scheme of planarization](image)

The rough surface of the tweezer-cut fiber touches a nanoscopically flat metal catalyst foil with an associated etching gas at elevated temperatures. The etching
temperature is adjusted to allow only catalyzed etching around the surface of metal
catalyst foil without allowing gas phase reaction. With the motorized nanometer
positioner, only asperities of the fiber touch the catalyst foil and are removed, then the
fiber is moved a little bit toward foil, more material is removed, and so on. Finally, we
expect that a nano-scopically flat surface will be imprinted on the surface of the fiber.

3.3.2 Instrumentation of Planarizer

The planarizing instrument has been constructed in a manner similar to the STM
device. In STM, the tunneling current and angstrom level of motion of piezoelectric drive
is controlled by feedback circuit enable a STM tip to keep certain distance from the
sample, and follow the morphology of the sample when a tip scan in 2-dimensional space.
STM also requires careful vibration isolation to minimize noise[43]. The same principle
was applied to the planarizer instrumentation. Nanometer scale motion control and
vibration isolation is needed to avoid folding over of asperities on the surface of the fiber
and provide for controlled etchback. Also, the main chamber of planarizer is required to
be small, rigid, and light so that resonance frequency of the instrument is higher than that
of environment.
Figure 3.10. (A) A picture of inchworm motor IW-810 (left one) was used for our system, (B) Schematic drawing of inchworm motor with dimension.

The EXPO Burleigh inchworm motor IW-810 was employed for motion control. The inchworm motor has the capability of 0.1 nm of motor resolution with total 1 inch translation, but it cannot be inserted inside of the chamber since it is driven by piezoelectric materials that cause a corona discharge in the range of 1 mtorr – 100 torr of gas pressure. This restriction required us to develop a mechanical feed through, so the inchworm motor is placed outside of the chamber and only the shaft moves through a mechanical feed through. Special care was also needed not to bring lateral force more than 1 N for accurate motion and stability.
Figure 3.11. (A) Cross sectional view of the main chamber and a mechanical feed through, (B) Self centering o-ring support for minimizing lateral force. (3D Solid Works was used for the drawing.)

As we see in Figure 3.11., the o-ring mechanical feed through was designed and the self centering o-ring support was developed to compress o-ring for vacuum seal without exerting lateral force to the shaft. In Figure 3.11.B, the cylindrical piece can pivot on the base part. This will in turn apply uniform compressive force to the o-ring.
Figure 3.12. (A) A picture of the main chamber of the planarizer (B) 2.75" CFF type button heater assembly from Heat Wave

For the main chamber (Figure 3.12.A), 2.75" six-port Conflat cube from Kurt J. Lesker was used, and a 2.75" CFF type button heater from Heat Wave Laboratory (Figure 3.12.B) was attached to the main chamber from the top. A gold coated heat shield was developed to localize heating just on the fiber to minimize heat transfer to the inchworm motor or whole chamber. The fiber sample was mounted to a hypodermic needle with ¼-28 thread, glued by silver paint. The shaft was lubricated by vacuum grease to avoid stick and slip problem that usually take place in o-ring feed through. For vibration isolation, soft rubber absorbers were used instead of the spring suspension and eddy current damping that is a standard technique in STM[43]. The spring suspension for our device
would be unstable since the center of mass is located higher than suspension plate (Figure 3.9.).

Feed back control was enabled through the feed back programs using lab view 7.0, and contact resistance between the asperities and a catalyst foil was measure by Fluke ohm meter that has the capability of maximum resistance up to 500 M Ohm. Every second, the resistance was measured, and the inchworm motor moved back and forth with 10nm - 100nm increment to maintain certain resistance.

3.3.3 Catalyzed Etching Chemistry and Results

Planarization of the SWNT spun fiber has been thoroughly tested with hydrogen gas and platinum foil. Molecular hydrogen can be effectively dissociated into atomic hydrogen on the surface of platinum since there is almost no kinetic barrier for H2 dissociation[44]. Atomic hydrogen on the catalytically active metal can migrate to nanotubes of asperities by the “spill over” mechanism[45, 46], and find defect sites and etch from the defects by methanation.

\[
\begin{align*}
H_2 + 2Pt & \rightarrow 2(Pt - H_{ads}) \\
(Pt - H_{ads}) + C & \rightarrow Pt + (C - H_{ads}) \\
(C - H_{ads}) + H_{ads} & \rightarrow CH_4(g)
\end{align*}
\]

The first step is a dissociation of molecular hydrogen, and the second step is spill-over in other words, surface diffusion. The final step is a formation of methane from the reaction between atomic hydrogen and carbon.
Figure 3.13. Methanation of a steam-activated granular carbon with respect to temperature[47].

In Figure 3.13, we can recognize that no methanation takes place without catalyst below 800 °C, and platinum is the best catalyst over 650 °C. To avoid a gas phase reaction and allow only a reaction around a Pt foil, 650 °C-800 °C temperatures were tried with variation of H₂ gas pressure from 10 mtorr to 10 torr. The fiber initially had a very rough surface since it was cut by tweezers. The best result was achieved at 700 °C and 1 torr of Hydrogen. The motion was controlled by a feedback program written with Labview to maintain a mega-ohm range of contact resistance. The total advancement was 11 µm. After planarization, the surface became smooth and flat, but was covered by a thick layer of carbonaceous materials that might be alkane species as identified from the Raman peak 1062 cm⁻¹ (Figure 3.14).
Figure 3.14. (A), (B), (C) SEM images from planarized sample with H₂, (D) Raman data from the planarized surface.

Oxygen gas was tried with platinum foil with temperature variation from 500 °C to 900 °C at 1 torr pressure. From our experience, we found that atomic oxygen is so aggressive that it etches nanotubes along the side wall even at low temperatures. For example, UV ozone or an inductively coupled oxygen plasma produced carbon oxide species name, “poo”. Here, we found similar effects came out as a result of planarization with oxygen. The surface became flat, but was covered by carbon oxide species that might be poly-cyclic aromatics decorated by oxygenated groups such as carbonyl groups or quinone groups (Figure 3.15.). Even at 500 °C, the formation of carbon oxide occurred.
Figure 3.15. (A) SEM image from planarization with 1 torr of oxygen at 500 °C (B) SEM image from planarization with 1 torr of oxygen at 900 °C.

Finally, carbon dioxide was tried with Pt and Ni foils at a wide range of temperature from 500 °C to 900 °C. The reaction between graphite and carbon dioxide is known as the Boudouard reaction[48].

\[
\begin{align*}
\text{C (graphite)} + \text{CO}_2(\text{g}) &= 2\text{CO(}g) \\
\Delta H^{\circ}_{298.15K} &= 41.21 \text{kcal/mol} \\
\Delta G^{\circ}_{1200K} &= -9.42 \text{kcal/mol}
\end{align*}
\]

This reaction is endothermic and, for a given carbon in the absence of catalyst, takes place several orders of magnitude slower than the catalyzed carbon and oxygen reaction at the same temperature. In general, catalysts are required to produce substantial gasification rates for the C-CO\textsubscript{2} reaction at temperatures below 900 °C[49]. A couple of experiments were tried at 10 mtorr at 500 °C, but we did not observe obvious evidence of etching (Figure 3.16.A). The bundles of nanotubes were folded over because the etching rate is much slower than our automated advance with the inchworm. The most promising results have been achieved at 1 torr of CO\textsubscript{2} and at 900 °C using Ni foil (Figure 3.16.B).
We observed very flat and clean surface without folding over after planarization. This seems to indicate that CO$_2$ can etch SWNTs only in presence of catalysts below 900 °C.

![Image](image.jpg)

**Figure 3.16.** (A) SEM image taken after planarization with CO$_2$ at 500 °C at 10 mtorr, Pt foil was used. (B) SEM image taken after planarization with CO$_2$ at 900 °C at 1 torr, Ni foil was used.

In conclusion, H$_2$, O$_2$, and CO$_2$ were tried as etching gases, and employed metal foil dissociated gas molecules into aggressive etching species. For H$_2$ and O$_2$ cases, thick layers of byproducts were observed. CO$_2$ gas at 900 °C produced flat and clean surfaces, but the quality of surfaces was not as good as the prepared surface by the focused ion beam cutting technique.
3.4 Electrochemical Method

Electrochemical polishing is well known as metal surface treatment to decrease surface roughness, and thus shine the surface. When an electric field is applied, the electric field at asperities is much higher than in crevices since electrons are more populated at asperities. If we draw equi-potential lines, we will be able to realize that the gradient of potential, and electric field is higher in asperities [50]. When positive voltage is applied to the metal surface, reactive ions or molecules in electrolyte solution will oxidize and thus remove asperities selectively due to the higher electric field [51]. The same principle could be adapted to planarize the cross sectional surface of the SWNT spun fiber.

From previous studies, electrochemical etching of SWNTs or MWNTs has been reported [52-54], but no study has been done on electrochemical polishing of nanotubes.

At the anode, an oxidation reaction takes place in the region of the double layer due to a very steep potential drop (Figure 3.17). The double layer consists of two layers in terms of ion density. At the inner layer, only ions are bound to the electrode, whereas solvent molecules are mixed with ions in the outer layer.

\[ \text{Re} \leftrightarrow O^x + e^- \]

**Figure 3.17.** Basic scheme of electrochemistry with concept of double layer.
The thickness of the double layer can be represented by the Debye length which can be calculated according to Debye-Huckel theory. Debye length is given by the equation: 

$$D = \frac{\varepsilon RT}{\sqrt{2\rho F^2 I}}$$

where $\varepsilon$ is permittivity, $I$ is ionic strength, $F$ is Faraday constant, and $\rho$ is density. From the calculation, we found that 0.01M or lower concentrate of solution was needed to enable Debye length to be longer than surface roughness for well defined electric field differences between asperities and crevices.

In the electrochemistry setup (BAS CV-50W Voltametric Analyzer, BAS Cell stand C3), there are three electrodes: a working electrode, a reference electrode, and an auxiliary electrode (Figure 3.19.). The electrode of interest is the working electrode, and the current flows between the working electrode and the auxiliary electrode driven by the voltage measured relative to the reference electrode. In the reference electrode, ‘Luggin capillary’ prevents the half circuit current from flowing such that we can measure voltage of the working electrode accurately.
Figure 3.19. Electrochemistry setup (BAS Cell stand C3), (A) The auxiliary electrode (B) The working electrode (C) The reference electrode (D) The SWNT spun fiber is mounted to the working electrode.

For the working electrode, the SWNT spun fiber was mounted with assistance of a hypodermic needle and silver paint as it is described in section 3.2.2. The auxiliary electrode was platinum, and the reference electrode was a Ag/AgCl electrode that has 0.22 V vs. the standard hydrogen electrode (SHE). To start with a well defined surface roughness (about 300nm-500nm), the sample was cut by cryo-microtome and oxygen plasma treated for 20 min.

We expected that selective etching of asperities would take place when the current begins to increase, since the etching with a small current will start from the asperities, whereas negligible current flows at the crevices. We selected the voltage for electrochemical polishing from linear sweeping voltammetry (LSV) data. The given
voltage was applied for appropriate amount of time, and the total charge was being recorded with respect to time by bulk electrolysis mode (Figure 3.20.).

![Graph showing current, voltage, and charge](image)

**Figure 3.20.** (A) Linear sweeping voltammetry in case of phosphoric acid. The voltage at which current begin to rise was used for polishing. (B) Bulk electrolysis in case of phosphoric acid. Total charge was recorded with respect to time.

Electrolyte solutions of water, acids, and bases were tested for polishing. The two principal reactions that describe the electrochemical oxidation of carbon in aqueous solutions[55] are

\[ C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \]

\[ C + H_2O \rightarrow CO + 2H^+ + 2e^- \]

Thus, carbon dioxide or carbon monoxide is produced as a result of electrochemical etching at the anode.

Water was tried at 2 V by selection of that voltage from LSV of water, and total charge during 4096 sec was 30 mC. After electrochemical etching, SEM images showed
that the surface of the sample became rougher with crack formation compared to that before treatment, contrary to our expectations (Figure 3.21.A and B).

**Figure 3.21.** Electrochemical etching with water and acid. (A), (B) SEM images taken before and after electrochemical etching with water, (C), (D) SEM images taken before and after electrochemical etching with phosphoric acid.

In acids, two major reactions take place in electrochemical oxidation of carbon[55]:

\[
2C + 4\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8\text{H}^+ + 8e^- \\
6C + \text{H}_2\text{O} \rightarrow C_6\text{O} + 2\text{H}^+ + 2e^-.
\]

The first reaction is an etching carbon reaction, evolving carbon dioxide, and the other is surface carbon oxide formation. We have tried phosphoric acid, nitric acid, sulfuric acid,
and even piranha with a variety of conditions. One of the examples is shown in Figure 3.21. C, D. 0.01 M phosphoric acid was tried at 1.5 V for 58 sec, and total charge was 0.5 mC. The surface roughness has been increased, and a very thin layer of surface oxide was formed on the surface. All the acids we have tested showed almost the same results as phosphoric acid. Usually, it was observed that higher concentration of acids produces thicker layer of carbon oxides, irrespective of their type.

Base was tried for electrochemical polishing, and the major reaction at the anode[55] is

\[ \text{C} + 6\text{OH}^- = \text{CO}_3^{2-} + 3\text{H}_2\text{O} + 4e^- \]

However, carbon monoxide, oxygen, and carbon oxide can be also produced as a side product. As base solutions, NaOH, KOH, LiOH were tried with various conditions. The experiment with 0.01 M NaOH showed promising results at 0.8 V and total charge 11 mC for 1023 sec. After electrochemical etching, the surface became very smooth, but it appeared to be covered by carbon oxide species. We have attempted to remove the oxide layer with 1 torr pressure of hydrogen at 750°C for 30 min in high vacuum chamber. The surface became cleaner, exposing bundles of nanotubes, but we were not able to make it perfectly clean. The bundles of nanotubes fell over the surface rather than remaining vertical, so this result was not appropriate for a preparing open-ended SWNT substrate.
Figure 3.22. SEM images taken before (A) and after (B) electrochemical polishing with NaOH, and SEM images taken after hydrogen cleaning in low magnification (C) and high magnification (D).

There is a report that 30 wt % KOH solution mixed with 2 wt % LiOH has the capability of dominantly producing carbonate ion at 1.14 V vs. Ag/AgCl electrode[56], but in our case, the result was very similar to NaOH case. The whole surface was covered by a smooth layer of carbon oxide species.

In conclusion, various electrolyte solutions that can be classified into three groups (water, acid, base) have been tried for electrochemical polishing. In the case of water and acid, the surface roughness increased with a formation of a very thin layer of carbon oxides. Our electrochemical polishing hypothesis was found to be not useful due to formation of oxide species. Once the insulating layer of carbon oxides is formed at the
surface of the asperities, the current is redirected to flow at the crevices that are now better conductors. Thus, selective etching just on the asperities did not take place. In case of base, a very thick layer of carbon oxide was formed, and exposed bundles of nanotubes were found to be thin and lying down on the surface after removing the oxide layer with hydrogen. That might indicate that sidewalls of bundles were also etched, and maybe etched faster that the tips of bundles. At some point, bundles of tubes could not support themselves and collapsed onto the surface. Although we were not able to find a way to polish the cross-sectional surface of the SWNT fiber preserving clean surfaces, we found that electrochemistry can etch single walled carbon nanotubes at ambient temperature with a simple setup.
4. Continued Growth from Microtome Cut Fiber

In this chapter, we describe a means to prepare open-ended SWNT substrate from microtome cut fiber and continued growth experiment. It starts from an etching scheme for removing a combed layer.

4.1 Oxygen Plasma Etching

Microtome cutting technique inevitably generates a combed layer where the sidewalls of nanotubes are exposed. Since each carbon atom is bound to three carbon atoms with 12eV binding energy, we need a highly aggressive etching species such as atomic oxygen to remove this combed layer.

![Diagram of etching process]

**Figure 4.1.** Proposed mechanism for side wall etching with atomic oxygen.

Atomic oxygen can react with carbon and produce CO, which has highest diatomic binding energy (11eV) in the universe. Single atomic oxygen might be able to attack sidewalls of tubes, but two oxygen atoms are more preferred thermodynamically. As illustrated in Figure 4.1, two oxygen atoms can be chemisorbed in the 1, 2 and 3, 4
positions of a carbon hexagon on the side of the tube, and one oxygen takes a carbon forming CO, while the other rotates to form a quinoid carbonyl. This quinoid carbonyl will then dissociate form a second CO. The net energy release for forming two CO molecules is 22 eV, which is higher than the energy cost of the 2 atom hole left behind on the side of the tube.

As a source of aggressive oxygen atoms, oxygen plasma was considered. The plasma state contains positive ions, negative ions, electrons and atoms generated by electric field, magnetic field or heat. In the case of inductively coupled oxygen plasma, electrons are accelerated by an AC electric field induced by an AC magnetic field from inductive coils according to Faraday’s law, and collide with molecules, generating atoms and positive and negative ions. Specifically, inductively coupled plasma can maintain a low plasma sheath voltage such that ion damage caused by sputtering can be avoided in contrast to the DC type plasma. This plasma sheath is a thin, positively charged layer that joins the charged plasma to the grounded chamber walls and to the specimen and specimen holder[57].

![Figure 4.2. Plasma chamber assembly showing high-frequency antenna located outside of the chamber[57].](image)
Our instrument (ICP type, Fischione Instruments, model 1020) was originally designed for removing hydrocarbon contamination on sample surfaces for better imaging in microscopy such as SEM and TEM. The output power is 40 W with 13.56 MHz radio frequency, and the chamber pressured during etching is 50 mtorr with 25 % oxygen and 75% argon. The plasma sheath voltage is maintained as low as 10-15 eV so that only carbonaceous contamination can be removed without causing sputtering[57].

As illustrated in Figure 4.3, the 50nm thick combed layer produced by the microtome cutting technique has been completely removed using inductively coupled oxygen plasma for 20 minutes. However, the surface was found to be covered by snow-like carbon oxide species, nicknamed “poo” that might be composed of oxygenated poly cyclic aromatic compounds. Since “poo” is weakly bound to the surface of nanotubes, most of “poo” was easily removed by washing the sample in 1 N HCl solution for 1 hour. HCl was employed not only to remove the “poo” but also to remove residual catalyst that is usually 1-4 wt. % of the fiber. The tubes left behind after oxygen plasma etching and
following HCl dipping were not perfectly clean tubes because of sidewall damage from atomic oxygen, so further treatment is imperative for preparing an open-ended SWNT substrate.

**Figure 4.4.** (A) Low magnification SEM image taken from oxygen plasma etched sample showing cross section of the fiber. (B) SEM image taken from the side of the fiber after oxygen plasma etching. (C), (D) before and after image with same magnification, respectively.

As shown in Figure 4.4., an interesting feature was produced at the side of the fiber during inductively coupled oxygen plasma etching. At the surface of the side of the fiber, nanotube bundles became aligned perpendicular to the fiber axis forming periodic pitches. Since the polarizability of nanotubes along the tube axis is high, nanotubes can be aligned
parallel to the direction of applied electric field [58]. Thus, the bundles of nanotubes at the side of the fiber can be aligned with the electric field exerted by the plasma sheath voltage while nanotubes are being etched and broken loose by the atomic oxygen. The periodic pattern is not clearly understood, but it seems to be caused by the interaction between circularly motion of ions and RF current induced on the surface of nanotubes or by plasma striations that are one of the characteristics in AC plasma[59].

4.2 UV Ozone

As an alternative source of aggressive atomic oxygen, the UV ozone method was also employed. The photodissociation of ozone following absorption in the ultraviolet Hartley band leads to the formation of excited state atomic oxygen[60].

\[ O_3 + h\nu \rightarrow O(^1D) + O_2 \]

At 248 nm wavelength, the quantum yield of this process is approximately 0.9 such that the UV ozone method is an effective way to create atomic oxygen[60].
Figure 4.5. (A) A picture of the overall UV ozone setup, (B) A picture of the main chamber, (C) Schematic drawing of the experimental setup for UV ozone with the formula for calculating zone of silence.

As shown in Figure 4.5.C, O₃ was produced from an ozone generator that produces 2.55 mol% O₃ from the gas mixtures of 25 % of O₂ gas balanced with Ar at 1 atm total pressure. The introduced O₃ molecules exit through a nozzle where they are photodissociated into O ('D) by 248 nm photons generated by a pulsed KrF excimer laser. The chamber pressure was maintained at 100 mtorr while being pumped out by a
mechanical pump with a pumping speed of 30 L/sec. This high pumping speed mechanical pump was employed to create a longer “zone of silence” region from the nozzle for the purpose of preventing a relaxation from the \(^1D\) state to \(^3P\) state of atomic oxygen by collisions. The zone of silence is the region where molecular collisions are suppressed, and the vertical length of the zone of silence can be calculated by the formula,

\[ x_M = \frac{2}{3} (d) \left( \frac{P_o}{P_b} \right)^{1/2}, \]

where \(P_o\) is the source pressure, \(P_b\) is the chamber pressure, and \(d\) is the diameter of orifice. The calculated zone of silence in our experimental condition was 8.5mm such that energetic \(^1D\) species can reach to the surface of the sample without collision if the distance between the orifice and the sample surface is maintained less than 8.5mm.

The laser was operated at 7 W time averaged power and 400 Hz repetition rate. A total of 4 million pulses were used for the etching process. As illustrated in figure 4.6., the whole combed layer has been etched away with this condition, but this method still could not avoid the formation of “poo”, the polycyclic aromatic oxide species shown in Figure 4.6.C. The “poo” was partially removed by dipping the fiber into 1 N HCl solution with reasoning similar to the case of oxygen plasma, but require further processing to remove all surface oxides and damaged tubes.

We did not employ a UV ozone technique as a standard procedure to etch away the combed layer, since it is dangerous because of UV laser and ozone and takes longer time compared to inductively coupled oxygen plasma to achieve complete removal.
Figure 4.6. (A) SEM image taken after microtome cutting, (B), (C) SEM image taken after UV ozone etching showing poo, (D) SEM image taken after followed by HCl dipping.

4.3 Hydrogen Cleaning

Atomic oxygen generated either by oxygen plasma or by a UV ozone has the ability of etching SWNTs effectively from the sidewall of a nanotube, but inevitably leaves behind a carbon oxide species nicknamed “poo”. As a first candidate for removing the poo, atomic hydrogen was considered. The C-H diatomic bond has an energy of 4 eV, whereas removal of carbon atom from the hexagonal lattice costs 12 eV. Without the ability of attacking the same carbon atom from the back side with many hydrogen atoms, there is no way this carbon atom can be removed from the side wall. Instead, hydrogen
atoms congregate at the exposed edges and start etching from there, because many hydrogen atoms are allowed to attack. This ability of atomic hydrogen enabled us to clean carbon oxide species and damaged tubes without creating damage to pristine nanotubes.

**Figure 4.7.** (A) SEM image taken after oxygen plasma etching and followed by HCl dipping, (B) SEM image taken after hydrogen cleaning with assistance of Fe/Ni catalyst, (C), (D) SEM images taken after final HCl dipping to remove catalyst (All scale bars are 1 μm in length).

To produce atomic hydrogen, a very thin layer (4.2 Å) of Fe/Ni (50-50 wt%) was deposited as catalyst by using an e-beam evaporator because the probability of dissociation of molecular hydrogen by itself is very low below 1000 °C. Then, 0.32 torr of H₂ was introduced during the cleaning process at 750 °C. As illustrated in Figure 4.7.B,
the surface has been cleaned by the hydrogen cleaning process leaving behind deposited catalyst particles. Finally, very clean bundles were exposed after dipping the fiber in 1N HCl solution to remove the partially deposited metal catalysts (Figure 4.7.D).

![Diagram of spill-over mechanism]

**Figure 4.8.** The scheme of spill-over mechanism.

Especially interesting from our point of view is that the whole surface became clean even though deposited catalyst formed islands on the surface of the surface. The mechanism for this phenomenon is believed to be a spill-over mechanism so that each hydrogen molecules dissociates on the surface of catalyst and spills over onto the nanotube surface to clean residual carbon oxides and damaged tubes. Previous studies have established hydrogen spill-over mechanism from platinum particles on graphite surface[46], and the mechanism was also suggested from the experiment with Pt and Pd particles on carbon nanotubes at room temperature[61].

As illustrated in Figure 4.7.D, finally, an open-ended SWNT substrate has been prepared by microtome cutting, oxygen plasma, HCl dipping, and hydrogen cleaning step. The growth experiment will be discussed in the next section.
4.4 Continued Growth

4.4.1 The Continued Growth Apparatus

The continued growth apparatus is a very unique system that consists of an ultrahigh vacuum (UHV) type e-beam evaporator, a high vacuum (HV) type main reactor, and the optical system including heating and temperature measurement as it is shown in Figure 4.9 and Figure 4.10.

Figure 4.9. Schematic drawing of the continued growth apparatus.
Figure 4.10. A picture of the continued growth apparatus. (A) Main reactor, e-beam evaporator, gas system, and pumping system. (B) Controllers for e-beam evaporator, Ar ion laser, thickness monitor, RGA, and pressure readout.

One of the outstanding features employed in this device is that the cross sectional surface of the fiber is heated by a 488nm Ar ion laser and the temperature is measured by black body radiation from the fiber. The radiation is detected by charge-coupled device (TEA/CCD512K, Princeton instrument) through the optics system that is precisely described in Appendix A, so that we can monitor the shape of the sample and measure the temperature in real time.
Figure 4.11. (A) A picture shows that the end of the SWNT fiber is glowing heated by Ar ion laser (B) The radiation image and temperature profile from the CCD camera.

Figure 4.11.B shows the temperature profile along the fiber axis and perpendicular to the fiber axis. The intensity of CCD camera was converted into the temperature through a calibration performed with a resistively heated tungsten wire that has a 100 \( \mu \text{m} \) diameter. The wire was located at the same position as the fiber, and the temperature of the wire was measured with an optical pyrometer while the intensity was being monitored with the CCD camera. We could measure the temperature reliably and comfortably through this calibration based upon the assumption that the emissivity of the SWNT fiber is the same as tungsten. Also, the temperature for etching or growing experiments is automatically maintained through a feedback program written with Labview by controlling output voltage of the laser and reading temperatures from CCD intensity.

Another merit of this system is that a UHV type home built e-beam evaporator is directly connected to the HV type main reactor through a gate valve. Thus, deposited
metal catalyst is not exposed to air, moisture or other contamination that might be a source of catalyst poisoning in a growth step.

The gas pressure of the main reactor can be measured by an ion gauge and an array of different range capacitance manometers. The pressure of the introduced gas is automatically maintained by an electrically controlled throttle valve (MKS), and the composition of the gas is analyzed by a quadruple Residual Gas Analyzer (RGA, AMETEK).
4.4.2 Continued Growth Procedure and Results

The methods to prepare an open-ended SWNT substrate have been extensively described in previous sections. Since it is important to start with a fiber free of residual catalyst and contaminants, the first step of the standard procedure is cleaning the fiber.

The SWNT fiber, containing no surfactant or polymer, was prepared through spinning 8 wt% of purified HiPco material in 102 % sulfuric acid into an ether or water coagulant bath[24]. The fiber was placed on a quartz boat and annealed in 3 % of hydrogen balanced with argon at three temperature steps of 110 °C, 350 °C, 800 °C for 2 hr. at each temperature at a total pressure of 1 atm in the furnace. Residual contaminants including sulfuric acid, SO₃, and other oxides were evaporated during this step. Residual catalysts (1-3 wt%) were mobilized by heat and hydrogen and brought out to the surface of the fiber, where they were easily removed by dipping the fiber into a 1N HCl solution.

Starting with this annealed fiber, the fiber pieces (about 5 mm) were microtomed perpendicular to the fiber axis as described in section 3.2.1, and washed with deionized water, and mounted to a stainless steel hypodermic needle, with the microtomed end protruding 2-3 mm for subsequent processing. The combed layer produced by the microtome was removed by 20 min. exposure to inductively coupled oxygen plasma but generated “poo” on the surface of the fiber as a result. The “poo” was partially removed using HCl dipping and completely removed by the hydrogen cleaning process, leaving behind very clean bundles of SWNTs with open-ends (Figure 4.12). For hydrogen cleaning, a very thin layer (4.2Å°) of Fe/Ni catalyst was e-beam evaporated onto the surface and subsequently heated to 730 °C with 0.32 torr of hydrogen for 30-40 min. All deposited catalysts for hydrogen cleaning were subsequently removed by 1N HCl dipping.
Having discussed open-ended SWNT substrate preparation, we will proceed to catalyst docking and growth. Before metal deposition, the fiber was briefly outgassed in $5 \times 10^{-6}$ torr H$_2$ at about 300 °C. This temperature is not high enough to close the ends of tubes because the open ends do not anneal closed until 800 °C[62-64]. Subsequently, a very thin layer (2.1Å) of Fe/Ni was evaporated while the temperature was maintained at 300 °C in a reducing environment of $5 \times 10^{-6}$ of H$_2$. Since evaporated platinum nanoparticles on HOPG (Highly Oriented Pyrolytic Graphite) dock to the step edges and form etching channels from the edges in hydrogen at elevated temperatures[65], the deposited
Fe/Ni atoms are expected to dock to defect sites or open ends of the tubes, forming nanometer-sized small particles in the open ends.

After catalyst docking, carbon feedstock such as ethanol or ethylene was introduced with balanced hydrogen. The temperature was rapidly raised to growth temperature 800-850 °C for 0.5-3 minutes to avoid non-nanotube carbon structure formation (amorphous carbon or graphite) that can cause catalyst poisoning. The best result has been achieved with 9.9 torr of ethanol and 0.1 torr of hydrogen at 800 °C for 80 minutes.

Figure 4.13. Continuous ropes (~25 μm) sprout from an edge of the open-ended SWNT substrate after growth with ethanol (9.9 torr) and hydrogen (0.1 torr) at 800C for 80 min. (A) Low magnification image. (B) The growth originated from lower right and grew to the upper left.

As illustrated in Figure 4.13, the morphology of the surface changed significantly after growth which was not observed for samples heated in just H₂. Loose SWNT ropes
sprouted from an edge of the SWNT substrate. In every case, the nanotube ropes were found rooted to the pre-existing nanotubes and tended to maintain the orientation of their seeds, although different ropes often grew along different directions. We suspect that these ropes initially grew along the fiber axis, but fell over onto the surface in the middle of the growth. This might cause the termination of the growth by blocking the pathway of growing nanotubes with particles and other tubes. To avoid the tubes falling-over, we need a higher density of open-ended tubes so that growing tubes can support each other and grow without stopping. In this case, we might have decreased the density of open-ended tubes during the aggressive oxygen plasma etching because the surface is shaped like a pine forest after treating with oxygen plasma, and nanotubes seem to grow only from top ends of each pine tree (Figure 4.13.).

To prove that the new ropes are continued growth of the existing SWNTs, we characterized the new ropes in comparison with pre-existing tubes using a Raman microscope (Renishaw Micro-Raman System 1000). Since Raman spectrum from the nanotubes is resonantly enhanced by matching inter-band transition energy and laser energy, multiple excitation sources of laser are desired to cover a broad range of tubes[37]. Three different excitation lasers (514.5, 633, and 780nm) were used and found to cover 150 different chiralities of tubes according to the Kataura plot[25, 66].

Because of the antenna effect of nanotubes, the Raman spectra from SWNTs are strongly suppressed when the polarization of laser is aligned perpendicular to the nanotube axis[67]. Taking advantage of this polarization dependence, we took the data by matching the polarization of the exciting laser to the direction of bundles grown from the substrate. The G peak signal ratio between parallel and perpendicular polarization of the
exciting laser relative to the direction of the aligned grown bundles was found to be 3:1 with 633 nm excitation laser (Figure 4.14). This indicates that the Raman signal we took with matching polarization is dominantly from well aligned grown bundles compared to the pre-existing tubes.

![Figure 4.14](image.png)

**Figure 4.14.** Polarized Raman spectra, an open-ended SWNT substrate (A) and a continued growth sample (B). The inset shows an open-ended SWNT substrate with the laser polarization parallel to the surface. Because of the isotropic nature, the Raman ratio (parallel vs. perpendicular) is 1.0±0.2 for an open-ended SWNT substrate. The deviation is arising from the imperfect alignment of SWNTs, and the small tilting angle between the sample and the laser polarization. For the continued growth samples with ropes falling over onto the surface, the Raman ratio was as high as 3. The Raman excitation line was 633 nm.
Figure 4.15. RBM data of continued growth. The blue line is from the substrate, the red line is from the new growth, the dotted line is from the control (The tubes were grown from Maruyama et al.'s recipe.)

From the RBM peak, we can estimate diameter through the equation \( d = \frac{223.5}{(\text{RBM}-12.5)} \) [30] and thus identify some of the \((n,m)\) candidates with same diameter. Then, we can finally decide chirality of tubes considering the candidate's interband transition energy because the Raman spectrum we took is resonantly enhanced.

As illustrated in Figure 4.15, the RBM data taken before and after growth were closely matched and new peaks did not show up in RBM spectra. The control data in Figure 4.15 was taken from the SWNT tubes on a quartz plate grown at 800 °C with 10 torr of ethanol[23] showing that newly nucleated tubes can be detected by three different lasers if they are in resonance window of three different lasers. From a comparison of the RBMs obtained from the control sample and those obtained from the before and after
spectra of our fiber, it appears highly suggestive that the new growth is indeed from the continued growth of pre-existing SWNTs and not new nucleation of tubes as observed in the control sample. Further work is required to prove the cloning or one-dimensional epitaxy mechanism in terms of single individual tubes.

Another example of continued growth form microtome cut fiber is shown in Figure 4.16. We can identify that the bundles at the edge were continuously grown and fall onto the surface.

Figure 4.16. Side views of another example. (A) A SWNT substrate that was etched with oxygen plasma and cleaned with hydrochloric acid. (B) The same position after (1) deposition of 4.2 Å Fe/Ni 50/50 wt% and heating in 0.32 torr H₂ at 350 °C for 30 minutes; (2) cleaning with hydrochloric acid; (3) deposition of 2.1 Å Fe-Ni; and (4) heating in a mixture of C₂H₅OH (8.4 torr) + H₂ (1.6 torr) at 735 °C for 80 minutes.
5. Continued growth from Focused Ion Beam Cut Fiber

5.1 Cleaning Process of FIB Cut Surface

As described in section 3.2.2, the focused ion beam cutting technique has the capability of preparing nanoscopically flat surfaces, but also inevitably generates a layer of amorphous carbon with embedded Ga ions.

<table>
<thead>
<tr>
<th>A</th>
<th>Wt %</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>79.32</td>
<td>85.05</td>
</tr>
<tr>
<td>O K</td>
<td>17.91</td>
<td>14.42</td>
</tr>
<tr>
<td>S K</td>
<td>0.81</td>
<td>0.33</td>
</tr>
<tr>
<td>CIK</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>FeK</td>
<td>0.17</td>
<td>0.04</td>
</tr>
<tr>
<td>NiK</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>GaK</td>
<td>0.27</td>
<td>0.05</td>
</tr>
<tr>
<td>P tL</td>
<td>1.44</td>
<td>0.1</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B</th>
<th>Wt %</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>79.24</td>
<td>84.26</td>
</tr>
<tr>
<td>O K</td>
<td>18.73</td>
<td>14.95</td>
</tr>
<tr>
<td>A lK</td>
<td>0.64</td>
<td>0.3</td>
</tr>
<tr>
<td>S nK</td>
<td>0.14</td>
<td>0.06</td>
</tr>
<tr>
<td>S K</td>
<td>0.86</td>
<td>0.34</td>
</tr>
<tr>
<td>CIK</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr K</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>F eK</td>
<td>0.17</td>
<td>0.04</td>
</tr>
<tr>
<td>N iK</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Ga K</td>
<td>0.03</td>
<td>0.0</td>
</tr>
<tr>
<td>P tL</td>
<td>0.08</td>
<td>0.01</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

**Figure 5.1.** EDX data of FIB cut surface (A), (B) Before and after dipping the fiber into the mixed solution of 1 N HCl and methanol at 60 °C overnight.

After FIB cutting, the 7-10mm long fiber pieces were dipped into the mixed solution that is made of 50% of methanol and 50% of 1N HCl at 60 °C overnight (about 8 hours). Methanol was added for better wetting ability that enables the HCl to penetrate into the surface of the fiber by capillary action. Since the melting temperature of Ga is so low
(Tm=29.77 °C) [68], at 60 °C, Ga should be a liquid state that will easily react with HCl. To avoid evaporation of the solution from the beaker, a watch glass was laid on top of the beaker, so that vapor was condensed back into the solution. Through this step, most of the embedded Ga has been removed as EDX data illustrates in Figure 5.1.

To minimize the effect from uncontrollable residual catalysts in the fiber, H₂ baking at elevated temperature followed by dipping the fiber into 1N HCl solution has been tried. In each cycle, temperature was ramped with three steps (110 °C, 350 °C, 800 °C) while resting at each step for one hour in 10 % H₂ balanced with Ar at 1 atm total pressure. After the first H₂ baking, the catalyst particles were exposed at the surface of the fiber, mobilized by heat and hydrogen in a manner similar to Ostwald ripening and then were subsequently removed by HCl. This cycle was repeated until no catalyst was observed at the surface after hydrogen baking. Usually, two or three cycles were enough, but this process could not remove the amorphous carbon layer.

![Image](image.jpg)

**Figure 5.2.** Residual catalysts cleaning scheme. (A) SEM image taken after hydrogen baking at the side of the fiber, (B) SEM image taken after followed by HCl dipping.
Two techniques have been successfully developed for removing amorphous carbon layer. The first one is hydrogen cleaning with assistance of catalysts in a HV reactor with a laser heating system similar to what has been described in section 4.3. We evaporated a very thin layer (2.8 Å) of Fe/Ni catalyst onto the cross sectional surface of the fiber at about 300 °C in a reducing environment of 1x10^-5 torr of hydrogen. Subsequently, hydrogen was introduced and maintained at 1 torr pressure at 750 °C for 40 minutes. After hydrogen cleaning, the fiber was dipped into 1 N HCl solution to remove catalyst. Finally, a nanoscopically flat and very clean SWNT substrate was revealed as shown in Figure 5.3.A.

![Figure 5.3. SEM images after cleaning process. (A) The surface has been cleaned by H₂ at 750 °C with assistance of catalysts. (B) The surface has been cleaned by 10 % of CO₂ at 950 °C.](image)

Carbon dioxide has been found to be ideal for removing amorphous carbon without any catalyst. As discussed in section 3.2.2, it is known that CO₂ itself can not etch graphite below 900 °C in the absence of catalyst[49] because this reaction is endothermic. As illustrated in Figure 5.3.B, it has been found that the amorphous layer on the surface was completely removed by 10 % of CO₂ balanced with argon at 950 °C for 20 minutes in
a quartz tube furnace without causing any damage to the nanotubes at the surface. We then tried an additional 20 minutes, but the surface remained the same and also flat. Thus, we suspected that the ends of tubes might be closed because the edge of the graphite can begin to be etched around 900°C[49].

5.2 End Opening and Characterizing Open Ends

For preparing an open-ended SWNT substrate, a characterizing method for open ends is really crucial because it is not possible to grow tubes continuously from closed-ended tubes. Previous studies for characterizing open-ended tubes were limited to gas adsorption technique[69, 70] that is not feasible for less than a 100 μm diameter surface. TEM might be another means, but it does not have the capability of giving information of the overall surface. Taking advantage of the observation that 10 % of CO₂ could not etch back the tubes at the surface at 950°C, we proceeded to try the same condition to HOPG surface and open ended SWNT bundles that were cut by an oxidative method.

As illustrated in Figure 5.4.A and B, the step edges on HOPG surface turned out to be etched back with a 2-3 nm/min etching rate by 10% of CO₂ at 950°C for 15min. Also, open-ended SWNT bundles (cut tubes) were etched back by a series of 120 pulses of CO₂ at 950°C as shown in Figure 5.4.C and D. The pulsed etching scheme was adopted to not remove all the short bundles. Each pulse of CO₂ contains 55 ml of CO₂ for 300 msec, separated by 1min.
Figure 5.4. AFM images of CO$_2$ etching for open end characterization. (A), (B) Before and after images of CO$_2$ etching on HOPG surface, (C), (D) Before and after images of CO$_2$ etching on open-ended SWNT bundles. (Courtesy of Valerie Moore et al.)
This experiment leads us to believe that CO$_2$ gas can etch back only open-ended tubes at 950 °C, this became a powerful tool for testing an end-opening scheme.

To open the ends of SWNTs, various methods have been tried including wet chemical methods such as hot and cold piranha(4:1, vol/vol 96 % H$_2$SO$_4$/30 % H$_2$O$_2$) [71], KMnO$_4$ [72], NaBr+O$_3$, and electrochemistry[73], but most of the wet chemical methods turned out to have a problem of producing a surface oxide layer. Two clean means of opening the ends of tubes were found to be a very short exposure of inductively coupled oxygen plasma and Ar ion sputtering respectively. The prepared flat and clean SWNT substrate was exposed to inductively coupled oxygen plasma for 10 to 20 sec. Figure 5.5. A and B showed that there was almost no change after 20 sec exposure to inductively coupled oxygen plasma, and no surface oxide was found to be formed on the surface. After treating with 10% of CO$_2$ at 950°C in a quartz tube furnace, the morphology has been significantly changed, and the surface roughness had increased from about 10 nm to about 200 nm as illustrated in Figure 5.5.C and D. This leads us to believe that short exposure to inductively coupled plasma is an effective means to open the ends of the tubes in our substrate.
Figure 5.5. End opening scheme with short exposure to oxygen plasma. (A), (B) SEM images taken before and after treatment with inductively coupled oxygen plasma, (C) SEM image taken after cleaning amorphous carbon. (D) SEM images taken after oxygen plasma treatment followed by 10% of CO₂ etching at 950 °C for 20 min.

As an alternative method, Ar ion sputtering had been tried because it can generate vacancies by knock-on or cascade processes without any contamination. First, we calculated the right amount of current density and voltage based upon the hypothesis that sputtering 30 carbon atoms (carbon atoms in the cap) per nanotube less than 10 nm from the surface open the ends. The voltage range of 500-1000 V was found to be the right voltage to keep the penetration depth less than 10 nm according to SRIM simulations with graphite. The number density of nanotubes on top of the surface is approximately $4 \times 10^{13}$ nanotubes/cm$^2$ calculated from the density of the fiber (1.1 g/cm$^3$), and thus we
need an Ar ion density of $1.2 \times 10^{16}$/cm$^2$ ($=1.65$ mC/cm$^2$), considering the sputtering yield as 0.1 according to SRIM simulation with graphite. The 3CM DC (CSC, Veeco) ion source was employed, and the experiment was performed at current density 0.25mA/cm$^2$ and 500V acceleration voltage at a normal angle to the surface for 1 minute (total charge: 15mC/cm$^2$). This condition seems a little bit aggressive creating about 300 sputtered atoms per nanotube but in actuality might be the right condition taking the channeling effect into account.

Figure 5.6. End opening scheme with sputtering. (A), (B) SEM images taken before and after sputtering, (C) SEM image taken after cleaning amorphous carbon, (D) SEM image taken after sputtering and followed by 10 % CO$_2$ etching at 950°C in a quartz tube furnace.
As illustrated in Figure 5.6, Ar ion sputtering by itself did not cause any damage or morphology change, but sputtering followed by 10% CO₂ etching at 950°C for 20 minutes in a quartz tube furnace increased surface roughness. This indicates that Ar ion sputtering is also a means of opening the ends of the tubes.

5.3 Catalyst Docking and Growth

The same deposition scheme described in section 4.4.2 has been adopted here. A very thin layer (2.1 Å) of Fe/Ni catalyst was deposited from the e-beam evaporator in a reducing environment of 1×10⁻⁵ torr of hydrogen at about 350°C. Since the surface is nanoscopically flat (Figure 5.3) and highly dense, most of deposited catalyst atoms are expected to dock to the open ends of the tubes directly, otherwise they will slightly diffuse around and find the ends of the tubes because the ends are more reactive compared to the sidewall of the tube. Through this process, very uniform diameter sized particles are expected to be nucleated in the open ends compare to previous method (Chapter 4).

The best result has been achieved from the sample that was cleaned by hydrogen with assistance of catalyst (Figure 5.3.A). The ends of tubes were etched open by a 20 sec exposure of inductively coupled oxygen plasma that has been proven as an effective means of opening the ends (Section 5.2.). The catalysts were deposited as described in the previous paragraph.

As soon as the catalyst was deposited, ethanol was introduced without hydrogen, and maintained at 10 torr by an automated throttle valve and feedback control. The temperature was increased to 800°C within 2 minutes to avoid non-nanotube carbon
deposition such as amorphous carbon that might cause catalyst poisoning. The growth
time was 30 minutes and the 2-3 μm extension of the fiber was observed in the real time
image from CCD camera.

![SEM images](image)

**Figure 5.7.** (A) SEM image taken from nanoscopically flat SWNT substrate by FIB
cutting, (B) SEM image taken after the growth experiment. (C),(D) High magnification
images taken from the edge of the fiber after growth experiment.

As illustrated in Figure 5.7, a significant change has been observed after the growth
experiment. Bundles of tubes have grown up seamlessly from the SWNT substrate. The
SEM images (Figure 5.7 C, D.) taken from the edge of the fiber shows that the grown
tubes are aligned vertically. This indicates that the tubes were grown with high density,
and that was not observed from the sample prepared by microtome cutting and oxidative etching scheme. This high density growth results from the nanoscopically flat SWNT substrate, and cleaning and end opening scheme without causing damage to the nanotubes while previous methods lost many open ends of the tubes during long exposure to oxygen plasma.

The Raman data in Figure 5.8 supports the belief that the grown tubes are not tubes of new chirality but tubes of the same chirality as the SWNT substrate, showing that the RBM peaks taken before and after growth experiment peaks all match.

![Raman data](image)

**Figure 5.8.** Raman data taken before and after growth experiment with three different lasers. Black line is from before growth, red line is from after growth, and green line is from controlled experiment (The tubes were grown with Maruyama et al.'s recipe.)
Raman data was collected with a Raman microscope (Renishaw Micro-Raman System 1000) using three different laser excitation lines (514 nm, 633 nm, 780 nm) to excite many chiralities of nanotubes because Raman data we collect is caused by resonant Raman scattering that occurs when the energy of the laser matches the interband transition energy of the nanotube. The green line in Figure 5.8 was taken from the tubes grown on quartz plate with Maruyama’s recipe[23] (10 torr of Ethanol, at 800°C), showing that newly nucleated tubes can be detected by three different lasers. To collect Raman signal from the top surface, the 2 μm diameter spot (50x objective) of the laser was focused onto the top surface, and the sample was tilted at a 45 degree angle from the direction of the laser so that we could avoid polarization mismatch[67]. The penetration depth of the three lasers calculated from UV-VIS absorption data of dispersed nanotubes is less than 100 nm considering the density of the fiber (1.11g/cm³). Thus, this leads us to believe that the Raman signal we collected after growth is not from the SWNT substrate but from the continuously grown bundles because the grown bundles were about 2-3 μm long. We collected spectra from several spots from the top surface at a 45 degree angle, and they agree with each other in terms of the frequency of RBM.
6. Continued Growth from Flipped-Over Vertically Aligned SWNT Film

6.1 Vertically Aligned SWNT Film Growth

A previous study reported that water plays a crucial role in the growth of a mm long SWNTs by activating catalyst during growth cycle[35]. According to Hata et al., water has the capability of removing amorphous carbon that poisons catalysts without causing damage to nanotubes. Continued growth is based upon the tip growth mechanism such that the growth is not terminated by a diffusion process of carbon feedstocks, but tip growth itself does not guarantee the prevention of catalyst poisoning. This motivated us to repeat Hata et al’s vertically aligned single-walled nanotube (V-SWNT) film growth with the assistance of water.

10 nm of Al₂O₃ was e-beam evaporated onto a silicon oxide surface, and additionally 1 nm of Fe was evaporated as a catalyst. The growth condition was ethylene: H₂: Ar = 100 sccm: 400 sccm: 600 sccm at 750°C at 1 atm total pressure for 10 min. The first few experiments, we tried with and without water, but no vertically aligned film grew. Later, we found that the pretreatment of deposited catalysts is imperative. Oxidation at 500°C in air for 10 min. followed by reduction at 750°C in 40 % of H₂ balanced with Ar for 5min., or alternatively oxygen plasma treatment for 1-2 min without reduction are found to be conditions that grow V-SWNT films.
Figure 6.1. AFM image and diameter analysis of the surface where 10 nm Al₂O₃ and 1 nm Fe were deposited onto Si wafer by e-beam evaporation. (Courtesy of Valerie Moore)

As shown in Figure 6.1, evaporated iron atoms form islands on the surface of Al₂O₃ with an averaged size of about 1 nm by diameter from AFM measurement. Since deposited catalyst particles went through heat treatment or plasma treatment causing a ripening effect, the diameters of grown SWNTs were larger than 1 nm. They varied from 1 nm to 7 nm as illustrated in Figure 6.2. The average height of a film was about 30 μm in the absence of water, and the maximum height achieved was 80 μm with 10 ppm of water, as measured by a water sensor (Super-dew, SHAW) that measures dew point of water vapor at the exhaust. To grow V-SWNT film, water was not critical but helpful when the right amount of water was involved.
Figure 6.2. (A) SEM image taken from the grown V-SWNT film, (B) TEM image taken from the V-SWNT film.

Figure 6.3. One example of Raman data from V-SWNT film. 780 nm laser was used to collect data.
Raman data were collected with a Raman microscope (Renishaw Micro-Raman System 1000) using three different lasers (514 nm, 633 nm, 780 nm), the polarization was matched exactly to the direction of the bundles to enhance signal[67]. As shown in Figure 6.3, sharp RBM were observed and G to D ratio was 6:1 indicating that the tubes have some defects or amorphous carbon. The diameter distribution as determined from Raman data ranges from 0.8 to 1.5 nm, but Raman data with the available excitation lasers can not detect large diameter tubes over 1.5 nm because the Raman spectra are resonanty enhanced. Also, Rayleigh line and notch filter make it difficult to detect nanotubes below 100-150 cm⁻¹ corresponding to 1.6-2.4 nm. Hence, this diameter measurement from Raman data is not conclusive.

![SEM images of V-SWNT film.](image)

**Figure 6.4.** SEM images of V-SWNT film. (A) Produced with acetone (B) Grown form 1.8 nm diameter sized Fe₃O₄ particles.

As illustrated in Figure 6.4, we have demonstrated V-SWNT film growth with acetone feedstock introduced with 150 sccm Ar and 100 sccm H₂ through a bubbler at 750°C, and achieved V-SWNT growth from 1.8 nm sized Fe₃O₄ particles[74] that were spin coated onto the deposited alumina surface.
6.2 The Flip-Over Technique and Continued Growth

When we tried continued growth from V-SWNT film, the first problem was that the top surface of V-SWNT film is covered by entangled bundles that are not appropriate for preparing open-ended SWNT substrates (Figure 6.4.A and B). Taking advantage of the fact that bundles at the bottom are aligned normal to the perfectly flat Si wafer substrate, we have tried flipping over the whole film to expose perfectly aligned flat ends.

Figure 6.4. (A), (B) SEM images show entangled bundles at the top of the SWNT film. (C) Scheme for flip-over technique using gold particle embedded cement.
As shown in Figure 6.4, ceramic cement (Omega CC High Temperature cement) was employed and mixed with gold powder (0.8-1.5 micron size, Alfa Aesar) with about 5:1 ratio on Si wafer. A few drops of liquid binder were added to the mixed powder and the mixtures are uniformly spread on the wafer. V-SWNT film were attached to cement mixtures and cured for 24 hours at room temperature or 4 hours at 65°C.

![Figure 6.5. SEM images from flipped-over V-SWNT film. (A) Low magnification image (B) High magnification image shows very clean and well aligned bundles.](image)

As illustrated in figure 6.5, the V-SWNT film has been flipped over, exposing the very flat surface and very well aligned clean bundles. The whole length of the film flipped over due to high tensile strength of nanotubes. Since gold particles were embedded in cement, charging effects which used to occur using the cement alone were not observed when we took SEM. This indicates that nanotube bundles made good contact to the surface.

An enhanced means of the flip-over technique has also been developed to transfer a film to a conductive surface. A 500 nm thick gold layer was deposited by sputtering or e-beam evaporator onto both Si wafer and V-SWNT film. The gold-coated V-SWNT film
was slightly pressed against the gold-coated Si wafer and baked in Ar at 800°C for 10 minutes to make two gold coated surfaces fused to each other for tight binding. After baking, the Si wafer with flipped-over film was detached from the Si surface where the V-SWNT film was originally grown. Through this means, we were able to flip over the whole surface of the grown film with contact to a conductive surface (Figure 6.6).

Figure 6.6. Scheme of flip-over technique using evaporated gold and a picture of result.

Continued growth has been demonstrated from flipped-over V-SWNT films. To open the ends of the tubes, the sample was treated by inductively coupled oxygen plasma for 20 sec. 0.7 Å thick Fe/Ni catalysts were deposited by e-beam evaporator as described earlier. Then, the sample was moved to a quartz tube furnace, and briefly reduced in 40% of H₂ balanced with Ar at 750°C for 10 sec. Subsequently, ethylene was added into a quartz tube furnace for growth for 10 min.
Figure 6.7. SEM images after growth experiment. (A) Bundles in the surface before growth, (B), (C), (D) Many groups of grown tubes have been observed.

As illustrated in Figure 6.7, many groups of grown tubes have been observed after the growth experiment. The tubes were found to be continuously extended from the open-ended substrate prepared with flipped-over V-SWNT film. The height of each group varied from 1 to 10 μm. A very interesting feature of this experiment is that we observed big catalyst particles on every grown group of the tubes as shown in Figure 6.7.B and C. This might be a strong evidence of the tip growth mechanism we expected in continued growth. Unfortunately, we could not collect Raman spectrum from the tubes we have grown because it was so hard to focus on the grown tubes selectively. We need further
investigation to confirm structure cloning and exploration to increase the efficiency of continued growth from flipped-over SWNT film.
7. Conclusion

This thesis described from the process of continued growth of SWNTs from through results. The hypothesis of continued growth starts with preparing an open-ended SWNT substrate and then docking nano-sized catalyst to the open ends. When carbon feedstock is introduced, activated catalyst decomposes the carbon feedstock. The carbon atoms diffuse around the catalyst and are added to the pre-existing SWNT substrate in a manner similar to one-dimensional molecular epitaxy. This growth follows a tip growth mechanism such that the growth will not be terminated by diffusion limit of carbon feedstock as base growth would due to the process of gas feedstock. If an armchair single crystal open-ended substrate is prepared, this approach provides a means to produce an armchair quantum wire.

Our goal is the demonstration of continued growth of SWNTs from an open-ended substrate with random chirality. Later efforts strove to increase the yield of armchair tubes using a laser ablation method at NASA.

To produce an open-ended SWNT substrate, we cut SWNT fiber perpendicular to the fiber axis. The microtome technique and the focused ion beam cutting technique were found to be an effective means of cutting the fiber. We developed an etching and cleaning scheme to prepare a SWNT substrate, and the ends of tubes were etched open by short exposure to an inductively coupled oxygen plasma. Also, we found that 10 % CO₂ balanced with Ar at 950°C has the ability to characterize the presence of open ends because it selectively etches open-ended tubes.
This thesis demonstrated continued growth of SWNTs from the microtome-cut fiber and the FIB cut fiber. The tubes grown from the FIB-cut fiber were found to be grown with higher density because the growth started from a nanoscopically flat, open-ended substrate. The radial breathing modes (RBM) in Raman spectra collected before and after the growth experiment matched, and new peaks did not show up. Since the RBM represents the chirality of nanotubes in resonant Raman scattering of SWNT, it appears highly suggestive that the new growth is indeed from the continued growth of pre-existing SWNTs and not new nucleation of tubes.

As an alternative approach, a vertically aligned SWNT film (V-SWNT film) was employed. A flip-over technique allowed us to prepare an open-ended SWNT substrate exposing the flat and clean bottom of the film. Many groups of tubes were observed to be grown from the flat substrate after a growth experiment. The interesting feature we found is that catalyst aggregated on the top the grown bundles forming large particles. This suggests that our growth followed a tip growth mechanism.

From our continued growth hypothesis, we expected that growth would not terminate because continued growth follows a tip growth mechanism. Our hypothesis might have been correct if we had started with chirality-selected and atomically flat SWNT substrate mono-dispersed catalyst in size docked to the ends of the tubes. In reality, we cannot control the chirality of tubes in the SWNT substrate or the catalyst size. This might cause a different growth rate for each tube such that the catalyst on different tubes meet each other at some point in the growth process, forming a large particle, which will become carbon-coated rather than allow SWNT growth. We might be able to achieve growing very long nanotubes if the size of the catalyst is kept small enough such that the catalyst
can not meet each other during the growth. However, the control of the catalyst size still remains a big challenge.

Continued growth of SWNTs has been demonstrated from our research for the first time. However, further study of the cloning process for production of one type of nanotube is needed as well as the control of catalyst size is needed to meet the “Armchair Quantum Wire” goal.

Our hope is that this basic research will provides a beginning to further efforts in developing the new technologies needed to provide for the world energy needs.
Appendix A. Laser Heating and Temperature Measurement System

Laser heating was employed to heat the end of the fiber in high vacuum chamber to provide a clean environment and allow for rapid heating. We used a CW Ar+ laser (488 nm, Innova 70-3) for the continued growth experiment.

![Diagram of laser heating system]

**Figure A-1.** Schematic drawing of laser heating system.

1. Mirrors: Ø1 inch BK-7 glass with AR coating of 488-515 nm specifically for Ar+ laser (CVI, Part# AR1-1025-45-s)
2. Galilean beam expander: 6×, on a stable rod cylindrical laser holders (Melles Griot)
3. Polarizer: zero order half wave plate with AR coating for 488 nm (CVI, Part# QWPO-488-10-2-R15) on a rotary mount
4. Focus lens: BK7 spherical plan-convex with a focus length of 150mm (CVI, Part# PLCX-25.4-77.3-C-425-675)
5. View ports: 1-1/3” fused silica view ports (MDC)

As shown in Figure A-1, the laser beam is expanded with 6x beam expander, and focused with a plano-convex lens mounted on a XYZ translator. The beam is directed...
into the chamber by a mirror and 1-1/3” fused silica view port. A half wave plate is employed to align the polarization of laser to the fiber axis to maximize absorption.

The beam of Ar+ laser has nearly a Gaussian TEM$_{00}$ profile with a beam waist of 1.5mm. The focal spot size at the fiber is 10.4 μm in diameter and the depth of focus is ±202 μm as calculated from the Gaussian beam optics approximation. Hence, the diameter of the beam where it impinges on the fiber can be adjusted to heat the whole cross-sectional surface of the fiber with 30-100 μm in diameter by translation of the lens in the z-direction.

**Pyrometer**

![Pyrometer Diagram]

Figure A-2, Schematic drawing for original temperature measurement system.

To measure the temperature of the fiber heated by the laser, an IR optics system was originally developed. We have employed IR optics parts which includes a Schwarzchild reflective objective (Ealing, Part# 25-0506), CaF$_2$ lens (f.l.=250mm), and gold or aluminum coated mirrors. Special feature in here is that the glowing image is monitored
by CCD camera in real time, and a missing spot in reflective aperture is guided by optics and analyzed by a spectrometer to give us temperature information. A PbS detector (Electro Optical System, PBS-050-TE2-H) employed in this setup has an operating wavelength 1.0-2.8 μm, and is electrically cooled down to -20C. In front of a spectrometer, a chopper is operated at 400Hz to reduce 1/f noise. The output voltage signal is transferred to a lock-in amplifier (Princeton Applied Research) that convert AC signal to DC signal, and finally analyzed by a computer with Labview software.

Figure A-3. (A) Data from black body source (Calibration factor is calculated with the theoretical black body radiation divided by radiation from black body source), (B) Data from the glowing fiber, (C) Measuring temperature by curve fitting, (D) Different correction factors in different days.
We determine the correction factor using a home made back body radiation source made with a cavity and aperture. The emissivity of the source is 0.99 and the temperature of the source was measured by a thermocouple. Since we know the temperature of the source, we can evaluate a correction factor through theoretical black body radiation divided by the radiation from black body source. A correction factor is caused by variation of the sensitivity of the detector with respect to wavelength and moisture that absorbs light in the range of 1-2.5 μm in air. As shown in Figure A-3.B and C, the radiation signal from the fiber through the 4 mm in diameter aperture (at the position of reflective aperture) was calibrated by correction factor, and the temperature was measured by black body radiation curve fitting. When the aperture is only 0.1 mm in diameter, the signal corresponding to a couple of microns on the fiber was too small to detect, and the correction factors varied day to day (Figure A-3, D). These problems lead us to measure the temperature of the fiber by the intensity on calibrated CCD using a heated tungsten wire (section 4.4.1).

This simplified setup is shown in Figure A-4.
Figure A-4. Schematic diagram of current setup.

W: CaF₂ window 1 inch × 1 mm (Infrared Optical Products); 1 mm minimum thickness to minimize the chromatic aberration, but provides sufficient mechanical strength.

F1: 15× all-reflecting Schwarzschild objective (Ealing, Part# 25-0506) with a numerical aperture of 0.28 and a working distance of 24.5 mm. Al coatings.

F2: CaF₂ lens (Thorlabs)

F3: Ø2 inch concave precision spherical mirror with Gold coating (Edmund)

M: Ø2 inch pyrex 7740 glass mirror (Edmund) with coatings
   M1: Au coating
   M2: Al coating

F4 and F5: Ø2 inch Paired convex lens with NIR Broad band AR coatings (T>99%, Thorlabs)

Long pass color glass filter (CVI, Part# CG-RG-610-1.00-3)

CCD camera: thermal electrically cooled TEA/CCD512 camera (Princeton Instruments).
Bibliography


