ABSTRACT

Title of Document: SEMICONDUCTING CARBON NANOTUBE TRANSISTORS: ELECTRON AND SPIN TRANSPORT PROPERTIES

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Single-walled carbon nanotubes (SWNTs) have attracted great interest both scientifically and technologically due to their long mean free paths and high carrier velocities at room temperature, and possibly very long spin-scattering lengths. This thesis will describe experiments to probe the charge-and spin-transport properties of long, clean individual SWNTs prepared by chemical vapor deposition and contacted by metal electrodes.

A SWNT field-effect transistor (SWNT-FET) has been shown to be sensitive to single electrons in charge traps. A single charge trap near a SWNT-FET is explored here using both electronic and scanned-probe techniques, and a simple model is developed to determine the capacitances of the trap to the SWNT and gate electrode.

SWNTs are contacted with ferromagnetic electrodes in order to explore the transport of spin-polarized current through the SWNT. In some cases spin-dependent
transport was observed, verifying long spin scattering lengths in SWNT. However, in many cases no spin-dependent effects were observed; these results will be discussed in the context of the present state of results in the literature.

Semiconducting SWNTs (s-SWNTs) with Schottky-barrier contacts are measured at high bias. Nearly symmetric ambipolar transport is observed, with electron and hole currents significantly exceeding 25 µA, the reported current limit in m-SWNTs. Four simple models for the field-dependent velocity (ballistic, current saturation, velocity saturation, and constant mobility) are studied in the unipolar regime; the high-bias behavior is best explained by a velocity saturation model with a saturation velocity of $2 \times 10^7$ cm/s. A simple Boltzmann equation model for charge transport in s-SWNTs is developed with two adjustable parameters, the elastic and inelastic scattering lengths. The model predicts velocity saturation rather than current saturation in s-SWNTs, in agreement with experiment.

Contact effects in s-SWNT-FET are explored by electrically heating the devices. These experiments resolve the origin of nanotube p-type behavior in air by showing that the observed p-type behavior upon air exposure cannot be explained by change in contact work function, but is instead due to doping of the nanotube. Modest doping of the SWNT narrows the Schottky Barriers and provides a high-conductance Ohmic tunnel contact from electrode to SWNT.
SEMICONDUCTING CARBON NANOTUBE TRANSISTORS:
ELECTRON AND SPIN TRANSPORT PROPERTIES

By

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# Table of Contents

Acknowledgements ........................................................................................................................................... ii

Table of Contents ............................................................................................................................................. v

List of Tables .................................................................................................................................................... viii

List of Figures ................................................................................................................................................... ix

Chapter 1 Introduction to Carbon Nanotubes .................................................................................. 1

1.1 Nanotube Overview .............................................................................................................................. 1

1.2 Electronic Band Structure .................................................................................................................... 3

1.3 Electronic Properties ............................................................................................................................. 9

Chapter 2 Nanotube Synthesis and Device Fabrication ............................................................. 12

2.1 Nanotube Chemical Vapor Deposition Synthesis .......................................................... 12

2.2 Electron-Beam Lithography and Electrical Contact Preparation .......................... 16

2.3 Annealing ........................................................................................................................................ 22

2.4 Electrical Measurement Setup ........................................................................................................ 23

Chapter 3 Scanning Probe Microscopy to Characterize Nanotube Devices ......................... 26

3.1 Introduction to Scanning Probe Microscopy .............................................................................. 26

3.2 Electrostatic Force Microscopy ................................................................................................. 30

3.3 Scanned Gate Microscopy ............................................................................................................. 37

3.4 Magnetic Force Microscopy ........................................................................................................... 42

Chapter 4 Single Electron Memory .......................................................................................... 43

4.1 Single Defect Detection Using Scanned Gate Microscopy ........................................... 43

4.2 Capacitance Analysis of a Single Electron Memory ..................................................... 46
Chapter 5 Magnetoresistance in Spin Valves with Nanotube Channels .......... 50
  5.1 Introduction to Magnetoresistance due to Spin-Valve Effect ............... 50
  5.2 Device Fabrication ........................................................................... 54
  5.3 Measurement Technique ................................................................. 58
  5.4 Result and Discussion ..................................................................... 60
Chapter 6 High-Bias Transport in Semiconducting SWNTs ..................... 71
  6.1 Introduction to High-Bias Transport in Nanotubes ......................... 71
  6.2 Unipolar Transport .......................................................................... 76
  6.3 Ambipolar Transport ....................................................................... 78
Chapter 7 High-Bias Transport of Semiconducting SWNTs in the Unipolar Regime 81
  7.1 Phenomenological Carrier Velocities under Electric Field .............. 81
  7.2 Experiment Results ......................................................................... 84
  7.3 Device Modeling .............................................................................. 85
  7.4 Carrier-Density and Potential Profiles in Velocity-Saturation Model ... 96
Chapter 8 Electron-Phonon Interactions in Semiconducting SWNTs .......... 100
  8.1 Overviews of Electron-Phonon Interactions in SWNTs ................. 100
  8.2 Numerical Study of Carrier Velocities in s-SWNTs Concerning Electron-
      Phonon Scatterings in a Single Subband ......................................... 101
Chapter 9 High-Bias Transport of Semiconducting SWNTs in the Ambipolar Regime
........................................................................................................... 115
  9.1 Introduction and Experimental Results ........................................ 115
  9.2 Device Modeling ............................................................................ 122
  9.3 Using EFM to Detect Electron-Hole Recombination in s-SWNTs ....... 130
9.4 Indirect Proof of Electron-Hole Recombination in s-SWNTs by SGM

Chapter 10 Contacts to Semiconducting SWNTs

10.1 Overview

10.2 Electrical Heating

10.3 Intrinsic s-SWNTs Behaviors with SBs

10.4 Cause of p-Type Behavior of s-SWNTs in Air

Chapter 11 Future Directions

Appendix A Deriving Electrostatic Potential from EFM Signal

A.1 Processes of Deriving Electrostatic Potential from EFM Signal

A.2 Linearity

Appendix B Matlab Codes

B.1 General Notes

B.2 Code for Device Modeling

B.3 Code for Calculating Average Carrier Velocity

Bibliography
List of Tables

Table 2-1. A recipe of nanotube growth. ................................................................. 15
Table 2-2. A recipe of nanotube device annealing. .................................................... 23
Table B-1. Symbols using in Section B-2................................................................. 175
Table B-2. Symbols using in Section B-3................................................................. 184
List of Figures

| Figure 1-1. Hexagonal lattice of a graphene. | 3 |
| Figure 1-2. SWNTs with different chiralities. | 4 |
| Figure 1-3. Graphite approximate electronic band structure and zone folding method. | 6 |
| Figure 1-4. Electronic band structure of SWNTs. | 8 |
| Figure 1-5. Transfer characteristic curves of metallic SWNT, and semiconducting SWNT. | 9 |
| Figure 2-1. Nanotube chemical vapor deposition setup. | 13 |
| Figure 2-2. An SEM image of nanotubes on Si substrate. | 16 |
| Figure 2-3. Scheme of lithography. | 19 |
| Figure 2-4. A nanotube selected to make a device. | 21 |
| Figure 2-5. A nanotube device. | 24 |
| Figure 3-1. Schematic diagram of STM. | 27 |
| Figure 3-2. SPM with electrical measurement setup. | 30 |
| Figure 3-3. Schemes of AC-EFM. (a) AC-device-EFM. (b) AC-tip-EFM. | 33 |
| Figure 3-4. Electrostatic force interaction between tip and sample. | 34 |
| Figure 3-5. A broken nanotube device. | 36 |
| Figure 3-6. EFM data. | 37 |
| Figure 3-7. Schemes of SGM. | 39 |
| Figure 3-8. SGM and AFM images. | 41 |
| Figure 4-1. Drain current $I_d$ as a function of gate voltage $V_g$ for the nanotube single electron memory device at a temperature of 5 K. | 44 |
Figure 4-2. SPM images of a nanotube single electron memory. ............................... 46
Figure 4-3. Schematic of a single electron memory device................................. 48
Figure 5-1. DOS of ferromagnetic metals and scheme of MR devices. .................. 51
Figure 5-2. Nanotube MR device and two-probe AC conductance measurement setup. ............................................................................................................................. 55
Figure 5-3. AFM and MFM images of FM electrodes. .............................................. 56
Figure 5-4. Nanotube four-probe spin valve device image and measurement setup. 59
Figure 5-5. Conductance vs. $B$-field of a two probe nanotube MR device at $T = 1.24$ K......................................................................................................................... 61
Figure 5-6. Conductance vs. $B$-field of a two probe nanotube MR device with continuous nine $B$-field sweeps at $T = 0.3$ K. ................................................................. 63
Figure 5-7. Conductance vs. $B$-field of a two probe nanotube MR device with three different $B$-field sweeps at $T = 0.3$ K................................................................................................. 64
Figure 5-8. Conductance vs. $B$-field at $T = 0.3$ K demonstrating a memory effect ... 65
Figure 5-9. MR effect with respect to $V_{sd}$ at $T = 0.3$ K........................................ 66
Figure 6-1. Scheme of phonon scattering in m-SWNTs.............................................. 72
Figure 6-2. Semiconducting nanotube transistor....................................................... 74
Figure 6-3. Scheme of a Si-SiO$_2$-CNT capacitor .................................................. 75
Figure 6-4. Color-scale plot of $I_d$ as a function of $V_d$ and $V_g$ at $T = 4.2$ K. ............ 76
Figure 6-5. Scheme of a s-SWNT band diagram at a unipolar bias region. .......... 77
Figure 6-6. Scheme of a s-SWNT band diagram at an ambipolar bias region. ....... 79
Figure 7-1. Different carrier velocity behaviors under the influence of $F$.............. 83
Figure 7-2. Experimental $I_d$ as a function of $V_d$ at $V_g$ from -9 V to -1 V, in 1 V steps. ................................................................. 85

Figure 7-3. Comparison between experimental data and simulation for several models with holes as majority carriers. ................................................................. 89

Figure 7-4. Saturation current $I_{sat}$ at different $V_g$ for experimental data and theoretical models discussed in text............................................................... 94

Figure 7-5. $I_d$ as a function of $V_d$ of constant-mobility model at $V_g$ from -9 V to -1 V, in 1 V steps................................................................. 94

Figure 7-6. Profiles of (a) band structure, (b) carrier density, and (c) carrier velocity in a s-SWNT channel without pinch-off happening ($V_d = -1$ V, $V_g = -9$ V) ....... 97

Figure 7-7. Profiles of (a) band structure, (b) carrier density, and (c) carrier velocity in a s-SWNT channel with pinch-off happening ($V_d = -5$ V, $V_g = -9$ V). ........... 98

Figure 8-1. Approximate electron-phonon scatterings in a single band. ................. 104

Figure 8-2. Nonequilibrium distribution function $g(k)$ under different $F$................. 105

Figure 8-3. $v$ vs. $F$ at different carrier densities with density increasing exponentially from $10^3$ cm$^{-1}$ to $10^7$ cm$^{-1}$ in $10^{0.5}$ cm$^{-1}$ steps. $l_{ac}$ and $l_{op}$ used for this calculation are 300 and 10 nm, respectively......................................................... 106

Figure 8-4. Fitting the calculation result of $v$ vs. $F$ by phenomenological equation of velocity saturation................................................................. 107

Figure 8-5. $v$ vs. $F$ at different carrier densities with density increasing linearly from $10^6$ cm$^{-1}$ to $10^7$ cm$^{-1}$ in $10^6$ cm$^{-1}$ steps. $l_{ac}$ and $l_{op}$ used for this calculation are 300 and 10 nm, respectively. ......................................................... 108

Figure 8-6. $v$ at $F = 100$ kV/cm as a function of carrier density $n$......................... 109
Figure 8-7. $v$ vs. $F$ at different carrier densities with density increasing exponentially from $10^3$ cm$^{-1}$ to $10^7$ cm$^{-1}$ in $10^{0.5}$ cm$^{-1}$ steps. $l_{ac}$ and $l_{op}$ used for this calculation are 150 and 10 nm, respectively. ................................................................. 111

Figure 8-8. $v$ vs. $F$ at different carrier densities with density increasing exponentially from $10^3$ cm$^{-1}$ to $10^7$ cm$^{-1}$ in $10^{0.5}$ cm$^{-1}$ steps. $l_{ac}$ and $l_{op}$ used for this calculation are 300 and 5 nm, respectively. ................................................................. 112

Figure 8-9. Comparison between the universal dispersion relation and the dispersion relation derived by tightbinding calculation and zone folding method for (7, 0) SWNT. ................................................................. 113

Figure 9-1. Drain current $I_d$ as a function of gate voltage $V_g$ (a) at drain voltage $V_d = -1$ V and temperature $T = 4.2$ K, and (b) at $V_d = 20$ mV and $T = 1.5$ K. ............ 118

Figure 9-2. Drain current $I_d$ as a function of gate voltage $V_g$ at drain voltages $V_d$ from -1 V to -9 V, in -2 V steps................................................................. 120

Figure 9-3. Calculated (a) position of the strong recombination and (b) current as a function of $V_g$. ................................................................. 125

Figure 9-4. Profiles of a s-SWNT device along channel position $x$......................... 127

Figure 9-5. Calculated band diagrams of a s-SWNT device. ................................. 129

Figure 9-6. Potential profiles deducted from AC-tip-EFM images of a s-SWNT device. ........................................................................ 132

Figure 9-7. Transfer characteristic of a s-SWNT device with small band gap........ 132

Figure 9-8. Transfer characteristic of a s-SWNT device. ........................................ 134

Figure 9-9. DC-SGM images with device transport schemes................................. 135

Figure 10-1. Drain current $I_d$ vs. drain voltage $V_d$ for SWNT with $V_d$ up to 50 V. .. 141
Figure 10-2. Transfer characteristics of a s-SWNT device................................. 143

Figure 10-3. Arrhenius plot of the current at various gate voltages in the low-
conductance state. .................................................................................................. 144

Figure 10-4. Activation energy $E_a$ vs. gate voltage $V_g$ in the low-conductance state.
............................................................................................................................ 145

Figure 10-5. Conductance vs $V_g$ at $T = 300$ K. .................................................. 147

Figure 10-6. Corresponding conductance versus gate voltage at room temperature, for
different SBs. ....................................................................................................... 149

Figure 10-7. Activation energy $E_a$ vs. gate voltage $V_g$ in the high-conductance state.
............................................................................................................................ 151

Figure A-1. EFM images, AFM corresponding image, and signal profiles from EFM
images. .................................................................................................................. 156

Figure A-2. EFM signals on the nanotube after the subtraction from the background
signal. .................................................................................................................. 158

Figure A-3. The converted potential profiles on the nanotube............................... 159

Figure A-4. EFM signals on the nanotube after the subtraction from the background
signal. .................................................................................................................. 160
Chapter 1

Introduction to Carbon Nanotubes

1.1 Nanotube Overview

Carbon nanotubes (CNTs) are novel materials which were discovered over a decade ago [1], and studied [2,3] intensively ever since. Single-walled carbon nanotubes (SWNTs) [4] consist of a single graphite sheet wrapped into a seamless tube, while multi-walled carbon nanotubes (MWNTs) have several concentric graphite shells. They are extremely tiny (in nanometer scale in diameters), but nonetheless have been studied individually in a variety of experiments [5-18]. They can be extremely long (nanotubes of length 4 cm [19] and 10 cm [20] have been reported, apparently limited only by the furnace sizes [20]), which is good for various applications. They are one of the few one-dimensional materials grown in nature, and have many exceptional mechanical [5,6], chemical [7-9], and electrical properties [10-18] which open doors to various kinds of researches and applications.

The carbon-carbon sp$^2$ bond in CNTs is one of the strongest chemical bonds in nature. Such bonds make CNTs very strong [21]. Combined with chemical cross-linked techniques [22], CNTs make the strongest fibers in the world, and CNTs have been suggested as a material for a continuous cable tethered to a satellite in geosynchronous orbit, an “elevator to space” [23].

Every carbon atom in SWNTs is a surface atom, which makes SWNTs electronic properties very sensitive to their environment, especially to the electron...
donors or acceptors which are physically absorbed on SWNTs. Such a unique material geometry makes SWNTs very good candidates for chemical sensors.

Based on unique electronic properties, SWNTs can be metallic or semiconducting as predicted theoretically [10,12] and observed experimentally [13-17], depending on their chirality. (Some metallic SWNTs will have a gap open due to surface curvature and become small-gap semiconducting SWNTs. [24]) Many electronics applications of SWNTs, such as molecular circuit interconnects [25], single electron transistors (SETs) [26], p-n junctions [27], high mobility field-effect transistors (FETs) [28], nonvolatile memory elements [29], logic circuits, field emission elements [30,31], and so on, have been proposed and realized.

Luttinger liquid (LL) behaviors are predicted in general one-dimensional electron systems due to non-negligible electron-electron interaction [11,32]. In CNTs, researchers have for the first time found experimental evidence of LL behavior [33,34].

Due to weak spin-orbital coupling in carbon-based material, spin-scattering lengths are predicted to be very long in CNTs. CNTs should be a very good conductor to preserve spin information during transport. Spin-related transport in both MWNTs [35] and SWNTs [36,37] have also been proposed and realized.

Containing such rich physics and applications, CNTs have attracted the attention of many researchers, including myself. My work is mainly concentrated on electrical properties of SWNTs, although I am also interested in other properties of CNTs.
1.2 Electronic Band Structure

To understand the CNT electronic band structure, we start with its family material: graphene, a single graphite sheet. Figure 1-1 shows a honeycomb graphene sheet, a simple two-dimensional hexagonal Bravais lattice, with bases containing two identical carbon atoms. Each black dot and red bar represents a carbon atom and a carbon-carbon sp² bond, respectively. The carbon-carbon distance $a_{C-C}$ in graphite is 1.42 Å.

![Hexagonal lattice of a graphene. $a_1$, $a_2$ are primitive vectors. $R$ is a nanotube rolling vector. In the case the figure represents, $R = 6a_1$.](image)

In structure, SWNT is a seamless tube of rolled graphene. Depending on how a graphene is rolled, various SWNTs can be formed. Conceptually, a rolling vector $R = na_1 + ma_2$ is picked on the graphite sheet, starting from one carbon atom and ending at another. Then the strip whose sides are perpendicular to $R$ and passing the start and the end of $R$ is determined. The strip is rolled along $R$, connecting the start and the end of $R$, to form the SWNT. A SWNT is usually characterized by a pair of
indexes \((n, m)\). Figure 1-2 shows three types of SWNTs: (a) armchair SWNTs with indexes \((n, n)\), (b) zigzag SWNTs with indexes \((n,0)\) and (c) chiral SWNTs with indexes \((n, m)\) other than the previous two specifically symmetric indexes.

\[
\begin{align*}
(a) & \quad \text{Armchair} \\
(n,m) &= (5,5) \\
(b) & \quad \text{Zigzag} \\
(n,m) &= (9,0) \\
(c) & \quad \text{Chiral} \\
(n,m) &= (10,5)
\end{align*}
\]

Figure 1-2. SWNTs with different chiralities. (a) (5, 5) armchair SWNT. (b) (9, 0) zigzag SWNT. (c) (10, 5) chiral SWNT. (courtesy R. E. Smalley)

SWNT electronic band structures are close related to graphene band structure due to the similarity between SWNTs and graphene. In 1947, P. R. Wallace wrote
down the graphene two-dimensional electronic dispersion relation of the $\pi$ bonding band (lower sign) and the $\pi^*$ anti-bonding band (upper sign)[38]:

$$E_{2D}(k_x,k_y) = \pm \gamma_0 (1 + 4 \cos(\frac{\sqrt{3} k_x a}{2}) \cos(\frac{k_y a}{2}) + 4 \cos^2(\frac{k_x a}{2}))^{\frac{1}{2}}$$  Equation 1-1

approximated by tight binding calculation, where $\gamma_0 = 2.89$ eV [39] is the nearest-neighbor carbon-carbon overlap integral, and $a = |a_1| = \sqrt{3}a_{C-C}$ is the length of primitive vectors ($a_{C-C} = 1.44$ Å in nanotubes, which is slightly larger than $a_{C-C}$ in graphite) [40,41]. The $\pi^*$ band and the $\pi$ band are degenerate at $K$ and $K'$ points. Figure 1-3(a) shows the graphene band structure in reciprocal space near the Fermi surface: the gray bands ($\pi^*$ band) are empty; the yellow bands ($\pi$ band) are filled; the six points at the hexagon corners ($K$, $K'$) are Fermi surfaces or Fermi points. Therefore, graphene is a semi-metal. Near the Fermi surface, the bands can be approximated to cones, and the dispersion relation is linear.
Figure 1-3. Graphite approximate electronic band structure and zone folding method. (a) Graphite approximate electronic band structure. Allowed $k$ state in a reduced zone (b) in $(7, 7)$ SWNT, and (c) in $(7, 0)$ SWNT.

Not all the $k$-states of graphene are available for SWNTs since they are quasi-one-dimensional material. Due to the tubular structure of SWNTs, the phase of the electron wavefunction has to be identical when traveling one complete circumference of the tube; that is, $k \cdot |\mathbf{R}| = 2\pi n$, where $n$ is an integer. This causes a quantization of
the wavevector along the circumferential direction, \( k_r \) [10]. Figure 1-3(b) and (c) show the examples of quantized \( k_r \) in graphene reciprocal space in an extended-zone scheme. The thick lines are allowed \( k \)-states, and the dashed lines represent identical states in a reduced-zone scheme. Such a method to determine SWNTs allowed \( k \)-states is called the zone folding method [40,41].

The energies corresponding to SWNTs’ allowed \( k \)-states make one dimensional subbands. When \( n - m \) is not multiple of 3, where \((n, m)\) are the indexes of a SWNT, the allowed \( k \)-states contain the Fermi points of graphene \((K, K')\), and the dispersion relation looks like Figure 1-4(a). The first subbands are crossing each other; there is no gap between them. The tube is metallic. Otherwise, the dispersion relation looks like Figure 1-4(b). There is a bandgap between the first valence bands and conduction bands. The tube is semiconducting. The bandgap is

\[
E_g = 2\Delta = \frac{2\gamma_D a_{c-c}}{d} \approx \frac{830 \text{ meV}}{d \text{ [nm]}},
\]

Equation 1-2

where

\[
d = a\sqrt{n^2 + m^2 + nm}/\pi
\]

Equation 1-3

is the diameter of the tube. Here we see nanotubes are direct bandgap materials.
Figure 1-4. Electronic band structure of SWNTs. (a) Metallic SWNT. (b) Semiconducting SWNT.

The dispersion relations of SWNTs can be approximated by the universal dispersion relations [18]:

\[ E(k) = \pm \sqrt{\left(\frac{\hbar v_{F,m} k}{2}\right)^2 + (\nu \Delta)^2} \], \quad \text{Equation 1-4} \]

where \( \nu = 0, 3, 6, 9, \ldots \) for metallic nanotubes, \( \nu = 1, 2, 4, 5, 7, 8, \ldots \) for semiconducting nanotubes, \( \hbar = \frac{h}{2\pi} \) (\( h \) is Planck’s constant), and \( v_{F,m} = 9.3 \times 10^7 \) cm/s is the Fermi velocity of graphene (the upper and lower signs are for conduction and valance bands, respectively). Each subband of the metallic nanotubes has a degeneracy of four (except \( \nu = 0 \) has degeneracy of two), but each subband of the semiconducting nanotubes has a degeneracy of two.
1.3 Electronic Properties

As mentioned in section 1.2, SWNTs are either metallic or semiconducting. This aspect of SWNTs has been confirmed experimentally in electronic transport measurement by many research groups. Figure 1-5 shows the transfer characteristic curves of two types of nanotube devices in FET geometry (this will be discussed in more detail in Chapter 2). Figure 1-5(a) shows a metallic SWNT device, where the conductance is almost independent of a gate bias. Figure 1-5(b) shows a semiconducting SWNT device, where the conductance is modulated by a gate bias, like a FET. Each of them is very useful and promising for future electronic applications.

![Figure 1-5. Transfer characteristic curves of (a) metallic SWNT, and (b) semiconducting SWNT.](image)

Nanotubes have long mean free paths for electron transport. Ballistic transport has been observed in both metallic [42,43] and semiconducting SWNTs [44] over micron length scales at low biases. In the diffusive regime, SWNTs can carry current density up to $10^9$ A/cm$^2$, as observed for both metallic [45] and
semiconducting SWNTs [46]. This current density is about 3 orders of magnitude better than that at which copper wires typically fail due to electromigration, while CNTs are robust at such high current densities in air and at elevated temperatures [47]. The current-carrying reliability studies of MWNTs under current densities greater than $10^9$ A/cm$^2$ show no observable failure in the nanotube structure and no measurable change in the resistance are detected up to 2 weeks [48]. CNTs are therefore very good for interconnections. Also SWNTs have extremely high mobility (over $10^5$ cm$^2$/Vs at room temperature) in the low electric field [28], and very high carrier velocity ($\sim 2 \times 10^7$ cm/s) in the high electric field regime [46]. Nanotubes are direct bandgap materials (with bandgap sizes a few hundreds of meV according to , Equation 1-2), and an electrically-driven infrared light emitter has also been demonstrated [49].

In my dissertation I will focus on CNTs electronic transport properties in several aspects. In Chapter 3 I will talk about how to use scanning probe microscopy (SPM) to characterize CNTs, especially in two techniques: electrostatic force microscopy (EFM) and scanned-gate microscopy (SGM). In Chapter 4 I will demonstrate using SGM technique detects a local defect in a nanotube single electron memory device. In Chapter 5 I will discuss spin-related magnetoresistance with CNTs as channels and recent progresses in this field. In Chapter 6 to 9 I will focus on high bias transport in semiconducting SWNTs in both unipolar and ambipolar regimes, and discuss how electron-phonon interactions affect semiconducting SWNT devices behave. In Chapter 10 I will introduce electrical high-power treatment to
undope CNTs devices in vacuum, concluding that air-exposed doping explains high on-currents in Schottky-barrier nanotube transistors.

The materials in Chapter 4 have been published in the open literature as Ref. [50], Chapter 6 and 7 as [46], and Chapter 10 as [51].
Chapter 2

Nanotube Synthesis and Device Fabrication

2.1 Nanotube Chemical Vapor Deposition Synthesis

Carbon nanotubes were originally discovered as products of the arc discharge between graphite rods [1]. Researchers have since found more methods to synthesize nanotubes, such as laser ablation [52], and chemical vapor deposition (CVD) [53,54].

The advantages of CVD growth include producing very long [19], clean (fewer defects) [55] SWNTs, and also producing large amounts of SWNTs [56]. Our group grows the nanotubes by CVD methods to meet the purpose of producing very long, clean (few defects) SWNTs directly on substrates. Also the system is simple to set up (see Figure 2-1).
Iron nanoparticles can catalyze the growth of CNTs and are used in our nanotube CVD growth [57]. The size of the iron nanoparticles is believed to determine the diameter of resulting nanotubes [58]. To prepare iron nanoparticles on the substrates (typically small chips of SiO2-capped Si), ferric nitrate (Fe(NO3)3) is dissolved in an isopropyl alcohol (IPA) solution, and then mixed well by stirring for a couple of hours. The concentrations of Fe(NO3)3/IPA solution directly control the density of catalyst particles for nanotube growth. The substrates are dipped in
Fe(NO$_3$)$_3$/IPA solution for 10 seconds and hexane for another 10 seconds to force Fe(NO$_3$)$_3$ to precipitate on the substrates. The substrates are placed in a quartz boat and then the boat is placed in the quartz tube, in the center of the oven (see Figure 2-1). After the gas lines are purged, Ar and H$_2$ are introduced to the quartz tube and the oven starts heating toward 850 °C. During the heating, iron nitrate is expected to be reduced to iron nanoparticle catalyst. After the temperature is stabilized at 850 °C, the carbon feedstock gases, such as methane and ethylene, are fed into the oven. The carbon feedstock gases are expected to decompose catalytically over the iron to carbon and hydrogen; carbon atoms interact with the iron nanoparticles, and nanotubes grow. Nanotube growth ends when the carbon feedstock gases are shut off and the oven is cooled.

Table 2-1 shows a typical example of nanotube growth. The growth parameters, such as gases, flow rates, flow times, and temperatures, are all adjustable to optimize the growth yield or for other purposes (such as length or density control).
Table 2-1. A recipe of nanotube growth.

<table>
<thead>
<tr>
<th>Action</th>
<th>Gas</th>
<th>Flow (sccm)</th>
<th>Temp (°C)</th>
<th>Time (minute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purge</td>
<td>Ar</td>
<td>730</td>
<td>RT</td>
<td>22</td>
</tr>
<tr>
<td>Heat</td>
<td>Ar</td>
<td>730</td>
<td>RT→650</td>
<td>15</td>
</tr>
<tr>
<td>Soak</td>
<td>Ar</td>
<td>730</td>
<td>650</td>
<td>5</td>
</tr>
<tr>
<td>Heat</td>
<td>Ar</td>
<td>730</td>
<td>650→730</td>
<td>2</td>
</tr>
<tr>
<td>Soak</td>
<td>Ar</td>
<td>730</td>
<td>730</td>
<td>3</td>
</tr>
<tr>
<td>Heat</td>
<td>Ar</td>
<td>730</td>
<td>730→800</td>
<td>3</td>
</tr>
<tr>
<td>Soak</td>
<td>Ar</td>
<td>730</td>
<td>800</td>
<td>3</td>
</tr>
<tr>
<td>Heat</td>
<td>Ar</td>
<td>730</td>
<td>800→850</td>
<td>5</td>
</tr>
<tr>
<td>Soak</td>
<td>Ar</td>
<td>730</td>
<td>850</td>
<td>10</td>
</tr>
<tr>
<td>Nanotube Growth</td>
<td>H₂</td>
<td>1900</td>
<td>850</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>1300</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₄</td>
<td>86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cool Down</td>
<td>Ar</td>
<td>730</td>
<td>850→RT</td>
<td>Wait for hours</td>
</tr>
</tbody>
</table>

Figure 2-2 shows an SEM image of nanotubes [59] grown according to the recipe of Table 2-1 with about 0.3 μg/ml (30μg/100ml) Fe(NO₃)₃/IPA. Most of the nanotubes are tens of microns long; some of the nanotubes are hundreds of microns long. The density of nanotubes is controllable by controlling the catalyst concentration. This sample, with long, well isolated nanotubes, is good for electrical device fabrication. By checking with atomic force microscopy (AFM, which will be described in next chapter), most of CVD-grown CNTs are thin (with diameters about 1~3 nm); therefore, most of them are expected to be SWNTs, although it is likely that some few-walled CNTs and small bundles of SWNTs are present.
2.2 Electron-Beam Lithography and Electrical Contact Preparation

When discussing the manufacture of electronic devices, lithography is the term used to describe the patterning of material on the surface of the substrate. Optical lithography, which uses light directed through a mask to create the pattern in a polymer resist layer (photoresist), is the most extensively used lithography technique in the electronics industry. In my study, however, electron-beam lithography is chosen to pattern thin films for device purposes because feature sizes from hundreds of microns down to tens of nanometers are easy to prepare. The major drawback of electron-beam lithography, that it is a serial process and therefore inherently slow due, is not a disadvantage here because each device is custom-designed for the particular nanotubes on a chip.

Making alignment marker patterns and nanotube contacts are two major steps during device fabrication with electron-beam lithography. Here we use a technique
called “find-and-wire” to fabricate nanotube devices. In the first lithography step, alignment markers are made randomly on a chip with already grown nanotubes. We find the nanotubes relative to the alignment markers. Then we wire the nanotubes we find through the second lithography. The chief advantage of the find-and-wire technique is that the wired nanotubes can be chosen for specific purposes.

Figure 2-3 explains how electron-beam lithography works. Figure 2-3(a) shows a clean diced chip or wafer. Figure 2-3(b) shows a chip with bi-layer resists. Resists are the chemicals which are easy to cover the whole surface of chips and whose chemical structures are sensitive to exposure to energetic beams (light or electrons, for instance). Depending on the dosage, the solubility of resists in some specific solvents (developers) can be varied. The bottom layer is methyl methacrylate (MMA), and the top is polymethyl methacrylate (PMMA). Typically, MMA is spun on with 4500 rpm for 45 seconds, and followed by 5 ~10 minutes baking at 150 °C on a hot plate. PMMA is spun on with 6000 rpm for 45 seconds, and followed by 5 ~ 10 minutes baking at 150 °C on a hot plate. The resist thicknesses of MMA and PMMA layers are about 300 and 100 nm, respectively. The bi-layer resist is used to create big undercuts and ease the lift-off process (described below) because MMA is more sensitive to electron dosage and easy to dissolve in Acetone (the solvent which is used for lift-off). Sometime a single PMMA layer is prepared if an e-beam mask with very big undercut is not needed and/or the MMA does not coat the chip surface evenly. Figure 2-3(c) shows a part of resists exposed under the electron beam. The patterns to be exposed are designed with CAD software, and the Nano Pattern Generation System (NPGS) is used to control a Scanning Electron Microscope (SEM,
FEI model XL-30). The electron beam scans the patterns, so the resist at the desired locations is exposed to the electron beam. Figure 2-3(d) shows the resist after development; a larger portion of the more sensitive MMA layer is removed by the developer, creating an undercut. The resist developer is methyl isobutyl ketone (MIBK):IPA = 1:3. Typically the exposed resist can be removed in developer within 20 ~ 70 seconds, then followed by IPA cleaning. Figure 2-3(e) shows the chip after deposition of the contact material (usually a metal film prepared by thermal evaporation). Figure 2-3(f) shows the result of the lift-off step. After the resist is dissolved (typically in acetone) the contact material in the developed patterns remains on the surface, while the contact material on the resist has been removed. To accomplish lift-off, typically the chip is soaked in acetone for a few hours for most deposited materials. For some materials (like permalloy), lift-off can be done within minutes. Afterward, the chip is rinsed with acetone and IPA, completing the lithography process.
In the find-and-wire scheme, the first lithography step is used to make alignment marker patterns usually after nanotube CVD growth. Cr/Au films are thermally evaporated to make alignment marker patterns because Au is easy to see under SEM. A Cr wetting layer is necessary for Au to stick on SiO₂. Typically Cr
and Au thicknesses are 1 and 30 nm, respectively, and the deposition conditions are not crucial in this step.

In nanotube device fabrication, locating nanotubes is the challenging (but fun) part owing to the random CVD nanotube growth. Figure 2-4(a) shows an alignment marker pattern. The zoomed-in picture shows a nanotube relative to the alignment markers. Many similar images have to be collected in order to get enough information to fabricate devices properly. In the Fuhrer lab, techniques were developed to take these kinds of images are with SEM rather than AFM [59], greatly speeding up the whole device fabrication process.
Figure 2-4. A nanotube selected to make a device.  (a) an alignment marker pattern. The zoomed-in picture shows a nanotube relative to alignment markers.  (b) a finished device with electrical contacts made of the same tube shown in the zoomed-in of (a).

The second lithography is needed for making electrical contacts to the selected nanotubes. Thermal evaporations for nanotube contacts are done with more
careful deposition conditions. The vacuum in the deposition chamber ranges from $3 \times 10^{-6}$ to $4 \times 10^{-7}$ torr to minimize the impurities in metals during evaporation. Figure 2-4(b) shows a finished device with the tube shown in the zoomed-in picture of Figure 2-4(a) contacted by four permalloy electrodes.

2.3 Annealing

Annealing has been found to often lower the contact resistance of nanotube devices [60]. It is not clear exactly how annealing results in better electrical contacts; likely possibilities are that impurities in the contact region are removed, the metal atoms in the contacts rearrange to form a better physical contact to the nanotubes, or that the gold diffuses through the wetting layer to make a better electrical contact to the nanotubes. The same oven system for nanotube growth (see Figure 2-1) is also used for annealing nanotube devices.

Table 2-2 shows a typical example of nanotube-metal contact annealing. The annealing parameters, such as gases, flow rates, flow times, and temperatures, are all adjustable to optimize the device performances.
<table>
<thead>
<tr>
<th>Action</th>
<th>Gas</th>
<th>Flow (sccm)</th>
<th>Temp (°C)</th>
<th>Time (minute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purge</td>
<td>Ar</td>
<td>1500</td>
<td>RT</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat</td>
<td>Ar</td>
<td>1500</td>
<td>RT→400</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soak</td>
<td>Ar</td>
<td>1500</td>
<td>400*</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cool Down</td>
<td>Ar</td>
<td>1500</td>
<td>400→RT</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2-2. A recipe of nanotube device annealing. (* indicate the temperature overshoot to 415 °C)

2.4 Electrical Measurement Setup

The major part of my research here is related to electrical measurements of nanotube devices. Figure 2-5 shows the device image, basic geometry and measurement setup. Figure 2-5(a) shows an SEM image of the nanotube device with the working parameters of the SEM. The CVD-grown nanotube is contacted by two Cr/Au electrodes. The ground, applied voltages $V_g$, $V_d$, and measured current $I_d$ are labeled; $V_g$ is applied to the conducting silicon substrate. The DC voltages applied to devices are sourced from a National Instruments BNC-2090 data acquisition device (DAQ), Keithley 2400 sourcemeter, Kepco BOP 100-1M power supply, or the auxiliary outputs of Stanford Research 830 Lock-in amplifier. The DC currents are translated into the voltage signals by Ithaco 1201 Current Preamplifier, and the voltages then are measured by National Instruments BNC-2090 DAQ or Agilent 34401A. The instruments are controlled by the computer programs written in
Labview or other comparable computer languages. The inset shows an AFM image of a section of the nanotube used to determine the diameter. Figure 2-5(b) depicts the side view of a nanotube device with device geometry.

![Figure 2-5](image)

Figure 2-5. A nanotube device. (a) an SEM image of a nanotube device with basic electrical setup. The inset is an AFM image, which is usually used to determine a nanotube diameter $d$. (b) side view of a nanotube device with device geometry. $t$ is the oxide thickness and $L$ is the channel length.

Electrical measurements are performed at one of several setups which have been established in our laboratory; three of these are described below.

Cascade Probe Station (Cascade Microtech):
This probe station has a 1000X optical microscope, good to visualize devices and probe movement. The operational temperature range is 200 K ~ 500 K, and the environment may be controlled by constant gas flow. An air table is available to isolate mechanical vibration. The Cascade probe station is especially suitable for the study of large numbers of devices; many devices with identical device geometry can be measured automatically because the stage position (and also the position of one probe) is controlled by computer.

Cryo-Probe Station (Desert Cryogenics):

This probe station also has a 1000X optical microscope. The operational temperature range is 1.5 K ~ 475 K, good for short-term low temperature measurements. The chamber can be pumped to $10^{-6}$ torr at room temperature and different gas environments can be established. An air table is available as well.

Cryostat (Desert Cryogenics):

Temperature operational ranges are 1.2 K ~ 325 K in $^4$He gas environment for $^4$He probe and 300 mK to 325 K in vacuum for $^3$He probe. The superconducting coil is able to produce magnetic field range from -9 to 9 Tesla.
Chapter 3

Scanning Probe Microscopy to Characterize Nanotube Devices

3.1 Introduction to Scanning Probe Microscopy

People use light to see the world around them. Optical microscopes were the first instruments to aid people in seeing small objects. However, because of diffraction of light, the sizes of the objects which can be imaged by optical microscopy are limited by the wavelength of visible light, which is on the order of 100 nm. Electron beams, whose wavelengths are much shorter than the wavelength of visible light, are used in electron microscopes, e.g. scanning electron microscopes and transmission electron microscopes.

People can also touch objects in the world around them. Instead of using our fingers, microfabricated cantilevers with sharp tips at the end can be used to touch small objects, and thus form an “image” of them. Scanning probe microscopy (SPM) includes a large group of microscopes which utilize this idea to image physical properties of materials, especially surface properties. The principles of SPM are founded on the invention of scanning tunneling microscopy (STM). STM was invented and demonstrated by Gerd Binnig and Heinrich Rohrer at IBM in Zurich [61], who therefore were awarded by Nobel Prize in 1986. The core of the SPM includes three parts: scanner (in xyz directions), probe (a sharp tip or a cantilever with a sharp tip), and feedback electronics (to maintain the constant interaction between tip
and surface). Atomic resolution imaging was achieved [62] by these simple pieces of equipment. Figure 3-1 shows the schematic diagram of STM.

![Figure 3-1. Schematic diagram of STM. (courtesy Digital Instruments)](image)

However, the applicability of STM is greatly limited by the need of conducting samples since tunneling current between the tip and the sample is used as a feedback signal; non-conducting samples are not accessible by STM. Another
feedback scheme is then needed in order to access non-conducting samples. Gerd Binnig and his colleagues again invented another SPM technique called atomic force microscopy (AFM) which uses the force between tip and sample as a feedback signal [63]. AFM is more sample-friendly and therefore used more widely in many areas of research. Atomic resolution in a clean and flat surface can also be attained with AFM [64]. AFM is a landmark of nanotechnology; without the help of SPM, nanotechnology likely could not have developed so fast. For general reviews of AFM, please read Ref. [65,66].

Nanotubes and nanotube devices are characterized by SPM by many researchers. STM is used to determined the atomic structures (chiralities and indexes \((n,m)\) of SWNTs from atomic resolution images and electronic properties from scanning tunneling spectroscopy [8,13-15]. AFM is used to measure diameters of nanotubes. Conducting tip AFM has been used to as one of the contact electrodes to measure nanotube electronic transport [67-70]; as a local gate to deplete carriers [71], study barriers in nanotube-metal contacts [72] or nanotube-nanotube junctions [71], and probe defects of nanotubes [73,74]; or in electrostatic force microscopy (EFM) to measure the conductance of nanotubes [75] and local electronic structure [76].

In our lab, there are two SPM setups: JEOL 4210 and DI Dimension 5000. Both of them have varieties of features. JEOL 4210 has vacuum capability \((2.6 \times 10^{-7} \text{ torr at room temperature})\) and temperature tunability from 130 K to room temperature by using the cooling stage and from room temperature to 773 K by using the heating stage (both stages have to be operated under vacuum conditions). DI Dimension 5000 has a very wide sample stage which allows large wafer scanning or
extra setups (for example probes for electrical measurements) on it. I have used the JEOL 4210 to do SPM characterize on nanotube devices because I need the features it offers.

In this chapter, I will focus mainly on two specific SPM techniques, EFM and scanned gate microscopy (SGM), to probe the electronic properties of nanotubes. My work was initiated by the previous work done by Prof. Adrian Bachtold and my advisor Prof. Michael Fuhrer in Berkeley [42]. At the end I will introduce one more commonly used SPM technique, Magnetic Force Microscopy (MFM). In Chapter 5 I will mention using MFM to characterize the magnetization of ferromagnetic contacts of nanotube spin-valve devices.

To be able to access the devices electrically while doing SPM scanning, an extra wiring setup is needed. Figure 3-2 shows the SPM system I used, JEOL-4210, combined with the setup of electrical connection to devices on a surface.
3.2 Electrostatic Force Microscopy

In nanotube devices, we are not able to do four-probe measurements to determine the intrinsic resistivity of nanotubes due to strongly invasive nature of the electrical contacts in one-dimensional systems; in order to measure voltage with an electrical contact, scattering into the contact is necessary to achieve electrochemical potential equilibrium, but such scattering adds significantly to the measured resistance. However, researchers are interested in the resistance distribution within a
nanotube device; to determine e.g. whether the contact resistance or the channel resistance dominates the device resistance. One way to measure the resistance distribution is to map the potential profile along the device while applying a voltage across to the device. EFM is a good candidate for this purpose [42]. EFM is a SPM technique utilizing the electrostatic force between the scanning tip and the samples to measure the capacitances between the tip and the surface, charge distribution, and the surface potentials [77-79].

The easiest EFM implementation is DC-EFM, so-called because the voltage between tip and sample does not oscillate. The electrostatic force between the tip and some local position of the sample $F$ is

$$F = -\frac{\partial U}{\partial z} \approx -\frac{\partial}{\partial z} \left( \frac{1}{2} C (V_{\text{tip}} - V_{\text{local}}(x, y) + \phi)^2 \right) = -\frac{1}{2} \frac{\partial C}{\partial z} (V_{\text{tip}} - V_{\text{local}}(x, y) + \phi)^2,$$

Equation 3-1

where $U$ and $C$ are the electrostatic energy and the capacitance between the tip and the local position of the sample, respectively; $V_{\text{tip}}$ and $V_{\text{local}}(x, y)$ are the potential of the tip and the local position of the sample, respectively; $\phi$ the work function difference between the tip and the local position of the sample. The force constant change $\Delta k$ due to the electrostatic force is

$$\Delta k \approx -\frac{\partial F}{\partial z} = \frac{1}{2} \frac{\partial^3 C}{\partial z^2} (V_{\text{tip}} - V_{\text{local}}(x, y) + \phi)^2.$$

Equation 3-2

The force constant change of the cantilever causes a shift of the natural frequency $\Delta \omega_0$, therefore, a phase shift of the amplitude of the tip cantilever

$$\Delta \phi \propto \Delta \omega_0 \propto \Delta k \propto (V_{\text{tip}} - V_{\text{local}}(x, y) + \phi)^2,$$

Equation 3-3
where the potential constant equals \( Q/k \). \( Q \) and \( k \) are the quality factor and the force constant of the cantilever, respectively. The DC-EFM signal is the phase shift \( \Delta \varphi \), which is sensitive to the surface potential. However, the DC-EFM phase shift signal is quadratic in the surface potential [42]. Thus it is hard to map the signal to the potential in data manipulation.

AC-EFM avoids this difficulty: as will be shown below, the signal of AC-EFM is linearly proportional to the surface potential, which helps to get quantitative information about the surface potential and reduces many difficulties in processing and understanding the data.

I will describe below a slightly modified version of AC-EFM compared to Ref. [42] which was necessitated by the lack of “lift mode” in the JEOL-4210 microscope. Lift mode (patented by the company Digital Instruments) is a technique in which the tip is scanned at a fixed height above the sample during the detection of electrostatic or magnetic forces in e.g. EFM or MFM. In my setup, the electrostatic force is detected at one frequency, simultaneous to the topographic scan which requires feedback at the tip oscillation frequency. My modified AC-EFM setup is sketched in Figure 3-3.
Like the usual “tapping mode” AFM, the tip is driven by the piezoelectric at frequency $\omega_{\text{tip}}$, which is very close the tip natural resonant frequency. The electronic feedback system controls the amplitude of tip, which determines the tip-sample distance. By doing tapping mode AFM, a topography image can be taken. While doing tapping mode AFM scanning, another AC bias with frequency $\omega$ (which is usually chosen to be close to tip natural resonant frequency, too) is then applied either
to the device (see Figure 3-3(a)) or the tip (see Figure 3-3(b)). Due to the electrostatic interaction between the tip and the sample, the tip also oscillates at frequency $\omega$. The amplitude and the phase of the tip oscillation at frequency $\omega$ are detected by the photo detector, and recorded with respect to x-y positions to form EFM images.

To quantitatively extract the surface potential, the following analysis is needed. The electrostatic interaction between the tip and the sample is depicted in Figure 3-4. The electrostatic force between the tip and some local position of the sample $F$ is also expressed by Equation 3-1.

![Figure 3-4. Electrostatic force interaction between tip and sample.](image)

For AC-device-EFM, an AC signal with frequency $\omega$ is applied to the device. The local surface potential at certain position $(x,y)$ has AC component $V_{\text{local}}(\omega,x,y)$. The amplitude signal $A(\omega,x,y)$ is proportional to the AC force component $F_{\text{ac}}(\omega)$. Therefore,

$$A(\omega,x,y) \propto F_{\text{ac}}(\omega) = -\frac{\partial U}{\partial z}(\omega) \approx \frac{\partial C}{\partial z} \cdot (V_{\text{tip}} + \phi) \cdot V_{\text{local}}(\omega,x,y), \quad \text{Equation 3-4}$$

which shows a linear relationship between $A(\omega,x,y)$ and $V_{\text{local}}(\omega,x,y)$.

For AC-tip-EFM, the AC signal $V_{\text{tip}}(\omega)$ is applied to the tip. Therefore,
\[ A(\omega,x,y) \propto F_{ac}(\omega) = -\frac{\partial U}{\partial z}(\omega) \approx \frac{\partial C}{\partial z} \cdot (V_{local}(x,y) - \phi) \cdot V_{tip}(\omega) , \]  

Equation 3-5

which also shows a linear relationship between \( A(\omega,x,y) \) and \( V_{local}(x,y) \).

AC-device-EFM and AC-sample-EFM have different advantages. The major advantage of AC-device-EFM is that the image shows strong signal at the positions electrical connected to the device and zero signals at all other place. The major advantage of AC-tip-EFM is that various DC device bias (\( V_d \) and \( V_s \)) dependent studies can be done, especially good for high DC device bias studies.

Figure 3-5 shows a broken nanotube device. Both AFM image in (a) and EFM image in (b) are taken simultaneously. The technique for this EFM image is AC-device-EFM. The top electrode is AC biased, while the bottom one is grounded. In the AFM topography image, the break of the tube can not be seen, although the transport data show that the device is not conducting; probably indicating the break is atomic in scale. In EFM image, a clear contrast is seen. The reason for that is due to the open circuit; the potentials of the top and the bottom parts of the nanotube are the same as top electrode (\( V_d = V_{ac, sample} \)) and the bottom (\( V_s = 0 \)), respectively. One important point: although the two images are taken simultaneously, there is no correlation between them. The topography information is not observed in EFM images.
Figure 3-5. A broken nanotube device. (a) AFM image. (b) EFM image. The break is not visible under AFM, but shows up clearly under EFM. The scan size is $5.4 \times 5.4 \mu m^2$. The two pictures are taken simultaneously.

Figure 3-6(a) shows another EFM image. There are two electrodes on the top and bottom of the image (see Figure A-1(a) in Appendix A for AFM image of the device). The top and bottom electrodes are DC biased, separately ($V_d = 0$ and $V_s = -1$ V). The technique for this EFM image is AC-tip-EM. There are EFM signal gradients from the top to the bottom both along the nanotube and on the bare SiO$_2$ substrate mainly due to the long-range capacitive coupling of the tip to the electrodes. After the signal background subtraction, the potentials at each point of the nanotube are able to be extracted (the detailed data processing is in Appendix A). Figure 3-6(b) shows the derived potential along the nanotube. The potential drops along the nanotube as expected. From the derived potential, we can say that at this specific bias condition, the major resistance of the device is distributed in the nanotube itself although the potential extraction near the contacts is more difficult and uncertain (see the discussion in Appendix A).
Figure 3-6. EFM data. (a) An EFM image of nanotube device. The top electrode is grounded ($V_d = 0$), while the bottom electrode is biased with -1 V ($V_s = -1$ V). The gate bias $V_g$ equals 0.4 V. The amplitude and frequency of AC tip bias $V_{ac,tip}(\omega)$ equals 0.2 V and 13 kHz, respectively. The scan size is $1.5 \times 1.5 \, \mu\text{m}^2$. (b) The potential profile along the nanotube extracted from (a). The black dashed lines indicate the edges of the electrodes. The processes of extracting nanotube potential profiles from EFM images is discussed in Appendix A.

3.3 Scanned Gate Microscopy

SGM is a SPM technique which treats an AFM conducting tip as a local gate to modulate the local charges or potentials of devices and monitor the conductances (or resistances) of devices [80,81]. By scanning a device, the regions which are sensitive the local field changes display very clearly in SGM images. SGM has been used to study 0D point contacts [80,82,83], quasi-1D electron gases [81], and 2D electron gases [84]. SGM has also been used to investigate defects and/or contacts on carbon nanotube devices [42,50,72-74,85-87].
The SGM techniques I have used consist of AC-SGM and DC-SGM. Figure 3-7 shows both SGM schemes over a nanotube device. While doing tapping mode AFM scanning, the conducting AFM cantilever also acts like a local gate over devices which are electrically biased. The major difference between AC-SGM and DC-SGM is that AC-SGM measures the AC current of the device responding to the vibration of the tip with respect to the local gate position over the device while DC-SGM measures the DC current.
Figure 3-7. Schemes of SGM. (a) AC-SGM. (b) DC-SGM.

Figure 3-8 shows the AFM and SGM images of a nanotube device with two contacts. Figure 3-8(a) is an AC-SGM image, and Figure 3-8(b) is an AFM image taken simultaneously with Figure 3-8(a). The first thing to notice is that the SGM image does not show the information of device topography. The only thing matter in the SGM image is whether the device charge transport reacts to the tip gate. In Figure 3-8(a), two nanotube positions near the contacts are very sensitive to the tip
gate. The contacts play a very important role in such bias conditions. Figure 3-8(c) shows AC-SGM image of the same device at different bias condition. In Figure 3-8(c), many positions along the nanotube are sensitive to the tip gate, even one section of nanotube reacts to the tip gate oppositely (the bright spot). The device behaves very differently at two bias conditions according to SGM images, which cannot be known in transport measurement only. Figure 3-8(d) shows a DC-SGM image of the same device. Unlike the unit of the signal in AC-SGM is arbitrary, the color scale in DC-SGM is the magnitude of the device DC current. At this particular bias condition, the tip enhances the device current while it is close to nanotube-metal contacts. From the image, we know the tip actually reducing the thickness of Schottky barriers of the contacts, which will be discussed more in Chapter 8.
Figure 3-8. SGM and AFM images. The scan sizes for all images are $6 \times 6 \mu m^2$. (a) AC-SGM image. The top electrode is biased with $-6 V$ ($V_d = -6 V$), while the bottom electrode is grounded ($V_s = 0$). The gate bias $V_g$ and the tip bias $V_{tip}$ are all equal to $-2 V$. (b) AFM image taken simultaneously with (a). (c) AC-SGM image taken at $V_d = 0$, $V_s = -4 V$ and $V_g = V_{tip} = -2 V$. (d) DC-SGM image taken at $V_d = -8 V$, $V_s = 0$, $V_g = -4.2 V$, and $V_{tip} = -4 V$.

Either AC-SGM or DC-SGM technique has its own advantages. AC-SGM has more spatial sensitivity, which provides more localized information on a small-scale device. DC-SGM images are easier to interpret in view of the fact that the signal is the DC current through the device.
In chapter 8, I will describe how DC-SGM and AC-tip-EFM are further used to characterize nanotube devices under high DC biases.

3.4 Magnetic Force Microscopy

Magnetic Force Microscopy (MFM) is a SPM technique which detects the magnetic field distribution of a surface by an MFM tip, an AFM tip coated by a magnetic material. Similar to DC-EFM described above, the magnetic force between the tip and some local position of the sample causes a phase shift of the amplitude of the tip cantilever, which is the signal of MFM. MFM is frequently used to detect magnetic moments on the surface of a magnet since the magnetic moment produces a strong magnetic field locally.
Chapter 4

Single Electron Memory

4.1 Single Defect Detection Using Scanned Gate Microscopy

Low power nonvolatile memory has been the subject of much research. The lowest power consumption electronic memory conceivable would have a node which stores a single electron [88-90]; such a device is called a single electron memory. There are many candidates for the readout elements in a single electron memory; a NTFET is one of them. NTFETs have advantages in that they are relatively easy to fabricate (a single processing step defines source, drain, and channel), they have high carrier mobility [28], and they are intrinsically nanoscale. The last two are necessary in order that small changes in charge produce large conductivity changes. Recently our group succeeded to make single electron memories using NTFETs [29,50]. These memory devices took advantage of the many charge traps intrinsic to the SiO$_2$ substrate, which were used as electron storage nodes. However, in a nanotube single electron memory the nanotube should only be sensitive to one single storage node. We then assumed that only one small piece of the nanotube is the readout and responsible for the single electron memory effect. SGM is then an ideal tool to test this assumption and identify the responsible piece of the nanotube.

Figure 4-1 shows $I_d$ as a function of $V_g$ of a p-type NTFET. $V_g$ is swept back and forth many times. Several discrete states are shown due to $I_d$ vs. $V_g$ is multi-valued. The most possible explanation for the device showing these discrete states is the charge storage node close to the nanotube readout contains few electrons; each
state corresponds to an electron storage configuration and the adjacent states are with one electron difference. The hysteresis loops are also shown between states. Any hysteresis loop is then available for a single electron memory.

Figure 4-1. Drain current $I_d$ as a function of gate voltage $V_g$ for the nanotube single electron memory device at a temperature of 5 K. Five discrete curves are seen, with no intermediate values of $I_d$. Hysteresis loops are evident in the figure. Several sweeps back and forth over $V_g$ ranges are shown. Arrows indicate sweep directions and switches. $\Delta V_{th}$ indicates the shift in $V_g$ between the $I_d$-$V_g$ curves; $\Delta V_{th} = 0.2$ V. $\Delta V_{w}$ indicates the shift in $V_g$ between the jumps between $I_d$-$V_g$ curves; $\Delta V_{w} = 1$ V.
Figure 4-2 show an AC-SGM image in (b) and its corresponding AFM-topography image of the device in (a), whose transport data are shown in Figure 4-1. The contrast in AC-SGM image indicates that the change of the device resistance responds to the conducting tip. Bright means large resistance change. The SGM signal along the nanotube is stronger which is consistent to that the nanotube is semiconducting; every piece of the nanotube reacts to the tip. One spot is particularly bright, but is not visible in corresponding AFM-topography image. We guess that this may be a single atomic-scale defect in the nanotube. The line trace alone the nanotube in Figure 4-2(c) shows the width of the peak is ~ 30 nm, which is not indicative of the actual size of the defect and probably limited by the size of the tip. However, here we still demonstrate the ability of SGM to detect a piece of nanotube, which is sensitive to local potential variance, in a nanotube device.
Figure 4-2. SPM images of a nanotube single electron memory. (a) AFM image and (b) AC-SGM image are taken simultaneously. The scan size is 2.26 × 2.26 µm². The bias settings are $V_d = 100$ mV, $V_g = 0$, and $V_{tip} = 4$ V. The arrows point to a possible atomic defect in the nanotube. The dotted line in (b) indicates the nanotube position, and the dash-dotted lines indicate the edges of the electrodes. (c) shows the line trace of the dotted line in (b) along the nanotube.

4.2 Capacitance Analysis of a Single Electron Memory

Figure 4-3 shows a probable schematic of our device described above. The charge trap (either at the SiO₂ surface or in the SiO₂ bulk) is coupled capacitively to the defect in the nanotube channel through a capacitance $C_{TC}$, and to the gate through a capacitance $C_{GT}$. There is also in additional capacitance between the gate and
channel, $C_{TC}$. In addition, a non-linear resistor $R_{TC}$ must be present between the nanotube channel and the charge trap to allow charging and discharging of the defect. Such a device structure has been considered in detail in Ref. [91], where it was shown that this structure forms the basis of a single electron memory. The $I_d-V_g$ characteristics of a transistor coupled to a charge trap in this way will show discrete curves, separated in gate voltage by an amount

$$\Delta V_{in} = \frac{eC_{TC}}{(C_{TC} + C_{GT})C_{GC}},$$

Equation 4-1

where $e$ is the electronic charge and $C_{GC}$ is the total gate capacitance given by

$$C_{GC} = C_{FC} + \frac{C_{TC}C_{GT}}{C_{TC} + C_{GT}}.$$

Equation 4-2

Periodic switching events will occur between curves with a spacing

$$\Delta V_w = \frac{e}{C_{GT}},$$

Equation 4-3

and the hysteresis width (the distance in gate voltage between the switching events between two charge states of the trap when increasing gate voltage and decreasing gate voltage) is determined by the nonlinear characteristics of the resistor $R_{TC}$ between channel and charge trap [91].
Figure 4-3. Schematic of a single electron memory device. Source and drain denote the contacts to the nanotube channel, the defect is the spot of high gate-voltage dependence on the nanotube observed in the scanned gate microscopy image in Figure 4-2(a), the gate is the conducting silicon substrate, and the trap is a charge trap located presumably at the surface or in the bulk of the SiO₂ dielectric.

For our device, we observe a threshold shift $\Delta V_{th} = 0.2$ V, and a write voltage periodicity $\Delta V_W = 1$ V (see Figure 4-1). These two numbers are insufficient to determine the three capacitances in Figure 4-3. We may estimate one of the capacitances, $C_{FC}$, by estimating the size of the defect region in the channel. From the SGM line trace (Figure 4-2(c)), the defect region is approximately 30 nm in extent (or perhaps smaller, this distance is comparable to the resolution of the image). This distance can be interpreted as the screening length in the nanotube at the defect. From Coulomb blockade measurements of other devices, we know that the gate capacitance per length of our nanotube transistors is approximately 10 aF/µm. This gives a capacitive coupling $C_{FC} \approx 0.30$ aF between the defect region and gate. Solving for the other capacitances, we find $C_{TC} = 0.14$ aF and $C_{GT} = 0.16$ aF. The total capacitance
of the charge trap $C_{TT} = C_{TC} + C_{GT} = 0.30$ aF. From this value we can make a rough estimate of the size of the charge trap. The self-capacitance of a sphere of radius $r$ is given by $C_{self} = 4\pi\varepsilon\varepsilon_0 r$, where $\varepsilon_0$ is the permittivity of free space and $\varepsilon$ the dielectric constant of the medium in which the sphere is embedded, $\sim 4$ for SiO$_2$. Setting $C_{TT} = C_{self}$ gives $r = 6.7$ Å, reasonable for a vacancy site or complex of dangling bonds in the SiO$_2$ dielectric.
Chapter 5

Magnetoresistance in Spin Valves with Nanotube Channels

5.1 Introduction to Magnetoresistance due to Spin-Valve Effect

Electrons have two degrees of freedom: charge and spin. Electron charges have been utilized in device aspect for decades and become the central part of modern electronic device technology, especially semiconductor technology [92]. On the other hand, electron spins are late to be noticed for device purposes compared with charges. An electron has two spin states, up and down, since it is a spin-½ fermion. In the Seventies, pioneering researchers [93] showed that tunneling between ferromagnetic films can depend on electron spins, which has inspired much research and applications in both academia and industry. The word “spintronics” (from “spin electronics”) is used to describe the manipulation of electron spins in solid materials in this new active field [94,95].

Materials which have non-zero magnetization in zero magnetic field (B-field) are called ferromagnetic (FM) materials. Such materials have different densities-of-state (DOS) for spin up and spin down, which causes unbalanced spin populations of spin up and spin electrons. Figure 5-1(a) depicts a FM material with magnetization pointing up or down, and its corresponding schematic DOS. The most common examples are iron, cobalt, nickel, and their alloys.
Electrons with different spins will experience different spin scattering strengths in FM materials because the DOS for spin-up and spin-down electrons at the Fermi level in FM materials are different; spin-up electrons travel more easily without spin scattering through the FM material with up magnetization than with down magnetization, and vice versa. For devices with a non-FM material sandwiched by two FM layers, the ease with which electrons go through depends on the configurations of the magnetizations of the two FM layers. For instance, when the
device is in the parallel state (p-state, see Figure 5-1(b)), spin-up electrons travel
easily although spin-down electrons are blocked. However, when the device is in the
anti-parallel state (ap-state, see Figure 5-1(c)), both spin-up and spin-down electrons
are blocked. The result is that the overall resistance of the device in the parallel state
is smaller than that in the anti-parallel state. Such an effect, called giant
magnetoresistance (MR), is already utilized in read-out heads of magnetic hard drives
as commercial products, while other applications are proposed, like magnetic random
access memory [96,97] and spin-FETs [98].

The MR ratio is defined

\[ MR Ratio = \frac{R_p - R_{ap}}{R_{ap}} = \frac{G_p - G_{ap}}{G_p}, \]  

Equation 5-1

where \( R_p \) and \( R_{ap} \) (\( G_p \) and \( G_{ap} \)) are the resistances (conductances) in the p-state and
ap-state, respectively. The simplest mechanism for giant MR effect (GMR) is that
electrons from layer one FM tunnel through non-FM layer to the other FM without
spin scattering. Suppose the conductance for spin-up (spin-down) electrons is
proportional to the multiplication of the spin-up (spin down) DOS fractions of the two
FM layers, then \( G_p \) and \( G_{ap} \) are

\[ G_p \propto a_1a_2 + (1-a_1)(1-a_2) \]  

Equation 5-2

and

\[ G_{ap} \propto a_1(1-a_2) + (1-a_1)a_2 \]  

Equation 5-3

respectively, where \( a_1 \) (\( a_2 \)) is the fraction of the major tunneling electrons (the
electrons with the spin parallel to the magnetization) of the first (second) FM layer.
The expected tunneling MR ratio (TMR) should be [93]
\[ TMR = \frac{2P_1P_2}{1 + P_1P_2}, \]  

Equation 5-4

where \( P_1 = 2a_1 - 1 \) (\( P_2 = 2a_2 - 1 \)) is spin polarization of first (second) FM layer.

The non-FM middle layer in MR devices not only can be an insulator, but also semiconductor, normal metal, or superconductor, depending on different purposes. In order to maximize GMR, the spin-polarized current injected from one FM layer needs to be preserved for a long distance while electrons are traveling in the non-FM layer so that the spin-polarized current can be detected by the other FM layer. In normal metals, such as copper [99] and aluminum [100], the spin-flip lengths \( \lambda_{sf} \) are 1000 and 650 nm at temperature 4.2 K, respectively, and 350 nm for both metals at 293 K. These metallic mesoscopic spin valves work very well, but lack tunablity. Semiconductors have a couple advantages, such as long \( \lambda_{sf} \) [101], carrier concentrations which can be tuned by chemical and electrical doping, and possible spin precession due to spin-orbit coupling [98]. However, the “conductivity mismatch” problem hinders the detection of the spin valve effect in FM-semiconductor-FM systems [102,103].

Carbon nanotubes are another possible candidate to transport spin-polarized current due to long mean free paths at room temperature and possibly very long spin-scattering lengths. MWNTs have been demonstrated to carry spin transport first [35,104,105], but SWNTs attract major interests for spin transport study lately [36,37,106-109] due to their one-dimensional electronic properties. In this chapter I would like to describe the work I have done with spin transport in SWNTs, and compare the results I have obtained with the results from other groups.
5.2 Device Fabrication

The device fabrication largely follows the procedures in Chapter 2 from section 2.1 to 2.3. Heavily n-doped Si chips with a SiO\textsubscript{2} layer of thickness $t = 500$ nm are used as device substrates. SWNTs are grown using a CVD. SEMs (Philips XL30 or Zeiss DSM 982 field-emission SEM (FESEM)) were used to locate the nanotubes, and electron-beam lithography followed by thermal evaporation of FM materials formed the contacts to a nanotube. The FM material we choose is permalloy (about 80% Ni, 20% Fe). It is known that permalloy possesses spin polarization $P = 45%$ [110,111], which is higher than pure FM metals. Thicknesses of the permalloy thin-film contacts are about 30–50 nm. The permalloy electrodes are designed with some specific aspect ratios, which define the easy axes and tune the coercivities [112]. Several aspect ratios are tried: $1 \times 4$ µm$^2$, $1 \times 8$ µm$^2$; $0.5 \times 2$ µm$^2$, $0.5 \times 4$ µm$^2$; $0.4 \times 4$ µm$^2$, $0.2 \times 12$ µm$^2$; $0.3 \times 4$ µm$^2$, $0.15 \times 12$ µm$^2$; $0.3 \times 4$ µm$^2$, $0.1 \times 12$ µm$^2$; $0.5 \times 2$ µm$^2$, $0.1 \times 14$ µm$^2$; suggested by the literature [99,100,112]. Larger electrodes made of Cr/Au connect permalloy contacts to outside of the world, allowing us to perform electrical measurements to the devices. Figure 5-2 shows a nanotube two-probe magnetoresistance device with measurement setup (described in next section).
Figure 5-2. Nanotube MR device and two-probe AC conductance measurement setup. The permalloy electrode thickness is 50 nm, sizes are $0.4 \times 4 \ \mu \text{m}^2$ and $0.2 \times 12 \ \mu \text{m}^2$, and the electrode separation is 200 nm.

Devices were annealed at $350 \sim 400 \ ^\circ \text{C}$ under Ar and H$_2$ flow to lower the contact resistance before measurements.

After the devices are fabricated, it is advantageous to know how the magnetizations of FM contacts interact with applied $B$-field. Magnetic force microscopy (MFM) is designed to measure the local $B$-field on the surface [113,114]. Therefore, MFM is very good at visualizing the magnetization of the FM contacts because the magnetic tip of MFM interacts with $B$-field produced by FM contacts. MFM scanning while applying B-field was performed in the laboratory of Professor Romel Gomez with the aid of his student Seok-Hwan Chung [112].

Figure 5-3 shows the AFM and MFM images of the nanotube magnetoresistance devices. AFM and MFM images are taken simultaneously. Figure 5-3(a) is an AFM image. Five permalloy rectangular contact pairs (one big pair on the top left corners and four small pairs on the bottom right) and several alignment
markers can clearly be seen, while two nanotubes can barely be seen. Figure 5-3(b) to (f) are MFM images, where only permalloy pairs show up. Bright areas indicate the local $B$-field of the areas pointing to one of the normal directions to the surface, and dark areas indicate the local $B$-fields pointing to the opposite direction.

Figure 5-3. AFM and MFM images of FM electrodes. (a) shows an AFM image of devices. The thin lines are nanotubes. There are two sizes of FM electrode pairs. The bigger pair on
the top-left corner has $1 \times 4$ and $2 \times 8 \ \mu m^2$ electrodes, while the other four pairs have $0.5 \times 2$ and $0.5 \times 4 \ \mu m^2$.  (b) shows a MFM image at zero B-field.  The previous field direction before ramping back to zero is positive (pointing right).  (c), (d) and (e) are MFM images taken at -18, -42, and -66 Gauss, respectively, while B-field is ramping toward negative direction.  (f) shows a MFM image while B-field ramps back to zero from negative direction.

Figure 5-3(b) is taken at zero applied $B$-field. The previous applied $B$-field direction before ramping back to zero is positive (pointing right).  All the magnetizations of the permalloy contacts remain in the previous applied $B$-field direction, which represents the ferromagnetism of the permalloy contacts.  The devices are defined in the p-state.  Also, all the permalloy contacts have single domain magnetization.  After ramping applied $B$-field to -18 Gauss, Figure 5-3(c) is then taken.  All the magnetizations of the contacts remain the same except the short electrodes of the big pair break into multi-domain.  Figure 5-3(d) is taken at applied $B$-field equal to -42 Gauss.  The magnetizations of both electrodes in the big pair point to the negative direction.  The big pair is in the p-state.  The small pairs are all in the ap-state; only the short electrodes change their magnetizations with applied $B$-field.  Figure 5-3(e) is taken at applied $B$-field equal to -66 Gauss, which is enough to flip the magnetizations of all the contacts.  The devices are all in the p-state again.  Figure 5-3(f) is taken when applied $B$-field ramps back to zero from the negative direction.

MFM provides valuable information to design permalloy electrodes to obtain single domain contacts, which are desired for the MR study. From the observations of MFM images, several tips for designing permalloy contacts can be found. First, long and thin electrodes have single domains, and also have larger coercivities.
Second, the permalloy pairs with long and thin electrode are stable in either p-state or ap-state. Third, to have large applied $B$-field window for a device in the ap-state, the aspect ratios of two contacts in a pair need to be very different.

Although the overall contact magnetization of a long and thin contact looks like single domain, some very small localized magnetization domains are still possible according to the MFM images (for example, some short electrodes of small pairs in Figure 5-3(d) and (f)). Because nanotubes are nanoscale material, such local magnetization domains may cause ambiguities when making MR measurements.

5.3 Measurement Technique

MR experiments are carried out in $^4$He or $^3$He systems in order to have a $B$-field supply and stable low temperature environment. Figure 5-2 shows the set-up of a standard two-probe AC technique to measure differential conductance (or differential resistance) of the device. This setup is for measuring differential conductance at zero DC bias; with some voltage dividers in front, measuring differential conductance at non-zero DC bias is achievable.

In order to observe MR effects purely from spin injection-accumulation-detection in spin valve devices, a four-probe non-local measurement is necessary [99,115]. Non-local measurement technique allows separating from spin injection-accumulation-detection, other spin related effects, such as magnetocontact resistance, anisotropic magnetoresistance, and Hall effect [99,115]. Figure 5-4 shows a nanotube four-probe spin valve device image and the four-probe non-local measurement scheme. For four-probe devices, two additional Cr/Au electrodes are added on the sides to contact nanotubes. An AC current is injected from the third to
the forth electrode while measuring the AC voltage between the first and the second electrodes. If the current injected is spin polarized and the spin scattering length in the non-FM material is longer than the channel length, a nonzero voltage should be expected and detected [99,100,115].

Figure 5-4. Nanotube four-probe spin valve device image and measurement setup.
5.4 Result and Discussion

The results of two-probe measurements are discussed first. The spin-valve nanotube devices do not show gate dependence at room temperature. The reason for that is the channel length \( L \) between two permalloy contacts (couple hundred of nm) is comparable to the thickness of gate dielectric and metal contact; the gate fields is hard to penetrate into the channels \([116,117]\). We thus can not distinguish whether the measured nanotubes are metallic or semiconducting. Figure 5-5 shows differential conductance \((G)\) vs. applied \(B\)-field from a particular nanotube MR device with \( L = 200 \) nm. The data is taken at temperature \( T = 1.24 \) K, DC source-drain voltage \( V_{sd} = 0 \), gate voltage \( V_g = 0.3 \) V, AC excitation voltage \( V_{ac} = 0.1 \) mV, and applied \(B\)-field sweep rate is about 1.8 Gauss/s. The dashed vertical lines, which guide \( G \) changes due to the device switches between p-state and ap-state, are at \( \pm 300 \) and \( \pm 1000 \) Gauss applied \(B\)-field. The 300 and 1000 Gauss are the coercivities of short and long permalloy electrodes \((0.4 \times 4 \, \mu m^2, 0.2 \times 12 \, \mu m^2)\), respectively. The coercivities of FM contacts and \(B\)-field window for ap-state are all larger than those in Figure 5-3 because the aspect ratios of permalloy contacts are larger.
Figure 5-5. Conductance vs. $B$-field of a two-probe nanotube MR device at $T = 1.24$ K. Negative MR effect is demonstrated. The positive $B$-field is pointing right. The arrows indicate the FM contact magnetizations. The first row is for sweeping $B$-field from negative to positive; the second row is from positive to negative.

According to applied $B$-field and the ramping history, the device is either in p-state or ap-state. If the nanotube MR devices works similar to magnetic tunneling junction devices, $TMR = 34\%$ should be expected according to Equation 5-4 and $P_1 = P_2 = 45\%$ for permalloy. However, the device in Figure 5-5 has higher conductance (lower resistance) when it is in ap-state rather than in p-state; the device possesses a negative $TMR$ of about -7\%. It is counterintuitive to have a device with a negative MR effect. The possible reasons or explanations are: (1) The local magnetic moments connected to the nanotube are not aligned with the net magnetization of the contact. (2) The electron spins precess in the nanotube. (3) Two permalloy contacts and the nanotube form a quantum dot where Kondo resonance occurs closer to the Fermi energy for the antiparallel magnetization orientation [118]. (4) Electron
tunneling through a SWNT quantum dot with asymmetric tunnel barriers is on resonance [109]. However I do not have further information to prove which one is more likely.

Figure 5-6 shows $G$ vs. applied $B$-field in nine continual sweeps from another device. The contacts of this device have the same geometry of the previous described one. The data is taken at temperature $T = 0.3$ K, DC source-drain voltage $V_{sd} = 0$, gate voltage $V_g = -0.47$ V, AC excitation voltage $V_{ac} = 0.01$ mV, and applied $B$-field sweep rate is about 4.5 Gauss/s. The permalloy evaporation conditions are the same. The channel length $L$ is also 200 nm. The coercivities of short and long permalloy electrodes are 300 and 500 Gauss, respectively. The long electrode has slightly smaller coercivity than that of the device in Figure 5-5. The average $TMR$ is about +3.5%; indicating a positive MR effect which is easier to understand in terms of spin injection-transport-detection. Although this device has some other switching and MR effects, it has better consistency in this set of sweeps.
Figure 5-6. Conductance vs. $B$-field of a two-probe nanotube MR device with continuous nine $B$-field sweeps at $T = 0.3$ K. Positive MR effect is demonstrated.

Sometimes, one of the peaks or both peaks are missing. Figure 5-7 shows $G$ vs. applied $B$-field in another three continual sweeps of the same device and the same settings in Figure 5-6 (except $V_g = 0$). In Figure 5-7(a) (the first sweep), the right sweep peak is missing, while in Figure 5-7(c) (the third sweep), the left sweep peak is missing. The reason is unclear; however the most possible explanation is somehow both FM contacts switch at the same time responding to the applied $B$-field. One
more thing to be noticed in this figure is *MR ratio* is ~ 17%, higher than the previous and closer to the expected 34% for the device without spin flipping predicted by the simple Julliere model.

Figure 5-7. Conductance vs. *B*-field of a two-probe nanotube MR device with three different *B*-field sweeps at *T* = 0.3 K. (a) and (c) show one peak is missing; (b) shows none of both peaks is missing.

Figure 5-8 shows the hysteresis effect of the same MR device. The settings are the same as those in Figure 5-7. Only the short electrode switches its magnetization. Around zero bias, the device can be either in p-state or ap-state depending on the history of the applied *B*-field. This memory effect has possible device applications in memories and transistors.
Figure 5-8. Conductance vs. $B$-field at $T = 0.3$ K demonstrating a memory effect. The arrows indicate the FM contact magnetizations.

Because both p-state and ap-state are stable, other settings may be changed to see how these two states behave. Figure 5-9(a) shows $G$ vs. $V_{sd}$ at both p-state and ap-state. The largest difference between both states is at zero $V_{sd}$ (0.3 mV offset due to small the offset of electronics (DAC board)). Roughly above 1.3 mV $V_{sd}$, the difference is diminishing. Figure 5-9(b) shows the calculated $TMR$ from Figure 5-9(a). The trend of decreasing $TMR$ with increasing $V_{sd}$ is clearly seen; however, the reasons for that are still unclear.
Figure 5-9. MR effect with respect to $V_{sd}$ at $T = 0.3$ K. (a) shows conductance vs. $V_{sd}$ while the device is at parallel state (solid line) or antiparallel state (dashed line) at zero $B$-field. (b) shows MR ratio vs. $V_{sd}$ derived from (a). Inset shows conductance vs. $B$-field at $V_{sd} = 1$ mV.

When larger $V_{sd}$ (larger 3 mV) is applied, some switching events happen (data not shown). The device transport behavior is very sensitive to all the settings, which makes the experiment very difficult.
In the previous two described devices, besides the major MR effect due to spin injection-transport-detection, there are also other magnetoresistance effects present, which are not fully identified. Sometimes the major MR effect can not be seen as well; this appears to be related to gate voltage $V_g$, temperature $T$, sweep rate of applied $B$-field. Even though all the factors are controlled, $G$ vs. applied $B$-field at different sweeps are not consistent. Such inconsistency prevents us from doing more systematic study of MR effect in nanotube devices.

Unfortunately, since the number of working devices is very small; the spin-flip length $l_s$ can not be extracted from the experiments. (Nevertheless, by assuming all the spin scattering events happen in the nanotube, the \( TMR \) should be

\[
TMR = \frac{2P_1P_2e^{-L/l_s}}{1 + P_1P_2e^{-L/l_s}}. \tag{5-5}
\]

Using \( TMR = 17\% \) observed in one device ($L = 200$ nm and $P_1 = P_2 = 45\%$ for permalloy), the lower bound of $l_s = 260$ nm can be extracted.) Only two out of tens of devices show any MR effects; the reasons for this are also not clear. Possible explanations are the following. (1) Strong spin-flip scattering could be present at the nanotube-metal interface. (2) Contact to the nanotube could be made through an intermediate non-magnetic region (such as amorphous carbon, or a section of the nanotube) (3) The contacts of devices are mechanical unstable. Atomic motion in the contacts generates telegraph noise. (4) Local magnetization fluctuations may play an important role due to the intrinsic nanoscale of nanotubes.

Four-probe spin valve nanotube devices have been fabricated and measured with both conventional and non-local measurement geometries. The non-local measurement geometry is described in Figure 5-4, while the conventional
measurement geometry injects the current from outside electrodes and measures the voltages with the inside electrodes. The comparisons and advantages between these two measurement geometries for spin-related transport are described in detail in Reference [115]. However, I failed to observe MR effects in four-probe spin-valve nanotube devices. One of the possible problems is conductivity mismatch [102,103]; the conductivity of non-FM layer is much less than those of contacts. Rashba [119] has suggested that making tunnel barriers between FM and non-FM layers will solve this problem. Another possible problem is additional current paths in the non-local measurement geometry due to the fact that the nanotubes may be MWNTs [120].

During the time I performed my research on nanotube spin valves, other research groups have also worked on this topic and have published some results. Recently, ferromagnetic semiconductors have been used as FM materials to contact nanotubes to solve the conductivity mismatch problem [107], and MR effects are seen [107]. However, the sizes of the contacts are not controlled, which makes single domain magnetization of FM contacts at all applied $B$-field impossible and the switching events complex. Moreover, MR effects are even observed at devices with one FM contact and one non-FM metal contact. The results, therefore, are confusing.

The group of van Wees (who has pioneered all-metal four-probe spin-valve experiments [99,100,115,121]) has also studied nanotube four-probe spin-valve devices in a non-local geometry [36]. MR effects due to spin injection-accumulation-detection have been reported. The results are promising, but more work is needed to determine the spin scattering length in nanotubes.
The Alphenaar group in University of Louisville has developed a shadow evaporation technique to fabricate short nanotube MR devices (channel length on order of 10 nm) [37], achieving a high yield of working MR devices. However, single-domain magnetization switching is lacking among devices according to the device geometry and transport results.

Electric-field control of spin transport has been realized recently by tuning resonant tunneling through a SWNT quantum dot in FM-SWNT-FM devices [109]. The spin-dependent transmission probability $T^\sigma$ for electrons with energy $E$ and spin $\sigma$ can be written as [109]

$$T^\sigma = \frac{\Gamma_1^\sigma \Gamma_2^\sigma}{(E - E_0^\sigma)^2 + (\Gamma_1^\sigma + \Gamma_2^\sigma)^2/4},$$

Equation 5-6

where $\Gamma_1^\sigma = \gamma_1(1 + \sigma P_1)$ ($\Gamma_2^\sigma = \gamma_2(1 + \sigma P_2)$) is the spin-dependent coupling to the first (second) ferromagnetic lead, $\gamma_1$ and $\gamma_2$ are the bare coupling and $E_0^\sigma$ is the spin-dependent energy level of the quantum dot. If the couplings to the leads are asymmetric (for example, $\Gamma_1^\sigma \ll \Gamma_2^\sigma$), when the transmission is off resonance, that is when $|E - E_0^\sigma| >> \Gamma_1^\sigma + \Gamma_2^\sigma$, $T^\sigma$ is small and proportional to $\Gamma_1^\sigma \Gamma_2^\sigma$, yielding the normal positive $TMR$ of $2P^2/(1 - P^2)$ (assuming $P_1 = P_2 = P$) [109]. On the other hand, when the transmission is on resonance, that is when $|E - E_0^\sigma| \ll \Gamma_1^\sigma + \Gamma_2^\sigma$, $T^\sigma$ is proportional to $\Gamma_1^\sigma/\Gamma_2^\sigma$, yielding an anomalous negative $TMR$ of $-2P^2/(1+P^2)$ [109]. By applying gate voltages, which change $E_0^\sigma$, the magnitude and the sign of $TMR$ can be tuned in a predictable way. Possibly this effect can explain my observation of negative $TMR$; however, my measurement of negative $TMR$ is apparently not tunable by gate as described above, especially when many random telegraph noise signals are present (data not shown).
Recent results on nanotube MR devices will likely generate much attention again in basic research as well as applications.
Chapter 6

High-Bias Transport in Semiconducting SWNTs

6.1 Introduction to High-Bias Transport in Nanotubes

One of the most striking aspects of carbon nanotubes is that they can carry extremely large current densities, exceeding $10^9$ A/cm$^2$ [45,48,122], orders of magnitude larger than those at which metal wires fail by electromigration [123]. In m-SWNTs, a saturation of 25 µA was observed at high drain biases in low contact resistance devices [45]. Yao et al. have first studied current saturation of 25 µA at high bias voltages in m-SWNTs and successfully explained the phenomenon in terms of scattering of electrons due to optical or zone-boundary phonon emission [45]; the phonon energy $hf$ is about 160 meV. The mean free path of optical phonon emission backscattering $l_{op}$ is ~ 10 nm. If the m-SWNT channel is much longer than $l_{op}$, such scattering processes then occur frequently and will establish a separation about 160 meV between the quasi-Fermi levels of left- and right-moving carriers (see Figure 6-1, duplicate from Ref. [45]). This inelastic phonon emission at energy $hf = 160$ meV explains the current limit of $(4e^2/h)(hf) \approx 25$ µA at high electric field [45,47,69], where $4e^2/h$ is the quantum conductance for the lowest two crossing subbands.
Figure 6-1. Scheme of phonon scattering in m-SWNTs. The solid lines represent the states occupied by carriers. The dashed arrow indicates the inelastic phonon emission.

The current-carrying capacity and reliability studies of MWNTs under current densities greater than $10^9$ A/cm$^2$ show that no observable failure in the nanotube structure and no measurable change in the resistance up to 2 weeks [48]. Also in contrast to metal wires, MWNTs do not fail continuously due to electromigration; instead, they fail via a series of sharp current steps, which correspond to the breakdown of MWNT shells [122,124]. By using electrical breakdown of MWNTs, it was found that metallic and semiconducting shells carry similar saturation currents $20 \sim 25$ µA [122,124]. Bourlon, et al. proposed a model of competition between electron-phonon scattering and Zener tunneling to further explain the geometrical dependence of saturation currents in metallic and semiconducting single shells in MWNTs [125].

Low contact resistance devices have been achieved with semiconducting SWNTs (s-SWNTs) by using palladium (high work function metal) to form ohmic contacts to the valence band of the s-SWNT [44]. Current saturation at 25 µA in ohmically-contact s-SWNT devices is not obvious in the data shown in the paper [44]; instead, the current seems to increase without limit (though this was not noted in...
the paper). Therefore, there is no reason to assume that the limit in s-SWNTs is identical to that in m-SWNTs. This is reasonable, since the electronic band structure is different: the equivalent zero-momentum phonon emission process in semiconducting nanotubes involves relaxation of electrons across the band gap, which is order of hundreds of meV, usually greater than the energy of zone-boundary and optical phonons.

Following the thoughts above, I recognized that high-bias transport experiments and studies on single s-SWNTs are lacking. I performed a series of high-bias experiments on s-SWNTs, and these experiments and modeling of the transport at high bias form the second half of my dissertation.

Figure 6-2 shows the measured $I_d$ vs. $V_d$ up to ±10 V at different gate biases $V_g$ for a s-SWNT-FET with $d = 2.4$ nm and $L = 20$ µm. Electrical measurements were performed by grounding the source electrode ($V_s = 0$) and applying $V_d$ to the drain, and $V_g$ to the gate, while measuring the drain current $I_d$. We note several striking features of the data. First, the data is highly symmetric under reversal of both $V_d$ and $V_g$, indicating good electron-hole symmetry in s-SWNTs due to the fact that the energy-band structure of the conduction band and the valence band are identical near the charge-degeneracy point [126]. Second, the currents significantly exceed 25 µA with no obvious evidence of saturation, which stands in contrast to the currents observed in metallic SWNTs. In Chapter 7 and 8 I will further discuss why s-SWNTs can have higher currents than metallic SWNTs.
Figure 6-2. Semiconducting nanotube transistor. Drain current $I_d$ as a function of drain voltage $V_d$ at gate voltages $V_g$ from -9 V to 9 V, in 1 V steps is measured. $V_d$ is applied up to 10 V. Temperature is 4.2 K.

When $V_g$ is greater (smaller) than the nanotube potential, electrons (holes) are expected to accumulate in the nanotube, and n-type (p-type) behavior is expected. Figure 6-3(a) (Figure 6-3(b)) show a Si-SiO$_2$-CNT capacitor accumulating electrons (holes) in the nanotube with applied biases $V_g > V_d & V_s$ ($V_g < V_d & V_s$). At finite positive (negative) gate voltages, the curves of Figure 6-2 show typical n-type (p-type) transistor behavior, i.e. saturation of $I_d$ at positive (negative) drain voltage. The saturation is followed by an increase in the current as $V_d$ becomes greater than $2V_g$. We interpret this increase in $I_d$ as the change from majority electron to majority hole current or vice versa. $V_d = 2V_g$ corresponds to the symmetric bias condition.
[127,128], equivalent to holding $V_g = 0$ and applying equal and opposite voltages to source and drain; at this point electron and hole currents should be equal.

Figure 6-3. Scheme of a Si-SiO$_2$-CNT capacitor. (a) For the case of $V_g > V_d$ & $V_s$. (b) $V_g < V_d$ & $V_s$. (c) $V_d > V_g > V_s$. (d) $V_d < V_g < V_s$. $V_s = 0$ in all cases.

Figure 6-4 shows a color-scale plot of $I_d$ as a function of $V_d$ and $V_g$, which is another way to represent the same data in Figure 6-2. The colors indicate the amount of current. The two dashed lines represent $V_g = V_s$ and $V_g = V_d$, which mark the boundaries separating the unipolar bias regimes from the ambipolar bias regimes. In the unipolar bias regimes, where $V_g$ is larger than both $V_d$ and $V_s$ for electrons to
accumulate, or \( V_g \) is smaller than both \( V_d \) and \( V_s \) for holes to accumulate, there are only majority carriers to take into account and minority carriers are few enough to be neglected. In the ambipolar bias regimes, where \( V_g \) is between \( V_d \) and \( V_s \) (see Figure 6-3(c) for \( V_d > V_g > V_s \) and Figure 6-3(d) for \( V_d < V_g < V_s \)), both majority carriers and minority carriers play important roles in the nanotube channel.

![Color-scale plot of \( I_d \) as a function of \( V_d \) and \( V_g \) at \( T = 4.2 \) K. The dotted line indicates \( V_g = V_d/2 \); the current minimum occurs along this line. The dashed lines are the boundaries between unipolar and ambipolar transport.](image)

6.2 Unipolar Transport

Figure 6-5 shows an example of a s-SWNT band diagram in the unipolar (hole conduction) bias regime (see Figure 2-5(b) for the scheme of device geometry). This band diagram results from a calculation performed as described in Chapter 7; most
importantly, contact effects are ignored. The Fermi level of the drain contact is 5 eV higher than that of the source contact due to $V_d = -5$ V is applied. The gradient of the bands denotes the electric field strength. The potential energy rises from the source contact to the drain contact with the largest slope occurring near the drain contact. The blue dashed line is the quasi Fermi level of holes in the nanotube, showing only holes are built up in the whole nanotube. Further discussion of s-SWNTs in the unipolar bias regimes will be found in Chapter 7.

Figure 6-5. Scheme of a s-SWNT band diagram at a unipolar bias region ($V_d = -5$ V, $V_g = -9$ V). The left and right sides are Fermi levels of the source and drain contacts, respectively. The vertical lines indicate the metal-nanotube junctions. The middle part is the nanotube, whose conduction and valence band edges are shown by two black lines. The quasi Fermi level of holes is indicated by the blue dashed line.
6.3 Ambipolar Transport

Figure 6-6 shows an example of a s-SWNT band diagram in the ambipolar bias regime, calculated as described in Chapter 7. In Figure 6-6 the contact effects are ignored as in Figure 6-5. The potential energy rises from the source contact to the drain contact with the largest slope occurring in the middle of the nanotube channel. The blue and red dashed lines are the quasi Fermi levels of holes and electrons in the nanotube, respectively. Holes are accumulated in the nanotube near the source while electrons are accumulated near the drain. In the middle, both types of carriers are present. This example of $V_d = -5 \text{ V}$ and $V_g = -2.5 \text{ V}$ is actually a symmetric bias case since $V_d = 2V_g$. It is equivalent to $V_g = 0$ and $V_d = -V_s = -2.5 \text{ V}$. Therefore, the picture is symmetric in terms of the source and the drain. The symmetric bias cases are indicated by a dotted line in Figure 6-4, where the current is at a minimum with variation of the gate voltage.
Figure 6-6. Scheme of a s-SWNT band diagram at an ambipolar bias region \( (V_d = -5 \text{ V}, \ V_g = -2.5 \text{ V}) \). The left and right sides are Fermi levels of the source and drain contacts, respectively. The vertical lines indicate the metal-nanotube junctions. The middle part is the nanotube, whose conduction and valence band edges are shown by two black lines. The quasi Fermi levels of electrons and holes are indicated by the red and blue dashed lines, respectively.

The ambipolar bias regime is a subject of much recent scientific and technological interest. In the ambipolar bias regime because electrons are injected from one contact into the s-SWNT and holes are injected from the other, electrons and holes meet in the channel (s-SWNT) and recombine rapidly due to strong Coulomb interaction between them. In part of the recombination, the energy will be relaxed by emitting light (photons). The light emitting process induced by applying electric bias in s-SWNTs is called electroluminescence, and was demonstrated by
IBM group [49,129]. Further discussions about s-SWNTs in the ambipolar bias regime will be in Chapter 9.
Chapter 7

High-Bias Transport of Semiconducting SWNTs in the
Unipolar Regime

7.1 Phenomenological Carrier Velocities under Electric Field

The movement of charges is current. In a solid-state system, the velocity of an electron is often described by

$$
\vec{v}(\vec{k}) = \frac{1}{\hbar} \frac{\partial E(\vec{k})}{\partial \vec{k}} = \frac{1}{\hbar} \nabla_{\vec{k}} E(\vec{k}) \tag{Equation 7-1}
$$

when the electron is occupied a state $\vec{k}$ with energy $E(\vec{k})$. However, there is no current in an equilibrium system due to the carriers moving in all directions, which produces zero net current. When there is a voltage difference between two ends of a conductor, a non-zero net current will flow due to unbalanced charge flows.

In a sample length $L$ shorter than the momentum relaxation length $l_e$ (mean free path) of electrons, the electrons transport is in the ballistic regime [41,130]. There the average electrons may traverse the device without scattering. On the other hand, when $L \gg l_e$, the transport is in the classical or diffusive regime, where the resistance of the sample is proportional to $L$, i.e. Ohm’s law is obeyed.

In classical transport, Ohm’s law can be rewritten to an average carrier velocity $\nu$ proportional the electric field $F$ which the carriers experience (consider one dimensional case):

$$
\nu = \mu F \tag{Equation 7-2}
$$
where $\mu$ is a material-dependent constant called mobility. In general, approximating mobility as a constant is only valid for low electric fields. As $F$ gets larger, $\mu$ is no longer a constant with respect to $F$, since more scattering mechanisms become available as the carriers gain more energy. In many materials the mobility follows a phenomenological equation,

$$\mu^{-1} = \mu_0^{-1} + \frac{|F|}{v_s},$$

Equation 7-3

where $\mu_0$ is the zero-field mobility and $v_s$ is the saturation velocity. Such behavior is called velocity saturation. Figure 7-1 shows different carrier velocity behaviors under the influence of $F$: The dashed line represents the constant mobility behavior, which shows the carrier velocity increasing linearly with $F$, while the solid line represents the saturation velocity behavior, which shows the carrier velocity saturates in the high $F$. (Here the values of $\mu_0$ and $v_s$ are taken from fits to this model for a particular nanotube device described later in this chapter.) Note that the dotted line shows the Fermi velocity of the carriers in a SWNT at high density, which should be the upper bound of the carrier velocity. The plot indicates that at modest experimentally accessible electric fields (comparable to those applied in Chapter 6, Figure 6-2) deviations from constant mobility are expected in SWNTs.
Figure 7-1. Different carrier velocity behaviors under the influence of $F$. The dashed and solid lines represent the constant mobility and the saturation velocity behaviors, respectively. The dotted line shows the Fermi velocity of the carriers. (The mobility of $2.7 \times 10^4$ cm$^2$/Vs is used for plotting constant mobility, $\mu_0 = 2.7 \times 10^4$ cm$^2$/Vs and $v_s = 2 \times 10^7$ cm/s for saturation velocity, and $9.3 \times 10^7$ cm/s for Fermi velocity of m-SWNT.)

In Chapter 6, we have briefly described applying high-bias to s-SWNTs. Such measurements help to know how the velocities of the carriers in s-SWNTs behave under the influence of high electric fields. In the unipolar bias regimes, the carrier velocities are simpler to analyze since there is only one type of carrier in the channel. Hence if we know the carrier density $n$ in a s-SWNT channel from the gate capacitance and measure the current $I$ under biases, along with (assuming that the carriers are electrons)

$$I = nev,$$

where $e$ is the electronic charge, we can easily estimate the carrier velocity. This estimation of the carrier velocity assumes that all the carriers move at this velocity,
and uses the charge-control model \((n \propto V_g)\) to determine the carrier density. It is well known that this is a very crude approximation, and the velocity extracted in this way is always less than the peak value. The approximation is too simplistic for the following reasons. In a semiconductor transistor, the velocity and density of the carriers are strong functions of position in the channel. As a result, device modeling is necessary to understand the device behaviors under different biases and the carrier behaviors under the effect of the electric fields [46].

7.2 Experiment Results

Before doing the modeling, I would like to describe the experimental results of high-bias transport of s-SWNTs in the unipolar regime that the device modeling is going to compare. We have investigated several s-SWNT devices with similar transport behavior. Some devices showed only unipolar p-type behavior; we associate these devices with Ohmically-contacted nanotubes or large-bandgap nanotubes. Only the ambipolar devices (having both good hole and electron conduction), which we assume to have small Schottky barriers (SBs) to both valence and conduction bands, are discussed in this chapter, because our goal is to extract both hole and electron behaviors in s-SWNTs, particularly under high \(F\). Under this condition, the SBs are very transparent and can be neglected in modeling.

The measured semiconducting nanotube diameters \(d\) range from 2 to 2.4 nm (with band gap about 0.35 \(\sim\) 0.42 eV), and the nanotube lengths between the contacts (channel length \(L\)) range from 10 to 20 \(\mu\)m. The measured nanotube diameters indicate they are SWNTs or small MWNTs. (We expect that in the case of a small MWNT with all semiconducting shells that the transport occurs primarily in the
outermost shell with the lowest bandgap.) Here we investigate high-bias transport up to bias voltages of 10 V, corresponding to average electric fields up to $5 \sim 10$ kV/cm.

We focus on the transport data from one particular device, with $d = 2.4$ nm and $L = 20 \, \mu m$. Figure 7-2 shows the experimental $I_d$ as a function of $V_d$ in the unipolar regime ($V_g$ is smaller than both $V_d$ and $V_s$) with holes as majority carriers at $V_g$ from -9 V to -1 V, in 1 V steps. This s-SWNT-FET device behaves as a normal p-type FET, with current saturating at negative $V_d$ and increasing at positive $V_d$. The current significantly exceeds 25 $\mu$A at positive $V_d$ as described in Chapter 6.

![Figure 7-2. Experimental $I_d$ as a function of $V_d$ at $V_g$ from -9 V to -1 V, in 1 V steps. The thick curve is for $V_g = -9$ V.](image)

7.3 Device Modeling

The model device geometry is schemed in Figure 2-5(b), with $L = 20 \, \mu m$, $d = 2.4$ nm, and $t = 500$ nm, to match the geometry of the device shown in Figure 7-2.
= 0 and \( x = L \) locate at left (source) and right (drain) ends of the nanotube (defined by the nanotube-contact junction). Here we have used the electrostatic gate capacitance per length

\[
c_{g,e} \approx \frac{2\pi \varepsilon_0}{\ln(4t/d)} \approx 0.2 \text{ pF/cm}, \quad \text{Equation 7-5}
\]

where \( \varepsilon_0 \) is the electric constant, \( \varepsilon \approx 2.45 \) the average dielectric constant of the oxide and vacuum.

First we examine the expected behavior for a perfectly ballistic (zero scattering) nanotube FET, in order to examine some of the qualitative behavior expected at high bias. We calculate the current using some assumptions and simplifications: (1) The nanotube is undoped (intrinsic semiconductor). (2) The electrode Fermi level is aligned with the middle of the nanotube gap. (3) The subbands are approximated by a hyperbolic band structure (as Equation 1-4 in Chapter 1):

\[
E(k) - (-e)V_{NT}(x) = \pm \sqrt{(h v_{F,m} k)^2 + (\nu \Delta)^2}, \quad \text{Equation 7-6}
\]

where the upper (lower) sign is for the valence (conduction) bands, \( V_{NT}(x) \) is the potential of the nanotube at position \( x \), \( k \) is the wave vector, \( v_{F,m} = 9.35 \times 10^7 \text{ cm/s} \) is the Fermi velocity of metallic nanotubes, \( \nu = 1 \) for first subbands, \( \nu = 2 \) for second subbands, and \( \Delta \) is half nanotube bandgap. (4) The device capacitance is dominated by capacitance to the gate since the channel length is fairly long compared with gate oxide thickness, and the charge density

\[
q(x) = \pm n(x)e = c_{g,e}(V_{NT}(x) - V_g) \quad \text{Equation 7-7}
\]

is determined locally, where
\[ n(x) = 4 \int dk (f(E(k_x) - \mu_s) + f(E(k_x) - \mu_d)) \]  \hspace{1cm} \text{Equation 7-8}

is the carrier density (the 4 from spin and subband degeneracies), \( k_x \) means \( k \) is in the range of \( k > 0 \) \((k < 0)\), and \( \mu_s \) \((\mu_d)\) is the chemical potential of source \( (\text{drain}) \) contact. (5) Zero temperature. (I believe that the temperature is not critical to the high-bias transport cases; the carriers should be very energetic.) (6) Contact resistance is neglected; i.e. the SBs at the contacts are transparent once the bias across the SBs exceeds one-half the band gap. The quasi-Fermi level of the right \( (\text{left}) \) moving carriers matches the Fermi level of the left \( (\text{right}) \) metal contact. The last two assumptions are reasonable for describing transport at biases greatly exceeding the SB height and the temperature. \( V_{NT} \) and \( n \) at the contacts are determined by satisfying the assumption (3), (4), (6) and bias conditions self-consistently. The current is then calculated by

\[ I = \frac{e}{4} \int dk (f(E(k_x) - \mu_s) + f(E(k_x) - \mu_d))v(k), \]  \hspace{1cm} \text{Equation 7-9}

where \( v(k) \) is described in Equation 7-1 \( (\text{in one dimension}) \). Here, only the lowest conduction bands or highest valence bands are considered to contribute to the current conduction.

The result of the ballistic model for holes as majority carriers is plotted in Figure 7-3(b). At low drain bias, the conductance is \( \frac{4e^2}{h} = 155 \mu\text{S} \), which is the signature of a perfectly ballistic SWNT [130]. Interestingly, this quantized conductance persists only over a small range of bias and gate voltages. At high positive drain bias, the current increases more slowly, with near-constant slope.
\[ \frac{c_{e,e} \frac{4e^2}{h}}{c_{e,e} + c_q} \approx 17 \mu S, \] where \( c_q = e^2D(E) \) is the quantum capacitance, with \( D(E) \) the energy-dependent density of states. Except for Fermi energies very near the band edge [60] \( c_q \) is well approximated by the quantum capacitance of a metallic SWNT \( c_{q,m} = \frac{8e^2}{h\nu_{F,m}} \approx 3.31 \text{ pF/cm} \). (In the ballistic case, only the right-moving branch of the conduction band is filled, and \( c_q = c_{q,m}/2 \approx 1.65 \text{ pF/cm} \).) The crossover from \( G = \frac{4e^2}{h} \) to \( G = \frac{c_{e,e} \frac{4e^2}{h}}{c_{e,e} + c_q} \) occurs once all the available holes in the valence band are moving toward the source at the Fermi velocity. At this point, further increase in the current can only come through increase in the hole density, which is limited by the voltage difference between gate and drain.
Figure 7-3. Comparison between experimental data and simulation for several models with holes as majority carriers. (a) Experimental $I_D$ as a function of $V_D$ at $V_g$ from -9 V to -1 V, in 1 V steps. The thick curve is for $V_g = -9$ V. (b) Ballistic model (c) current saturation model, and (d) velocity saturation model are plotted for the same gate voltages as the experimental data. Note the different vertical scale for (b).
At negative high drain bias, the current saturates because no more holes are added by increasing negative drain bias, since now the amount of holes is controlled by the voltage difference between gate and source.

Figure 7-3 compares the experiment data (reproduced in Figure 7-3(a) from Figure 7-2) with the ballistic model (Figure 7-3(b)) as well as two other models discussed below. The ballistic model reproduces many of qualitative features of the experimental data in Figure 7-3(a): a high conductance region at low bias, saturation at negative bias, and current increasing roughly linearly at positive bias. Particularly the linear increase at positive bias is striking; in conventional metal-oxide-semiconductor FETs (MOSFETs) the current increases supra-linearly at positive bias. The linear increased is easily understood in terms of the nearly constant Fermi velocity in SWNTs at high $E_F$; further increase of the carrier energy does not increase the velocity (and the current).

Quantitative comparison between Figure 7-3(a) and Figure 7-3(b) shows that the current and conductance are significantly higher in the ballistic model than those in the experiment. This is reasonable: since the channel length is tens of microns, we do not expect ballistic transport.

We next examine two models for the field-dependent velocity in the nanotube. In the first, the current saturation model, we assume that the maximum difference in the left- and right-moving quasi-Fermi levels is set by optical phonon scattering at $hf \approx 160$ meV. The current is then limited to $4ef \approx 25 \, \mu A$ as observed in metallic nanotubes [45], and as has been suggested for semiconducting nanotubes [44]. The empirical $I$-$V$ relation
where $I_0 = 25 \, \mu A$ is the saturation current for metallic SWNT, was suggested in Ref. [45]. If we represent this relation in terms of mobility $\mu$ and $F$, we have:

$$
\mu^{-1} = \mu_0^{-1} + ne \left| \frac{F}{I_0} \right|,
$$

where $\mu_0$ is the zero-field mobility and $n$ is the carrier density.

Again using the assumptions above with the average quasi-Fermi level of the carriers in the nanotube near the nanotube/metal junctions matching the Fermi level of the metal contacts, we calculate the current

$$
I(x) = q(x)\mu F(x),
$$

where $F(x) = -\nabla V_{NT}(x)$ and $q(x) = c_{ge}(V_{NT}(x) - V_g)$ are functions of position $x$.

Note that the current $I$ is constant throughout the whole channel (independent of $x$).

The result of the current saturation model for hole conduction is shown in Figure 7-3(c), where the fitting parameters are $I_0 = 25 \, \mu A$ and zero-field hole mobility $\mu_0 = 2.7 \times 10^4 \, cm^2/Vs$. Comparing the calculation (Figure 7-3(c)) with experiment (Figure 7-3(a)), disagreement is seen in several aspects. First, rather than saturating at $25 \, \mu A$ at high positive drain bias, the measured current increases with roughly constant slope. Second, the current at negative bias is larger than that in experiment. $I_0 = 25 \, \mu A$ was chosen assuming only the first valence subbands participate in the conduction and the physics is similar to metallic SWNT; however, no choice of $I_0$ gives a good fit. Specifically, $I_0 = 50 \, \mu A$, which might correspond to two contributing subbands, is significantly worse.
The qualitative agreement of the ballistic model with the measured current suggests that the charge-controlled model of the nanotube transistor, namely $I_d \propto q$, is correct. However, the charges must not move with Fermi velocity, but somewhat slower. In conventional semiconductors, typically the electric-field-dependent carrier velocity is observed to saturate to a constant value at high electric field. Empirically, the carrier mobility often follows Equation 7-3, which means at low $E$-field regime, the carrier velocity $v$ increases linearly with $E$-field with slope $\mu_0$; at high $E$-field, $v$ saturates at $v_s$. Perebeinos, et al. have calculated the electron-phonon interaction within a tight binding model and derived the $\mu$-$F$ relation for a single electron [131], and Equation 7-3 fits their result very well [131]. The calculation of current under the velocity-saturation model is the same as that in the ballistic model except $v = \mu F$, $\mu$ is described by Equation 7-3, and the pinch-off effect is included. Pinch-off happens because the carrier velocity is limited at $v_s$. To maintain constant current in nanotube, the channel needs finite amount of charge even when $V_d$ approaches $V_g$. (The pinch-off effect will be discussed more in the next section.) We include the pinch-off effect in velocity saturation model as follows: when we calculate $I_d$ vs. negative $V_d$, the magnitude of current eventually starts to decrease as $V_d$ is beyond a threshold voltage $V_{d,th}$; i.e. the maximum of $I_d$, $I_{d,max}$, occurs at $V_{d,th}$. The current is fixed at $I_{d,max}$ when $V_d$ is greater than $V_{d,th}$. The same procedure is applied to the source when $V_d$ is positive.

The $I$-$V$ curves of the velocity-saturation model for hole conduction are plotted in Figure 7-3(d), where the fitting parameters are hole saturation velocity $v_s = 2 \times 10^7$ cm/s and zero field hole mobility $\mu_0 = 2.7 \times 10^4$ cm$^2$/Vs. Simply speaking, $\mu_0$
is determined by fitting the current at low drain bias; \(v_s\) is determined by fitting the current at high negative drain bias. The unipolar majority-electron bias regime (\(V_g\) larger than both \(V_d\) and \(V_s\)) is very similar to the majority-hole regime, indicating symmetric conduction and valence band structure. By a similar analysis, we find the electron saturation velocity is also \(\sim 2 \times 10^7\) cm/s. Directly comparing compared the results of modeling (ballistic, current saturation, and velocity saturation) with the experimental data in Figure 7-3, and we find the best agreement with the velocity-saturation model. Also, the reason the currents in s-SWNTs can be higher than 25 \(\mu\)A is that no matter how many the carriers are, all of them move with \(\sim 2 \times 10^7\) cm/s in high electric fields. This also indicates that higher-order subbands participate the carrier transport.

In order to compare the models more quantitatively, we plot in Figure 7-4 the saturation current \(I_{\text{sat}}\) at different \(V_g\) for the experimental data and the current-saturation and velocity-saturation models. Also included is a calculation carried out for a constant hole mobility of 5000 cm\(^2\)/Vs (the \(I_d-V_d\) curves are shown in Figure 7-5). Figure 7-4 shows that the experimental behavior fits the velocity-saturation model very well - the velocity-saturation model predicts linear \(I_{\text{sat}}\) vs. \(V_g\), as seen in the data. The current-saturation model always produces sublinear \(I_{\text{sat}}\) vs. \(V_g\), while the constant-mobility model has \(I_{\text{sat}} \sim V_g^2\) similar to conventional long channel MOSFETs [92]. Note that it is probable that an even better fit in Figure 7-4 might have been obtained for slightly different fitting parameters; the calculations are time consuming, so this has not been done.
Figure 7-4. Saturation current $I_{\text{sat}}$ at different $V_g$ for experimental data and theoretical models discussed in text. $I_{\text{sat}}$ is $I_d$ at $V_d = V_g$.

Figure 7-5. $I_d$ as a function of $V_d$ of constant-mobility model at $V_g$ from -9 V to -1 V, in 1 V steps. The thick curve is for $V_g = -9$ V.
The saturation velocity is smaller than the peak carrier velocity of $4.5 \times 10^7$ cm/s calculated in Ref. [132] for a 2.4 nm diameter nanotube at an electric field of $\sim 5$ kV/cm, and $5 \times 10^7$ cm/s in Ref. [131] using a one-electron model, but is still more than twice as high as in silicon inversion layers [133]. The one-electron model is good for low carrier density cases. However, in the device operation regime, the carrier density is high ($\sim 10^9$ cm$^{-1}$). The measured saturation velocity is lower than the calculated saturation velocity suggests increasing carrier density may reduce the saturation velocity. In Chapter 8, I will discuss how the saturation velocity should decrease with carrier density increase.

Though a simple model of velocity saturation describes the experimental data surprisingly well, some problems remain. First, contact effects are not considered, which causes poor agreement around $V_d = 0$ and $V_g = 0$. In Chapter 10, I will investigate the contact effects of s-SWNT-FETs. Second, the experimental current at high positive drain bias does not increase as fast as expected, indicating that $v_s$ may decrease slightly with increasing charge density. The phenomenological Equation 7-3 fits the one electron case fairly well [131]. However, it is not at all clear whether their results extrapolated to many electrons would give current saturation or velocity saturation (since these are identical in a one-electron model). In Chapter 8, I will explore the carrier behavior in s-SWNTs under the considerations of electron-phonon interactions.
7.4 Carrier-Density and Potential Profiles in Velocity-Saturation Model

In the previous section I modeled a s-SWNT device and found the best agreement with the velocity-saturation model, with a saturation velocity $v_s$ of $2 \times 10^7$ cm/s. Here I would like to discuss more details about the charge distribution and potential profile along the nanotube channel in the velocity-saturation model.

Plugging Equation 7-3 into Equation 7-2, the carrier velocity as function of $F$ in the velocity-saturation model is obtained:

$$v = \mu_0 F \frac{v_s}{v_s + \mu_0 |F|} \quad \text{Equation 7-13}$$

When $F >> v_s/\mu_0$, $v$ approaches $v_s$; When $F << v_s/\mu_0$, $v \approx \mu_0 F$.

Figure 7-6 shows an example of the profiles of band structure, carrier density, and carrier velocity of a s-SWNT channel at $V_d = -1$ V, $V_g = -9$ V. The average electric field is about 0.05 V/µm = 0.5 kV/cm, which is smaller than $v_s/\mu_0 = 0.74$ kV/cm. The overall channel has fairly uniform carrier density due to the potential difference from source to drain is small. The potential drop ($F$), and therefore the carrier velocity, are not varying much as well.
Figure 7-6. Profiles of (a) band structure, (b) carrier density, and (c) carrier velocity in a s-SWNT channel without pinch-off happening ($V_d = -1 \text{ V}$, $V_g = -9 \text{ V}$).

Figure 7-7 shows another example of the profiles at $V_d = -5 \text{ V}$, $V_g = -9 \text{ V}$. The overall potential gradient is higher than the previous example because the magnitude of applied $V_d$ is larger. The average electric field is about 0.25 kV/cm, which is larger than $v_s/\mu_0$. The carrier density and the carrier velocity show pronounced variation along the nanotube channel, by almost a factor of two. The trends of the carrier density and the carrier velocity are inverted because the current is constant through the whole channel. Near the drain contact the carrier density can not go lower.
because the carrier velocity in the velocity-saturation model is limited at $v_s$, no matter how we increase $F$; the carrier density is fixed and the potential is set correspondingly. That means the carriers in the nanotube near the drain contact are very away from equilibrium with the carriers in the drain contact; pinch-off happens. The carriers near the drain contact move with the speed close to saturation velocity $v_s$.

Figure 7-7. Profiles of (a) band structure, (b) carrier density, and (c) carrier velocity in a s-SWNT channel with pinch-off happening ($V_d = -5$ V, $V_g = -9$ V).
The discussions above are for hole conduction. Due to electron-hole symmetry of SWNTs, the electron conduction acts in the same manner.
Chapter 8

Electron-Phonon Interactions in Semiconducting SWNTs

8.1 Overview of Electron-Phonon Interactions in SWNTs

When electrons travel in a crystal material, they usually suffer scatterings so that they lose their phase information, momentums or energies. There are several major scattering sources in solid state systems, such as defects, impurities, lattice vibrations (phonons). In CNTs, especially SWNTs, which are quasi-one-dimensional materials, scattering happens in a special manner. Only forward and backward scattering are available, which largely reduce the scattering probability and make CNTs very good charge conductors. Phase information of traveling electrons, which produces quantum phenomena, is usually lost easily in a very short range, and I will not discuss it here. It is known that CVD growth methods produce nanotubes largely free of defects and impurities [55,134]; in one study, high-quality CVD-grown SWNTs were confirmed to contain one defect per 4 µm on average [134]. Therefore, electron-phonon interactions causing relaxation of electron energies and/or momenta consume many researchers’ efforts in order to understand electronic transport properties in CNTs.

Yao et al. have first studied current saturation of 25 µA at high bias voltages in m-SWNTs and successfully explained the phenomenon in terms of scattering of electrons due to optical or zone-boundary phonon emission [45]. The mean free path of nearly elastic acoustic phonon scattering \( l_{ac} \) is \( \sim 300 \) nm, and the mean free path of optical phonon emission backscattering \( l_{op} \) is \( \sim 10 \) nm from the data fitting. Dai’s
group [47] and McEuen’s group [69] have also confirmed Yao’s conclusions experimentally. Both groups have performed length dependent measurements on m-SWNTs, and extracted the mean free paths at low and high energies (Dai: $l_{ac} \sim 300$ nm, $l_{op} \sim 15$ nm; McEuen: $l_{ac} \sim 1600$ nm, $l_{op} \sim 10$ nm). The current through short (< ~ 150 nm) m-SWNTs can be significant higher than 25 µA [47,69]. Transport through very short (~ 10 nm) m-SWNTs is free of significant phonon scattering and thus ballistic and quasiballistic at the low- and high-bias voltage limits, respectively [47].

Electron-phonon scattering in s-SWNTs has also been studied, at least theoretically. Pennington et al. have studied electron-phonon scattering in a single charge carrier picture, and found out the charge carrier drift velocity can be as high as $5 \times 10^7$ cm/s in s-SWNTs [132]. Negative differential mobility is even predicted at high electric fields [132]. Perebeinos et al. also used a single carrier picture in multiple subbands predicted velocity saturation behavior [131], as discussed in Chapter 7. However, it is not at all clear whether their results extrapolated to many electrons would give current saturation or velocity saturation (since these are identical in a one-electron model). The carrier density in s-SWNT-FETs usually changes according to gate capacitance and voltages. Therefore I would like to discuss the numerical study I have done on carrier velocities under the influences of phonon scatterings in s-SWNTs in different carrier density regimes.

8.2 Numerical Study of Carrier Velocities in s-SWNTs Concerning Electron-Phonon Scatterings in a Single Subband

In solid state systems, the nonequilibrium distribution function $g$ is used to describe the dynamics of the charge carriers (both electrons and holes). In carbon
nanotubes which are one-dimensional materials, the number of electrons in the n-th subband at time $t$ in a phase space volume $dxdk$ at point $(x, k)$ is $2g_n(x, k, t)dxdk/2\pi$ [135], where two is from the spin degeneracy of electrons. In equilibrium, $g$ is given by the Fermi distribution:

$$g_n(x, k, t) = f(E_n(k)) = \frac{1}{e^{(E_n(k) - \mu)/k_BT} + 1}, \quad \text{Equation 8-1}$$

where $E_n(k)$ is the universal energy dispersion of the n-th subband, $k_B$ is Boltzmann constant, $T$ is the temperature. However, when an applied electric field is present, $g$ deviates from Fermi distribution [135]. In this section, I simply consider the carriers in a single subband, so the subscript is dropped for simplicity.

The dynamics of $g$ is governed by Boltzmann equation:

$$v(k)\frac{\partial g(x, k, t)}{\partial x} + \frac{eF}{\hbar} \frac{\partial g(x, k, t)}{\partial k} + \frac{\partial g(x, k, t)}{\partial t} = \left( \frac{dg}{dt} \right)_{\text{collision}}, \quad \text{Equation 8-2}$$

where the right side of the equation is the distribution change rate due to the collisions. In steady state, $\frac{\partial g(x, k, t)}{\partial t} = 0$, and further assuming no carrier density variation along $x$ so that $\frac{\partial g(x, k, t)}{\partial t} = 0$, then

$$\frac{eF}{\hbar} \frac{\partial g(k)}{\partial k} = \left( \frac{dg}{dt} \right)_{\text{collision}}. \quad \text{Equation 8-3}$$

The collision term in Boltzmann equation can be simply described by relaxation lengths if there are multiple sources of scatterings:

$$\left( \frac{dg}{dt} \right)_{\text{collision}} = \sum_{s, k} \frac{v(k)}{l_s} ((1 - g(k))g(k') - g(k)(1 - g(k'))), \quad \text{Equation 8-4}$$
where the first term in right side of Equation 8-4 denotes the carriers scattering in to state \( k \) from state \( k' \), while second term denotes the carriers scattering out from state \( k \) to state \( k' \), and \( s \) stands for different types of scatterings. Here I approximate the electron-phonon scattering into two categories: nearly elastic scattering mainly with low energy acoustic phonons and strongly inelastic scattering mainly with optical phonons or zone-boundary phonons; the scattering strengths are characterized by \( l_{ac} \) and \( l_{op} \), respectively. Figure 8-1 shows approximate electron-phonon scatterings in a single band. The filled and empty circles indicate the states which are occupied and empty, respectively. The arrows indicate some possible scattering transitions. The arrow 1 indicates an elastic electron-phonon scattering, while the arrow 2 and 3 indicate inelastic electron-phonon scatterings. Because the optical phonon energies and zone-boundary phonon energies are all about 160 meV with small dispersion, the emission energy of phonons required by inelastic electron-phonon scatterings is simply set at 160 meV (phonon absorption is not considered because the population of phonons of 160 meV is very small at room temperature). The transitions 1 and 2 toward empty states are permitted; however, the transition 3 toward filled states is prohibited simply because of the exclusion principle.
Figure 8-1. Approximate electron-phonon scatterings in a single band. The filled and empty circles indicate the states which are occupied and empty, respectively. The arrows indicate some possible scatterings. The scatterings toward empty states are permitted; however, the scatterings toward filled states are prohibited simply because exclusion principle.

By solving Equation 8-3, the nonequilibrium distribution function \( g(k) \) corresponding to each \( F \) is obtained. Figure 8-2 shows \( g(k) \) at three different \( F \). Note that the dashed curve represents the Fermi distribution at \( T = 300 \) K, which is symmetric with respect to \( k = 0 \). Under \( F \) the distribution has higher weight in one \( k \) direction than in the opposite, which causes a nonzero average carrier velocity (drift velocity); therefore nonzero current. When \( F \) gets higher, the asymmetry gets more pronounced. \( g(k) \) has a sharp decline at the point where the corresponding energy of the state is about 160 meV when \( F \) is high. This occurs because once carriers have the energies higher than 160 meV, they start to emit phonons and relax to lower energy states.
Figure 8-2. Nonequilibrium distribution function $g(k)$ under different $F$. The dashed curve represents the Fermi distribution at $T = 300$ K. The bandgap of the universal dispersion relation used in this calculation is 0.4 eV.

After obtaining $g(k)$ and then evaluating the average carrier velocity (drift velocity)

$$v = \frac{\sum_k g(k)v(k)}{\sum_k g(k)}$$

Equation 8-5

at many different $F$, the $v$-$F$ relationship can be determined.

First, motivated by experiments in m-SWNTs [45,47,69], we choose values for the numerical calculation of $l_{ac} = 300$ nm and $l_{op} = 10$ nm. Figure 8-3 shows average carrier velocity (drift velocity) $v$ as a function of applied electric field $F$ at different carrier density $n$ with density increasing exponentially from $10^3$ cm$^{-1}$ to $10^7$ cm$^{-1}$ in $10^{0.5}$ cm$^{-1}$ steps. Note that a carrier density of $10^3$ cm$^{-1}$ is identical to one carrier in a 10 µm nanotube. The curves with low carrier densities collapse to a
single curve line with velocity-saturation like behavior. Similar velocity-saturation behavior for a single carrier picture in multi-subbands was predicted by the group [131].

Figure 8-3. $v$ vs. $F$ at different carrier densities with density increasing exponentially from $10^3$ cm$^{-1}$ to $10^7$ cm$^{-1}$ in $10^{0.5}$ cm$^{-1}$ steps. The curves with low carrier densities collapse to a single curve line with velocity-saturation like behavior. As the density greater than threshold density $\sim 10^6$ cm$^{-1}$, the velocity decreases with increasing the density. $l_{sc}$ and $l_{op}$ used for this calculation are 300 and 10 nm, respectively.

Figure 8-4 compares the numerical results to the phenomenological equation of velocity saturation, Equation 7-3, which is also suggested in [131]. The blue star points in Figure 8-4 represent the same numerical calculation data of the curve for $n = 10^6$ cm$^{-1}$ in Figure 8-3. The red dashed curve is the fit using Equation 7-3. They agree with each other fairly well with the fitting parameters $\mu_0 = 8.2 \times 10^3$ cm$^2$/Vs and $v_s = 4.5 \times 10^7$ cm/s, obtained by least-squares fitting. Here we see the velocity-
saturation behavior is preserved in the numerical calculations even at finite carrier densities. However, as the density increases beyond a threshold density $\sim 10^6$ cm$^{-1}$, the velocity decreases with increasing density.

![Graph](image)

**Figure 8-4.** Fitting the calculation result of $v$ vs. $F$ by phenomenological equation of velocity saturation.

Figure 8-5 shows $v$ as a function of $F$ at different carrier densities with density increasing linearly from $10^6$ cm$^{-1}$ to $10^7$ cm$^{-1}$ in $10^6$ cm$^{-1}$ steps. The scattering lengths used here are the same as those in Figure 8-3. Although the velocity still seems to saturate at high $F$, the saturation velocity decreases monotonically with increasing density.
Figure 8-5. $v$ vs. $F$ at different carrier densities with density increasing linearly from $10^6 \text{ cm}^{-1}$ to $10^7 \text{ cm}^{-1}$ in $10^6 \text{ cm}^{-1}$ steps. At high electric fields the velocity decreases with increasing the density. $l_{ac}$ and $l_{op}$ used for this calculation are 300 and 10 nm, respectively.

The blue star points in Figure 8-6 shows $v$ at $F = 100 \text{ kV/cm}$ as a function of carrier density $n$ (a) in logarithmic scale from the data in Figure 8-3, and (b) in linear scale from the data in Figure 8-5. The trend of the saturation velocity with respect to the carrier density is easily noticed. As discussed previously, the saturation velocity does not vary with the carrier density at low carrier densities, but falls nearly linearly at high carrier densities. If Equation 7-4 and current saturation were obeyed, we would expect the saturation velocity to be inversely proportional to carrier density. This is a reasonable expectation when considering only a single valence and conduction subband (excluding inter-subband scattering) and very strong optical phonon scattering; here one might expect the current to saturate 25 $\mu$A at high electric fields, once the difference between quasi-Fermi levels for left- and right-moving
carriers is 160 meV. The red dashed lines in Figure 8-6 indicate the $v$-$n$ relation corresponding to a current of 25 µA. That the calculated (blue star) points are higher than the red dashed lines at high carrier densities and electric fields implies the current is higher than 25 µA. Therefore, in our model, it is possible that the current can exceed 25 µA in s-SWNTs even though phonon emissions are strong and inter-subband scattering is neglected.

![Graph](image)

Figure 8-6. $v$ at $F = 100$ kV/cm as a function of carrier density $n$ (a) in logarithmic scale and (b) in linear scale. The red dashed lines indicate the $v$-$n$ relation corresponding to a current of 25 µA.

Now I would like to explore the effects of varying $l_{ac}$ and $l_{op}$ in the relations of $v$-$F$. Figure 8-7 shows $v$ as a function of $F$ similar to Figure 8-3, but with scattering lengths $l_{ac} = 150$ nm and $l_{op} = 10$ nm. The general qualitative behaviors of velocity saturation in Figure 8-7 and Figure 8-3 are the same. The quantitative difference is that the low field mobility is smaller when $l_{ac}$ is shorter. $l_{ac}$ affects low $F$ transport
more because elastic scatterings do not need high carrier energies to activate. When $l_{op}$ is varied (see Figure 8-8 with scattering lengths $l_{ac} = 300$ nm and $l_{op} = 5$ nm), the qualitative behavior (velocity saturation) is in general not changed as well; however, at high $F$ the saturation velocity increases and the saturation behavior become better when $l_{op}$ gets shorter. $l_{op}$ affects high $F$ transport more because inelastic phonon emissions only happen when carriers have high energies. Also, at high $F$ the saturation velocity *increases* when $l_{op}$ gets shorter because once carriers have energy to emit phonons, they emit right away and relax to low energy states, which have small velocity; in the other words, there are very few carriers at states with velocities in the opposite direction of average carrier velocity. The fitting parameters $\mu_0 = 8.2 \times 10^3$ cm$^2$/Vs and $v_s = 4.5 \times 10^7$ cm/s in Figure 8-4 are a little off from $\mu_0 = 2.7 \times 10^4$ cm$^2$/Vs and $v_s = 2 \times 10^7$ cm/s of experimental results. The variance of $\mu_0$ suggests that $l_{ac}$ is longer than 300 nm in the experimental sample discussed in Chapters 6 and 7. This is not surprising; low-field mobility is expected to a strong function of diameter [132,136], and also likely varies depending on processing conditions. The discrepancy of $v_s$ I believe is mostly due to the fact that the carrier density is $10^6$ cm$^{-1}$ in Figure 8-4, but order of $10^7$ cm$^{-1}$ in the experiments described in Chapter 7, hence the carrier-density-dependence of the velocity should be taken into account to better understand the data.
Figure 8-7. \( v \) vs. \( F \) at different carrier densities with density increasing exponentially from \( 10^3 \text{ cm}^{-1} \) to \( 10^7 \text{ cm}^{-1} \) in \( 10^{0.5} \text{ cm}^{-1} \) steps. \( l_{ac} \) and \( l_{op} \) used for this calculation are 150 and 10 nm, respectively.
Figure 8-8. $v$ vs. $F$ at different carrier densities with density increasing exponentially from $10^3$ cm$^{-1}$ to $10^7$ cm$^{-1}$ in $10^{0.5}$ cm$^{-1}$ steps. $l_{ac}$ and $l_{op}$ used for this calculation are 300 and 5 nm, respectively.

I have considered expanding my numerical study to the multi-subband case. However, while I was working on this subject, IBM group published their results on it [137]. They have calculated the mobility in s-SWNTs as a function of carrier density and electric field, for different tube diameters and temperatures. They have found that at a critical density, $n_c$ about $3.5$ to $5.0 \times 10^6$ cm$^{-1}$, the average carrier velocity saturates at about one-third of the Fermi velocity of graphene. Below $n_c$, the velocity reaches a maximum and then experiences negative differential mobility with increasing field. Above $n_c$, the velocity increases with field strength with no apparent saturation, which is also seen in my numerical calculation for the lowest conduction band or highest valence band transport. It is interesting that my simple model produces many features of the more detailed calculations of [137]; this indicates that I have indeed captured the essential physics of scattering in s-SWNTs in my model.

Theorists have predicted negative differential conductance or negative differential mobility in s-SWNTs at high-bias transport [131,132], which is not shown in my numerical study. One of the reasons is that for simplicity of my study the electronic dispersion relation is approximated by universal dispersion relation [18], where the carrier velocity is asymptotically approach to the Fermi velocity of graphene as energy increases (see Equation 1-4). However, the real electronic band structures flattens at very high energies. Figure 8-9 show the comparison between the universal dispersion relation and a more accurate dispersion relation derived by tight
binding calculation and zone folding method for (7, 0) s-SWNT. We see that the universal dispersion relation is a very good approximation to the tight binding calculation, but yet there is still some small discrepancy between them. The universal dispersion relation has non-negative curvature; the dispersion relation derived by tight binding calculation and zone folding method shows negative curvature. Therefore, as more and more carriers have very high energies, the average velocity decreases, causing negative differential conductance or negative differential mobility. Another possible reason is that my calculation restricts at single subband, no band edges of higher subbands are available; however they are available in multi-subband calculation.

Figure 8-9. Comparison between the universal dispersion relation and the dispersion relation derived by tightbinding calculation and zone folding method for (7, 0) SWNT.
Recently Pop et al. [138] have experimentally observed negative differential conductance in freely suspended SWNTs (both m-SWNTs and s-SWNTs) but not in those lying on substrates. But here the reason is not simply because of the negative curvature of the bands, but rather because of significant self-heating effects including electron scattering by hot nonequilibrium optical phonons [138,139]; there is no thermoconductivity through the substrates in freely suspended SWNT devices. Lazzeri et al. [139] predict an effective temperature for optical phonons of thousands of Kelvins. Hot phonon scatterings thus can reveal more about high bias transport in SWNTs.
Chapter 9

High-Bias Transport of Semiconducting SWNTs in the Ambipolar Regime

9.1 Introduction and Experimental Results

Semiconducting SWNTs have almost identical conduction and valence bands near the Fermi level as described in Chapter 1. It is possible to inject electrons and holes from the contacts into the s-SWNT at same time if the applied bias to the s-SWNT is larger than the bandgap of the s-SWNT [46,49,128]. Electrons are injected from one contact into the s-SWNT and holes are injected from the other [46,49,128]. When electrons and holes meet in the channel, they recombine rapidly due to strong Coulomb interaction between them [92,135,140]. Part of the energy they carry will be relaxed during the recombination. It is possible to emit light (photons) because the s-SWNT bandgap is direct, and the momentum of a photon is small, which conserves the momentum in the process. The process is usually referred as “light recombination”. IBM research group have demonstrated optical emission in infrared range induced electrically from s-SWNT devices [49,127,129]. Sometimes recombination relaxes energy in other ways, such as phonons. It is called as “dark recombination”. The efficiency of the radiative recombination has been found to be quite low; about $10^6$ to $10^7$ photons per electron-hole pairs [141] for the devices with substrates. More recently, it was found that the partially suspended nanotubes exhibit
an increase of 2 to 3 orders of magnitude from the nanotubes with substrates [142], resulting the efficiency about $10^{-3}$ to $10^{-4}$.

Sometimes the recombination involves three charged particles, two electrons plus one hole or one electron plus two holes; the electron-hole pair annihilates and gives its energy to the additional particle. Such a process is called Auger recombination. Although the probability for three particles to meet is smaller than for two particle processes, Auger recombination is still sometimes favorable because the energy and the momentum are conserved easily.

Above discussions are all based on an independent charge picture, where charges do not interact with each other. However, one electron and one hole in s-SWNTs have been predicted to bind together to form an exciton due to Coulomb interaction [143-147], which lower the total electronic energy of the system. When excitons are involved in the recombination, two particles participate in Auger recombination: one excition plus one free charge, or two excitons. The exciton energy is large (order of 100 meV in s-SWNTs) due to nanotube’s 1D nature, which severely modulate the light emission spectrum away from the energy gap [148,149]. The evidence of exciton existence in s-SWNTs is found in femtosecond transient absorption optical spectroscopy measurements [150] and suggested in fluorescence spectroscopy experiments [148,151].

In Chapter 6, I have briefly described that we are able to inject both electrons and holes into a s-SWNT when applying $V_d < V_g < V_s$ (for injecting electrons from drain and holes from source) or $V_d > V_g > V_s$ (for injecting electrons from source and holes from drain). In this chapter I would like to provide another evidence of
electron-hole recombination indeed happens in s-SWNTs by transport measurement and device modeling.

Figure 9-1(a) shows $I_d$ as a function of $V_g$ at $V_d = -1$ V from the device whose unipolar data are described in Chapter 7. This device behaves as an ambipolar semiconductor although p-type (hole) conduction is slightly better than n-type (electron) conduction. Because of the ambipolar behavior, we assume the presence of SBs at the electrodes for electrons and holes, but a smaller SB for holes. The maximum transconductances $g_m$ for holes and electrons are $\sim 2.5$ and $2.0 \, \mu\text{A/V}$, respectively, which correspond to field-effect mobilities $\mu_{\text{FE}} \approx 2.5 \times 10^4$ and $2.0 \times 10^4 \, \text{cm}^2/\text{Vs}$ (here we have used the electrostatic gate capacitance per length $c_{\text{g-e}} \approx 2\pi\varepsilon\varepsilon_0/\ln(4t/d) \approx 0.2 \, \text{pF/cm}$ where $\varepsilon_0$ is the electric constant, $\varepsilon \approx 2.45$ the average dielectric constant of the oxide and vacuum). (The field effect mobility $\mu_{\text{FE}}$ is slightly smaller than the zero-field mobility $\mu_0 = 2.7 \times 10^4 \, \text{cm}^2/\text{Vs}$ determined using the data in the range $-0.1 \, \text{V} < V_d < 0.1 \, \text{V}$ discussed in Chapter 7, due to finite $V_d = -1$ V used here.) The on-state conductances $G \approx 13$ and $7 \, \mu\text{S}$ for hole and electron indicate mean-free-paths $l = LG/2G_0$ of at least 1.6 and 0.9 $\mu$m. These values are comparable to the highest measured values for SWNTs [28] though contact resistance due to SBs may play a significant role in this case. In fact, large $V_d$ and large voltage difference between gate and the contacts are needed such that the SBs are thinning enough to be transparent for charges to tunnel through. Figure 9-1(b) shows $I_d$ as a function of $V_g$ at $V_d = 20 \, \text{mV}$, illustrating p-conduction is much better than n-conduction at relatively low drain biases due to the high and thick SBs for n-conduction. The maximum hole transconductance is $\sim 0.1 \, \mu\text{A/V}$, which corresponds
to $\mu_{FE} \approx 5 \times 10^4 \text{ cm}^2/\text{Vs}$. The on-state $G \approx 20 \mu\text{S}$ indicates a mean-free-path $l$ at least 2.5 $\mu$m. ($\mu_{FE}$ and $G$ derived from Figure 9-1(b) is larger because $V_d$ is smaller and the temperature is lower; presumably fewer scatterings happen in this measurement.)

Figure 9-1. Drain current $I_d$ as a function of gate voltage $V_g$ (a) at drain voltage $V_d = -1 \text{ V}$ and temperature $T = 4.2 \text{ K}$, and (b) at $V_d = 20 \text{ mV}$ and $T = 1.5 \text{ K}$. The solid and dashed lines correspond to linear (left) and logarithmic (right) scales, respectively. The dotted line in (b) corresponds to a transconductance of 0.1 mA/V.
Figure 9-2(a) shows $I_d$ vs. $V_g$ at different $V_d$. Here, as usual, the gate voltage is measured relative to the grounded source electrode. Figure 9-2(b) shows the same data plotted with the gate voltage measured relative to the drain electrode. In each case we subtract from $V_g$ the value $V_{off} = 0.7$ V in order to make Figure 9-2(a) and Figure 9-2(b) appear symmetric under reversal of the horizontal axis. They are symmetric because the source and the drain contacts are identical; they are called source or drain contact only according to where the ground and the bias are applied respectively. We interpret $V_{off}$ as the gate voltage at which the center of the nanotube is charge-neutral; it is non-zero due to the work function difference of the nanotube with respect to the Si substrate and metal electrodes, and likely also includes contributions from charges in the dielectric [29] and/or doping of the nanotube by adsorbates [8]. We define $V_{g'} = V_g - V_{off}$. In Figure 9-2, the currents in the ambipolar region are shown by solid lines, while the currents in the unipolar regions are shown by dashed lines. As noted in Chapter 6, the minimum current appears at $V_{g'} = V_d/2$, which is clearly seen in Figure 9-2. Also, the curves with high $V_d$ collapse into a curve at negative $V_{g'} - V_s$ in Figure 9-2(a) and at positive $V_{g'} - V_d$ in Figure 9-2(b) because the current saturation due to pinch-off effect in unipolar range described in Chapter 7 and strong electron-hole recombination, which will be described next.
Figure 9-2. Drain current $I_d$ as a function of gate voltage $V_g$ at drain voltages $V_d$ from -1 V to -9 V, in -2 V steps. Temperature is 4.2 K. The gate voltage in (a) is measured relative to the grounded source electrode, while (b) shows the same data plotted with the gate voltage measured relative to the drain electrode. In each case we subtract from $V_g$ the value $V_{off} = 0.7$ V. The currents in ambipolar regions are shown by solid lines, while the currents in ambipolar regions are shown by dashed lines.

It is notable that the gap in conduction between unipolar electron conduction and unipolar hole conduction at low bias (e.g. $V_d = -1$ V in Figure 9-2) is significantly larger than the bandgap ($\sim 350$ meV for this sample). I assume that this is due to the SB contacts, which do not conduct until a finite bias is applied across them. I model
this with a parameter $V_c$; the contacts are opaque for biases less than $V_c$, and once the bias across the contact exceeds $V_c$, the contacts are considered to be transparent. When both $|V_{g'} - V_d|$ and $|V_{g'} - V_s|$ are smaller than the threshold voltage $V_c$ to overcome the SB, both hole current $I_h$ (the left branches) and electron current $I_e$ (the right branches) are in the off state or in the subthreshold region (remember $V_s = 0$ all the time). When $V_{g'} - V_d$ (or $V_{g'} - V_s$) is smaller than $-V_c$ the hole current starts to flow in the linear region, and likewise for the electron current when $V_{g'} - V_s > V_c$ (or $V_{g'} - V_d > V_c$). Once $|V_d| > 2V_c$, there is no longer a conduction gap because at least one of the hole current ($I_h$) and electron current ($I_e$) is in the linear region, but a conduction dip with minimum at $V_{g'} = V_d/2$ instead, where $I_h = I_e$. (From Figure 9-2, $V_c$ is estimated about 1.3 V.) The data suggests that the total current through the device $I_d \neq I_h + I_e$ but rather $I_d = \max(I_h, I_e)$ indicating nearly complete recombination of electrons and holes. This is consistent with recent reports [127,141,152] demonstrating that holes and electrons efficiently combine in the nanotube radiatively or irradiatively. Photoexcited carrier lifetimes in nanotubes attributed to interband carrier recombination are reported [152] to be 5 ~ 20 ps, much shorter than the carrier transit time in our device of ~ 100 ps, which is the channel length $L$ divided by the carrier saturation velocity.

The discussion above helps us to understand the device behaviors in ambipolar regions only very qualitatively. A more dedicated device modeling like that described in Chapter 7 is needed to have a more complete understanding of the devices operated in ambipolar regions.
9.2 Device Modeling

The modeling device geometry is described in Chapter 7, with \( L = 20 \, \mu m, d = 2.4 \, nm, \) and \( t = 500 \, nm, \) to match the geometry of the device whose transfer characteristics are shown in Figure 9-1 and Figure 9-2. Also as customary, \( V_d \) and \( V_g \) are applied to the drain and the gate, respectively, and the source is grounded \((V_s = 0)\). The contact effects are entirely neglected in the modeling; we assume that at large \( V_d \) and large voltage difference between gate and the contacts the SBs are thinned enough to be transparent for charges to tunnel through easily. The contact effects will be further addressed in Chapter 10.

Considering there are both electrons and holes existing in the channel, the charge density (charge per unit length) contributed by electrons and holes are

\[
q_e(x) = -en_e(x) \quad \text{and} \\
q_h(x) = en_h(x)
\]

Equation 9-1

respectively, where \( n_e(x) \) and \( n_h(x) \) are the electron and hole carrier densities, respectively. (Note that electrons have negative charges.) The total charge density

\[
q(x) = q_e(x) + q_h(x) = e_{ee}(V_{NT}(x) - V_g).
\]

Equation 9-2

The electron and hole flow rates are

\[
J_e(x) = n_e(x)\mu(-F(x)) \quad \text{and} \\
J_h(x) = n_h(x)\mu F(x),
\]

Equation 9-3

where \( F(x) = -\nabla V_{NT}(x). \) (Note that electrons move opposite to the direction of \( F(x) \).) Here I use the result from velocity-saturation model illustrated in Chapter 7 and 8 to the carrier velocity under the influence of \( F(x) \):
\[ \mu(x) = \frac{\mu_0 v_x}{v_x + \mu_0 |F(x)|} \]

Equation 9-4

(the same as Equation 7-3 and Equation 7-13). The total current is also contributed by electron and hole currents

\[ I = I_e(x) + I_h(x), \]

Equation 9-5

where

\[ I_e(x) = -eJ_e(x) = en_e(x)\mu F(x) \]

and

\[ I_h(x) = eJ_h(x) = en_h(x)\mu F(x). \]

Equation 9-6

(In our device definition, the current \( I_d \) flowing from drain to source is measured, which is toward the negative direction in our device modeling; therefore \( I_d = -I \).)

In the absence of recombination, carrier continuity in steady state gives

\[ \frac{\partial J_e(x)}{\partial x} = \frac{\partial J_h(x)}{\partial x} = 0. \]

Equation 9-7

However, if electron-hole recombination is considered, then

\[ \frac{\partial J_e(x)}{\partial x} = \left( \frac{dn_e}{dt} \right)_{\text{recombination}} \]

and

\[ \frac{\partial J_h(x)}{\partial x} = \left( \frac{dn_h}{dt} \right)_{\text{recombination}} \]

Equation 9-8

where \( \left( \frac{dn_e}{dt} \right)_{\text{recombination}} \) and \( \left( \frac{dn_h}{dt} \right)_{\text{recombination}} \) are the electron and hole density change rates due to recombination, respectively. If the independent charge picture is applied and a single recombination process involves one electron and one hole, then electron and hole density change rates equal the recombination rate:
\[
\frac{\left( \frac{dn_e}{dt} \right)_{\text{recombination}}}{\left( \frac{dn_h}{dt} \right)_{\text{recombination}}} = -k(n_e(x)n_h(x) - n_i^2), \quad \text{Equation 9-9}
\]

where \( k \) is the recombination constant, and \( n_i \) is the intrinsic carrier density which only depends on temperature. The carrier density change rates due to recombination are negative because the carriers disappear when they recombine.

Putting all these things together with the average quasi-Fermi level of the carriers in the nanotube near the nanotube/metal junctions matching the Fermi level of the metal contacts, the current are evaluated in ambipolar bias conditions. Figure 9-3(b) shows the calculated currents in different ambipolar bias conditions with parameters \( v_s = 2 \times 10^7 \text{ cm/s}, \mu_0 = 2.7 \times 10^4 \text{ cm}^2/\text{Vs}, k = 5 \times 10^6 \text{ cm}^2/\text{s} \) and \( n_i = 10^4 \text{ cm}^{-1} \). The calculated currents in Figure 9-3(b) reproduce many features of measured results in Figure 9-2: (1) as we expected from the discussion and the measured result in previous section, there is a current minimum for each \( V_d \) at the symmetric bias \( (V_g = V_d/2) \); (2) the current increases roughly linearly after away from the symmetric bias; (3) the displacement between each curve is nearly the same. (1) results from electron-hole recombination, while (2) and (3) result from the charge carriers having velocity-saturation behavior.
Figure 9-3. Calculated (a) position of the strong recombination and (b) current as a function of $V_g$.

Figure 9-4 shows the calculated (a) potential profiles, (b) recombination rate profiles, and (c) electron current and hole current profiles of a s-SWNT device along channel position $x$, which give more details to understand the device (the parameters are all the same as those used in Figure 9-3). Note that the colors of the curves in Figure 9-4 correspond to the biases at the points with the same color dots in Figure 9-3(b). We first look at the blue curves, which show the device is under a symmetric
bias situation \((V_d = -5 \text{ V}, \ V_g = -2.5 \text{ V})\). The first expression is that all blue curves are symmetric about \(x = 10 \mu\text{m}\), the middle of the channel, as anticipated. At the middle of the channel, several phenomena are observed: (1) \(V_{NT} = V_g\); (2) the largest potential gradient; (3) the largest recombination rate; (4) \(I_e = I_h\). This is because the majority and minority carriers swap roles here, and thus the multiplication of the electron and hole densities in Equation 9-9 is the largest. Thus we observe that under a symmetric bias situation, at the middle of the channel (1) the electric field is the largest; (2) the carriers move the fastest.
Figure 9-4. Profiles of a s-SWNT device along channel position $x$. (a) Potential. (b) Recombination rate. (c) Electron current and hole current. $V_d = -5$ V are all the case. Different colors indicate different gate bias (cyan, red, blue, green, and magenta indicate $V_g = -0.5$ V, -1.5 V, -2.5 V, -3.5 V, and -4.5 V, respectively). In (c), the dashed and dotted lines represent electron and hole currents, respectively. Note that the blue lines shows a symmetric bias case ($V_g = V_d/2$).

When $V_g$ is tuned, the position of the symmetric axis shifts. The red ($V_d = -5$ V, $V_g = -1.5$ V) curves in Figure 9-4 indicate $V_g$ is tuned toward $V_s$, and thus the
symmetric axis shifts toward source contact. Similar results are shown in the cyan curves, while reverse results are shown in the green and magenta curves, where $V_g$ is tuned toward $V_d$ and the symmetric axis shifts towards the drain. Figure 9-3(a) shows how fast the position of the symmetric axis ($L_m$) shifts as a function of $V_g$. It moves relatively fast around the symmetric $V_g$ bias, and slows down away from the symmetric $V_g$ bias. Figure 9-3 matches the electroluminescence experiments in Ref [153], in which the position of localized light emission from a s-SWNT was measured, very well. Also, the recombination range expected from Figure 9-4(b) is about several µm, which is the same order of the electroluminescence light spot due to electron-hole recombination [49].

Calculated band diagrams of a s-SWNT device are plotted in Figure 9-5 to summarize the results from the modeling. Figure 9-5(a) shows a band diagram with a symmetric bias ($V_d = -5$ V, $V_g = -2.5$ V) while Figure 9-5(b) shows a band diagram away from the symmetric bias ($V_d = -5$ V, $V_g = -1.5$ V). The arrows are symbols of electron-hole recombination, and in the regions marked by dashed ellipses strong recombination happens.
Figure 9-5. Calculated band diagrams of a s-SWNT device at (a) $V_d = -5$ V, $V_g = -2.5$ V (symmetric bias) and (b) $V_d = -5$ V, $V_g = -1.5$ V. The arrows are symbols of electron-hole recombination, and in the regions marked by ellipses strong recombination happens.

I have also tried the modeling with three-independent-charge Auger recombination, whose recombination rate is proportional to

$$n_e^2(x)n_h(x) + n_e(x)n_h^2(x) = (n_e(x) + n_h(x))n_e(x)n_h(x).$$  

Equation 9-10

The results of the modeling are similar to those of two-independent-charge recombination. The main reason for that is $n_e(x) + n_h(x)$ varies only very slightly

129
through the whole nanotube since the current is identical and the carrier velocity is always close to saturation velocity at large electric fields through the whole nanotube.

While I was doing the device modeling in ambipolar regimes, there were two other groups executing the same device modeling [153,154]. IBM used an infinite recombination rate, which makes the electric field infinite and produces other unphysical results at the position where $V_{NT} = V_g$. [153]. And although Guo et al. properly considered the recombination rate, the carrier velocity is described by a constant mobility [154], which is non-realistic at high bias regimes. Therefore, my modeling results should be more realistic than theirs.

9.3 Using EFM to Detect Electron-Hole Recombination in s-SWNTs

From the modeling of the previous section, we have found that potential slopes are larger at strong electron-hole recombination regions and that the region of largest slope shifts when $V_g$ is altered. This indicates that electron-hole recombination can be studied indirectly by measuring the potential profile in the nanotube. One tool for this is EFM, which I have discussed already in Chapter 3. In this section I would like to show an example of how I attempted to measure the local potential of a s-SWNT device in the ambipolar regime using EFM.

Figure 9-6(a) shows an AFM image of a s-SWNT with two metal contacts. The nanotube is not visible in the height scale because the diameter is ~ 4 nm but the contact height is ~ 100 nm. Because its diameter is large, this nanotube should have a small band gap; the expected energy gap for a 4 nm s-SWNT is 210 meV. Figure 9-7 shows the transfer characteristic of this s-SWNT device. The current is somewhat larger than the current of the device in Figure 9-2. EFM is performed on this device
with different biases. Figure 9-6(b) shows an exemplary EFM image at $V_{\text{top}} = -0.2$ V, $V_{\text{bottom}} = -2.2$ V, $V_{g} = -0.2$ V and $V_{\text{ac,tip}} = 0.2$ V. It is clearly seen that the EFM signal is increasing from the top to the bottom, which indicated that the potential is varying along the nanotube. Note that the biases in Figure 9-6(b) are equivalent to holding $V_{\text{top}} = 0$ and applying $V_{\text{bottom}} = -2$ V and $V_{g} = 0$. In the measurement I held $V_{g} = -0.2$ V and varied $V_{\text{top}}$ and $V_{\text{bottom}}$ at the same amount in order to minimize the voltage difference between the tip and the substrate; however, they are equivalent to holding $V_{\text{bottom}} = -2$ V and $V_{g} = 0$ and varying $V_{g}$.
Figure 9-6. Potential profiles deducted from AC-tip-EFM images of a s-SWNT device. (a) An AFM image of a s-SWNT with two metal contacts. The scan range is $5.3 \times 8.1 \ \mu m^2$. (b) An exemplary EFM image at $V_{\text{top}} = -0.2 \ \text{V}$, $V_{\text{bottom}} = -2.2 \ \text{V}$, $V_g = -0.2 \ \text{V}$. (c),(d) The potential profiles along the nanotube for different $V_{\text{top}}$ and $V_{\text{bottom}}$. $V_{\text{top}}$ and $V_{\text{bottom}}$ of each curve are shown as flat potentials in the contact regions ($x < 0$ for the top contact and $x > 7 \ \mu m$ for the bottom contact). Note that $V_g = -0.2 \ \text{V}$ and $V_{\text{ac,tip}} = 0.2 \ \text{V}$ are hold constant.

![Graph showing transfer characteristic](image)

Figure 9-7. Transfer characteristic of a s-SWNT device with small band gap. The measurement was done at room temperature in vacuum (base pressure $P_b = 3.8 \times 10^{-7} \ \text{torr}$).

Figure 9-6(c) and Figure 9-6(d) shows the potential profiles along the nanotube drawn from AC-tip-EFM images for different $V_{\text{top}}$ and $V_{\text{bottom}}$ and fixed $V_g = -0.2 \ \text{V}$. $V_{\text{top}}$ and $V_{\text{bottom}}$ of each curve are shown as flat potentials in the contact regions ($x < 0$ for the top contact and $x > 7 \ \mu m$ for the bottom contact). The curves correspond to $V_g$ moving from -2 V to 2 V in 1 V steps and sustaining $V_{\text{top}} = -2 \ \text{V}$ and $V_{\text{bottom}} = 0$ (Figure 9-6(c)), or $V_{\text{top}} = 0$ and $V_{\text{bottom}} = -2 \ \text{V}$ (Figure 9-6(d)). The potentials vary monotonically as expected, and the potential drops at the contacts are
not dominant; the nanotube is resistive. However, the large variation in potential gradient expected (see Figure 9-5) is not observed. There is no clear trend of potential variation shifts when regulating $V_g$. Several rounds on this device and other devices were tested, but I still failed to observe the effects shown in Figure 9-5. The most likely explanation is simply that the nanotube is not much longer than the recombination length, so the spatial variation of slope changes cannot be seen.

9.4 Indirect Proof of Electron-Hole Recombination in s-SWNTs by SGM

From the discussions in Chapter 3, we know a conducting AFM tip can serve as a local voltage variation probe, and the study of the transport responses of devices to the probe is called SGM. In this section I will discuss application of this technique to s-SWNT devices in the ambipolar transport regime to indirectly study electron-hole recombination.

Figure 9-8 shows a transfer characteristic of a s-SWNT device with $d = 2.7 \text{ nm}$, and $L \sim 6 \mu\text{m}$. The inset shows the AFM image of the device. Again the nanotube is not visible because of the height scale. Therefore, a dashed line is used to highlight where the nanotube is. The device shows fairly symmetric electron and hole behaviors. The blue and red lines are a guide to the eye to indicate the qualitative behavior of the electron and hole currents. The double-side arrow roughly shows the $V_g$ range where both electron and hole currents are significant. SGM of this device is operated in this range.
Figure 9-8. Transfer characteristic of a s-SWNT device. The measurement was done at room temperature in vacuum (base pressure $P_b = 6.5 \times 10^{-7}$ torr). The blue and red lines help to guide the sight of the electron and hole currents. The double-side arrow shows the $V_g$ range to operate SGM. The inset shows the AFM image of the device. The dashed line in the inset highlights where the nanotube is.

Figure 9-9 shows DC-SGM images with device transport schemes. The color scale is the device DC current. Bright spots in the images mean the current of the device is boosted when the tips above such positions. $V_{tip} = -4$ V, $V_{top} = -8$ V and $V_{bottom} = 0$ are fixed for all images. $V_g$ from (a) to (g) is varied around the symmetric bias from -4.5 V to -3.3V in 0.2 V steps.
Figure 9-9. DC-SGM images with device transport schemes. The color scale is the device DC current. $V_{tip} = -4$ V, $V_{top} = -8$ V and $V_{bottom} = 0$ are fixed for all images. $V_g$ from (a) to (g) is varied from -4.5 V to -3.3V in 0.2 V steps. The device transport schemes are corresponding to the images on the left.

Figure 9-9(d) represented the symmetric bias situation ($V_g = -3.9$ V). There are two bright spots above the nanotube near the top and the bottom contacts. The phenomenon is easy to understand in terms of electrons and holes simultaneously injected to the nanotube; electrons are injected from the top contact, while holes from the bottom. When the tip is close to the nanotube near the top contact, the tip voltage
$V_{\text{tip}} = -4 \text{ V}$ is positive with respect to the top contact voltage $V_{\text{top}} = -8 \text{ V}$, and thus the tip enhances the electron current from the top contact $I_{e,\text{top}}$, probably by thinning the SB at the top contact. Similarly, the tip voltage $V_{\text{tip}} = -4 \text{ V}$ is negative with respect to the bottom contact voltage $V_{\text{bottom}} = 0 \text{ V}$, and the tip enhances the hole current from the bottom $I_{h,\text{bottom}}$ when the tip is close to the nanotube near the bottom contact. Because of the high recombination of electrons and holes, the total current through the device $I_d \approx \max(I_{e,\text{top}}, I_{h,\text{bottom}})$. In the case, $I_{e,\text{top}}$ and $I_{h,\text{bottom}}$ have similar magnitudes (see the sketch next to Figure 9-9(d)), so raising either of them will enhance the total current. Hence the tip always enhances conductance of the device whenever the tip is above the nanotube near the contacts. Analogous circumstances happen when $V_g$ is not very far away from the symmetric situation (see Figure 9-9(b), (c), (f), and (g)).

However, when $V_g$ is far away from the symmetric situation, things start to change. In Figure 9-9(a) only one bright spot appears on the nanotube near the bottom contact when $V_g \approx -4.5 \text{ V}$. The reason for that is $I_{h,\text{bottom}} \gg I_{e,\text{top}}$ due to the potential difference between the gate and the nanotube near the bottom contact is much larger than that between the gate and the nanotube near the top contact (see the sketch next to Figure 9-9(a)). Since $I_d \approx \max(I_{e,\text{top}}, I_{h,\text{bottom}})$, when $I_{h,\text{bottom}}$ is enhanced by the tip, $I_d$ increases and a bright spot appears on the nanotube near the bottom contact, but when $I_{e,\text{top}}$ is enhanced by the tip, $I_d$ stays the same as $I_{h,\text{bottom}}$ so no clear feature appears on the nanotube near the top contact. The same arguments can be applied to the case in Figure 9-9(g).
From the arguments in this section, several of our assumptions about s-SWNTs can be confirmed by this SGM study: (1) Both electrons and holes can be injected into s-SWNTs simultaneously around symmetric biases. (2) The total current is determined by the currents (charges) near the contacts. (3) Variation of nanotube potentials near the contacts affects the currents (charges) near the contacts. (4) Nearly perfect electron-hole recombination happens, at least for devices of this length ($L \sim 6 \mu m$).
Chapter 10

Contacts to Semiconducting SWNTs

10.1 Overview

Semiconducting SWNTs have advantageous materials properties for FET applications: intrinsic nanoscale dimensions (i.e. “ultra-thin body”) [155], high mobility [28], and high carrier velocity [46]. These advantages come from the bulk properties of s-SWNTs. However, as in normal semiconductors, the contacts are always an issue to be considered. In general, Schottky barriers (SBs) are formed between metal electrodes and a s-SWNT. In contrast to conventional planar bulk semiconductor junctions, the depletion width for nanotubes varies exponentially with inverse doping [156]. In addition, ineffective screening of the long-range Coulomb interaction in 1D nanotube contacts makes a very long-range (logarithmic) tail in the charge distribution [116,156]. These effects in s-SWNTs have been suggested to open new possibilities for device design [156].

As-fabricated s-SWNT in an FET geometry (SWNT-FETs) are typically found to be p-type [16,17], and doping was originally assumed to be the cause. Tans et al. [16] argued that SWNT-FETs were p-type due to doping by the electrodes (i.e. negative SB), while the IBM group [17] argued that the positive threshold indicated a uniform p-doping of the nanotube itself, such as by adsorbed oxygen [8]. However, until now in the literature the only evidence for doping in nanotube devices is the positive threshold voltage.
Later the group of Avouris et al. posited that p- vs. n-type behavior was determined entirely by the SWNT/electrode interface [157,158], and explicitly rejected doping. They also argued that the effect of oxygen is to reduce the SB height of the SWNT/electrode interface [159,160]. Avouris et al. modeled the (short-channel) s-SWNT-FET as a ballistic Schottky barrier FET (SB-SWNT-FET), in which the conductance is modulated by the gate field through narrowing of the SBs through which electrons tunnel [157]. SB-SWNT-FETs thus display unusual vertical scaling [161], large subthreshold swings [28,158], and ambipolar behavior [46,128,162]. (Subthreshold swing S is defined as \((d\log I_d/dV_g)^{-1}\) for a FET in the exponential turn-on regime. SB-SWNT-FETs have an exponential turn-on (due to the narrowing of the SBs) that occurs when the Fermi level lies within the band. This is referred to as “subthreshold” behavior, but is not subthreshold because in the SB device there are already holes present in this region.) Even though they rely on tunneling, high on-currents may be realized in SB-SWNT-FETs with thin gate dielectrics, due to the nanoscale diameter of s-SWNTs and their small effective mass. More recently negative SB height “ohmic” contacts to nanotubes have been established through the use of other metals (e.g. Pd) [44], and provide another route to high on-currents, and additionally provide near-ideal subthreshold swings.

It appears that in the literature there is no uniform agreement of nanotube p-type behaviors in air: whether nanotubes are p-doped or p-type behaviors were only determined by the SB heights at the SWNT/electrode interfaces. Also, whether doping is a major factor in device performance is far from settled. In this chapter, we will resolve the uncertainty of nanotube p-type behaviors in air by showing that the
observed p-type behavior cannot be explained by contact work function, but is instead to be due to doping of the nanotube. Moreover, we will show that, in addition to SB-SWNT-FETs with thin dielectrics, and negative SB contacts (e.g. Pd), doping provides a third route to obtain high on-currents in a SWNT-FET. Modest doping of the SWNT narrows the SBs and provides a high-conductance tunnel contact from electrode to SWNT. This tunnel contact is “ohmic”: in the on-state its conductance does not depend strongly on temperature or gate or drain voltages [70], though in the off-state it provides poor subthreshold swings [155].

10.2 Electrical Heating

SWNTs were grown using a CVD process and device fabrication is the same as that described in Chapter 2. Electrical measurements were performed by grounding the source electrode \( V_s = 0 \) and applying \( V_d \) to the drain, and \( V_g \) to the gate, while measuring the drain current \( I_d \) in a \(^4\)He cryostat or in ambient. High electrical bias (up to \( \pm 50 \) V) is applied to s-SWNT devices in vacuum, causing electrical heating due to high power dissipation (> 1 mW) in the devices. The measured nanotube diameters \( d \) range from 1.6 to 4.2 nm, with most around 2 nm.

Figure 10-1 shows \( V_d \) up to \( \pm 50 \) V was applied to a s-SWNT \((d = 2.2 \) nm and \( L = 9 \) µm) device at \( V_g = 0 \). The device conducts well originally at low bias (sweep 1). After applying large \( V_d \) (sweep 1), the conductivity is lower when \( V_d \) is ramped down (sweep 2) compared with sweep 1. A low-conductance gap of width ~ 10 V is seen in the low-bias region when \( V_d \) returns to small values (sweep 3). This gap at low bias due to the application of high \( V_d \) is irreversible while the device remains in vacuum; the original conductance at zero gate voltage can not be recovered by
application of $V_g$ or $V_d$; it is different from the previously-observed hysteresis [29] in SWNT-FETs due to charge trapping in the gate dielectric. The original conductance at zero gate voltage is completely recovered when the device is exposed to atmospheric gas (not shown). The device can be cycled between these two states (which we will refer to as “high-conductance state” and “low-conductance state”) repeatedly by applying high $V_d$ or exposing it to air. Applying large $V_d$ to m-SWNT devices does not change the $I_d$-$V_d$ characteristic (see the inset of Figure 10-1).

![Figure 10-1](image)

Figure 10-1. Drain current $I_d$ vs. drain voltage $V_d$ for SWNT devices. Main panel shows $I_d$ vs. $V_d$ for a semiconducting SWNT with $V_d$ up to 50 V at $V_g = 0$ and $T = 1.4$ K. The arrows and numbers indicate sweep directions and sequence of sweeps of $V_d$. Inset is $I_d$ vs. $V_d$ for the same $V_d$ range for a m-SWNT device ($d = 2.0$ nm and $L = 9$ µm) at $T = 5$ K. (In this case a gate voltage $V_g = V_d/2$ was applied during the sweep of $V_d$.)
10.3 Intrinsic s-SWNTs Behaviors with SBs

Figure 10-2 depicts transfer curves of the same s-SWNT device at different temperatures $T$ in the high-conductance state (Figure 10-2(a)) and in the low-conductance state (Figure 10-2(b)). In both cases $V_d = 0.1$ V. Note that for all data in this chapter the drain voltage is low (0.1-0.25 V), much lower than the biases studied in Chapters 6-9; here the contact barriers may play a significant role. The device shows ambipolar behavior in both states [46,128] (data of higher positive $V_g$ in the high-conductance state is not shown), but in the low-conductance state the ambipolar behavior is very symmetric; at all temperatures the hole and electron on-currents are the same order of magnitude, and the subthreshold swings $S$ are similar. (Note that majority-carrier currents are studied in all cases; minority carrier current and recombination current do not play a role, due to the low drain field. The devices are “ambipolar” only in the sense that at positive gate voltage we measure majority-electron current, and at negative gate voltage we measure majority-hole current.) Around $V_g = 0$ (-3 V $< V_g < 3$ V) in the low-conductance state, $S$ values for holes and electrons are very large (on order 10 V/decade), and the current decreases very quickly with temperature.
We first examine the temperature dependence of the conductance in the low-conductance state in the region near $V_g = 0$. Figure 10-3 shows the data from Figure 10-2(b) at several $V_g$ values on an Arrhenius plot. An effective activation energy $E_a$ can then be extracted. Figure 10-4 shows $E_a$ as a function of $V_g$ extracted from Figure
10-3; over a large range (-3 V < \( V_g < 3 \) V) \( E_a \) has a fairly constant value of \( \sim 150 \) meV, and is similar for electrons (\( V_g > 0 \)) and holes (\( V_g < 0 \)). The estimated energy gap for this nanotube of diameter \( d = 2.2 \) nm is \( E_g = 380 \) meV [39]. (Here the overlap integral we use is 2.89 eV [39], a more precise value from Roman spectroscopy.) We interpret \( E_a \) as the SB height [163], which is similar for electrons and holes, indicating midgap alignment of the metal Fermi level.

![Figure 10-3](image)

Figure 10-3. Arrhenius plot of the current at various gate voltages in the low-conductance state: the six curves represent \( V_g \) values ranging from -5 V to 0 V, in steps of 1 V.
Due to the competition between tunneling and thermionic emission, the measured activation energy is less than the SB height, but approaches the true SB height in the limit of an intrinsic SWNT with thick gate dielectric at small $V_g$ [163], as in our case here. At higher carrier density (due to doping or large $V_g$) the barrier is thinned, enhancing the tunneling contribution and lowering the measured activation energy compared to the true SB height. A thorough treatment of tunneling vs. thermionic emission in SWNT/electrode junctions is given in [163]. Here we verify for the first time the prediction of Ref. [163] that the activation energy indeed gives the expected SB height in the intrinsic SWNT at low $V_g$. The only previous reports in the literature which extract an activation energy for SWNT-FETs on thick dielectric use a large positive or negative gate voltage to put the device in the on-state [162,164]; in these cases the activation energy are smaller than the SB height due to
tunneling. This effect is also seen in our work at large gate voltages; see Figure 10-4, in which the activation energy is already lower than \( \sim 25 \) meV at \( V_g = -5 \) V.

The current shows a dip (arrows in Figure 10-2(b)) near \( V_g = 0 \) with a width of \( \sim 0.4 \) V. In order to interpret this feature, we must discuss the gate coupling, i.e. the shift in Fermi level with gate voltage. The gate coupling is given by

\[
\frac{dE_F}{d(eV_g)} = \frac{C_g}{C_g + C_q} \cdot \frac{C_g}{C_g + C_s + C_d}
\]

Equation 10-1

where \( C_s, C_d, \) and \( C_g \) are the electrostatic capacitances of the nanotube to the gate, source, and drain, and \( C_q \) is the quantum capacitance of the nanotube, equal to \( e^2 D(E) \)

where \( D(E) \) is the density of states. In the bandgap, in the absence of charge traps, the quantum capacitance is zero, and the first term is unity. The second term approaches unity for our long-channel devices. Therefore, the gate coupling is expected to be near unity when the Fermi level lies in the bandgap. We then interpret the \( \sim 0.4 \) V width of the dip in current as the Fermi level crossing the gap of the nanotube. The width is close to the expected value of the gap \( E_g = 380 \) meV, and in that region the activation energy is \( \sim 170 \) meV (see Figure 10-4), approximately \( E_g/2 \).

The dip occurs near \( V_g = 0 \) indicating the s-SWNT is nearly intrinsic. Outside of this region the effective SB height is expected to be lowered by thermally-assisted tunneling [163]. We conclude that the low-conductance state corresponds to an intrinsic s-SWNT with symmetric SBs for electrons and holes.

10.4 Cause of p-Type Behavior of s-SWNTs in Air

We now turn to the high-conductance state produced by exposure to air. As seen in Figure 10-5, the device has higher on-conductance in the p-type region.
compared to the low-conductance state, while on-conductance in the n-type region is nearly unchanged. The subthreshold swing in the p-type region is smaller than in the low-conductance state, but still much larger than the $k_B T \ln 10/e \approx 60 \text{ mV/decade}$ ($k_B$ is Boltzmann’s constant, and $e$ is the electronic charge) expected for an ideal MOSFET at room temperature [92]. The off-conductance (minimum conductance) is nearly identical to that in low-conductance state. We explore two possible explanations for the hole conduction enhancement observed upon air exposure: the metal electrode work function is increased, or the nanotube is doped.

Increase in metal work function should result in the following effects. First, n-type conduction should be suppressed because of increasing SB height for electrons [157]. Careful calculations by Heinze et al. [157] show that the electron conductance

![Figure 10-5. Conductance vs. $V_g$ at $T = 300$ K. The dashed and solid lines are taken in the high-conductance state and the low-conductance state, respectively.](image)

Figure 10-5. Conductance vs. $V_g$ at $T = 300$ K. The dashed and solid lines are taken in the high-conductance state and the low-conductance state, respectively.

Increase in metal work function should result in the following effects. First, n-type conduction should be suppressed because of increasing SB height for electrons [157]. Careful calculations by Heinze et al. [157] show that the electron conductance
is indeed strongly modified by the band lineup (see Figure 10-6 (courtesy Fig. 1(b) in Ref [157]) – note that here the barrier to electrons is being made smaller and that to holes is increasing, but the situation would be identical for increasing barrier to electrons since electron-hole symmetry is assumed). This is not surprising. The s-SWNT channel is an intrinsic semiconductor with near-perfect electron-hole symmetry; the conductance of the SWNT channel itself should be nearly identical for electrons and holes. When the Fermi level lies in the conduction band, the conductance of the channel is dominated by the large SBs at the source and drain. Increasing the size of these barriers (making the work function more negative) exponentially reduces the conductance. In contrast, Figure 10-5 shows that n-type conductance is nearly identical in the high- and low-conductance states. Second, the off-conductance (minimum conductance) should decrease exponentially as the barrier for electrons increases, which is also not seen in Figure 10-5. The observation of very similar off-conductance in the high-conductance and low-conductance states indicates similar SB heights. Therefore, we rule out metal contact work function change as the explanation for the high-conductance state.
Figure 10-6. Corresponding conductance versus gate voltage at room temperature, for different SBs. The SB height for electrons is indicated for each curve. (Device geometry: 50 nm metal contacts on the left and right; a ground plane 120 nm and a top gate 100 nm away from the nanotube. Courtesy Fig. 1(b) in S. Heinze et al., Physical Review Letters 89, 106801 (2002))

In contrast, p-type chemical doping of s-SWNTs upon air exposure can explain our experimental results. Chemical doping not only increases free carriers in nanotubes, but also changes the SB thickness by varying the depletion width \( W_p \) [156]. The depletion width for nanotubes varies exponentially with the inverse of the doping density \( D_p \) [156]:

\[
W_p \approx \frac{d}{2} \exp\left(\frac{2\varepsilon \varepsilon_0 E_F}{e^2 d N D_p}\right),
\]

where \( \varepsilon_0 \) is the electric constant, \( \varepsilon \approx 2.45 \) the average dielectric constant of the oxide and vacuum, and \( N \approx 38 \text{ nm}^{-2} \) is carbons atoms per unit surface area. In Figure 10-2(a), the gate voltage needed to remove all the carriers is \( \approx 1.6 \text{ V} \). Assuming a gate capacitance per length \( c_g \approx 0.20 \text{ pF/cm} \) in our device geometry [28,46], we
estimate the doping level $D_p$ is about $2.0 \times 10^6 \text{ cm}^{-1} \approx 7.6 \times 10^{-4}$ holes/carbon. Then $W_p \approx 5.5 \text{ nm}$, which is at least one order of magnitude smaller than the SB thickness controlled by electrostatic gating in our device geometry [116,157]. The thin SB due to a thin depletion width and the unchanged SB heights for both valence and conduction bands easily explain why the on-current is enhanced in p-type conduction, while off-current is not changed in the high-conductance state compared with the low-conductance state. Note that in the high-conductance state, the temperature dependence of the conductance at negative $V_g$ is small or negligible (see Figure 10-2(a)), and the measured activation energy is much smaller than in the low-conductance state. (Figure 10-7 shows $E_a$ in the high-conductance state as a function of $V_g$ extracted from Figure 10-2(a)) This arises not because of a reduction in SB height for holes (which would necessitate an increase in SB height for electrons), but rather due to tunneling dominating thermionic emission as the SB is thinned by hole-doping. Therefore, the activation energy underestimates the SB height when doping is present.
The exact nature of the chemical doping remains unclear. The obvious possibility is that oxygen adsorbs on the s-SWNTs, accepting electrons. Oxygen is known to affect the thermopower and resistivity of bulk SWNT samples [8]. Jhi et al. [165] predicted that adsorbed O$_2$ donated 0.1 hole per adsorbed molecule to the SWNT. However, a recent paper [166] exploring s-SWNTs with one section suspended across a trench found that the s-SWNT section bound on the SiO$_2$ substrate is p-type doped (with a similar doping magnitude observed here), and the suspended s-SWNT is undoped; this raises the possibility that SWNT doping arises from an interaction with the SiO$_2$ substrate. For solution-processed SWNTs on Au electrodes, annealing produced n-type FETs, and exposure to O$_2$ restored p-type operation, interpreted there as due to changes in metal work function [159]. However, the origin of n-type behavior in the annealed FETs remains unclear, so a complete picture is
lacking. More controlled study to clarify the origins and the effects of chemical doping, and its dependence on device processing and ambient conditions is required.

In conclusion, we have shown that dissipating high power in a SWNT-FET can reveal its intrinsic undoped behavior. In ambient environment, s-SWNTs on SiO₂ substrates are doped, and such chemical doping offers a new route to high on-currents in SB-SWNT-FETs. It is notable that the effects demonstrated here also form the basis of an electronically-programmable FET: application of a high electrical current is sufficient to reduce the on-current by two orders of magnitude and effectively remove a particular FET from a circuit.
Chapter 11

Future Directions

Unfortunately I was not able to obtain understandable or conclusive results on spin valve measurements in nanotube-based devices during my graduate study; the spin valve effect I see is not consistent. However, I believe that the experiments should be successful if more reliable devices could be constructed by making good tunneling barriers between nanotube and ferromagnetic leads. This would allow systematic study and understanding of spin transport in nanotubes.

My expectation is that high bias transport is insensitive to temperature since it is far from equilibrium. Measuring the temperature effect to prove this prediction would be useful. From the Boltzmann equation calculation we know the carrier density in nanotubes plays an important role to determine the carrier velocity. Extending the nanotube device modeling of Chapter 7 to include the results from Chapter 8 (saturation velocity depending on carrier density) would be a logical next step, which I unfortunately was unable to finish during my Ph.D. The comparison of high bias experiments in metallic nanotubes, small bandgap and large bandgap semiconducting nanotubes will be interesting, too, to investigate the dependence of the current-carrying capacity on bandgap (and subband spacing) as well as on carrier density. Because the band structures of different kinds of nanotubes at high energy are similar, current-carrying capacity at high gate voltages (high carrier densities) should be very similar.
I will also try to expand my simple Boltzmann equation calculation to m-SWNTs, and compare that to the experimental results. It will be nice to consider first a two-subband calculation, including interband scattering transitions because the second subband is reachable in the gate field that researchers typically apply. Recent experiments on single layer graphite (graphene) and few-layer graphite [167-175] open the possibility of studying transport at high bias in these new all-carbon nanostructures. They are structurally similar to nanotubes, but two dimensional materials. Expanding the Boltzmann equation calculation to anticipate what happens in truly two dimensional systems will be very interesting. In addition, if the experimental results can come out at the same time, that should be a remarkable work.

There remains a mystery in the ambipolar transport at high bias in s-SWNTs: the current dips in the $I-V_g$ characteristic curves are sharper than what is calculated considering electron-hole recombination (Chapter 9). EFM in this bias region can provide the potential distribution along the nanotube, and may give us a hint. I attempted to accomplish EFM on devices in the ambipolar regime, but the results were inconclusive; longer devices will likely greatly improve the results. Also, high bias EFM in the unipolar region will also tell us about the details of the pinch-off effect in nanotubes, which currently relies on assumptions in my device modeling.
Appendix A

Deriving

Electrostatic Potential from EFM Signal

A.1 Processes of Deriving Electrostatic Potential from EFM Signal

Figure A-1(a) shows an AFM image; (b), (d), (f), (h) show a series of EFM images; (c), (e), (g), (i) show the corresponding EFM signals vs. the position along the vertical direction. The technique for this series of EFM images is AC-tip-EFM, as described in Chapter 3. The device is biased at $V_d = 0$, $V_s = 0$ in (b), (c); $V_d = 0$, $V_s = -1$ V in (d), (e); $V_d = -1$ V, $V_s = 0$ in (f), (g); $V_d = -1$ V, $V_s = -1$ V in (h), (i). The goal is to get electrostatic potential profile of a nanotube while the device is biased at $V_d = 0$, $V_s = -1$ V or $V_d = -1$ V, $V_s = 0$. The images taken at $V_d = 0$, $V_s = 0$ and $V_d = -1$ V, $V_s = -1$ V are for reference.
Figure A-1. EFM images, AFM corresponding image, and signal profiles from EFM images. The scan sizes for all images are $1.5 \times 1.5 \, \mu m^2$. (a) AFM image. The nanotube is barely seen between electrodes. (b), (d), (f), (h) EFM images. The top and bottom electrode biases ($V_d$ and $V_s$) for all images are labeled. The gate bias $V_g$ equals 0.4 V. The amplitude and frequency of AC tip bias $V_{\text{ac,tip}}(\omega)$ equals 0.2 V and 13 kHz, respectively. (c), (e), (g), (i) corresponding signal profiles. The blue solid and red dashed lines represent the signal profiles on the nanotube and bare substrate ($SiO_2$), respectively.

The nanotube only can be barely seen in AFM image, but it seen clearly in EFM images. The position of nanotube can be determined from both AFM and EFM
images. The EFM signals on the nanotube can be traced. The blue solid lines in
Figure A-1(c), (e), (g), (i) are the signal profiles on the nanotube. The red dashed
lines are the signal profiles on the substrate. Presumably the EFM signals on the
nanotube come from both the nanotube potentials and the substrate potentials. The
remaining signal after subtracting the blue solid curves from the red dashed curves
indicate the signals from the nanotube potentials only.

Figure A-2 shows the EFM signals from the nanotube only. When the device
is biased at $V_d = V_s = 0$, the whole nanotube should have the same potential 0 since
the nanotube is conducting. Similarly, the whole nanotube have potential -1 V when
$V_d = V_s = -1$ V. The top and bottom blue dashed curves in Figure A-2 therefore mean
the EFM signals form the nanotube when the nanotube whole potentials are 0 and –1
V, respectively. Also as expected, the signals of the device biased at $V_d = 0, V_s = -1$
V and $V_d = -1$ V, $V_s = 0$ are between the signals at $V_d = V_s = 0$ and $V_d = V_s = -1$ V
because the nanotube potentials supposedly are between 0 and -1 V when $V_d = 0, V_s =
-1$ V or $V_d = -1$ V, $V_s = 0.$
If we assume the EFM signal difference and the potential difference is linear (we will check the linearity in the next section), that means,

$$V_1 - V_2 \propto A(V_1) - A(V_2),$$

Equation A-1

where $A(V)$ is the EFM signal with the nanotube potential $V$, then we can derive the potential of nanotube at any position when $V_d = 0$, $V_s = -1$ V or $V_d = -1$ V, $V_s = 0$ by

$$\frac{V - (-1)}{0 - (-1)} = \frac{A(V) - A(-1)}{A(0) - A(-1)}.$$

Equation A-2

Figure A-3 shows the result of linear interpolation. At different bias conditions, the potentials and, therefore, the resistance distribution are very different. This is why EFM provides unique transport information. As we observe, the derived potentials near the contacts show greater uncertainty. In other words, when the nanotube gets closer to the contacts, the potentials there are harder to extract. This is
because the device geometry near the contacts changes dramatically; the contacts are much taller than the rest of device. Also, the signals from the contacts are very strong. It is harder to eliminate large signals from the contacts to get small signals from the nanotube properly.

Figure A-3. The converted potential profiles on the nanotube.

A.2 Linearity

Here we would like to check whether the assumption “linearity”, or basically Equation A-1, is a proper idea. Figure A-4 shows the EFM signals from nanotube only, as Figure A-2. Each curve is at $V_d = V_s$ from -1 V to 0 in 0.2 V steps. If Equation A-1 is true, each curve in Figure A-4 should be equally spaced to the adjacent curves. The curves look more or less equally spaced in the middle, but not near the contacts. Also, when the biases increase, the nonlinearity effect will get larger. Few possible reasons make the analysis near the contacts worse. Besides the
reasons mentioned in the previous section, there might be some data processing errors which come from the uncertainty of nanotube positions near the contacts. Even though the linearity test fails near the contacts, the derived potentials away from the contact are still reliable. Sometimes we can extrapolate the potential profiles of nanotubes toward the contacts, and estimate the contact resistances accordingly.

Figure A-4. EFM signals on the nanotube after the subtraction from the background signal. $V_g = 0.5 \text{ V}$ and $V_{ac,tip} = 0.2 \text{ V}$ are for all curves. Each curve is at $V_d = V_s$ from -1 V to 0 in 0.2 V steps.
Appendix B

Matlab Codes

B.1 General Notes

This code is not fully developed, and I am not very professional in code writing. So the codes might not be very easy to understand. The texts or sentences which start by “%” or “%%” are short explanations of the codes; they do not belong to the code itself.

B.2 Code for Device Modeling

%% analytically calculate the hole current of the device at different bias conditions when the carriers experience velocity saturation at high electric field

%% calculate nanotube potential at the contacts when the quasi-Fermi levels of nanotube bands are in equilibrium with the Fermi levels of the contacts

% constants; MKS unit
vFm=9.35e5;
h=6.626e-34;
qe=-1.6e-19;

% ground chosen and geometry factors and parameters
Vs=0;
Cg=0.2e-10;
del=0.2*1.6e-19;

for k=1:199;
    for l=1:19;
        Vd(k,l)=(-k+100)*0.1;
        Vg(k,l)=l-10;
        dE0d=abs(qe*1);
        dE0s=abs(qe*1);
        if qe*(Vd(k,l)-Vg(k,l))>del
            E0dgueq=eq*Vd(k,l)-del;
            while dE0d>abs(qe*1e-6)
                if (qe*Vd(k,l)-E0dgueq-del)>0
                    nde(k,l)=2*4/h/vFm*(abs((qe*Vd(k,l)-E0dgueq)^2-del^2))^0.5;
                else
                    nde(k,l)=0;
                end
                E0d(k,l)=qe*(qe*nde(k,l)/Cg+Vg(k,l));
                dE0d=abs(E0d(k,l)-E0dgueq);
                E0dgueq=E0dgueq+1e-3*(E0d(k,l)-E0dgueq);
            end
        end
    end
if (qe*(Vd(k,l)-Vg(k,l))>=0)&(qe*(Vd(k,l)-Vg(k,l))<=del)
\[ E_{0d}(k,l) = qe \cdot V_g(k,l) \]
\[ n_{de}(k,l) = 0 \]
end

if \( qe \cdot (V_g(k,l) - V_d(k,l)) > \text{del} \)
\[ E_{0dguess} = qe \cdot V_d(k,l) + \text{del} \]
while \( dE_{0d} > \text{abs}(qe \cdot 1e^{-6}) \)
if \( (E_{0dguess} - qe \cdot V_d(k,l) - \text{del}) > 0 \)
\[ n_{dh}(k,l) = 2 \cdot 4 / h / vFm \cdot (\text{abs}((qe \cdot V_d(k,l) - E_{0dguess})^2 - \text{del}^2))^{0.5} \]
else
\[ n_{dh}(k,l) = 0 \]
end

\[ E_{0d}(k,l) = qe \cdot (-qe \cdot n_{dh}(k,l) / C_g + V_g(k,l)) \]
\[ dE_{0d} = \text{abs}(E_{0d}(k,l) - E_{0dguess}) \]
\[ E_{0dguess} = E_{0dguess} + 1e^{-3} \cdot (E_{0d}(k,l) - E_{0dguess)) \]
end
end

if \( (qe \cdot (V_g(k,l) - V_d(k,l)) \geq 0 \) \& \( (qe \cdot (V_g(k,l) - V_d(k,l)) \leq \text{del}) \)
\[ E_{0d}(k,l) = qe \cdot V_g(k,l) \]
\[ n_{dh}(k,l) = 0 \]
end

if \( qe \cdot (V_s - V_g(k,l)) > \text{del} \)
\[ E_{0sguess} = qe \cdot V_s - \text{del} \]
while \( dE_{0s} > \text{abs}(qe \cdot 1e^{-6}) \)
if (qe*Vs-E0sguess-del)>0
    nse(k,l)=2*4/h/vFm*(abs((qe*Vs-E0sguess)^2-del^2))^0.5;
else
    nse(k,l)=0;
end
E0s(k,l)=qe*(qe*nse(k,l)/Cg+Vg(k,l));
dE0s=abs(E0s(k,l)-E0sguess);
E0sguess=E0sguess+1e-3*(E0s(k,l)-E0sguess);
end
end
if (qe*(Vs-Vg(k,l))>=0)\&(qe*(Vs-Vg(k,l))<=del)
    E0s(k,l)=qe*Vg(k,l);
    nse(k,l)=0;
end
if qe*(Vg(k,l)-Vs)>del
    E0sguess=qe*Vs+del;
    while dE0s>abs(qe*1e-6)
        if (E0sguess-qe*Vs-del)>0
            nsh(k,l)=2*4/h/vFm*(abs((qe*Vs-E0sguess)^2-del^2))^0.5;
        else
            nsh(k,l)=0;
        end
        E0s(k,l)=qe*(-qe*nsh(k,l)/Cg+Vg(k,l));
    end
end
\[ d\text{E}0s = |E0s(k, l) - E0\text{sguess}|; \]
\[ E0\text{sguess} = E0\text{sguess} + 1e^{-3} \times (E0s(k, l) - E0\text{sguess}); \]
end
end
end
if (qe \times (Vg(k, l) - Vs) \geq 0) \& (qe \times (Vg(k, l) - Vs) \leq del)
\[ E0s(k, l) = qe \times Vg(k, l); \]
\[ nsh(k, l) = 0; \]
end
end
end
phid = E0d/qe; % phid is nanotube potential at drain
phis = E0s/qe; % phis is nanotube potential at source

%%% Calculate the hole current analytically when carrier experience velocity saturation.

% geometry factors and parameters
Cg = 0.2e-10;
L = 20e-6;
% undetermined parameters
mu0 = 2.7;
vs = 2e5;
for k=1:199;
for l=1:19;
    if (Vd(k,l)>0)&(Vg(k,l)<0)
        if phis(k,l)>1/mu0*(L*vs+phid(k,l)*mu0-...
            (L^2*vs^2+2*L*vs*mu0*(phid(k,l)-Vg(k,l)))^0.5)) % when
pinch off happens at source
            I(k,l)=1/(L/mu0+(phid(k,l)-phis(k,l))/vs)*Cg*...
            (1/2*(phid(k,l)^2-phis(k,l)^2)-...
            Vg(k,l)*(phid(k,l)-phis(k,l)));
        else % when pinch off does not happen
            I(k,l)=-Cg*vs*((L*vs)^1.5+2*(L*vs)^0.5*mu0*(phid(k,l)-Vg(k,l))-...
            L*vs*(L*vs+2*mu0*(phid(k,l)-Vg(k,l)))^0.5-...
            mu0*(phid(k,l)-Vg(k,l))*(L*vs+2*mu0*(phid(k,l)-Vg(k,l)))^0.5)/...
            (mu0*(L*vs+2*mu0*(phid(k,l)-Vg(k,l)))^0.5);
        end
    elseif (Vd(k,l)<0)&(Vg(k,l)<=Vd(k,l))
        if phid(k,l)>1/mu0*(L*vs+phis(k,l)*mu0-...
            (L^2*vs^2+2*L*vs*mu0*(phis(k,l)-Vg(k,l)))^0.5)) % when
pinch off happens at drain
            I(k,l)=1/(L/mu0-(phid(k,l)-phis(k,l))/vs)*Cg*...
            (1/2*(phid(k,l)^2-phis(k,l)^2)-...
\[ V_g(k,l) \times (\phi_d(k,l) - \phi_s(k,l)) \]

\[
\text{else} \ % \ \text{when pinch off does not happen} \\
I(k,l) = C_g \times v_s \times ( (L \times v_s)^{1.5} + 2 \times (L \times v_s)^{0.5} \times \mu_0 \times (\phi_s(k,l) - V_g(k,l)) - \\
L \times v_s \times (L \times v_s + 2 \times \mu_0 \times (\phi_s(k,l) - V_g(k,l)))^{0.5} - \\
\mu_0 \times (\phi_s(k,l) - V_g(k,l)) \times (L \times v_s + 2 \times \mu_0 \times (\phi_s(k,l) - V_g(k,l)))^{0.5}) / \\
(\mu_0 \times (L \times v_s + 2 \times \mu_0 \times (\phi_s(k,l) - V_g(k,l)))^{0.5}); \\
\text{end} \\
\text{end} \\
\text{end} \\
\text{end} \\
\]

%% numerically calculate the hole current of the device at different bias conditions when the carriers experience velocity saturation at high electric field

%% calculate potential at the contacts

function [\phi_0, \phi_L, V_d, V_g] = potentialcalculate_atcontacts;

%% constants

vFm=9.35e5;

h=6.626e-34;

qe=-1.6e-19;
%% ground chosen and geometry factors and parameters

Vs=0;
Cg=0.2e-10;
del=0.2*1.6e-19;

for k=1:199;
    for l=1:199;
        Vd(k,l)=(-k+100)*0.1; % Vd from 9.9 to -9.9 V
        Vg(k,l)=(l-200)*0.1; % Vg from -19.9 to -0.1 V
        dE0d=abs(qe*1);
        dE0s=abs(qe*1);
        if qe*(Vd(k,l)-Vg(k,l))>del
            E0dguees=qe*Vd(k,l)-del;
            while dE0d>abs(qe*1e-6)
                if (qe*Vd(k,l)-E0dguees-del)>0
                    nde(k,l)=2*4/h/vFm*(abs((qe*Vd(k,l)-E0dguees)^2-del^2))^0.5;
                else
                    nde(k,l)=0;
                end
            end
            E0d(k,l)=qe*(nde(k,l)/Cg+Vg(k,l));
            dE0d=abs(E0d(k,l)-E0dguees);
            E0dguees=E0dguees+1e-3*(E0d(k,l)-E0dguees);
        end
    end
end
if (qe*(Vd(k,l)-Vg(k,l))>=0)\&(qe*(Vd(k,l)-Vg(k,l))<=del)

E0d(k,l)=qe*Vg(k,l);
nde(k,l)=0;
end

if qe*(Vg(k,l)-Vd(k,l))>del

E0dgess=qe*Vd(k,l)+del;
while dE0d>abs(qe*1e-6)

if (E0dgess-qe*Vd(k,l)-del)>0

ndh(k,l)=2*4/h/vFm*(abs((qe*Vd(k,l)-E0dgess)^2-del^2))^0.5;
else

ndh(k,l)=0;
end

E0d(k,l)=qe*(-qe*ndh(k,l)/Cg+Vg(k,l));
dE0d=abs(E0d(k,l)-E0dgess);
E0dgess=E0dgess+1e-3*(E0d(k,l)-E0dgess);
end
end

if (qe*(Vg(k,l)-Vd(k,l))>=0)\&(qe*(Vg(k,l)-Vd(k,l))<=del)

E0d(k,l)=qe*Vg(k,l);
nde(k,l)=0;
end

if qe*(Vs-Vg(k,l))>del
E0sguess=qe*Vs-del;

while dE0s>abs(qe*1e-6)
    if (qe*Vs-E0sguess-del)>0
        nse(k,l)=2*4/h/vFm*(abs((qe*Vs-E0sguess)^2-del^2))^0.5;
    else
        nse(k,l)=0;
    end

E0s(k,l)=qe*(qe*nse(k,l)/Cg+Vg(k,l));
dE0s=abs(E0s(k,l)-E0sguess);
E0sguess=E0sguess+1e-3*(E0s(k,l)-E0sguess);
end
end

if (qe*(Vs-Vg(k,l))>=0)&(qe*(Vs-Vg(k,l))<=del)
    E0s(k,l)=qe*Vg(k,l);
    nse(k,l)=0;
end
end

if qe*(Vg(k,l)-Vs)>del
    E0sguess=qe*Vs+del;
    while dE0s>abs(qe*1e-6)
        if (E0sguess-qe*Vs-del)>0
            nsh(k,l)=2*4/h/vFm*(abs((qe*Vs-E0sguess)^2-del^2))^0.5;
        else
            nsh(k,l)=0;
        end
    end
end
\[ E_{0s}(k,l) = qe \cdot \left( -qe \cdot n_{sh}(k,l)/C_g + V_{g}(k,l) \right) \]
\[ dE_{0s} = \text{abs}(E_{0s}(k,l) - E_{0sguess}) \]
\[ E_{0sguess} = E_{0sguess} + 1e^{-3} \cdot (E_{0s}(k,l) - E_{0sguess}) \]
\[ \text{if } (qe \cdot (V_{g}(k,l) - V_s) \geq 0) \land (qe \cdot (V_{g}(k,l) - V_s) \leq \text{del}) \]
\[ E_{0s}(k,l) = qe \cdot V_{g}(k,l) \]
\[ n_{sh}(k,l) = 0 \]
\[ \text{end} \]
\[ \text{end} \]
\[ \phi_L = E_{0d}/qe; \]
\[ \phi_0 = E_{0s}/qe; \]

%%% calculate hole current with considering pinch off

for l=199:-1:1 % for loop for different Vg

k=101;

Idone(k,l) = currentcalculate_negVd(Vg(k,l),phi0(k,l),phiL(k,l)); % call function currentcalculate_negVd to calculate current

for k=102:199 % for loop for Vd

Idone(k,l) = currentcalculate_negVd(Vg(k,l),phi0(k,l),phiL(k,l));
if abs(Idone(k,1)-Idone(k-1,1))<abs(Idone(k-1,1)*0.0001);

    break;

elseif abs(Idone(k,1))<abs(Idone(k-1,1));

    break;

elseif abs(Idone(k,1)-Idone(k-1,1))>abs(Idone(k-1,1)-Idone(k-2,1))

    break;

end

end

for kk=k:199

    Idone(kk,1)=Idone(k-1,1);

end

end

%%% calculate hole current self consistently with negative Vd

function [Idone,potential,field]=currentcalculate_negVd1(Vg,phi0,phiL);  %
%%% numerically calculate the hole current when the carriers experience velocity saturation

%%% constants
qe=-1.6e-19;

%%% geometry factors
Cg=0.2e-10;
L=20e-6;
%% parameters
mu0=2.7;
vs=2e5;

%% calculation
%step
dx=1e-8;
%guess current
I=-0.5e-6;

phi(2001)=100; % away from real phiL
%calculate current
while abs(phi(2001)-phiL)>0.001;
    phi(1)=phi0;
    nh(1)=Cg/(-qe)*(phi0-Vg);
    phiprime(1)=I*vs/(I*mu0+(-qe)*mu0*vs*nh(1));
    for xindex=1:2000
        phi(xindex+1)=phi(xindex)+phiprime(xindex)*dx;
        nh(xindex+1)=Cg/(-qe)*(phi(xindex+1)-Vg);
        phiprime(xindex+1)=I*vs/(I*mu0+...
                        (-qe)*mu0*vs*nh(xindex+1));
    end
end
Idone=I;
if phi(2001)<phiL;
    I=I*(1-0.001);
else phi(2001)>phiL;
    I=I*(1+0.001);
end
end
potential=phi;
field=-phiprime;

<table>
<thead>
<tr>
<th>vFm</th>
<th>Fermi velocity of metallic nanotubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Planck constant</td>
</tr>
<tr>
<td>Qe</td>
<td>Electron charge</td>
</tr>
<tr>
<td>Vs</td>
<td>Voltage at the source contact (zero because the source is grounded)</td>
</tr>
<tr>
<td>Cg</td>
<td>Electrostatic capacitance of nanotube per length</td>
</tr>
<tr>
<td>del</td>
<td>Half of nanotube bandgap</td>
</tr>
<tr>
<td>Vd</td>
<td>Voltage at the drain contact</td>
</tr>
<tr>
<td>Vg</td>
<td>Voltage at the gate</td>
</tr>
<tr>
<td>E0d</td>
<td>Potential energy of nanotube right at the drain contact</td>
</tr>
<tr>
<td>E0s</td>
<td>Potential energy of nanotube right at the source contact</td>
</tr>
<tr>
<td>E0dg</td>
<td>Guess of E0d for iteration</td>
</tr>
<tr>
<td>E0sg</td>
<td>Guess of E0s for iteration</td>
</tr>
<tr>
<td>nde</td>
<td>Electron density of nanotube right at the drain contact</td>
</tr>
<tr>
<td>nse</td>
<td>Electron density of nanotube right at the source contact</td>
</tr>
</tbody>
</table>
Table B-1. Symbols using in Section B-2.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ndh</td>
<td>Hole density of nanotube right at the drain contact</td>
</tr>
<tr>
<td>nsh</td>
<td>Hole density of nanotube right at the source contact</td>
</tr>
<tr>
<td>phid</td>
<td>Potential of nanotube right at the drain contact</td>
</tr>
<tr>
<td>phis</td>
<td>Potential of nanotube right at the source contact</td>
</tr>
<tr>
<td>L</td>
<td>Channel length</td>
</tr>
<tr>
<td>mu0</td>
<td>Zero–field mobility</td>
</tr>
<tr>
<td>vs</td>
<td>Saturation velocity</td>
</tr>
<tr>
<td>I</td>
<td>Current from the drain contact to the source contact</td>
</tr>
<tr>
<td>dx</td>
<td>Step size of nanotube channel</td>
</tr>
<tr>
<td>phi</td>
<td>Potential of nanotube</td>
</tr>
<tr>
<td>nh</td>
<td>Hole density of nanotube</td>
</tr>
<tr>
<td>phiprime</td>
<td>Derivative of potential of nanotube with respect to nanotube position</td>
</tr>
<tr>
<td>field</td>
<td>Electric field along nanotube</td>
</tr>
</tbody>
</table>

B.3 Code for Calculating Average Carrier Velocity

```matlab
%% Calculate carrier velocity from nonequilibrium carrier distribution
function by solving steady-state Boltzmann eq.; single band

%% Calculate fermi function
T=300; % unit is K
delta=0.2; % unit is eV
L=20e-6; % unit is m
```
for j=1:9
n(1,j)=2*10^((j-1)/2); % charge density is ~ n x 10^5 electron /m;
[gf,k,E,vf,nf,jp,jn,ip,in]=fermi1_k(n(1,j),T,delta,L); % call function

fermi1_k

%%% calculate velocity

for i=1:50
V(i,1)=0.2*i;
[v(i,j),count(i,j),ndone(i,j)]=velocity11(V(i,1),gf,L,vf,jp,jn,ip,in); % call
function velocity11
end
for i=51:60
V(i,1)=10+1*(i-50);
[v(i,j),count(i,j),ndone(i,j)]=velocity11(V(i,1),gf,L,vf,jp,jn,ip,in);
end
for i=61:68
V(i,1)=20+10*(i-60);
[v(i,j),count(i,j),ndone(i,j)]=velocity11(V(i,1),gf,L,vf,jp,jn,ip,in);
end
end
function [g,k,E,vf,nf,jp,jn,ip,in]=fermi1_k(n,T,delta,L); % A separate function to calculate fermi function; T's unit is K; charge density is ~ n x 10^5 electron /m; delta's unit is eV

% constant; MKS unit
kb=1.38e-23;
qe=1.6e-19;
hbar=1.055e-34;
vfm=9.35e5;

hbaromega=0.16; % unit is eV
k0=delta*qe/hbar/vfm; % unit is 1/m

dk=2*pi/L; % unit is 1/m
delk=dk/(100e-6/L); % unit is 1/m; one delk contain 4/(100e-6/L) e

for i=1:50001 % hyperbolic dispersion relation
    k(i,1)=delk*(i-25001);
    E(i,1)=hbar*vfm*(k(i,1)^2+k0^2)^0.5/qe; % unit is eV
    vf(i,1)=vfm*k(i,1)/(k(i,1)^2+k0^2)^0.5;
end

%%% calculation Fermi distribution
kguess=n/2*dk/4; % 4 means 2 bands and 2 spins
muguess=hbar*vfm*(kguess^2+k0^2)^0.5/qe; % guess mu;
nguess=0;
while abs(nguess-n)>n*1e-3
    for i=1:50001
        g(i,1)=(exp((E(i,1)-muguess)*qe/(kb*T))+1)^(-1);
    end
    nguess=4*sum(g)/(100e-6/L);
    if nguess>n
        muguess=muguess*(1-1e-1);
    else
        muguess=muguess*(1+1e-1);
    end
end

nf=nguess;

%%% find the states which are hbaromega=0.16 eV lower than each state k
for i=1:50001
    kp(i,1)=(((k(i,1)^2+k0^2)^0.5+hbaromega*qe/hbar/vfm)^2-k0^2)^0.5;
    kn(i,1)=(((k(i,1)^2+k0^2)^0.5-hbaromega*qe/hbar/vfm)^2-k0^2)^0.5;
end

i=1;
while int32(kp(i,1)/delk+25001)>50001
    i=i+1;
end

ip=i; % ip is the index of kp larger than 50001

i=1;
while imag(kn(i,1))==0
    i=i+1;
end

in=i; % in is the index of kn starting becoming complex

for i=1:(in-1) % kn is real upto to in-1
    jp(i,1)=int32(kp(i,1)/delk+25001);
    jn(i,1)=int32(kn(i,1)/delk+25001);
end

for i=in:25000
    jp(i,1)=int32(kp(i,1)/delk+25001);
end

i=25001;
jp(i,1)=int32(kp(i,1)/delk+25001);

for i=25002:(50002-in)
    jp(i,1)=50001+1-int32(kp(i,1)/delk+25001);
end
for i=(50002-(in-1)):50001
    jp(i,1)=50001+1-\text{int32}(kp(i,1)/\text{delk}+25001);
    jd(i,1)=50001+1-\text{int32}(kn(i,1)/\text{delk}+25001);
end

function [v,count,ndone,gnew]=velocity11(V,g,L,vf,jp,jn,ip,in);
A separate
function to calculate nonequilibrium carrier distribution by solving Boltzmann
equation and then calculate average carrier velocity

kb=1.38e-23;
qe=1.6e-19;
hbar=1.055e-34;
vfm=9.35e5;
lpb=10e-9; \% unit is m
le=300e-9; \% unit is m

\text{dk}=2*\pi/L; \% unit is 1/m
\text{dt}=2.07e-15*(L/10e-6);
\text{delk}=\text{dk}/(100e-6/L); \% unit is 1/m; one delk contain 4/(100e-6/L) e

count=0;
kgain=qe*V/L*dt/hbar; \% unit is 1/m
igain=int32(kgain/delk);

v=1; vold=0;

while abs(v-vold)>vold*1e-2 % check whether v stabilize

for j=1:500 % g evolve 500*dt

for i=(-igain+1):0

    gnew(i+igain,1)=0;

end

for i=1:(ip-1) % jp is bigger than 50001 upto ip-1

    gnew(i+igain,1)=g(i,1)+(1/le*(g(50002-i,1)-g(i,1))-... 

    1/lpb*(g(i,1)*((1-g(jn(i,1),1))+(1-g(50002-jn(i,1),1))))*(-vf(i,1))*dt; % multiply -vf because ratio of vf and le or lpb is positive

end

for i=ip:(in-1)

    gnew(i+igain,1)=g(i,1)+(1/le*(g(50002-i,1)-g(i,1))+... 

    1/lpb*((1-g(i,1))*(g(jp(i,1),1)+g(50002-jp(i,1),1))-... 

    g(i,1)*((1-g(jn(i,1),1))+(1-g(50002-jn(i,1),1))))*(-vf(i,1))*dt;

end

for i=in:25000

    gnew(i+igain,1)=g(i,1)+(1/le*(g(50002-i,1)-g(i,1))+... 

    1/lpb*((1-g(i,1))*(g(jp(i,1),1)+g(50002-jp(i,1),1))))*(-vf(i,1))*dt;

end

for i=25001:25001

    gnew(i+igain,1)=g(i,1)+(1/le*(g(50002-i,1)-g(i,1))+... 

end

181
\[ \frac{1}{\text{lpb}}((1-g(i,1))(g(jp(i,1),1)+g(50002-jp(i,1),1)))*vf(i,1)*dt; \]

end

for i=25002:(50002-in)

\[ gnew(i+igain,1)=g(i,1)+(1/le*(g(50002-i,1)-g(i,1))+... \]

\[ \frac{1}{\text{lpb}}((1-g(i,1))(g(jp(i,1),1)+g(50002-jp(i,1),1)))*vf(i,1)*dt; \]

de\n
for i=(50002-(in-1)):(50002-ip)

\[ gnew(i+igain,1)=g(i,1)+(1/le*(g(50002-i,1)-g(i,1))+... \]

\[ \frac{1}{\text{lpb}}((1-g(i,1))(g(jp(i,1),1)+g(50002-jp(i,1),1)))-... \]

\[ g(i,1)*((1-g(jn(i,1),1))+(1-g(50002-jn(i,1),1)))))*vf(i,1)*dt; \]

de\n
for i=(50002-(ip-1)):(50001-igain)

\[ gnew(i+igain,1)=g(i,1)+(1/le*(g(50002-i,1)-g(i,1))-... \]

\[ \frac{1}{\text{lpb}}((1-g(i,1))*((1-g(jn(i,1),1))+(1-g(50002-jn(i,1),1)))))*vf(i,1)*dt; \]

de\n
g=gnew;

de\n
end % end of 500 evolutions

count=count+500;

dol=e=v;

done=4*sum(gnew)/(100e-6/L);

d=v=sum(gnew.*vf)*4/(100e-6/L)/done;

de\n
end % end of evolution
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>Delta</td>
<td>Half of nanotube bandgap</td>
</tr>
<tr>
<td>N</td>
<td>Carrier density</td>
</tr>
<tr>
<td>L</td>
<td>Channel length</td>
</tr>
<tr>
<td>kb</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>qe</td>
<td>Unit charge</td>
</tr>
<tr>
<td>hbar</td>
<td>Planck constant divided by $2\pi$</td>
</tr>
<tr>
<td>vfm</td>
<td>Fermi velocity of metallic nanotubes</td>
</tr>
<tr>
<td>hbaromega</td>
<td>Optical or zone-boundary phonon energy</td>
</tr>
<tr>
<td>dk</td>
<td>Wavevector spacing</td>
</tr>
<tr>
<td>delk</td>
<td>Wavevector step in the calculation</td>
</tr>
<tr>
<td>k</td>
<td>Wavevector</td>
</tr>
<tr>
<td>E</td>
<td>Energy</td>
</tr>
<tr>
<td>vf</td>
<td>Fermi velocity</td>
</tr>
<tr>
<td>muguess</td>
<td>Guess of chemical potential</td>
</tr>
<tr>
<td>kp</td>
<td>The state with $hbaromega$ higher than state $k$</td>
</tr>
<tr>
<td>kn</td>
<td>The state with $hbaromega$ lower than state $k$</td>
</tr>
<tr>
<td>jp</td>
<td>Index of kp</td>
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<td>Index of kn</td>
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<tr>
<td>in</td>
<td>Limit of jn</td>
</tr>
<tr>
<td>lpb</td>
<td>Optical or zone-boundary phonon scattering length</td>
</tr>
<tr>
<td>le</td>
<td>Acoustic phonon scattering length</td>
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<tr>
<td>dt</td>
<td>Time interval of every iteration</td>
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<tr>
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<td>Description</td>
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<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>kgain</td>
<td>The increase of k due to electric field</td>
</tr>
<tr>
<td>igain</td>
<td>Corresponding index increase of kgain</td>
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<tr>
<td>v</td>
<td>Average carrier velocity</td>
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<td>Nonequilibrium carrier distribution</td>
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<tr>
<td>Count</td>
<td>Number of iteration</td>
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Table B-2. Symbols using in Section B-3.
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