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ELECTRICAL AND THERMAL TRANSPORT IN CARBON NANOTUBES FOR MOLECULAR DEVICE APPLICATIONS

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**SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY**

2005

Electrical and Thermal Transport in Carbon Nanotubes for Molecular Device Applications

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SUMMARY

The effects of oxygen and nitrogen on the growth of carbon nanotubes using microwave plasma enhanced chemical vapor deposition (MPECVD) system are studied. It is found that the hydrogen, oxygen and nitrogen plasma pretreatments of nickel catalyst are important to affect the morphology and composition of the nickel (Ni) catalyst film, and subsequently influence the quality of CNT films, such as impurity, defect concentration and CNT number density. Oxygen plasma treatment is found to reduce the grain size of the nickel film. Nitrogen atoms involved in plasma can incorporate into Ni films and form nickel nitride phase that can greatly suppress the formation of carbon passivation layer on the catalyst.

The thermal conductivities of vertical aligned multiwalled carbon nanotube (MWNT) films with thickness range from 10 to 50 μm have been studied using a pulsed photothermal reflectance (PPR) technique. It is found that the measured thermal conductivity of the MWNT films is around 15 W/mK and independent of the CNT length. A thermal conductance model is developed to obtain the effective thermal conductivity of MWNT films by taking the CNT volume filling fraction into account. Phonons are believed to dominate the heat transport in MWNTs through comparing the thermal conductivity with the electrical conductivity. The phonon mean free path is estimated to be 20 nm.

Temperature effects on the full Raman spectra of SWNTs, MWNTs, carbon nanofibers (CNFs) and highly ordered pyrolytic graphite (HOPG) sample are investigated. It is found that the Raman peak positions shift to low frequency with increasing temperature. The variation rate

of the G peak frequency as a function of temperature in SWNTs is a factor of 2~3 larger than the corresponding G peak frequency variation rates of MWNTs, CNFs and HOPG samples from room temperature up to 673 K. The line shapes of the RBM features for SWNTs are also found to be sensitive to the temperatures. The softening of inter-atomic force constant due to thermal expansion of C-C bonds and the relaxation of the weak van der Waals interaction between the SWNTs in a bundle with increasing temperature are suggested to be the main origins of the reversible spectral variations.

Carbon nanotube based field effect transistors (CNTFETs) have been fabricated using a burning-out process. The on/off ratio of the CNT channel current is more than 10^4 . In the burning-out process, the high current induced Joule heating can greatly reduce the CNT-metal contact resistance and improve the performance of CNTFETs. The CNTFETs show a strong memory effect with clear hysteretic behaviors. The charge retention time of the CNTFETs is around 7 days. The mechanism of the memory effect has been studied.

Chapter 1

INTRODUCTION

1.1 Motivation

In the ultra large scale integrated (ULSI) circuit era, the dimension of the microelectronic devices has been greatly scaled down in order to achieve high speed, low cost, and high performance. For example, currently, the microprocessing unit (MPU) physical gate length is 45 nm and it probably will be reduced to 13 nm 10 years later. The half pitch of dynamic random access memory (DRAM) lines would decrease from 100 nm in 2003 to 32 nm in 2013, as shown by the technological roadmap in Table 1.1.

Table 1.1 Technology roadmap for semiconductor [1]

Year	2001	2003	2006	2010	2013	2016
DRAM ^a ½ Pitch (nm)	130	100	70	45	32	22
MPU ^b /ASIC ½ Pitch (nm)	150	107	70	50	35	25
MPU physical Gate length (nm)	65	45	28	18	13	9
Nominal power supply V _{dd} (V)	1.2	1.0	0.9	0.6	0.5	0.4
Static power dissipation per device (10 ⁻⁹ W)	5.6	10	53	97	140	110

^aDynamic random access memory

^bMicroprocessing unit

However, it is now generally accepted that silicon based microelectronic devices will be reaching some fundamental scaling limits in a decade or so. This realization has sparked an intense study for new device principles, technologies and materials. Carbon nanotubes (CNTs), a kind of new material for nano-electronics were firstly discovered by Iijima in 1991[2]. They are extremely small by nature, around nanometer-scale in their diameter and up to few tens of microns in their length. These low dimensional nanostructures have unique electrical, mechanical and thermal properties that are superior to those bulk or thin film silicon materials used so far. For example, the strong sp^2 carbon bonds and void boundary scattering in CNTs could endow them extremely high thermal conductivity, ~ 6600 W/m.K at room temperature[3], even higher than that of CVD diamond. In addition to their excellent current carrying ability (10^9 A/cm²)[4] and small diameter, CNTs can be used as high reliable electron source of field emission display (FED)[5], integrated circuits heat sink, multi-layer interconnections, and molecular conducting wires in nanodevices.

Traditional microelectronic devices are fabricated on semiconductor wafers with sub-micron structures by thin film deposition, lithography, etching etc. This technology is referred to “top down” approach. In contrast, in “bottom up” approach, the devices are directly assembled from low dimensional nanostructures, i.e. carbon nanotubes, silicon nanowires, etc. Since the characteristic size of these materials is already in nanometer-scale, the critical lithography process used in the “bottom up” approach is no more necessary.

Single-wall carbon nanotubes (SWNTs) have unique electronic properties. They can be metallic or semiconducting, depending on their diameters and chiralities[6]. Together with

their excellent thermal and mechanical properties, SWNTs are a promising material for molecular devices, such as diodes[7], single electron transistors[8], field effect transistors[9], chemical sensors and memories, etc.[10, 11]. These CNT based nano-devices have excellent performance.

1.2 Objectives

The main objectives of this project are summarized as follows:

To improve the CNT film quality through using N_2 and O_2 in the MPECVD technique. The effects of N_2 and O_2 on the Ni catalyst and CNT growth are addressed in detail.

To investigate the thermal conductivity of MWNT films. Previously measured thermal conductivity of CNT films may not reflect intrinsic CNT thermal conductivity due to the effect of volume filling fraction. Furthermore, for a steady-state method, convection and radiation heat loss could lead to an uncertainty of determining the thermal conductivity. To resolve these problems, we have applied a pulsed photothermal reflectance (PPR) technique to the thermal conductivity measurement. In this technique, heat loss can be negligible. A refined model has been developed to correct the effect of volume filling fraction in the MWNT films to obtain the intrinsic thermal conductivity of MWNTs.

To study the influences of measurement temperature on the Raman spectra of CNTs. We present a systemic study of temperature effects on the full Raman spectra of highly

purified SWNTs, MWNTs, carbon nanofibers (CNFs), and highly oriented pyrolytic graphite (HOPG) samples. The different temperature coefficients of Raman peaks between different carbon materials are discussed and temperature dependence of Radial Breathing Mode (RBM) peaks for SWNTs is also addressed in detail.

To fabricate SWNT based field effect transistors (CNTFETs) using burning-out process. Fabrication of carbon nanotube field effect transistors is associated with placing a single SWNT across predefined metal electrodes. Unfortunately, in most cases more than one SWNT bridge the electrodes. These CNTs may consist of both metallic SWNTs (m-SWNTs) and semiconducting SWNTs (s-SWNTs). How to efficiently remove away the m-SWNTs while leaving the s-SWNTs undamaged and the thermal effect induced by high current are studied.

To study the mechanism of the memory effects of the CNTFETs. Influences of water and alcohol molecules adsorbed on the CNTs surface on the hysteresis phenomena are studied. Both “bottom contact” and “top contact” structured CNTFETs are fabricated for the study.

1.3 Major Contributions of the Thesis

The major contributions of this work are summarized as below.

1. A CNT growth process has been optimized. It is found that oxygen and nitrogen in the process can greatly enhance the quality of the CNTs. The grain size of nickel catalyst can

be decreased with interaction with oxygen under the plasma assistance. In nitrogen plasma, nickel nitride phase can effectively suppress the formation of carbon passivation layers on the catalyst.

2. Thermal conductivity of aligned MWNTs has been determined using pulsed photothermal reflectance (PPR) technique. Taking a volume filling fraction into account, the effective thermal conductivity is estimated to be about 200 W/m.K and is independent of the CNT length from 10 to 50 μm . The heat transport in MWNTs is dominated by phonons whose mean free path is estimated to be 20 nm.
3. We suggest that the electron transport in the aligned MWNT films is diffusive rather than ballistic. The ratio of the electrical conductivity in the longitudinal direction to that in the transverse direction is from 20 to 30. The anisotropic electrical conductivity can be attributed to different number of tube-tube junctions in the longitudinal and transverse directions.
4. The Raman spectra for carbon nanotubes at different temperatures are studied. We find that the G peak position shifts to low frequency with increasing temperature. The variation rate of the peak frequency as a function of temperature for SWNTs is a factor of 2~3 larger than the corresponding variation rates of MWNTs, CNFs, and highly ordered pyrolytic graphite (HOPG) samples from room temperature to 673 K. The line shapes of the RBM features are also found to be sensitive to temperature. The softening of the interatomic force constant due to thermal expansion of C-C bonds and the relaxation of the weak van

der Waals interaction between the SWNTs in a bundle with increasing temperature are suggested to be the main origins of the reversible spectral variations.

5. Carbon nanotube based field effect transistors (CNTFETs) are fabricated using burning-out process. The m-MWNTs can be efficiently burned out by applying a large current while the s-SWNTs are protected under certain gate voltage. The CNTFETs show good performance with high on/off ratio more than 10^4 . The high current induced joule heating can greatly reduce the metal-CNT contact resistance and improve the performance of the CNTFETs
6. CNTFETs fabricated by burning-out process show strong memory effects with a retention time of 7 days. Two factors can contribute to the memory effects of CNTFETs. (1) Charges could be injected from CNTs to the oxide and remain trapped there; (2) Water molecules adsorbed on the tube wall and SiO_2 surface can also act as charge trapping centers. Alcohol molecules around the CNTs has a strong influence on the threshold voltage of CNTFETs. The memory effect of the CNTFETs can be improved by changing the device configuration, such as “bottom contact” structure.

1.4 Organization of the Thesis

The thesis is organized as follows:

Chapter 1 describes the motivation, objectives, major contributions and organization of the thesis.

Chapter 2 gives a literature review of carbon nanotubes, including CNT structure, growth techniques, the theories and measurements of thermal and electrical transport in CNTs. The applications of carbon nanotubes are also introduced in this chapter.

In Chapter 3, the detailed growth process of MWNTs using microwave-plasma enhanced chemical vapor deposition technique is presented. Atomic force microscope (AFM), scanning electron microscope (SEM) and X-ray diffraction (XRD) are used to characterize the Ni catalyst and CNTs. The mechanism of growth of carbon nanotube with the aid of Ni catalyst and the roles of oxygen nitrogen plasma are also discussed.

Chapter 4 describes the thermal and electrical transport in aligned MWNTs films with thickness from 10 to 50 μm . Pulsed photothermal reflectance (PPR) is employed to investigate the thermal conductivity and two probe I-V method is used to study the electrical conductivity of the MWNT films. A three-layer model is employed to simulate the measured temperature curves. The issues of heat loss and the thermal contact resistance between CNTs and Au are calculated to justify the accuracy of our measurement of the thermal conductivity. A thermal conductance model is proposed to eliminate the CNT volume filling fraction effect to get the intrinsic thermal conductivity of the MWNTs.

Chapter 5 describes the Raman scattering characteristics of SWNTs, MWNTs, nanofibers (CNFs) and HOPG. The influence of temperature on the RBM peaks of SWNTs is discussed in detail.

In Chapter 6, the electrical transport in single-wall carbon nanotubes (SWNTs) is examined. The fabrication and performance of carbon nanotube field effect transistors (CNTFETs) are summarized. Thermal effect induced by high current through SWNTs and memory effects of the CNTFETs are also discussed in this chapter.

In Chapter 7, the main conclusions of this project are drawn and the future work is proposed.

Chapter 2

LITERATURE SURVEY

2.1 Introduction

Carbon nanotubes (CNTs) are unique nanostructures with remarkable electronic, thermal and mechanical properties, such as high thermal conductivity[3], high strength and stiffness[12]. Single-wall carbon nanotubes (SWNTs) can be metallic or semiconducting depending on their diameters and chiralities. These unique properties make CNTs the promising materials for nanoelectronic applications.

2.2 Structure of CNTs

The structure of CNTs has been explored early by high resolution transmission electron microscopy (TEM) and scanning tunneling microscopy (STM) techniques[13]. Olk *et al.*[13] confirmed that the CNTs are seamless graphene cylinders. Basically, CNTs can be divided into multiwalled carbon nanotubes (MWNTs) and single-wall carbon nanotubes (SWNTs) in terms of the number of graphite layer in the CNTs. A SWNT has a single layer of graphite and usually is around 1.4 nm in diameter, while a MWNT has more than one graphite layer and have larger diameters. There are three kinds of SWNTs in terms of index number (n,m), which will be discussed in the following paragraph. Figure 2.1 shows the schematic structures of (a) three kinds of SWNTs and (b) a three-layer MWNT.

(a)

(b)

Figure 2.1 Schematic structures of (a) three SWNTs with different index number and (b) a three-layer MWNT.

Usually, the structure of SWNTs can be described in terms of the chiral vector $\mathbf{R} = n\mathbf{a}_1 + m\mathbf{a}_2$, which connects two crystallographically equivalent sites on a 2D graphite sheet, (Point A and B), as depicted in Fig. 2.2. The chiral vector can be defined by the chiral vector index number (n, m) , where n and m are integers. The chiral angle θ between the chiral vector $\mathbf{R}$ and the zigzag line, the armchair line and the unit vector $\mathbf{a}_1$, $\mathbf{a}_2$ of the hexagonal honeycomb lattice of the graphene sheet are shown in Fig. 2.2[14]. Three distinct types of nanotube structures can be generated by rolling up the graphene sheet into a cylinder.

Figure 2.2 Chiral vector of a carbon nanotube.

If R lies along the Armchair line ($\theta = 30^\circ$), then it is called an "Armchair" nanotube. If $\theta = 0^\circ$, then the tube is of the "zigzag" type. Otherwise, if $0^\circ < \theta < 30^\circ$ then it is a "chiral" tube. The nanotube diameter d is given by

$$d = \sqrt{3}a_{c-c}(m^2 + mn + n^2)^{1/2} / p, \quad (2.1)$$

Where a_{c-c} is the C-C bond length, the chiral angle θ is given by

$$q = \tan^{-1} \left[\sqrt{3}n / (2m + n) \right], \quad (2.2)$$

The values of n and m determine the CNT diameter and chirality, or "twist" of the nanotube. The chirality in turn affects many physical properties of CNTs. For example, a SWNT is considered metallic if the value $n - m$ is divisible by three. Otherwise, the nanotube is semiconducting. Consequently, when tubes are formed with random values of n and m , we would expect that two-thirds of nanotubes would be semi-conducting, while the other one third would be metallic, which happens to be the case[15].

2.3 Growth of Carbon Nanotubes

Arc-discharge is a convenient way to generate a variety of carbon materials because of the high temperature of the plasma ($> 3000^\circ\text{C}$)[16]. This technique has been used for the synthesis of single-wall, multiwalled carbon nanotubes, and ropes of single-wall

nanotubes[17]. The details of the synthesis of CNTs include the use of carbon rod electrodes of 5-20 mm diameter separated by ~ 1 mm with voltage of 20-25 V across the electrodes and a DC electric current of 50-120 A flowing between the electrodes. The arc is typically operated in ~500 torr Helium atmosphere. The by-product of the arc-discharge growth process is multi-walled graphite particles in polyhedron shapes. The carbon arc method for generating multiwalled carbon nanotubes appears very simple, but it is clear that obtain high yields of CNTs is not obvious and requires careful control of the experimental conditions[18].

Another efficient route for synthesis of SWNTs employs the laser vaporization of a graphite target. It was claimed that both MWNTs and SWNTs could be produced in this way. Usually, a Co-Ni/graphite composite target was used and laser pulses are used to evaporate the target. Flowing argon gas sweeps the entrained nanotubes from the high temperature zone to the water-cooled Cu collector[19]. The by-products are usually fullerenes, graphitic polyhedron with enclosed metal particles and amorphous carbon.

Chemical vapor deposition (CVD) methods have been successful in making carbon fiber, filament and nanotube materials[20, 21]. A schematic experimental setup for CVD growth is depicted in Fig. 2.3. The growth process involves heating a catalyst material to high temperatures in a tube furnace and flowing a hydrocarbon gas through the tube reactor for a period of time. Both MWNTs and SWNTs can be prepared through CVD method.

Figure 2.3 Schematic experimental setup for CVD growth of CNTs.

The general nanotube growth mechanism in CVD process involves the dissociation of hydrocarbon molecules catalyzed by the transition metal, dissolution and saturation of carbon atoms in the metal nanoparticles[18]. The precipitation of carbon from the saturated metal particle leads to the formation of tubular carbon solids in sp^2 structure. The experimental results support the occurrence of two stages in the growth process. In the first stage, the formation of a primary tube is initiated by a small metal particle on the substrate. The carbon tends to nucleate on the side of the metal drop. The primary tube consists of perfect graphite layers cylindrically rolled around the metal particle. The metal particle may be found at the tip of the tube or some times at the bottom of the CNTs, which are commonly referred to the “top-growth” or “bottom-growth” mechanism, respectively, as shown in Fig. 2.4. The second

stage may consist of the thickening of the primary tube by the carbon deposition on the outer surface of the tube.

Figure. 2.4 Two general growth models of nanotubes.

Metal catalysts for CVD process are usually Fe, Fe₂O₃, Ni, Co, Pt, etc. The catalyst is critical for the growth of CNTs. The catalyst particle size and uniformity affect the diameter and uniformity of the grown CNTs. Also the gas stock, substrate temperature, gas flow ratio, deposition pressure are important factors to affect the quality of CNT films, such as defects density in the tube walls, impurity concentration in the CNT films and CNT number density. Alignment of the growth of carbon nanotubes can be achieved by the catalyst pattern and applying electric field in the deposition process.

CVD approaches are more popular and widely used to produce CNTs. CVD process with metal catalyst has several advantages over other synthesis methods. The CNTs can grow at relatively low temperatures and the diameter of the CNTs can be controlled by controlling the size of the metal catalyst particles. Furthermore, it is relatively easy to obtain vertically aligned CNTs with CVD technique[22].

2. 4 Thermal Conductivity of CNTs

Diamond and in-plane graphite display the highest measured thermal conductivity of any known materials at moderate temperature. In graphite the thermal conductivity is generally dominated by phonons and limited by the small crystallite size within a sample. Thus the apparent long range crystallinity of CNTs has led to speculation that the longitudinal thermal conductivity of carbon nanotubes could be comparable or even exceed the in-plane thermal conductivity of graphite.

In semimetals and semiconductors include CNTs, lattice thermal conductivity, k_l is usually much larger than electron thermal conductivity k_e [23]. According to kinetic theory, the lattice thermal conductivity is determined by $k_l = Cv l/3$, where C , v and l are the specific heat, sound velocity or phonon group velocity, and phonon mean free path, respectively. The strong sp^2 bonds in CNTs give rise to high sound velocity. In addition, lack of scattering of phonons by boundary and defects in perfect CNTs could result in long phonon mean free path. All these contribute to the high thermal conductivity of CNTs.

In 1999, Hone, Whitney and Zettle[24] pointed out that the thermal conductivity for a single CNT rope at room temperature could vary between 1800 - 6000 W/m.K. Also in that year, Che, Cagin and Goddard numerically calculated the thermal conductivity of a (10, 10) nanotube to approach 2980 W/m.K[25]. In 2000, Berber, Kwon, and Tomànek[3] using molecular dynamic simulations suggested unusually high value of 6,600 W/m.K for the thermal conductivity at room temperature. They theorized that these high values would be due to the large phonon mean free paths. All these groups stated that these values for CNT thermal conductivity are comparable to diamond or a layer of graphite.

Hone *et al.*[24] used a comparative method and determined the thermal conductivity of aligned SWNT film around 200 W/m.K. Yi *et al.*[26] employed 3 ω method and obtained thermal conductivity of 25 W/m.K at room temperature for MWNT film. Li *et al.* [27] developed a thermal probe method which can measure the thermal conductivity of a single CNT and yield a value of 3000 W/m.K for a single MWNT. Also, there are some other measurement techniques used for thermal conductivity measurements, including infrared emission[28], laser surface reflectance[29], Raman scattering[30], liquid crystal[31], etc. All these methods can be classified into two groups: steady state methods and transient state methods. Laser surface reflectance technique belongs to transient state methods. Compared to the above mentioned steady state methods, one advantage of transient methods is that heat loss can be minimized if the experimental conditions is optimized.

It can be seen from above, the experimental results of CNT thermal conductivities of different groups deviate each other greatly. Since CNTs are in nano-meter scale and 1 D materials, which make CNTs greatly different from bulk materials. Firstly, thermal conductivity of CNTs is different in axis direction and transverse direction, e.g. thermal conductivity in CNTs is a tensor, not a scalar. The thermal conductivity along the axis direction is much higher than that in transverse direction, suggesting that aligned CNT films should have much higher thermal conductivity than that of randomly ordered CNTs. Secondly, SWNTs and MWNTs usually have different thermal conductivity since the interlayer interaction also plays a role in the thermal transportation in MWNTs. Finally, a single CNT should have different thermal conductivity with their bulk counterpart, such as CNT films. The number density of CNTs, inter-tube interaction, impurity density, and alignment of the CNT film have strong influences on the observed thermal conductivity. So far, there are still many challenging issues remained in these fields, such as the influences of CNT diameter and length on the CNT thermal conductivity.

2.5 Electronic Properties of CNTs

Usually, MWNTs exhibit metallic property and are similar to graphite due to their large diameters, while SWNTs are greatly different with MWNTs. The electronic properties of SWNTs are very sensitive to their diameters and chiralities. The physics behind this sensitivity of the electronic properties to their structure can be understood within a band-folding picture[32]. The Fermi surface of an ideal graphite sheet consists of the six corner K points around the hexagonal Brillouin zone. When forming a tube, owing to the periodic

boundary conditions, the electron wave-vector along the circumferential direction become quantized. Only a certain set of k states of the planar graphite sheet is allowed. The allowed set of k 's, indicated by the lines in Fig. 2.5, depends on the diameter and the helicity of the tube. Whenever the allowed k 's include the point K, shown in the (7, 1) case, the system is a metal with a nonzero density of states at the Fermi level, resulting in a one-dimensional metal with 2 linear dispersing bands. When the point K is not included, shown in the (8, 0) case, the system is a semiconducting with a energy gap depending on the tube diameter[14].

Figure 2.5 Allowed k -vector of the (7,1) and (8,0) tubes (solid lines) mapped onto the graphite Brillouin zone.

The general rules for a SWNT with index of (n, m) are: (n, n) tubes are metals; If $n-m$ can be divided by 3: $n-m=3j$, where j is an integer, the SWNTs are very tiny-gap semiconductors; otherwise, SWNTs will be large gap semiconductors. Figure 2.6 shows the band structure calculated by tight-binding approach for (12, 0), (13, 0) and (5, 5), respectively[6]. For most experimentally observed carbon nanotube sizes, the gap in the tiny-

gap variety which arises from curvature effects would be so small that, for most practical purpose, all the $n-m=3j$ tubes can be considered as metallic at room temperature.

Figure 2.6 Energy band diagram of three kinds of SWNTs.

Electron transport through single-wall carbon nanotubes (SWNTs) has generated considerable interest. SWNTs provide a nearly perfect model system for one dimensional conductors, in which electron–electron correlations have a profound influence on the properties of conduction electrons. They offer several clear advantages over other 1 D system. For example, comparing with semiconductor quantum wire, SWNTs are atomically uniform and well-defined. Strong confinement around the circumference leads to a large spacing between 1D subbands (~ 1 eV for a ~ 1 nm tube in contrast to ~ 10 meV for typical semiconductor quantum wires), which means that the 1D nature is retained up to room temperature or above. Moreover, because of the tubular structure, the Peierls distortion, which normally makes other molecular wire semiconducting, becomes energetically unfavorable in carbon nanotubes[14]. At low temperatures, a number of interesting mesoscopic phenomena

have been observed, such as single-electron charging[33], resonant tunneling through discrete energy levels[34], and proximity-induced superconductivity[35]. At relatively high temperatures, tunneling conductance into the nanotubes displays a power-law suppression as a function of temperature and bias voltage, which is consistent with the physics of the 1D Luttinger liquid[36]. Metallic SWNTs (m-SWNTs) are able to carry a remarkable high current density and the main scattering mechanism for high energy electrons is due to optical or zone-boundary phonons[37].

Due to the 1D nature, the CNT-metal contacts usually exhibit high resistance of ~ 1 M Ω . m-SWNTs have an ideal intrinsic two terminal resistance of only $h/4e^2$ or 6.5 K Ω [38]. Thus the bias voltage dropped almost entirely across the contacts and tunneling phenomena could dominate the transport. Thermal annealing can efficiently reduce the CNT-metal contact resistance. Similar reduction in contact resistance was achieved by using planarized or briefly annealed gold electrode[37].

2.6 Applications of Carbon Nanotubes

2.6.1 Electron Field Emission Display

MWNTs and m-SWNTs are good candidates of electron emitters for their small tip, which greatly enhance the localized electric field. In addition, they have good thermal conductivity and excellent current carrying ability, which greatly improve the reliability of the field emission display. Some of the first experiments on field emission from nanotube were carried out by Walt De Heer and colleagues[5]. With an aligned CNT cathode, a current

density of up to 0.1 Acm^{-2} at a voltage of approximately 700 V was reported. This level of emission should be sufficient to produce an image on a phosphor-coated display. In our group, at an average field of $2\text{-}5 \text{ V}/\mu\text{m}$, a high density of electron field emission current of $0.01\text{-}0.1 \text{ mA}/\text{cm}^2$ from high density nanotube films has been obtained[39].

2.6.2 CNT based Electronic Devices

Electronic properties of SWNTs are strongly determined by their diameter and chirality. However, pentagon-heptagon pair defects can be introduced into the hexagonal network of a single carbon nanotube, leading to a change in the helicity of the tubes and their electronic structure. These structures could be the building blocks of nanoscale electronic devices made entirely of carbon nanotube[7]. CNTs can also be used for chemical sensors[40, 41], bio-sensors[42] and actuators[43]. These applications can be implemented using the conductance change of CNTs upon interaction with outside inputs, such as gases, biomolecules, pressures, etc. One important application of s-SWNTs is field effect transistors (FET)[9]. Ballistic CNTFET was studied by Ali Javey *et al* [44]. Quantum spin field effect transistor was reported by Wang *et al* [45]. These results demonstrate that CNTs are promising materials for nano-electronic applications. The basic structure of CNTFETs is shown in Fig. 2.7 (a). A s-SWNT acts as conducting channel across the source and drain electrodes. Highly doped Si substrate act as the back gate to control the “on” and “off” of the CNT channel. SiO_2 act as gate oxide. Due to the small size and high thermal conductivity of the SWNTs, CNTFET based integrated circuits should have high integration density, high speed and high reliability in comparison with Si based ICs. In addition, CNTFET can be used as memory devices[46, 47], as shown in Fig 2.7 (b). Charges can be injected from the CNTs

to dielectrics and remain trapped there, causing a hysteretic behavior. If some chemical gases, such as NH_3 , CO and NO are sprayed onto the CNTFETs, the CNT channel conductance and the threshold voltage of the CNTFETs will change correspondingly. High sensitivity CNTFET gas, chemical or biosensors have been made. Figure 2.7 (c) shows a simple structure of a typical CNTFET gas sensor.

Figure 2.7 Schematic structures of (a) CNTFET, (b) CNTFET memory, (c) CNTFET gas sensor.

Chapter 3

GROWTH OF CARBON NANOTUBES

3.1 Introduction

Growth of high quality carbon nanotubes (CNTs) is critical important for CNT electrical applications. Currently, chemical vapor deposition (CVD) is a very common method to fabricate CNTs. The CVD techniques can be divided into thermal CVD, hot-filament CVD (HFCVD), microwave plasma-enhanced CVD (MPECVD), plasma jet CVD, etc. Different deposition technique produce CNTs with different morphology.

In this work, we employ MPECVD technique to prepare CNTs. In this technique, The CNTs can be grown at relatively low temperature, ~600-700 °C. The quality of CNTs is influenced by many factors, such as deposition pressure, microwave power, substrate temperature, gas flow ratio, particle size of catalyst, etc. All these parameters need to be optimized to increase the CNT number density and reduce defect and impurity concentration in CNT film.

Specially, metal catalysts play an important role in the growth of carbon nanotubes. For example, the diameter, length and purity of CNTs can be controlled by the grain size and morphology of the metal catalyst. Usually, acid treatment, such as HNO₃ and HF dipping can roughen the surface of metal catalyst films and make smaller catalyst particles[48]. It was also

found that some gases, such as oxygen, nitrogen, or ammonia, introduced to MPECVD growth can also affect the morphology and qualities of CNTs[22].

In our group, high number density nanotubes were produced with the aid of iron-oxide particles[49]. The CNTs can grow within a large process window. For example, the H_2/CH_4 flow ratio can vary from 10 to 160. However, at the same process conditions, it is difficult to produce CNTs with nickel(Ni) catalyst. In this chapter, we investigated the influences of plasma treatment on the CNT growth. The effects of oxygen and nitrogen on the growth of carbon nanotube using Ni catalyst are studied in detail.

3.2 Microwave Plasma Enhanced Chemical Vapor Deposition System

In this project, we use the 1.5 kW AsTex high pressure microwave plasma chemical vapor deposition (MPECVD) system (HPMS, 2.45GHz frequency). Figure 3.1 shows the configuration of the MPECVD system. 2.45 GHz microwave is generated and conducted into the chamber through the rectangular wave-guide. The introduced gases can be excited by the high energy of microwave and form plasma region. Substrate temperature is controlled by a RF heater and monitored using a thermal couple buried in the substrate holder.

Different from other kinds of plasma, the microwave can oscillate electrons in microwave frequency. Collision of electrons with gas atoms and molecules generates highly ionized species. Due to the high energy of microwave, usually the CNTs can be prepared under low temperature[50].

Figure 3.1 Schematic diagram of the MPECVD reactor.

3.3 Experimental Details

Chapter 3: Growth of carbon nanotubes

Ni thin films with thickness of 50 nm were deposited on (100) orientated single crystalline silicon substrate using an e-beam evaporator. To enhance the adhesion of the Ni film to the silicon substrates and roughen the nickel film surface, Ni coated silicon substrates were first annealed at 400°C in nitrogen atmosphere for 5-10 min and then dipped into diluted nitric solution for 5-10 seconds. Methane (CH₄) was used as feedstock for carbon source. In addition, H₂, O₂ and N₂ were added to assist CNT growth. In the first stage, Ni coated substrate was pretreated in a gas-mixture of Group A, H₂, Group B, H₂ + N₂, and Group C, N₂ + O₂ plasma for 10 min, respectively. In the second stage, a gas mixture was introduced into the chamber at a fixed flow ratio of H₂/CH₄=300/20 sccm (Group A) and H₂/CH₄/N₂=300/20/50 sccm (Groups B and C). Deposition pressure and deposition time were 35 Torr, and 10 min, respectively. Microwave power was maintained at 1.3 kW. The substrate temperature monitored using a thermal couple buried in the sample holder was kept at 700°C. The detailed process parameter can be seen from table 3.1

Table 3.1 Process condition of the MPECVD growth of CNTs

	Stage 1 (plasma pretreatment)	Stage 2 (CNT growth)
Time (Min)	10	10
Pressure (Torr)	35	35
Microwave power (kW)	1.3	1.3
Group A (sccm)	H ₂ (300)	H ₂ (300)/CH ₄ (20)
Group B (sccm)	H ₂ (300)/ N ₂ (20)	H ₂ (300)/CH ₄ (20)/N ₂ (50)
Group C (sccm)	N ₂ (250) /O ₂ (5)	H ₂ (300)/CH ₄ (20)/N ₂ (50)

After the pretreatment in the first stage, the nickel coated substrates were taken out from the chamber and the surface morphologies of nickel films were examined by Atomic Force Microscope (AFM) (Shimadzu SPM-9500J2). Their AFM images are shown in Fig. 3.2. One can see clearly that Ni grain size in Group A is around 50-100 nm. Some interconnections and voids between the grains exist. With the treatment of $H_2 + N_2$ plasma, the grain size could be reduced a little bit, ranging from 30-80 nm, as seen in Fig.3.2 (b). In group C, the Ni grain size is further reduced to about 20-50 nm after $N_2 + O_2$ plasma treatment. It is also noticed that nickel particles are round in shape and have large inter-grain distance compared to Group B and A. It is reported that small round grains (20 ~ 50 nm) can easily act as nucleation seeds for nanotubes. CNTs are difficult to grow on large rectangular catalyst grains, resulting in the formation of carbonaceous particles[51, 52].

Figure 3.2. AFM images of nickel films after (a) H_2 , (b) $\text{H}_2 + \text{N}_2$ and (c) $\text{N}_2 + \text{O}_2$ plasma pretreatment.

The influence of different pretreatments on CNT growth can be seen in Fig. 3.3. The CNT morphologies of different groups were examined using field emission scanning electron microscopy (FE-SEM, 6340F). Low number density and short length of CNTs are obtained for Group A. Due to the large grain size of Ni catalyst, CNTs grew non-uniformly. Some regions were covered with tangled CNTs, while others with amorphous carbon and carbonaceous particles, see Fig.3.3 (a). CNT number density is increased significantly for Group B, as shown in Fig. 3.3 (b). The CNTs are 50-80 nm in diameter and several micrometers in length. However some large carbon particles can still be observed. In group C, the number density of CNTs is even higher and fewer carbonaceous particles are found than that in Group B. One can see the CNT number density greatly increases, e. g. the impurities decreases from A to C. On the other hand, In group A, the CNTs are tangled with each other and form cage structure, while in Group B and C, the CNTs are more straight and longer, suggesting a small defect density in the CNTs formed[51].

Figure 3.3. SEM images of carbon nanotubes of Group A, B, and C.

3.4 Effects of Oxygen and Nitrogen

Although H_2+N_2 plasma pretreatment does not influence Ni grain size very much, the composition of Ni particles was changed, as confirmed by X-ray diffraction (XRD, Siemens D5005 X-ray diffractometer) results. XRD was performed at a grazing incidence angle ($\alpha=1^\circ$)

to investigate the composition of the catalyst. Figure 3.4 shows the XRD profile of nickel catalyst before CNT deposition for the three groups. There are only several Ni peaks for Group A, indicating that H_2 plasma pretreatment did not change pure nickel film composition. Several Ni_3N peaks detected in Group B suggest that the nickel film chemically reacted with nitrogen during the $N_2 + H_2$ plasma pretreatment. The plasma treatment plays a role in the incorporation of Ni and nitrogen. NiO peak was detected in group C, indicative of chemical reaction between Ni and O_2 at $700^\circ C$. The oxidation process can further reduce the Ni grain size, which is beneficial to the CNT growth.

Figure 3.4 XRD spectrum of nickel films after (a) H_2 , (b) $H_2 + N_2$ and (c) $N_2 + O_2$ plasma pretreatment.

Growth of CNTs can be described as follows: The decomposition of hydrocarbon on the front surface of the fine Ni particles produce hydrogen and carbon, which then dissolves in Ni particles in the initial stage. The dissolved carbon then diffuses through the particles, to be deposited on the trailing face forming the tube structure[18]. On the one hand, the round Ni grains are easier to act as nucleation seeds for CNTs, as CNTs cannot grow with large rectangular Ni grains. This is consistent with the results reported by other research group[51]. Many carbonaceous particles are formed on the surface of the rectangular or irregular catalyst grains. On the other hand, the excess carbon will release its energy by forming graphite cap on nickel particle surface. Once the cap is formed, the growth of CNTs will be prohibited. In other words, nickel catalyst is easily passivated by excess carbon. In Fig. 3.3 (a), most of nickel catalysts are covered by carbonaceous layers, which prohibit CNT growth.

In the “scooter” model, Smalley’s[19] group suggest that an individual nickel atom becomes chemisorbed to the edge and ‘scoots’ around the periphery, assisting the arrangement of incoming carbon atoms into the hexagonal rings, as shown Fig. 3.5. If the nickel particles have sufficient high mobility to keep visiting every site of the tube circumference frequently to ensure the tube open, CNTs will keep growing. According to this explanation, we can interpret the enhancement effect of nitrogen on CNT growth on basis of two possible mechanisms. (1) Under the aid of $H_2 + N_2$ plasma, ionized nitrogen reacted with nickel and formed Ni_3N and Ni_4N phase. The nitride could dissolve the excess carbon efficiently, so that the carbon passivation layers on nickel nitride particles are suppressed. The nitride enhancement mechanism was also proposed by Jung *et. al.*, who demonstrated CNTs could be deposited in $CH_4 + NH_3$ environment and the nitride surface layer on the catalyst can suppress

the passivation efficiently[22]. Although growth temperature and gas flow ratio of $H_2:CH_4$ can be precisely controlled to eliminate formation of passivation layer, the addition of nitrogen makes CNT growth in a wider range of H_2/CH_4 ratio. (2) Due to the more charges of nitrogen ion compared to hydrogen ion, the ionized nitrogen atom may possess higher kinetic energy. Impinging process transfer more energy from nitrogen ions to nickel nitride particles to keep them more active. Thus the CNTs growth is efficiently enhanced.

Figure 3.5 Illustration of ‘scooter’ mechanism for growth of CNTs.

3. 5 Conclusions

This chapter study the growth of carbon nanotubes (CNTs) using microwave plasma enhanced chemical vapor deposition (MPECVD) technique. Influences of O_2 and N_2 on nickel

catalyst particles, in turn, on CNT growth are investigated. After $O_2 + N_2$ plasma pretreatment, Ni grain size is greatly reduced. Under the aid of plasma, nitrogen can react with Ni, the newly formed Ni_3N and Ni_4N phase could greatly suppress the formation of carbon passivation layer on nickel nitride particles. What's more, the chemical activity of catalyst is enhanced in the presence of ionized nitrogen. Yield of CNTs is therefore significantly increased and defect concentration in the CNT film is greatly reduced.

Chapter 4

THERMAL AND ELECTRICAL TRANSPORT IN MULTIWALLED CARBON NANOTUBES

4.1 Introduction

Carbon nanotube (CNT) is a type of very attractive material for many unique properties because of its nanometer size tubular structure. Extremely high thermal conductivity has been theoretically predicted for CNTs, due to large phonon mean free path in strong carbon sp^2 bond network of CNT walls[3]. Che *et al.*[2] used equilibrium molecular dynamics to simulate the thermal conductivity of single-wall carbon nanotube (SWNT) and suggested that it is dependent on the concentration of vacancies and defects in the CNTs. Theoretical value of it approaches 2980 W/m.K along the tube axis, which is even higher than that of good conventional thermal conductors, such as diamond.

So far, some experimental results of thermal conductivity for single-wall and multiwalled carbon nanotubes (MWNTs) have been reported[53, 54, 26]. However the values deviate each other very largely, from 20 to 3000 W/mK. The measurement techniques include comparative method[53] and 3 w method[55]. Although these studies provide considerable knowledge of heat transport along CNTs, some problems still need be clarified. Firstly, previously measured thermal conductivity of bulk CNTs may not reflect intrinsic CNT thermal conductivity due to the effect of volume filling fraction. Here intrinsic means the pure

CNT thermal conductivity. Normally the measured bulk CNT film thermal conductivity was contributed by CNT as well as air contained in a specific area, so the value of the thermal conductivities are greatly affected by the CNT film density. Secondly, for a steady-state method, radiative heat loss could lead to an uncertainty in determining the thermal conductivity. Finally, in practical CNT electronic applications, such as CNT based transistors, bio/chemical sensors etc, CNT length dependence of thermal conductivity will be considered as one of a few key factors in design. However, the relevant results have not been reported yet.

Compared to SWNTs, MWNTs have large diameter and more rigidity[56], which could reduce the contact resistance between the MWNTs and metal electrodes. Large diameter CNTs have been predicted to have a larger mean free path l_e for elastic scattering for a given defect density[57]. Together with high current carrying capability (10^9A/cm^2) and high thermal conductivity, vertical aligned MWNT array are excellent candidates for field emission cathode arrays and integrated circuit heat sink.

In this chapter, thermal and electrical transport properties of MWNTs, which were prepared by microwave plasma chemical vapor deposition technique, were investigated using pulsed photothermal reflectance (PPR) and the two-terminal I - V methods. In section 4.2, the transmission line theory is introduced followed by the PPR system. A three-layer model is employed to simulate the results to obtain the thermal properties of the MWNTs. Thermal contact resistance and heat loss issues are also discussed in this chapter. In section 4.3,

electrical transport in MWNTs is also characterized and the anisotropic transport property are discussed in detail. Finally, we give some main conclusions.

4.2 Thermal Conductivity Measurement

4.2.1 Pulsed Photothermal Reflectance(PPR) system

Figure 4.1 shows the experimental setup of the PPR system. This technique basically consists of a pump laser and a probe laser. The pump source is a Nd:YAG laser(continuum Surelite 110Hz) operating at a wavelength of 532 nm with a pulse width(FWHM) of ~8ns. To enhance the heat absorption, a metal layer, preferably gold, is deposited on top of the sample surface. The probe laser is a continuous wave(cw) He-Ne 1mW laser(single frequency Coherent, model 200), whose amplitude noise(RMS) is 0.1% for the frequency range of 10 Hz to 10 MHz and the amplitude fluctuation is about 1.9 %.

When the Nd:YAG laser pulse is incident on the top gold layer, the sample surface temperature rises sharply, and then relaxes with time. This gives rise to a temperature profile which depends on the thermal properties of the underlying sample and the thermal resistance between the layers. Heating up of the sample induces a change in the refractive index on the gold layer. A probe beam is incident to the center of the pump spot to monitor the induced changes. Since the temperature and the reflectivity of gold are inversely related, the temperature profile can be obtained by capturing the changes in the reflected probe beam. The signals are captured using a photodetector(New Focus DC Photoreceiver 1801) with a rise time of 3 ns, and are displayed on the oscilloscope(HP Oscilloscope 54522A) which has a bandwidth of 500 MHz and sample rate of 2 GSa/s (2.5 G sample data point per second). To

extract the thermal conductivity from the obtained signal, analytical expression of heat conduction is used to fit the measured temperature profile.

Figure 4.1 Photothermal reflectance experiment setup. (1) Pump Nd: YAG laser, (2) Probe He-Ne laser, (3) Lens, (4) Sample, (5) Attenuator, (6) Filter, (7) Photodetector, (8) Oscilloscope.

Photothermal techniques have gained popularity in measuring thermal properties of thin films and bulk materials. This is mainly due to its non-contact nature together with easy sample preparation. Photothermal techniques can be classified into either modulation or pulsed measurement techniques. The advantage of using pulsed photothermal technique is that

real-time signal can be achieved. This is useful in monitoring the thermal treatment process. In addition, the signals obtained using the pulse technique are usually in a very short time scale, and the convective heat losses can be neglected.

In order to extract the thermal properties of a thin film from its thermal response, an analytical model has been developed by solving the heat diffusion equation. For an N layer system, this would involve solving N differential equations with 2N coefficients to be determined. Ang[58] illustrated the use of Laplace transform technique to obtain the temperature profile for a three-layer system. However, direct evaluation of the coefficients in the frequency domain solution is rather complex. Using the transmission-line theory proposed by Hui and Tan[59], the frequency domain solution for a multilayer system can be easily obtained. By performing an inverse Laplace transform on the frequency domain solution, we can obtain the transient temperature profile.

4.2.2 The Transmission-Line Technique

The analogy between thermal conduction and electrical conduction is well-established[60, 61]. Here, only the relevant results are given. For most thermal transient problems, the amount of temperature above the ambient, i.e. the temperature excursion $T(z, t) = T_2(z, t) - T_1(z, t)$ is that of interest. The Laplace transform of the temperature excursion $\bar{T}(z, s)$ is equivalent to the voltage $V(z)$, and the heat flux $-K \partial \bar{T}(z, s) / \partial z$ to the current $I(z)$, where K is the thermal conductivity, t is the time, s is the frequency and z is distance along the heat flux direction.

From these analogies and the heat conduction equation expressed in frequency domain [62], one can obtain the following frequency domain (or s domain) of the transmission-line equations:

$$\frac{dV(z)}{dz} = -\frac{1}{K} I(z) , \quad (4.1)$$

$$\frac{dI(z)}{dz} = -rcsV(z) , \quad (4.2)$$

where r is the density and c is the specific heat. Equation (4.1) is basically the definition of heat flux and Equation (4.2) is the one-dimensional heat conduction equation in the s domain. If we differentiate Eq. (4.1) with respect to z , and then substitute Eq. (4.2) into the resulting expression, a voltage wave equation will be obtained. Similarly, a current wave equation can be obtained by differentiating Equation (4.2) with respect to z , and substituting Equation (4.1) into the resulting expression. The resulting voltage and current wave equations are:

$$\frac{d^2V(z)}{dz^2} - g^2V(z) = 0 , \quad (4.3)$$

$$\frac{d^2I(z)}{dz^2} - g^2I(z) = 0 , \quad (4.4)$$

where g is defined as $\sqrt{s/a}$ and $a = K/rc$ is the thermal diffusivity.

If we consider a transmission-line terminated by a load impedance Z_L as shown in Fig. 4.2,

Figure 4.2 Transmission-line with current source $Q(s)$ terminated in a load impedance Z_L .

the traveling-wave solution to Eq. (4.3) and (4.4) can be written as:

$$V(z) = V^+(0)[\exp(-gz) + \Gamma(0)\exp(gz)], \quad (4.5)$$

$$I(z) = \frac{V^+(0)}{Z_c}[\exp(-gz) - \Gamma(0)\exp(gz)], \quad (4.6)$$

where Z_c is the characteristic impedance given by $1/k\gamma$, $\Gamma(0)$, the ratio of the reflection coefficient at $z = 0$, is defined as the voltage $V_-(0)$ associated with the reflected wave $\exp(\gamma z)$ divided by the voltage $V_+(0)$ associated with the incident wave $\exp(-\gamma z)$, which is given as $V_-(0)/V_+(0)$, alternatively, $\Gamma(0)$ can be represented as:

$$\Gamma(0) = \frac{Z_L - Z_c}{Z_L + Z_c}, \quad (4.7)$$

The input impedance at $z = -d$ is given by:

$$Z_{in}(-d) = Z_c \frac{Z_l - Z_c \tanh(gd)}{Z_c + Z_l \tanh(gd)}, \quad (4.8)$$

The thermal characteristics of a film (K, α) of thickness d can be represented by its analogue transmission line characteristics (γ, Z_c). The load impedance, Z_l , corresponds to the thermal impedance of the rear surface of the film. The current source, $Q(s)$, corresponds to the shape of a heat pulse which strikes the film's front surface.

Using the transmission-line concepts stated above, the surface temperature of a film of the corresponding voltage at $z = -d$, $V(-d)$, is given by:

$$V(-d) = Q(s) Z_{in}(-d), \quad (4.9)$$

For a single layer film, the input impedance $Z_{in}(-d)$ is given by Eq. (4.8). For multiplayer films, one can iterate the Eq. (4.8) to obtain the input impedance for two and three-layer samples. Since $V(-d)$ corresponds to the temperature excursion in the frequency domain, $T(z,s)$, the temperature excursion in the time domain can be obtained by performing an inverse Laplace transform of Eq. 4.9

$$T(-d, t) = \frac{1}{2\pi j} \int_{s-j\infty}^{s+j\infty} T(-d, s) \exp(st) ds, \quad (4.10)$$

where σ is chosen such that all the singularities of $T(-d, s)$ lie on the left-hand side of the complex s plane.

To facilitate the calculation of Eq. (4.10), numerical approximation method is used.

The mathematical formula of Stehfest method[63] is given by:

$$f(t) \approx \frac{\ln 2}{t} \sum_{n=1}^N c_n F\left(\frac{n \ln 2}{t}\right), \quad (4.11)$$

where the coefficient C_n is given by:

$$C_n = (-1)^{n+N/2} \sum_{K=(n+1)/2}^{\min(n, N/2)} \frac{k^{N/2} (2k)!}{((N/2 - k)! k! (k-1)! (n-k)! (2k-n)!)}, \quad (4.12)$$

4.2.3 Experimental Details

Groove structures are chemically etched on high resistivity silicon (100) substrates. The depth and width of the structure are 10-50 μm and 3-5 mm, respectively. Nickel thin films with thickness ranging from 0.5 to 100 nm are selectively deposited on the groove structured silicon substrates. The Ni films in the groove structures serve as catalyst for growing CNTs in $\text{CH}_4 + \text{H}_2 + \text{N}_2$ microwave plasma. Substrate temperature, reactant gas flow ratio of $\text{H}_2 : \text{CH}_4 : \text{N}_2$, microwave power and deposition pressure are 720°C, 200:20:10 sccm, 1300 W, 35 Torr, and up to 10 mins, respectively. The length and diameter of the MWNTs are ranging from 10 to 50 μm and 40 to 100 nm, respectively. To enhance heat absorption in our PPR measurement, 1.2- μm thick gold foil is closely attached to the top of the CNT films. Procedures of the sample preparation are shown in Fig. 4.3. Figure 4.4 (a) show the HR-TEM

picture of one MWNT. The inset of Fig. 4.4 (a) shows the detailed wall structure of the nanotubes. Figure 4.4 (b) shows the schematic illustration of the samples for thermal and electrical property measurement.

Figure 4.3 Procedures of the CNT samples preparation.

During the measurement, the gold foil is struck by a Nd: YAG laser pulse with a pulse width (FWHM) of 8 ns, spot size of 3 mm, pulse energy of 30.3 μJ , and frequency of 10 Hz. Immediately after the laser pulse striking, the sample surface temperature rises sharply and then drops to room temperature. Estimated surface temperature excursion of about 31 K is about 10% of the measuring temperature. The temperature decay time is governed by thermal conduction properties of the CNT film underneath the gold foil. A focused continuous He-Ne laser is reflected from the gold foil surface, probing the light reflection variation of the gold foils. Since the reflectivity is very sensitive to the surface temperature[64], by inverting the obtained signal, a temperature excursion profile can be obtained. The system was calibrated by measuring the thermal conductivity of silicon dioxide film.

(a)

(b)

Figure 4.4 (a) HR-TEM images of the MWNTs and (b) schematic illustration of the samples for thermal and electrical property measurement.

4. 2. 4 Results and Simulation

We use a three-layer model to simulate heat transport in Au/CNTs/Si structure. To minimize the effect of thermal transport through intertube airspace, the effective thermal conductivity is deduced from the difference in the temperature profiles of Au/CNTs/Si and Au/airgap/Si.

Figure 4.5 shows the measured and fitted normalized surface temperature profiles for Location A “Au/airgap/Si” and Location B “Au/CNTs/Si”, respectively. To obtain the thermal conductivity of CNTs, the temperature profile is fitted using a 3-layer heat conduction model. The silicon substrate is modeled as an infinite medium, because heat diffusion length in silicon is 3.7×10^{-4} m[65], which is less than the thickness of silicon substrate. The Laplace transform of surface temperature profile, $T(s)$, can be described by

$$T(s) = \frac{Q(s)}{e_1 \sqrt{s}} \left[\frac{(\cos h_2 \sqrt{s} + e_{32} \sinh h_2 \sqrt{s}) \cosh h_1 \sqrt{s} + (e_{31} \cosh h_2 \sqrt{s} + e_{21} \sinh h_2 \sqrt{s}) \sinh h_1 \sqrt{s}}{(e_{31} \cosh h_2 \sqrt{s} + e_{21} \sinh h_2 \sqrt{s}) \cosh h_1 \sqrt{s} + (\cosh h_2 \sqrt{s} + e_{32} \sinh h_2 \sqrt{s}) \sinh h_1 \sqrt{s}} \right], \quad (4.13)$$

where $e_i = \sqrt{r_i C_i K_i}$, $e_{ij} = e_i / e_j$, $h_i = d_i / \sqrt{a_i}$. $i=1,2,3$. Subscripts 1, 2 and 3 stand for the Au foil, CNTs or airgap and silicon substrate, respectively. r , C , K , e , a , and d are the bulk density, specific heat, and thermal conductivity, thermal effusivity and thermal diffusivity of each layer, respectively. $Q(s)$ is the Laplace transform of the Nd:YAG laser pulse, in a form of

$$Q(s) = \frac{1}{2} \left[1 + \operatorname{Erf} \left(\frac{b}{g} - \frac{gs}{2} \right) \right] \exp \left[-bs + \frac{1}{4} g^2 s^2 \right], \quad (4.14)$$

where $b=2.0 \times 10^{-6}$ s and $g=5.764 \times 10^{-9}$ s for the laser pulse we used.

Figure 4.5 Measured (dot line) and fitted (solid line) surface temperature of the (A) air gap and (B) 40- μ m MWNT film.

In order to fit the temperature excursion profile, Eq. (4.13) is inversely Laplace transformed into time domain using Stehfest numerical method[63]. The bulk density of $1.93 \times 10^4 \text{ kg/m}^3$ and specific heat of 129 J/kg.K for Au are used in the fitting[66]. The thermal conductivity for silicon substrate is taken as 148 W/m.K [65]. Fitting parameters are the thermal conductivities of Au foil and CNT films, and the thermal diffusivity of the CNT films. One can see that the simulated curves fit the measured temperature profiles reasonably well for $40\text{-}\mu\text{m}$ thick CNT film (B) and airgap (A). The average fitted thermal conductivity of the CNT film is about 15 W/m.K . We have measured CNT films with different thickness from 10 to $50 \mu\text{m}$, and the fitted values are listed in Table 4.1. It is found that the thermal conductivity for the four CNT films ranged from 12 to 17 W/m.K . The variation range of the fitted thermal conductivity depends on the signal to noise ratio. One can see that the thermal conductivity does not show a CNT film thickness dependence. In other words, it is independent of the length of CNTs.

Table 4.1. Thermal properties vs. thickness (or length) of the MWNT samples

Nanotube length (μm)	12	25	40	46
Thermal conductivity K_{Au} (W/m K)	268-288	182-243	267-295	250-310
Thermal conductivity K_{tube} (W/m K)	13-17	12-16.5	13-17	14-17
Thermal diffusivity $\alpha_{\text{tube}}(10^{-5} \text{ m}^2 \text{ s}^{-1})$	1-2.6	1-10	5-9	0.7-1

The fitted thermal conductivity for airgap is around 0.0264 W/m.K , consistent with the literature value of 0.026 W/m.K [65]. It is also noticed that the average thermal conductivity of Au foil is about 260 W/m.K , only about 80% of Au bulk value. Hartmann *et al.*[67] have

confirmed that thermal conductivity of Au film is strongly dependent on the film thickness due to the influence of surface and grain boundary scattering. In addition, voids and microcracks within the gold foil may also reduce thermal conductivity efficiently[68].

4.2.5 Contact Thermal Resistance

Contact thermal resistance between the gold foil and CNTs does not affect our CNT thermal conductivity very much. With our CNTs length 10-50 μm and CNT thermal conductivity of 12-17 W/m.K. The CNT thermal resistance can be expressed by $R_{th}=d/K$, where d and K are the length and thermal conductivity of the MWNTs, respectively. The sample thermal resistance could be $0.8\text{-}2.9\times 10^{-6} \text{ m}^2\text{K/W}$, which is contributed by both CNT thermal resistance and the contact thermal resistance. Figure 4.6 shows how the thermal resistance varies as a function of the thickness of CNT films. A contact thermal resistance of $2.2\times 10^{-8} \text{ m}^2\text{K/W}$ is obtained by extrapolating the linear fitting to zero film thickness and it is one or two orders of magnitude smaller than the CNT thermal resistance. Therefore the contact thermal resistance can be ignored. In addition, the boundary thermal resistance caused by acoustic mismatch is even one order of magnitude smaller than the obtained contact thermal resistance[69]. Thus, contribution from acoustic mismatch is negligible as well.

Figure 4.6. Thermal resistance of Au/CNTs as a function of the CNT length.

4.2.6 Heat Loss

Heat loss in the measurement also does not affect the obtained thermal conductivity. First, it has been found that, in transient thermal conductivity measurement by a flash technique, the heat loss is noticeable when the temperature decay time is more than 30 ms and 5 s[70, 71], respectively. In our measurement, the temperature rise is 20-30 K above the environment temperature (room temperature) and the temperature excursion duration is only $\sim 400 \mu\text{s}$. By comparing our experimental conditions with those used in flash technique[70, 71], we suggest that the radiative heat loss in our measurement is not significant. Second, using the three layer model described in the text, the surface temperature of gold foil $T^*(s)$ with heat loss will be

$$T^*(s) = Q(s) \left\{ \frac{(\cosh_2 \sqrt{s} + e_{32} \sinh_2 \sqrt{s}) \cosh_1 \sqrt{s} + (e_{31} \cosh_2 \sqrt{s} + e_{21} \sinh_2 \sqrt{s}) \sinh_1 \sqrt{s}}{[(e_{31} \cosh_2 \sqrt{s} + e_{21} \sinh_2 \sqrt{s}) \cosh_1 \sqrt{s} + (\cosh_2 \sqrt{s} + e_{32} \sinh_2 \sqrt{s}) \sinh_1 \sqrt{s}] e_1 \sqrt{s}} \right\}, \quad (4.15)$$

$$+ h_{c,r} [(\cosh_2 \sqrt{s} + e_{32} \sinh_2 \sqrt{s}) \cosh_1 \sqrt{s} + (e_{31} \cosh_2 \sqrt{s} + e_{21} \sinh_2 \sqrt{s}) \sinh_1 \sqrt{s}]$$

where h_c and h_r are the convective and radiative heat transfer coefficients, respectively. For the case of convective heat loss, according to the definition of h_c ,

$$h_c = \frac{-K_{air} dT / dz}{T}, \quad (4.16)$$

where $T = T_2 - T_1$, T_2 is the gold surface temperature with a maximum value of 55°C, T_1 is the ambient temperature of 25°C, and dT/dz is the temperature gradient normal to the gold foil. h_c can be evaluated to be 24 W/m².K using the thermal conductivity of $K_{air} \sim 0.027$ W/m.K. Substituting $d_{Au} = 1.2 \mu\text{m}$, $K_{Au} = 240$ W/m.K, $e_1 = 2.16 \times 10^4 \text{ W s}^{1/2} \text{ m}^2 \text{ K}^{-1}$, $h_1 = 1.95 \times 10^{-4} \text{ s}^{1/2}$, $d_2 = 40 \mu\text{m}$, $K_{tube} = 15.5$ W/m.K, $e_2 = 1.81 \times 10^3 \text{ W s}^{1/2} \text{ m}^2 \text{ K}^{-1}$, $h_2 = 4.82 \times 10^{-3} \text{ s}^{1/2}$, $e_3 = 1.56 \times 10^4 \text{ W s}^{1/2} \text{ m}^2 \text{ K}^{-1}$ and $h_c = 24$ W/m².K into Eq. (4.15). Through inverse Laplace transform, the value of $[L^{-1} T^*(s) - L^{-1} T(s)] / L^{-1} T(s) \sim 10^{-4}$. This indicates that the influence of the convective heat loss on the gold foil temperature profile can be ignored.

As for the radiation effect, using Au emissivity of $e_m = 0.07$, the Stefan-Boltzmann constant $S_{SB} = 5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4$, $T_2 = 329 \text{ K}$ and $T_1 = 298 \text{ K}$, the maximum value of h_r is evaluated as:

$$h_r = e_m S_{SB} (T_2^2 + T_1^2)(T_2 + T_1) = 0.49 \text{ W} / \text{m}^2 \cdot \text{K} , \quad (4.17)$$

Since $h_r/h_c \sim 0.02$, the radiative heat loss should be much smaller than the convective heat loss.

Thus, radiative heat loss can be also neglected.

4.2.7 Volume Filling Fraction

The obtained thermal conductivity of the CNT films is not as high as those reported values, as mentioned in the introduction. Let us examine the effect of intertube airspace, which is highly resistive to heat conduction. A thermal conductance model is shown in Fig. 4.7. The total thermal conductance of the CNT films is contributed from the effective thermal conductance of CNTs and the airgap, i.e.

$$\frac{K_{tube}}{d} = \frac{K_{tube}^* d}{d} + K_{air} \frac{1-d}{d} , \quad (4.18)$$

where K_{tube}^* is the effective thermal conductivity for the CNTs, K_{tube} is the fitted thermal conductivity for the CNT film, K_{air} is the thermal conductivity for air. d is the CNT volume filling fraction and d is the thickness of the tube films or airgap. Through weighing the groove-structured sample before and after CNTs growth and assuming the mass density of MWNT $\rho \sim 1.34 \text{ g/cm}^3$ [26, 72], the value of d is determined to be about 7-8% for the four samples. By substituting the average values of K_{tube} and K_{air} into Eq. (4.18), we have $K_{tube}^* = 2 \times 10^2 \text{ W/m.K}$. This is much lower than reported by Berber *et al* [3]. For isolated SWNTs

without defects, the thermal conductivity may exceed that of diamond. For CNT array, the thermal conductivity directly depends on the packing density. Even for the most densely packed array of cylinders, hexagonally packed, the necessary void spaces inside each nanotube and in the interstices between tubes can significantly reduce the thermal conductivity of the CNT array.

Figure 4.7 Schematic illustration for thermal resistance model.

4.2.8 Heat Transport Mechanism in MWNTs

To have a better understanding of the thermal transport in CNTs, other fitting parameters shown in Table 4.1 should be addressed here. One can see that the thermal diffusivity a is diverging with the thickness of the CNT films. Using the relation $a \sim K^*/rC$ and using the mass density of MWNT $r \sim 1.34 \text{ g/cm}^3$, the specific heat C of the MWNTs can

be calculated out around 1.7×10^3 J/kg.K. This is larger than the published value of 470 J/kg.K[26]. Benedict *et al.*[73] predicted that the specific heat could depend on the diameter of CNTs. Phonon dominant specific heat is directly related with the phonon density of state(PDOS). Small diameter CNTs have large strain due to their large curvatures in comparison with large diameter CNTs. This particular strain effect is thought to be the reason for the differences in the PDOS, which will further affect the specific heat. Interestingly, our MWNT diameters distribute from 40 to 100 nm, indeed larger than those CNTs used in Yi *et al.*'s experiment[26], where the diameters were from 20 to 40 nm.

Electrical conductivity S of the same tube films is determined to be $1.6\text{--}5 \times 10^{-1} \Omega^{-1} \cdot \text{cm}^{-1}$. Using the Wiedemann-Franz law[23], the ratio of K/ST ($T=300$ K) for our sample is around $1\text{--}4 \times 10^{-4} (\text{V/K})^2$, which is three or four orders of magnitude larger than the free-electron Lorenz number of $2.45 \times 10^{-8} (\text{V/K})^2$. Therefore, we suggest that the thermal conductivity of MWNTs is dominantly contributed by phonons, or $K \sim Cvl$, where v is the characteristic sound velocity for CNTs and l is the phonon mean free path. With $K_{\text{tube}}^* = 200$ W/m.K and $v = 10^4$ m/s[74], we have $l \sim 20$ nanometers, which is smaller than that calculated by Kim *et al.* [27]. For our MWNTs, due to the large length of our tube samples (10~50 μm), boundary scattering could not be the main reason to reduce the phonon mean free path. Inter graphene layer and intertube coupling as well as the defects scattering are more likely to reduce the phonon mean free path[3,25,27]. The defects here mean pentagonal defects, heptagonal defects and pentagonal-heptagonal pairs, which lead to form positive, negative curvature or stepped surface on CNT walls, respectively[18]. These defects interrupt the localized CNT periodic structure and act as phonon scattering centers, resulting lower phonon mean free

path. The influence of the defects and inter-layer coupling effects on the thermal conductivity reduction can be estimated. We use the value ~ 6600 W/mK reported by *Berber et al.*[3], it could be reduced to 660 W/mK for MWNT array if the conclusion that interlayer interactions quench the thermal conductivity of graphite by nearly 1 order of magnitude is applicable to CNTs. Then the defects could further reduce the thermal conductivity from 660 to 200 W/m.K.

Maruyama[75] proposed that thermal conductivity of CNTs may converge when the tube length is much longer than the phonon mean free path. As was confirmed by Che's[25] simulation, if the CNT length is larger than 15 nm, theoretical thermal conductivity converges to a value of 2980 W/m.K. In our case, the length of MWNTs ranges from 10 to 50 μm , much far beyond the phonon mean free path of 20 nm. Therefore, the thermal conductivity should not depend on the CNT length for our CNT films. This expectation is confirmed by our measurement, as shown in the Table I.

Using equilibrium and nonequilibrium molecular dynamics simulations with accurate carbon potential, Berber[3] predicted the thermal conductivity of (10,10) SWNT of $K \sim 6600$ W/m.K at room temperature. In contrast, Maruyama[75] obtained the thermal conductivity of (5,5) SWNT of $K \sim 600$ W/m.K at room temperature using phantom technique, ten times smaller than Berber's results. Kim *et al.*[27] through measuring a microfabricated suspended device, determined the thermal conductivity of 3000 W/m.K for a single MWNT. However, Hone *et al.*[53] measured the thermal conductivity of crystalline ropes of SWNTs and obtained a value of 35 W/m.K at room temperature, in the same order of magnitude as the

value observed by Yi *et al.* [26] for the bundles of MWNTs. One year later, the former authors reported a value of 200 W/m.K for magnetically aligned SWNT film[54]. From above, we can see that for a single tube, either single-wall or multiwalled, the thermal conductivity is from 600 to 6000 W/m.K, significantly higher than the values of 15-200 W/m.K for bulk CNT samples, including CNT films, CNT ropes and aligned CNT array. It should be pointed out that for isolated single CNT involved measurements, heat loss to its surrounding may affect the accuracy of measurement, overestimating its thermal conductivity. In contrast, for bulk CNT samples, heat loss to inter-air-gaps among the tubes could be much smaller than isolated single CNT due to very high CNT number density and very small air gaps among them. The small thermal conductivity for bulk CNT samples may also result from intertube coupling[3,5,27] and high density of defects which efficiently scatter the flow of phonons in CNTs[26]. Further investigation is needed to clarify these issues.

4.3 Electrical Measurements of MWNT Films

4.3.1 Experimental Details

The electrical resistance of the testing samples was measured in the longitudinal direction on low-resistivity silicon substrates, and in the transverse direction on high-resistivity silicon substrates using two probes and a picoammeter (HP 4155A), as shown in Fig. 4.8 (a) and (b). Taking the volume geometric correction into account, the corresponding electrical conductivity σ of the MWNT films in the longitudinal and transverse directions can

be determined. The electrical conductivity in the longitudinal direction $S_{//} = (1-5) \times 10^3 \Omega^{-1} \text{ m}^{-1}$ is three orders of magnitude larger than that of highly doped silicon substrate ($1-5 \Omega^{-1} \text{ m}^{-1}$, $400 \mu\text{m}$), and the corresponding substrate resistance is 3 ~ 4 orders of magnitude lower than the longitudinal MWNT resistance. The transverse conductivity $S_{\perp} = (1-3) \times 10^2 \Omega^{-1} \text{ m}^{-1}$ is three or four orders of magnitude larger than that of high resistivity ($0.02-0.05 \Omega^{-1} \text{ m}^{-1}$) silicon substrate. The corresponding transverse resistance of the substrate is still two orders of magnitude larger than that of MWNTs. The substrate effects can therefore be safely neglected.

Figure 4.8 Schematic diagram of the electrical measurement in (a) longitudinal direction and (b) transverse direction.

4.3.2 Results and Discussion

For the two-terminal current-voltage (I - V) measurement, linear current-voltage curves were obtained in the longitudinal and transverse directions. The electrical resistance in the longitudinal direction as a function of the thickness of MWNT films is plotted in Fig. 4.9. It

can be clearly seen that the resistance linearly increases with increasing in thickness of MWNT films, obeying the Ohm's law. This finding is consistent with a diffusive transport rather than ballistic transport of electrons in the MWNT films[4, 76, 77, 78]. The diffusive transport phenomena can be explained as follows: Metal-MWNTs contacts give rise to an extra potential on the C atoms on the MWNTs surface, and thus have a great influence on the electrical transport properties of MWNTs. MWNTs growing over metal layers always exhibit a diffusive transport[79]. Impurities and defects in the tube walls act as the scattering centers and greatly reduce the electron phonon mean free path. This may also contribute to the diffusive transport in our MWNT films.

Using the Büttiker-Landauer relation[80], the longitudinal electrical resistance of the MWNTs can be described by:

$$R = \frac{h}{4e^2} + R_i + R_{c1} + R_{c2} , \quad (4.19)$$

where $h/4e^2$ is the quantized contact resistance between the MWNTs and the Au foils. R_i , R_{c1} , and R_{c2} are the intrinsic resistance from the scattering process, the tube-tube junction resistance and the metal-MWNTs contact resistance, respectively. R_i and R_{c1} should vary linearly with the thickness of the MWNT films. By extrapolating the nice linear fitting to zero film thickness in Fig. 4.9, we can determine $R_{c2} = 240 \text{ K}\Omega$. Correspondingly, the electrical conductivity in the longitudinal and transverse directions is $S_{//} = (1-5) \times 10^3 \Omega^{-1} \text{ m}^{-1}$ and $S_{\perp} = (1-3) \times 10^2 \Omega^{-1} \text{ m}^{-1}$, respectively. By taking the MWNTs volume filling fraction of 7-8 % into account, the effective electrical conductivities are $S_{//}^* = (1-4) \times 10^4 \Omega^{-1} \text{ m}^{-1}$ and $S_{\perp}^* = (5-25) \times 10^2$

$\Omega^{-1} \text{ m}^{-1}$. The anisotropy of the electrical conductivity of the MWNT films, $S_{\parallel}^*/S_{\perp}^*$, ranges from 20 to 30 for 10-50 μm long CNTs.

Figure 4.9 Electrical resistance vs. the thickness of the MWNT films.

The anisotropy of the electrical conductivity suggests most MWNTs in our samples grew perpendicularly to the substrates. With PPR technology, it is difficult to measure the thermal conductivity perpendicular to the MWNT growth direction for our samples. However, it has been suggested that $K_{\perp}/K_{\parallel}$ is identical in our oriented and unoriented MWNT films. The anisotropy in the thermal conductivity should therefore follow the anisotropy in the electrical conductivity [53,54] or:

$$\frac{S_{\perp}^*}{S_{\parallel}^*} = \frac{K_{\perp}^*}{K_{\parallel}^*}, \quad (4.20)$$

Thus, transverse thermal conductivity $K^{\perp}$ could be around 6-10 W/mK for our samples. It is believed that the phonon coupling between the graphene layers in a single MWNT should have graphite-like behavior. However, cylindrical MWNTs also produce LA mode, corresponding to the phonon motion along the nanotube axis; TA modes, corresponding to the phonon motion perpendicular to the nanotube axis, and a twist mode, corresponding to the phonon motion around nanotube axis. The anisotropy of the thermal conductivity of our MWNT films may partly result from the fact that the velocity of the phonons in LA mode is higher than that in TA mode. Similar observation is also found in SWNTs[14].

The values of $S^{\parallel}$ are 20 to 70 times smaller than that of in-plane graphite[81]. The small $S^{\parallel}$ of our MWNTs could result from several factors including the MWNT transverse coupling, existence of defects, impurities, tube-tube junctions, and some degree of misalignment. The finding of $S^{\parallel}$ being much larger than $S^{\perp}$ would be attributed to the following effects: The intrinsic MWNT resistance is much lower than the tube-tube contact resistance, because fewer tube-tube contacts are crossed for a given length of MWNTs in the axis direction as compared with the perpendicular direction[82]. In addition, $S^{\perp}$ is greatly affected by the number density of MWNTs, or the MWNT filling fraction.

For our MWNT samples, $S^{\parallel}/S^{\perp}$ ranges from 20 to 30 and this ratio is much lower than the corresponding ratio of the in-plane conductivity to the out-of-plane conductivity of 10^3 - 10^4 for graphite[83]. Interestingly, $S^{\perp}$ is found to be much higher than the out-of-plane conductivity of graphite. Carbon has four valence electrons and three of them are strongly bound to neighbor carbon atoms forming graphene with very high in-plane rigidity. The fourth

electron is delocalized and shared by all the atoms forming p bond, thus leading to a high in-plane conductivity. However, the out-of-plane conductivity for graphite is very small because of the weak interplane coupling interaction.

Figure 4.10 shows the schematic diagram of electron transverse (perpendicular to the nanotube axis) transport across MWNTs. Figure 4.10 (a) schematically illustrates the carrier transport within a single MWNT. There are two routes for electrons moving from Position A to Position B, i.e., tunneling and circum-navigating processes. Electrons could tunnel from one shell to another shell (Route 2), similar to the out-of-plane electron transport in graphite. The electron transfer in the circumference direction (Route 1) should be similar to that of graphite due to the large diameter of MWNTs, in which curvature effects can be neglected. Thus, high electrical conductance of a single MWNT could be mainly contributed by the outmost-shell transport.

Figure. 4.10 (b) schematically illustrates the transverse transport in MWNT arrays. Because of a large ratio of the CNT length to the diameter, ~ 500 , and a fairly high number density of the MWNTs in the samples, tube-tube junctions could be easily formed in our MWNT films. Electrons transport from Position A to C would be greatly influenced by the tube-tube junctions. The junctions act as energy barriers which limit the overall electron mean free path in the MWNT films, so that the electrical conductance is significantly reduced by the junctions. The tube-tube junction resistance is determined by inter-tube hopping processes similar to the inter-plane hopping in 3D graphite. Since the total transverse conductance in MWNTs is contributed by the circum-navigating processes and inter-tube hopping processes

whereas only the hopping processes dominates the out-of-plane transport in graphite, which can partly explain that $S^{\wedge}$ for our sample is larger than that of the out-of-plane conductance in graphite.

Figure 4.10. Schematic diagram of the electron transverse transport in MWNTs.

4.4 Conclusions

Thermal and electrical transport in MWNT films have been studied. The thermal conductivity of MWNT films with film thickness or CNT length from 10 to 50 μm is investigated by pulsed photothermal reflectance (PPR) technique. The average thermal conductivity is found to be about 15 W/m.K and independent of the CNT length. Taking the volume-filling fraction of CNTs into account, the effective thermal conductivity for the MWNTs is about 2×10^2 W/m.K. Convection and radiation heat loss can be neglected due to the small time duration of the measurement.

Two probe I-V method has been employed to examine the anisotropic electron transport in the MWNT films. It is found that the electron transport in the nanotubes is diffusive rather than ballistic. The ratio of the electrical conductivity in the longitudinal direction to that in the transverse direction is from 20 to 30. The anisotropic electrical conductivity can be attributed to different number of tube-tube junctions in the longitudinal and transverse directions.

A comparison between the obtained effective thermal conductivity and electrical conductivity suggests that heat transport in the MWNTs is dominated by phonons. Phonon mean free path is estimated to be 20 nm, much smaller than the CNT length. This is consistent with our observation that the observed thermal conductivity is independent of MWNT length.

Chapter 5

RAMAN SCATTERING OF CARBON NANOTUBES

5.1 Introduction

Raman scattering, an inelastic photon scattering process by the phonons, is widely used for characterizing the structure of crystal materials. It is a nondestructive method and suitable for carbon materials, such as diamond, graphite, carbon fibers and carbon nanotubes, etc. The Raman spectra of carbon materials usually show a highly dispersive band in 1300-1400 cm^{-1} , so called D-band which results from the lattice disorder (or the reduction in crystallite size); G-band in 1500-1600 cm^{-1} due to the in-plane atomic displacements; second order of D band in 2500-3000 cm^{-1} and second order of G band in 3100-3300 cm^{-1} [84, 85]. In addition to these bands, SWNTs uniquely have a radial breathing mode (RBM) at 100-200 cm^{-1} [32]. Usually the Raman spectra of carbon nanotubes (CNTs) are affected by many factors. They can be classified into two groups: (1) the internal factors, such as diameter, length, chirality, and crystalline degree and (2) the external factors, such as temperature, external pressure, doping concentration and the excitation photon energy, etc. All the factors have certain degree of influences on the position, intensity, line width, and line shape of the Raman peaks.

With the applications of carbon nanotubes in the low dimensional, high-speed, and high power nanodevices, electrical and thermal management become important issues for nanotechnology. Current crowding and localized heating in submicron interconnects are

known to strongly affect the reliability of CNTs based devices. The heat induced changes in the diameter and length of CNTs would consequently affect the optical phonon frequency and electronic properties of CNTs. Temperature dependent Raman spectra can provide us the structural, thermal and electronic properties of CNTs. So far, quite a few research groups have demonstrated that the Raman frequencies decrease with increasing of temperatures due to the phonon softening effect of C-C bond force-constant[86,87,88,89]. However, the temperature dependence of the positions and line-shape of RBM peaks of SWNTs are still not sufficiently well documented.

Moreover, the temperature variation in most previous experiments was directly achieved through changing the intensity of the excitation laser beam. The CNT temperature was monitored using the ratio of intensity of the Stokes peak to that of the Anti-Stokes peak. However, the temperature determined from the Stokes/Anti-Stokes ratios is strongly affected by systematic errors, because the ratio is not sensitive to the temperature. Calibration must be carefully done[90]. In addition, laser heating is a local heating technique. The temperature dependence of the Raman peak positions will be influenced by the temperature gradient, not reflecting the intrinsic properties of the materials. This is because the temperature gradient leads to a certain degree of thermal expansion, resulting in an extra stress and the Raman peak position shifting.

In this chapter, we studied the temperature dependence of the Raman spectra of single-wall carbon nanotubes (SWNTs), multiwalled carbon nanotubes (MWNTs), carbon nanofibers (CNFs) and highly ordered pyrolytic graphite (HOPG). Section 5.2 described the experimental

details. General results about the Raman peaks are presented in section 5.3. Comparison of the temperature sensitivity of Raman peak position between the samples and the temperature dependent line-shape of the RBM peaks in SWNTs are also discussed in this section.

5.2 Experimental Details

The SWNTs used in this work were purchased from MER corporation. The purity of the SWNTs is above 95% after purification. The average diameter of the SWNTs are ~ 1.4 nm and length is range from several to few tens of microns. We find that most SWNTs are in the form of bundles with bundle diameters of 15~20 nm. The MWNTs were produced by microwave plasma chemical vapor deposition (MPECVD) method. The MWNTs are 50-80 nm in diameter, and several microns in length. The freestanding CNFs produced by Nanocs International Inc. (New York, U.S.A.) are 500-1000 nm in diameter, and few tens of microns in length. The HOPG samples were purchased from Advanced Ceramics. The Raman scattering was carried out using the Renishaw Raman system with an Argon laser excitation at 514.5 nm (2.41 eV) under ambient conditions. The spectral resolution was about 2 cm^{-1} . The laser beam power was controlled below $0.2\text{ }\mu\text{W}$ in a spot size of $1\text{ }\mu\text{m}^2$ to avoid laser-heating. The SWNTs were piled up on a fused quartz substrate to avoid charge transfer effect and the sample was placed on the THMS 600 electrical heating stage, which controlled the sample temperature from RT up to 673K. The heater could provide a uniform temperature profile over the sample size. The peak positions, relative intensities and full width at half-maximum (FWHM) of the Raman peaks were obtained by fitting the spectra using several Lorentzian line shapes.

5.3. Results and Discussion

5.3.1 General Results

TABLE 5.1. The frequencies of the observed Raman peaks at RT for the SWNTs, MWNTs, CNFs and HOPG.

	D	G	D*	G*
SWNTs	1334 cm^{-1}	1591 cm^{-1}	2672 cm^{-1}	3180 cm^{-1}
MWNTs	1335 cm^{-1}	1593 cm^{-1}	...	...
CNFs	1330 cm^{-1}	1589 cm^{-1}	...	...
HOPG	...	1582 cm^{-1}	2727 cm^{-1}	

Figure 5.1 shows the Raman spectra of SWNTs, MWNTs, CNFs and HOPG at different temperatures from 298 to 673 K. Table 5.1 list the observed Raman peaks at RT for the four kinds of materials for comparison.

(a)

(b)

(c)

(d)

Figure 5.1. The Raman spectra of SWNTs(a), MWNTs(b), CNFs(c) and HOPG sample(d) at different temperatures.

The temperature dependent Raman spectra of our SWNTs are shown in Fig. 5.1 (a). One can clearly find the peaks attributed to RBM with A_{1g} symmetry at $140\text{--}220\text{ cm}^{-1}$. These peaks are not observed in the CNFs and HOPG sample. MWNTs were also found to have RBM peaks, whose frequencies are affected by the individual CNT diameter and inter-layer interactions[91, 92, 93]. However we could not observe the RBM peaks from our MWNTs, possibly due to the low purity of the samples. The D peaks at $1300\text{--}1360\text{ cm}^{-1}$ are caused by disordered sp^2 carbon structure. The G peaks relevant to tangential mode at $1560\text{--}1600\text{ cm}^{-1}$, the faint peaks contributed by a combination between the tangential mode and RBM mode,

i.e, ($\omega_{\text{tang}} + \omega_{\text{RBM}}$) at 1720-1740 cm^{-1} [94], the D^* peaks, the second order of D peak, at 2620-2680 cm^{-1} and the G^* peaks at 3150-3180 cm^{-1} , the second order of G peak, are also observed in SWNTs. With increasing temperature from RT up to 673 K, the D, D^* , G and G^* peaks shift towards low frequency direction and the temperature dependences of the peak frequencies are shown in Fig. 5.2. It is seen that each set of data points can be fitted using a linear function, shown as solid straight lines. The slopes S (or the peak frequency variation rates with respect to temperature) is indicated in the figure 5.2 (a). The relations of $S_{G^*} \sim 2S_G$ is consistent with the assignment of the G^* peak as the second harmonic of the G peak. Since the frequency of the G peak is related to tangential C-C stretching, a well-accepted speculation that the frequency downshifting is likely associated with the softening of the force constant due to thermal expansion of C-C bonds[87,88,89] is still applicable here to interpret our observation. Interestingly, the Raman spectra of the HOPG sample also exhibit the temperature dependence, shown in Fig. 5.2 (b). Such phenomenon was not observed in the experiments with laser heating method[88,89] where an increase in the laser power density could not efficiently increase the temperature of the HOPG due to its high thermal conductivity.

It is worthy mentioning that the peak intensity of SWNTs as a function of the temperature. Since the SWNTs are powder-like, the SWNTs could easily swell during heating up, they may not restore the position before heating. This could be the reason for a small change in the intensity after the heating cycle.

(a)

(b)

Figure 5.2. The frequencies for the D, G, D* and G* peaks as a function of temperature. The data are fitted using linear functions indicated in the figure.

It is interesting to make a comparison between HOPG and other carbon materials. The D-bands can be clearly observed in SWNTs, MWNTs and CNFs, indicating the disorder structures in these samples, while it is hardly to be detected in the HOPG sample, as the HOPG basal plane has a perfect sp^2 structure[88]. Although HOPG has no first order D-band intensity, the second order D* can be observed at twice the frequency of the D band, because the physical origin of this second order Raman band could be caused by a strong coupling between electrons and phonons with the same wave vector in the vicinity of the K point of the 2D Brillouin zone, where the electronic energy bands exhibit unique linear k-dependence phonon and electron dispersion relations[94]. From Tab. 5.1, one can notice that the frequency of D* peak in SWNTs is almost 50 cm^{-1} lower than in that HOPG, probably due to the phonon softening effect induced by the curvature of the graphene sheet. C. Thomsen also observed that the second order of D peak was softened by 30 cm^{-1} over the value of graphite, which can be interpreted by *ab initio* approach[95].

5.3.2 Temperature dependence of the Raman Peak Frequencies

Although the frequencies of the Raman peaks for the SWNTs, MWNTs, CNFs and HOPG sample are temperature sensitive, the temperature sensitivity of the Raman peak frequencies are quite different. The S values obtained from the slope of the solid line in Fig.5.2. are listed in Tab. 5.1. The S value for the G band of the SWNTs is 0.04, a factor of 2~4 larger than those of the MWNTs, in consistence with Huang *et al*'s results[89]. This finding suggests that the lengthening of the C-C bonds caused by thermal expansion in SWNTs is likely to be significantly larger than the large size carbon materials. The physical

reason is that in the environment of very high curvature (or very small diameter) of SWNTs, the C-C bonds are lengthened up to $\sim 1.44 \text{ \AA}$, about 1.5% larger than that of graphite[96]. The force constant of the lengthened C-C bonds can be much easily softened with increasing temperature.

TABLE 5.2. The slopes of the fitted straight line for the D, G, D* and G* peaks of the SWNTs, MWNTs, CNFs and HOPG in Fig.5.2.

Slope, S (cm^{-1}/K)	D	G	D*	G*
SWNTs	-0.0083	-0.0407	-0.0234	-0.0811
MWNTs	-0.0084	-0.0158	...	...
CNFs	-0.0056	-0.0124	...	...
HOPG	...	-0.0167	-0.0209	

There is another explanation of the different G peak temperature coefficient. Since the frequency of E_{2g} mode is related to the C-C stretching[32], the frequency decrease is associated with the lengthening of C-C bond. The higher temperature coefficient for the SWNTs suggests that the C-C bond length is easily stretched compared to the MWNT, CNF and HOPG samples, probably due to the curvature effect. Since SWNTs are constructed by rolling a single layer of graphite into cylindrical structure, the relative azimuth of C-C bonds would be different from those in planar graphite due to the small diameter of SWNTs. The bonds of C_1 - C_2 , C_1 - C_3 and C_1 - C_4 have an azimuth angle γ between each other in the radial direction, as shown in Fig.5.3, So that the force constant of C_1 - C_2 bond has a radial component and a tangential direction component, as indicated in the upper right corner in Fig. 5.3. The azimuth angle γ decreases with decreasing the SWNT diameters, for example, for (15, 15), (10, 10) and (7, 7) SWNTs, $g_1 > g_2 > g_3$. The radial component of the C-C force constant increases while the tangential component decreases with decreasing the azimuth

angle γ , e.g. CNT diameter. Thus, the tangential component of C-C force constant in SWNTs should be smaller than that in planar graphite[87]. For the MWNTs and CNFs with diameters larger than 50 nm and 500 nm, the curvature effect can be neglected. The vibration properties for tangential G mode of the MWNTs and CNFs are very close or identical to that of the HOPG sample. Consequently, the G mode, resulted from the vibration of carbon atoms in the tangential direction, should have a larger frequency temperature coefficient in the SWNTs than those in MWNTs, CNF and HOPG sample. These two probably make the SWNTs' C-C bonds easy to lengthen upon increasing the temperature.

Figure 5.3. Schematic illustration of the C-C azimuth angle in SWNTs.

5.3.3 Radial Breathing Mode (RBM) Peaks of SWNTs

The RBM features at 140-220 cm^{-1} shown in Fig.5.1 are a unique characteristic of SWNTs. From simple relations between the peak frequency and the nanotube diameter d (in a unit of nm), i.e. $w_{\text{RBM}}=248/d$ (cm^{-1}) [97], or $w_{\text{RBM}}=224/d + 14$ (cm^{-1}) [98], the tube diameters are estimated to be from 1.2 (for $w_{\text{RBM}}=210$ cm^{-1}) to 1.6 nm (for $w_{\text{RBM}}=150$ cm^{-1}). It has been well established that the natural line-width of the RBM peaks is around 3~4 cm^{-1} [86,99,100]. However, it can be broadened up to 10 cm^{-1} due to extrinsic SWNT broadening processes associated with point defects, finite-size effects, etc[86]. Analysis of our RBM line shapes indicates that the RBM features at room temperature (RT) can be well fitted using several Lorentzian peaks at 148, 157, 172, 180, 189, 199 and 208 cm^{-1} , as shown in Fig. 5.4 (a). The FWHM of the Lorentzian peaks are fixed at 8.4 cm^{-1} , as the damping constant for the RBM is not expected to be strongly dependent on the nanotube diameter from 1.0 to 1.6nm[90]. We have tried to use minimum number of phonon frequencies to fit RBM bands and found that 7 peaks are necessary to give a best fitting. The number of phonon frequencies were determined by the line shape of the Raman bands and the fitting was performed using the multi-peak fitting function in the software provided by Renishaw Raman system. The integrated intensity of the three Lorentzian peaks at 172, 180 and 189 cm^{-1} dominates the intensity of the entire RBM features, suggesting that the majority of our SWNTs are of a diameter of ~1.4 nm. Since the line-widths of these symmetric RBM peaks are insensitive to temperature up to 600K[86,99], we also fit the RBM peaks at higher temperatures using a set of 8.4 cm^{-1} -FWHM Lorentzian peaks, as shown in Figs.5.4 (b-d). Interestingly, with increasing temperature, the line shape of the entire features begins to narrow down. At 673 K, the

Lorentzian peaks with $w_{\text{RBM}} \leq 165 \text{ cm}^{-1}$ and $w_{\text{RBM}} \geq 200 \text{ cm}^{-1}$ completely vanish. The temperature dependent variation of the RBM features is qualitatively consistent with Jorio et al's observation for bundled SWNTs[86], but against the findings where entire RBM features downshift with increasing temperature[87,101,102].

The activation of the RBM features is associated with the transitions between the pair of electronic density of state (DOS) singularities in the valence and conduction bands with the energy separations of $E_{ii} = E_{Ci} - E_{Vi}$, where $i = 1, 2, 3, \dots$. When the energies of the incident or scattered photons are in resonance with E_{ii} , the Raman peaks will be enhanced. In other words, the Raman spectra only reflect the characteristic features of the SWNTs whose E_{ii} are very close to the photon energy of incident laser beam E_{laser} , or inside the resonant window of $|E_{\text{laser}} - E_{ii}| \leq 0.2 \text{ eV}$ [94]. Note that the DOS is nanotube diameter and chirality dependent. The energy separation between the highest-lying valence-band singularity and the lowest lying conduction-band singularity can be expressed as $E_{11}^{(M)} = 6a_{C-C}\gamma_0/d$ and $E_{11}^{(S)} = 2a_{C-C}\gamma_0/d$ for the metallic and semiconducting SWNTs, respectively, where γ_0 is the nearest neighbor carbon-carbon overlap energy and a_{C-C} the nearest neighbor carbon-carbon distance[103,104].

A thorough interpretation to the temperature dependent RBM peaks in Fig.5.4 is difficult at this moment. However, we would like to give our consideration in terms of following speculations. 1) If the simple relations of $w_{\text{RBM}} \propto 1/d$ mentioned above are still valid at high temperatures, the RBM peak frequencies could downshift due to thermal radial expansion of the SWNTs. However, the speculation only predict a downshifting of the entire RBM features without a significant change in the line shapes, inconsistent with our

observation. Furthermore, molecular dynamics simulations[101] and x-ray diffraction studies[105] suggest that the thermal radial expansion of SWNTs is extremely small even at 700K, $dd/d \approx (700\text{K}) \times (8 \times 10^{-7}/\text{K}) \sim 6 \times 10^{-4}$, and thus may not play an important role in the temperature dependent variation of the RBM features. 2) Although the thermal expansion of SWNTs is found to be extremely small, the C-C bond length $a_{\text{C-C}}$ could expand at a much higher rate than the radial and axial tube dimensions through enhancing the out-of-plane atomic vibrations with increasing temperature[101]. It should be noted that the energy separation of E_{ii} is determined by the ratio of $a_{\text{C-C}}$ to d , rather than d itself, referring to the equations for both $E_{11}^{(M)}$ and $E_{11}^{(S)}$ discussed above. As a result, E_{ii} could be increased and, therefore, shift into the resonant energy window to activate larger diameter SWNTs in the Raman scattering process. In other words, those smaller nanotubes, whose E_{ii} are in the resonant energy window, but close to the high end of it at RT, might possess higher E_{ii} and be out of the window, becoming inactive at high temperatures. In the meantime, the larger diameter nanotubes with E_{ii} slightly lower than the low end of the energy window at RT might be able to move into the window at high temperatures, contributing to the Raman signals. Therefore, the temperature dependent RBM peaks in Fig.5.4 could basically reflect the tube diameter distribution viewed through different energy windows. According to this speculation, the big Lorentzian peaks at 172, 180 and 189 cm^{-1} in the RBM features at RT could remain at the positions at high temperatures, while the disappearance of the peak at 208 cm^{-1} could be due to its corresponding E_{ii} out of the energy window. However, the vanishing of the peak at 157 cm^{-1} is not well understood. 3) As discussed above, the softening of the interatomic force constant is responsible for the downshift of the D and G peaks. In addition, the influence of the relaxation of the weak van der Waals interaction between the tubes in a bundle on the

temperature dependent spectral changes may not be negligible[101]. The weak van der Waals interaction is found to cause a small net increase in E_{ii} , leading to a 4~40 cm^{-1} up-shift in the RBM peak frequencies for isolated SWNTs with respect to the corresponding value for the bundled SWNTs[106]. The softening of the intertube force constant could restore E_{ii} . Competition between a possible increase in E_{ii} caused by the increase of the ratio of a_{C-C} to d and a possible decrease in E_{ii} caused by the softening of the intertube force constant might eventually determine whether E_{ii} increases or decreases with increasing temperature. If the two opposite tendencies are comparable, E_{ii} , or the energy window, could remain unchanged and, thus, the major Lorentzian peaks at RT could remain between 170 to 190 cm^{-1} at high temperatures. The peaks with $w_{\text{RBM}} \leq 165 \text{ cm}^{-1}$ and $w_{\text{RBM}} \geq 200 \text{ cm}^{-1}$ could be simply smoothed out by significant broadening of the line shapes at high temperatures since their E_{ii} are close to the two ends of the energy window[86].

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Figure 5.4. The deconvolution of the RBM features at 298, 373, 573 and 673 K, respectively.

The FWHM of the multi-Lorentzian peaks are fixed at 8.4 cm^{-1} , while their intensities and peak positions are determined by the best fitting to the line shape.

5.4 Conclusions

This chapter investigated the temperature dependence of the Raman spectra of SWNTs, MWNTs, CNFs, and HOPG samples. The temperature of the samples are uniformly increased using THMS600 electrical heating stage. It is found that all the detectable Raman peaks shift to low frequency with increasing temperature and the frequency shifts are reversible, indicating that the changes are associated with the carbon-carbon distance variation. The Raman peak frequencies of SWNTs are more sensitive to the temperature than those of MWNTs, CNFs and HOPG due to the curvature effect of SWNTs. For SWNTs, the line shapes of the RBM features are also found to be sensitive to temperature. The broad RBM

features from 140 to 220 cm^{-1} at room temperature narrows down to a range of 170~190 cm^{-1} at 673 K. The reversible temperature-dependent spectral changes can be interpreted through the softening of the interatomic force constant due to thermal expansion of C-C bonds and the relaxation of the weak van der Waals interaction between the tubes in a bundle with increasing temperature.

Chapter 6

ELECTRON TRANSPORT IN SWNTS AND CNT BASED DEVICES

6.1 Background

SWNTs can be divided into two groups, metallic SWNTs (m-SWNTs) and semiconducting SWNTs (s-SWNTs) depending on their chirality. When a graphene sheet is rolled up into a small tube, the allowed electron wave vector components perpendicular to the tube axis become quantized, resulting in 1D subbands in the electronic band structure of SWNTs[107]. For the subband near the Fermi energy E_f , the electron energy (E) versus the wave vector (k) is shown in Fig. 6.1 for a (a) m-SWNT and (b) s-SWNT. The dark lines represent the filled electron states. The subband structure depends on the indices number (n , m) of SWNTs.

Figure 6.1. Energy band diagram near the fermi level for a (a) metallic SWNT and (b) semiconducting SWNT.

At room temperature, electrons near Fermi level in a m-SWNT can have a long electron mean free path on the order of microns. For a SWNT a few microns long, electron flow from one end of the tube to the other end without scattering with phonons, electrons, defects, and boundary. This situation is often referred to ballistic electron transport. In a s-SWNT or a MWNT, it is generally believed that electron flow subjects to collision or scattering, resulting in a diffusive transport. These theoretical predictions have been supported by a variety of experiments[108,109,110].

The ballistic electron transport property of electrons near Fermi level in m-SWNTs arises from its unique lattice structure. The SWNT has a periodic lattice structure in axis and circumferential direction and is only one atom thick in radial direction, resulting in no electron boundary scattering in the SWNTs. However, the ballistic transport of electron in m-SWNTs at low field does not mean zero electrical resistance. For a perfect ballistic conductor, the current is carried through the contacts by infinitely many subbands or modes. But inside the size-confined ballistic conductors, the current is carried by only a few subbands due to quantization. This requires a redistribution of the current among the current carrying modes at the interface, leading to interface resistance. According to Landauer formula, for a conductor with current carried by M subbands, the resistance that one would measure between two perfect contacts is [111].

$$R_c = \frac{h}{2e^2MT_r} \approx \frac{12.9k\Omega}{MT_r}, \quad (6.1)$$

where h , e and T_r are Planck's constant, electron charge, and transmission coefficient, respectively. The transmission coefficient T_r represents the average probability that an electron injected at one end of the conductor will transmit to the other end. In a m-SWNTs, currents are carried by two 1D subbands[107]. This suggests a contact resistance of 6.5 k Ω for a perfect contact.

Compared to the low field transport property, the electron-phonon scattering mechanism can be different at a high field for m-SWNTs. The high field electron states for a metallic SWNTs is shown in Fig. 6.2 (a) for a low electric field. At low field, the two bands are filled up to the vicinity of the Fermi Level. The allowed electron-phonon scattering event is the backscattering of electrons between the two states near the Fermi level, as shown by the arrow in Fig. 6.2 (a). This transition requires a phonon with the energy equal to the small energy difference and a wave vector equal to the wave vector difference between the two states. Only few low phonon states satisfy the energy and momentum conservation, the probability of such as electron-phonon scattering event is small[112]. However, at high field, the forward-moving states are filled to a much higher energy level than the backward moving states, as shown in Fig. 6.2 (b). The transition of electron from the forward moving state to the backward one is possible by emitting an optical phonon at a frequency ω of 1300 cm⁻¹. This electron-optical phonon scattering event may have a higher probability than the electron-acoustic phonon scattering at low fields, since the optical phonons have higher density of states than the acoustic ones[113]. Yao *et al.*[37] have demonstrated that the m-SWNT current saturates at about 25 μ A at applied voltage exceeding a few volts. They proposed that the

current saturation is due to electron-optical phonon scattering at high electrical field. If this is the case, heat dissipation in the bulk is expected at high field.

Figure 6.2. Electron-phonon scattering mechanism at a (a) low and (b) high electric field.

Semiconducting SWNTs (s-SWNTs) usually have small energy gap range from 0.3 to 1.2 eV[18]. Gate effect in Si MOSFETs can also be used in these one dimensional semiconductors[114]. The first carbon nanotube based field effect transistor (CNTFET) was developed by Tan *et al.*[9]. The CNTFET exhibits p-type characteristics. Initially, it was naturally assumed that the gate voltage modified the nanotube conductance, in analogy with the channel of an ordinary Si FET. However, there has been increasing evidence that Schottky barrier at the contacts may play an important role[115]. In fact, ordinary FETs require Ohmic contacts for effective switching, while CNTFET operate as unconventional schottky barrier transistor.

The p-type behavior suggests the electric transport in CNTFET is dominated by holes. Several factors can be attributed to the origins of holes. One possibility is that doping come

from cleaning and handling CNTs in oxidizing acids. Another comes from the work function difference between the CNT and metal[114]. Since Schottky barrier (SB) forms at the metal-CNT contact. For CNTs, the SB is sensitive to the metal work function[116]. It is necessary to point out that oxygen can also play a role in the p-type characteristics. The metal work functions are well known to be sensitive to adsorbed gases[117]. In most experiments, the metal contacts and CNTs have been directly exposed to O_2 . Thus, one inevitable effect of gases is to change the metal work functions. In air, the barrier for electrons is high because of the pinning of the Fermi Level (E_f) close to the valence band maximum at the CNT-metal interface. Decreasing the gate voltage leads to reducing the thickness of the schottky barrier and allowing flowing for holes. The energy band diagram of CNT-metal contact in air is shown in Fig. 6.3.

Figure 6.3. Energy band diagram of the CNT-metal contact in the presence of oxygen.

In this chapter, we shall report on the fabrication of CNTFETs using burning-out process and characterize the performance of the CNTFETs. The thermal effects induced by high current will be discussed. We shall also study the memory effect of our CNTFETs.

6.2 Fabrication of CNTFETs

6.2.1 Introduction

Fabrication of the carbon nanotube based field effect transistors (CNTFETs) is often associated with spinning SWNT suspension on predefined metal electrodes. Unfortunately, it is often found that more than one SWNT, even a SWNT rope bridge the electrodes. These CNTs may contain metallic SWNTs (m-SWNTs) and semiconducting SWNTs (s-SWNTs), resulting in a high off channel current. To our knowledge, there is still not any efficient technique to selectively synthesize high quality s-SWNTs. To retain s-SWNT on the electrodes, IBM research group broke down m-SWNTs in SWNT ropes by applying a high current to the source-drain electrodes[118]. Under a large current, the m-SWNTs can be electrically broken down, while the s-SWNTs are protected by applying a positive gate voltage to the gate electrode to switch them off. Different from IBM's method that a constant current was employed to burn-out the m-SWNTs, we increase the drain-source voltage step by step, the measured source-drain current curves do provide us additional information to understand the electrical breakdown process. For example, the current becomes saturated at high field due to the optical phonons emission, which is directly related to the destruction of m-SWNTs.

6.2.2 Experimental Details

The SWNTs used in this work were purchased from MER corporation. They are several microns in length and 1.4 nm in diameter with a band gap up to ~600 meV[19]. The SWNTs were ultrasonic dispersed in alcohol solution for 10 min. A drop of CNT alcohol

suspension was spun onto the predefined Ti/Au electrodes, which were prepared on SiO₂ coated highly doped silicon substrate. More than 90% of the source-drain electrodes can be bridged with the SWNTs. A schematic illustration of a typical CNTFET cross section is shown in Fig. 6.4 (a). The highly doped p-type silicon substrate serves as the back-gate. 500 nm-thick SiO₂ thin film was thermal grown above the silicon substrate. 10 nm thick Ti and 90 nm thick Au were deposited on the SiO₂ followed by lift-off process. The spacing between the source and drain electrodes is 1, 2, 3, 4, 5 and 6 μm , respectively. The top surfaces of the samples were examined by atomic force microscopy (AFM, Shimadzu9500J2), as shown in Fig. 6.4 (b). The burning-out process and the CNTFETs electrical measurement were performed at ambient condition using HP-4156B semiconductor analyzer.

(b)

Figure 6.4 (a) Schematic illustration for the cross section of the CNTFET, (b) AFM image of a CNTFET. The scale bar is 800 nm.

6.2.3 Results and Discussion

6.2.3.1 Burning-out Process

An AFM image of the top view of the CNTFETs is shown in Fig. 6.4 (b). One can see that one SWNT rope bridges the electrodes. The height of the rope is about 8 nm. According to Philip, *et al.*'s observations [118], the current is uniformly distributed in a bundle of SWNT rope, because the individual nanotubes can simultaneously be in good contact with the external electrodes. Thus, the total conductance between the source and drain is $G(V_g) = G_m + G_s(V_g)$, where G_m and $G_s(V_g)$ are the conductance contributed by m-SWNTs and s-SWNTs, respectively. It has been suggested[119, 120, 121] that the p-type behavior of a

SWNT channel is a contact characteristic rather than a bulk effect of the SWNT. The schottky barrier height or thickness at the contact between the s-SWNT and metal electrodes is a function of the gate voltage and determines the performance of the CNTFET. The energy band diagram of the s-SWNT-metal contact with oxygen adsorption is presented in Fig. 6.3. When a proper positive gate voltage with respect to the source is applied to the substrate, the Schottky barrier thickness is increased and block the holes. Thus the s-SWNT channel is turned off[120].

Figure 6.5 shows the electrical fabrication process of the CNTFETs. The initial I_{ds} - V_{ds} curves as a function of gate voltage is shown in Fig. 6.5 (a). The V_{gs} varied from -5 to 5 V in a step of 2 V, and V_{ds} varied from -0.1 to +0.1 V in a step of 1 mV. It can be seen that at a given V_{ds} , I_{ds} decreases with increasing the V_{gs} , indicating that the holes dominated the electrical transport. The as-prepared devices did show a gate effect but the on/off ratio of the channel current was about 3. The low on/off ratio could be attributed to the existence of m-SWNTs in the SWNT rope channel. When the s-SWNTs channel are turned off by a positive gate voltage, the current could still flow from the source to drain through those m-SWNTs, resulting in a high off current of 3 nA. We found that I_{ds} reached its minimum value at $V_{gs} \geq 5$. It means that the s-SWNT channels were completely turned off when $V_{gs} \geq 5$ V. In other words, the threshold voltage of the CNTFET is 5 V. To disable the active m-SWNTs in the CNT rope, a gate voltage of 5 V was applied to turn off and protect the s-SWNTs. At the same time, V_{ds} was repeatedly scanned from 0 to 15 V, as shown in Fig. 6.5 (b). At the V_{ds} of around 3.5 V, the I_{ds} increased first and then decreased with time. The details were shown in the inset of Fig. 6.5. (b). The maximum value of I_{ds} dropped from 1.3 μ A to 0.8 μ A due to burning-out

some m-SWNTs under the high current. After the first burning-out process, the I_{ds} - V_{ds} curves as a function of the gate voltage were checked and shown in Fig. 6.5 (c). It can be seen the gate effect became stronger than that of the as-prepared one and the on/off ratio was increased to 5 with an off current of 2 nA. The incomplete pinch-off of I_{ds} indicated that some m-SWNTs still existed in the ropes. In the second burning-out process, larger range V_{ds} were applied. The V_{ds} repeatedly scanned from 0 to 14 V. The I_{ds} reached a maximum value of 106 μ A in curve A, and consequently collapsed to curve B and curve C, as shown in the inset of Fig. 6.5 (d). Figure 6.5 (d) shows the output characteristics of the CNTFET after the second burning-out process. The transfer characteristics were shown in Fig. 6.5 (e). The final device showed a strong gate effect with on/off ratio more than 10^4 . For $V_{gs} \geq 5$ V, the I_{ds} was undetectable, it was $\sim 10^{-12}$ A, indicating that all the m-SWNTs contacting the source and drain electrodes were burned out.

(a)

(b)

(c)

(d)

(e)

Figure 6.5. (a) Output characteristics of a as-prepared CNTFET, (b) I_{ds} - V_{ds} curves of first burning-out process at $V_{gs} = 5$ V, (c) Out-put characteristics of the CNTFET after the first burning-out process, (d) Output characteristics of the CNTFET after second burning-out process. Inset: I_{ds} - V_{ds} curves of the second burning-out process at $V_{gs} = 5$ V, (e) Transfer characteristics of the final CNTFET.

Although the p-type characteristics of CNTFETs origin from the CNT-metal Schottky contact effects, we can still estimate the effective hole density and mobility of the CNTFET. The total charge of the s-SWNTs is $Q = CV_{gt}$, where C is the CNT capacitance with respect to the silicon back-gate, V_{gt} is the threshold voltage to turn off the s-SWNTs. The CNT capacitance per unit length with respect to the back gate is $C/L = 2\pi\epsilon_0\epsilon/\ln(2h/r)$, where r , L , h , and ϵ are the CNT radius, CNT channel length, SiO₂ layer thickness and the average dielectric constant, respectively. Through Fig. 6.5 (d) and (e), using $\epsilon \approx 3$, $r = 4$ nm, $L = 1000$ nm, $h = 500$ nm, and $V_{gt} = 5$ V, the one dimensional hole density $r = Q/eL \approx 7 \times 10^6$ cm⁻¹. The hole mobility m_h can also be determined from the equitation, i.e., $dI/dV_g = m_h (C/L^2)V_{ds}$. At $V_{ds} = 100$ mV, the value of m_h is around 36 cm²/Vs, which is comparable to the earlier reported value, ~ 20 cm²/Vs[114].

6.2.3.2 Problems in the Burning-out Process

There exist some problems with the burning-out fabrication process. When a very huge SWNT rope with a diameter more than one hundred nanometers bridges the electrodes, the m-SWNTs encapsulated in the center of the SWNT rope are difficult to be selectively burned-out. If a higher breakdown current is applied, some s-SWNTs should be sacrificed. We often find that m-SWNTs could not be completely removed even at $V_{ds} = 24$ V, under which both s-SWNTs and m-SWNTs can be burned out together. These problems make the yield of the CNTFETs only about 20 %. We find that the CNT suspension concentration, the ultrasonic dispersive power and spin speed are very critical factors to influence the yield. Through optimizing these parameters, the yield can be increased to 60 %.

6.2.3.3 Thermal Effect

From Fig. 6.5 (b), we can see that the I_{ds} increases first and then decreases after a few scans. This phenomenon is frequently observed in our experiments. The increase of I_{ds} can be attributed to the thermal effect of m-SWNTs. The high current in m-SWNTs generates joule heating could anneal the defects in the tube wall. This could reduce the intrinsic resistivity of the m-SWNTs. Moreover, much joule heating solidates the contact between the CNTs and the electrodes, which reduces the contact resistance. This is very similar to the annealing effect. Further increase in I_{ds} must generate more extra heat and burn-out the m-SWNTs in the channel, leading to a decrease in I_{ds} . Why some m-SWNTs were destroyed in the first burning-out process while others survived? It can be interpreted in terms of different defect concentration in the m-SWNTs. Under air exposure, defects and dangling bonds could provide various chemical precursors to oxidation process[122]. The perfect crystalline-structure of m-SWNTs could endure higher current. In the second burning-out process, the higher current produces much joule heat that promotes the formation of defects in the CNTs first and results in rapid oxidation.

Figure. 6.5 (e) shows the transfer characteristic curve of the CNTFET. For $V_{gs} > 4$ V, the I_{ds} - V_{ds} curves remain around 10^{-12} A, exhibiting an excellent pinch-off capability. For $V_{gs} < 0$, the I_{ds} - V_{ds} curves saturate at around $V_{gs} = -7$ V, indicating that the CNT-metal contact resistance R_C begin to dominate the total resistance $R = R_{CNT} + 2R_C$ [114], where R_{CNT} is the gate dependent CNT channel resistance. The saturation current value corresponds to the $R_c = 0.35$ M Ω , a factor of 3 smaller than the reported value for a similar device structure[114].

Similarly the CNT-metal contact resistance can be roughly estimated to be around 3-4 M Ω from Fig. 6.5 (a) and (c). This means the CNT-metal contact resistance decreased after the burning-out process. It is also noticed that the I_{ds} of Fig. 6.5 (d) is larger than those of Fig. 6.5 (a) and (c) at the same bias condition even after losing some conductive m-SWNTs. For example, at $V_{gs} = -5V$, $V_{ds} = 100$ mV, the I_{ds} of Fig. 6.5 (e) is around 140 nA, while the corresponding value of Fig. 6.5 (a) and (c) are around 10.5 nA. This means the performance, e.g., the “on-state” impedance of the CNTFET is greatly reduced by decreasing of CNT-metal contact resistance. These interesting findings can be explained by the thermal annealing effect as follows:

Usually the CNT-metal contacts exhibit high resistance. In addition to quantum mechanical contact resistance, there are other source of contact resistance, such as that produced by poor coupling between the CNT and the electrodes, or Schottky barriers at metal/semiconducting tube. In our experiments, the coupling between the CNT-metal contacts could be greatly reduced by the thermal effect. The thermal-annealing for the CNT-metal contact can be effective in the temperature range from 180 to 800°C[37, 121]. During the burning-out process, the high current induced heat can increase the temperature of m-SWNTs to around 750° C, which is close to thermal oxidization temperature of CNTs in air[18]. The generated joule heating solidities the contact between the metal and SWNTs, thus efficiently reducing the CNT-metal contact resistance. It is necessary to point out that the current-induced heat within m-SWNTs can be transferred to the adjacent s-SWNTs in the same rope, which can also make a similar annealing effect and reduce the s-SWNT-metal contact resistance. Usually, the transferred heat is not enough to burn-out the s-SWNTs, partly due to the high thermal contact resistance between the SWNTs and the heat loss through air

convection. However, if too high burning-out voltage is applied, the extra heat produced by m-SWNTs will also burn-out the adjacent s-SWNTs.

From Fig. 6.5 (a), one can see that at $V_{gs} = -5$ V, the saturation current carried by m-SWNTs at $V_{gs} = 5$ V is only one third of the total channel current at $V_{gs} = -5$ V (on/off ratio = 3), which means that the on-state ($V_{gs} = -5$ V) total conductance of s-SWNTs is much larger than that of m-SWNTs. Thus, even after losing some m-SWNTs, the on-state channel conductance could be greatly increased if the contact resistance between s-SWNTs and metal is reduced due to the thermal annealing effects.

Figure 6.6 shows the detailed I-V curves of second burning-out process. The decrease of CNT-metal contact resistance is also reflected from the bias-dependence of dI/dV shown in the inset of Fig.6.6. Before I_{ds} decreases (Curve A), the dI/dV slowly increased with increasing V_{ds} until reached a saturation value, as shown in the left inset of Fig. 6.6. After the drop down of I_{ds} (Curve B), the dI/dV rised sharply at first, reached a peak value at $V_{ds} = 3.5$ V and then decreased with further increasing of bias voltage V_{ds} , as shown in the right inset of Fig. 6.6. This observation is consistent with Yao *et.al*'s[37] report. The curve A corresponds to high contact resistance and the curve B curves correspond to low contact resistance. On the condition of low contact resistance, more voltage will drop on the bulk of carbon nanotubes. At high field, the saturated current in m-SWNTs can be attributed to the optical phonon emission (OPE)[37]. The plot dI/dV vs V_{ds} on a log-log scale for the high contact resistance is also shown in the upper left corner of Fig. 6.6. The differential conductance scaled as a power law with respect to the bias voltage, $dI/dV \propto V^{0.35}$, which is in good agreement with the

Luttinger-Liquid behavior reported by Bockrath et al.[123]. The bias dependence of dI/dV in the low bias region can be attributed to the suppressed tunneling density of states in a Luttinger liquid[124].

In Fig. 6.6, one can see that the current dropdown exhibits a two-step feature. First step is from curve A to curve B, and second step is from curve B to curve C. The current saturation appears at the curve B. One may think the conductance dI/dV decrease may result from the burning-out some m-SWNTs at high bias region of curve B, not from the optical phonon emission. In our experiments, we found the saturation curve B is stably repeated for 3 scan times and then drop to curve C. It means the curve B contains 3 I_{ds} - V_{ds} curves with same shape. If the conductance decrease at high bias region in curve B is due to the loss of m-SWNTs, then the shape of curve B at the second or third scan time should be different from the first scan. Figure 6.7 shows the output characteristics and burning-out I-V curves of another CNTFET. At the V_{ds} scanning from 0 to 6V, the current drops down from curve A to curve B, in which the current becomes saturated at 3 V and I-V curve is stable repeated for long time (> 10 s). When the V_{ds} scans from 0 to 7 V, the I-V curve maintains the same shape with curve B from 0 to 6 V, 7s later, curve B sharply collapsed to curve C due to the burning-out m-SWNTs, as shown in the inset of Fig. 6.8, in which hollow hexagon line correspond to scanning from 0 to 6 V, and the solid black line correspond to scanning from 0 to 7 V. This confirmed that the OPE mechanism is the main reason to cause the conductance decreases at the high voltage in m-SWNTs.

Figure 6.6 I_{ds} - V_{ds} curves of burning-out process Inset (upper left): log-log scale of dI/dV vs voltage. (Left): Linear scale of dI/dV vs voltage at high current. (Right) Linear scale of dI/dV vs voltage at low current.

Figure 6.7 Output characteristic of another CNTFET. Inset: Burning-out I-V curves and related dI/dV vs V_{ds} curves.

Another observation is that most of m-SWNTs are efficiently burned-out when the current saturation appears due to optical phonon emission (OPE). Figure 6.8 shows the percentage of the burned-out m-SWNTs as a function of burning-out voltage V_{ds} . One can see that at the beginning of OPE, the percentage of the burned-out m-SWNTs sharply increased. This means the OPE directly related to the destruction of SWNTs. The strong electron-lattice scattering induces thermal effect. The optical phonon emission results in energy dissipation and finally destructure tube structure. This may also provide us a method to efficiently control

the burning-out process. For example, we can find a safe burning-out voltage range, in which the m-SWNTs can be efficiently burned-out while the s-SWNTs leave undamaged.

Figure 6.8. Percentage of the burning-out of m-SWNTs vs burning-out voltage.

6.3 Memory Effect in CNTFETs

Memory effects are found in the CNTFETs fabricated by burning-out process. Figure 6.9 shows the memory effect of a typical CNTFET. Hysteretic behavior of drain current as a

function of gate voltage is clearly observed at room temperature. The threshold voltage shift is around $V_{T2}-V_{T1} \sim 6$ V when the gate voltage sweep between -9 and 9 V. A current on/off ratio up to 10^2 can be achieved. After a pulsed (3s) voltage of 12 V was applied to the gates of CNTFETs, the devices were removed from the testing stage and stored under ambient conditions. The I_{ds} was monitored at $V_{gs}=0$ and $V_{ds}=1$ V once a day on the testing stage(HP4156B). The I_{ds} was found at a certain level with a fluctuation range of $250 \sim 320$ nA over a period of at least 7 days.

Figure 6.9 Hysteretic behavior of drain current as a function of gate voltage.

It is also found that the hysteresis effect increase with the sweeping range of the gate voltage, as shown in Fig. 6.10. The threshold voltage shift increases form 2 to 7 V corresponding to the gate voltage sweeping range increasing from (-8 ~ 8 V) to (-15 ~ 15 V).

Figure 6.10. Threshold voltage shift increase with increasing the gate voltage sweeping range.

The charge storage mechanism in the CNTFET can be attributed to the charge injection or removal from the dielectric through the SWNTs[125]. The diameter of the SWNT is very small, which causes a very high electric field at the nanotube surface so that charges are easily injected from nanotube to SiO_2 and remain trapped, as shown in Fig. 6.11.

Figure 6.11. Diagram of avalanche injection of holes from CNTFET channel to bulk oxide traps.

Above results demonstrate the CNTFETs may have the potential capability of non-volatile memory. If a large negative gate voltage is applied to the back gate with respect to the CNT, holes will be injected from CNTs to the oxide and remain in the traps causing a decrease of threshold voltage, corresponding to the “writing” operation. When large positive gate voltage is applied to the gate, the holes in the oxide traps can be removed, corresponding to the “erasing” operation.

Interestingly, it is found that the hysteric effect decrease with time and the threshold voltage shift reduce and saturate to a constant value after 3 days, as shown in the Fig. 6.12. We find that as-prepared CNTFETs have strong memory effects. However, the effects gradually become small with time, e.g. the threshold voltage shift gradually reduces and

saturates to constant values after 3 days, as shown in Fig. 6.12. For example, at the gate voltage sweeping range of $-9 \sim 9$ V, the threshold voltage is about 6 V and for an as-prepared CNTFET is 6 V and then gradually decreases and saturates at 3 V.

Figure 6.12. Threshold voltage shift decrease with time and saturate to a constant value.

This observation could be explained as follows. The as-prepared CNTFETs adsorbed alcohol and water molecules during their fabrication processes. Once the water molecules adsorbed at the CNT surface, they could trap the charges ejected from CNTs, causing the memory effect[126]. While the role of alcohol molecules is different from that of water molecules. The adsorption or reaction of the alcoholic molecules could dope the SWNTs or they could change the substrate potential by electrochemical adsorption to silicon oxide

surface, filling out the charge traps, which also have a great influence on the threshold voltage [127, 128]. The number of alcohol and water molecules on the CNT walls decrease with time due to desorption at room temperature, weakening the memory effect in CNTFET. Figure 6.13 represents the water molecules around the CNTs in as-prepared and 3 days later CNTFETs.

Figure 6.13. Cross section of (a) As-prepared CNTFET, (b) CNTFET 3 days later.

To confirm the above assumption, following experiment was carried out. A small drop of alcohol (IPA) solution was dropped on a CNTFET, which had been kept in clean room for more than 3 days. Figure 6.14 shows the hysteretic curves of the CNTFET memory before and after dropping IPA solution on it. One can clearly see that the threshold voltage shift increases from 2 to 4 V after dropping IPA solution on it. One can also notice that the conductance of the CNTFET after dropping IPA is clearly lower than that before at the negative gate bias region. This observation is consistent with Ref. 127. The conductance change could be attributed to the chemical adsorption and reaction between the SWNT and alcoholic molecules. This property suggests a potential application for chemical sensors.

Figure 6.14 Hysteretic curves of CNTFET memory before and after IPA dropped.

In order to study the influence of the CNTFET structures on the memory effect, both “top-contact” (in which the SWNT is on the top of the metal electrodes) and “bottom contact” (in which the SWNT is under the metal electrodes) structures are used, as shown in Fig. 6.15. The fabrication process of the two kinds of CNTFETs and FE-SEM images of actual devices are shown in Fig. 6.16 and Fig. 6.17, respectively. Figure 6.18 shows the dependence of the threshold voltage shift on the gate voltage sweeping range. One can clearly see that the “bottom-contact” CNTFETs have stronger memory effects than those of the “top-contact” CNTFETs. Threshold voltage shifted for the “bottom-contact” CNTFETs is 1~2 V larger than

that for the “top-contact” CNTFET in the gate voltage sweeping range from 12 V (-6 ~ 6V) to 30 V (- 15 ~ 15 V). This suggests that the CNTFET memory effects are sensitive to the device structure.

(a)

(b)

Figure 6.15. (a) Top-contact and (b) bottom-contact CNTFET structure.

The basic process flow for the two kinds of devices as follows:

Figure 6.16. Fabrication process of CNTFET for (a) Bottom contact, (b) Top contact.

Figure 6.17. FE-SEM top view of (a) Overall device layout, (b) Detailed metal electrode layout, (c) Top contact CNTFETs and (d) Bottom contact CNTFET.

Figure 6.18. Comparison of the threshold voltage shift between the “top contact” and “bottom contact” CNTFETs.

The explanation could be twofold. On the one hand, the charge storage of CNTFETs is partly related to the water molecules around the CNTs. The SiO_2 surface-bound water molecules can stay for a longer time. In ambient air, the thermally grown SiO_2 surface consists of Si-OH silanol groups and is hydrated by a network of water molecules that are hydrogen bonded to the silanol groups[126]. In “bottom contact” structure devices, the CNTs are close to the SiO_2 surface, as well as the water molecules bonded to the SiO_2 surface. As shown in Fig. 6.19. Therefore, the charge storage capacitance for the “bottom contact” devices should be larger than that for “top contact” devices. On the other hand, the memory effects are also caused by charges injecting from SWNTs into SiO_2 layer. This memory effect is mainly

dominated by the high electric field near the SWNTs. However, the electric field around the cylindrical SWNT decreases rapidly with distance. The gap between the SWNT and SiO_2 for the “top-contact” devices is likely larger than the “bottom contact” devices. As a result, the charges injection capability for the “top-contact” devices is smaller than that for the “bottom contact” devices.

Figure 6.19 Schematic illustration of water molecules around CNT in (a) Top contact CNTFET and (b) Bottom contact CNTFET.

6. 4 Conclusions

Carbon nanotube based field effect transistors (CNTFETs) were fabricated by electrical burning-out process. Though applying a proper gate voltage, the semiconducting SWNTs (s-SWNTs) can be efficiently protected, while the metallic SWNTs (m-SWNTs) can

be burned out by applying high source-drain current.. The conductance of the CNTFETs can be modulated by the gate voltage more than 4 orders of magnitude. The effective hole mobility is around $36 \text{ cm}^2/\text{Vs}$ at $V_{\text{ds}} = 100 \text{ mV}$. Through optimizing the parameters of the CNT suspension concentration, the ultrasonic dispersive power, and spin speed, the yield of the CNTFETs can be increased from 20 to 60 %.

It is found that the SWNT-metal contact resistance can be greatly reduced due to the thermal effect in the burning-out process. The current saturation of m-SWNTs at high field induced by optical phonon emission is directly related to the destruction of m-SWNTs.

Memory effect is observed at room temperature by sweeping gate voltage. The CNTFETs show a good charge retention capability with the charge storage time around 7 days at ambient condition. The following two processes could be responsible to the memory effect. (1) Charge injection from carbon nanotube (CNT) to the dielectrics. (2) Water and alcohol molecules adsorbed on the CNT and SiO_2 surface also contribute to the charge rearrangement.

Chapter 7

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

1. The influences of O₂ and N₂ plasma on nickel catalyst, in turn, on CNT growth are investigated. Ni grain size is greatly reduced after O₂+N₂ plasma pretreatment. The newly formed Ni₃N and Ni₄N phases could significantly suppress the formation of carbon passivation layers on nickel nitride particles. The chemical activity of Ni catalyst is enhanced in the presence of O+N plasma. Yield of CNTs is therefore significantly increased.
2. The average thermal conductivity of carbon nanotube films, with the film thickness from 10 μm to 50 μm, is approximately 15 W/m.K at room temperature and independent of the tube length. Taking a small volume filling fraction of CNTs into account, the effective nanotube thermal conductivity could be 2×10^2 W/m.K, which is smaller than the thermal conductivity of diamond and in-plane graphite by a factor of 9 and 7.5, respectively. By comparing the thermal conductivity with the electrical conductivity, we suggest that the heat transport in CNTs is dominated by phonons instead of electrons. The electrical conductivity of the MWNT films exhibited anisotropic characteristics with respect to the nanotube axis and the electron transport was diffusive rather than ballistic.

3. Temperature dependence of the Raman spectra of SWNTs, MWNTs , CNFs, and HOPG was investigated. The characteristic Raman peak frequencies are found to decrease with increasing temperature. The Raman peak frequencies of SWNTs are more sensitive to temperature than those of MWNTs, CNFs and HOPG due to the curvature effect of SWNTs. The broad RBM features for the SWNTs from 140 to 220 cm^{-1} at room temperature narrows down to a range of 170~190 cm^{-1} at 673 K. The reversible temperature-dependent spectral changes can be interpreted through the softening of the interatomic force constant due to thermal expansion of C-C bonds and the relaxation of the weak van der Waals interaction between the tubes in a bundle with increasing temperature.

4. Though applying a proper gate voltage, the semiconducting SWNTs (s-SWNTs) can be efficiently protected, while the metallic SWNTs (m-SWNTs) can be burned out by applying high source-drain current. The SWNT-metal contact resistance is found to be greatly reduced due to the thermal effect in the burning-out process. The conductance of the CNTFETs can be modulated by the gate voltage more than 4 orders of magnitude. The hole mobility is around 36 cm^2/Vs at $V_{\text{ds}} = 100$ mV. Through optimizing the parameters of the CNT suspension concentration, the ultrasonic dispersive power, and spin speed, the yield of the CNTFETs can be increased from 20 % to 60 %.

5. Memory effects (Hysteretic behavior) are observed at room temperature by sweeping gate voltage from -15 to 15 V and from 15 to -15 V. The CNTFETs show a good charge retention capability with a time of about 7 days at ambient condition. The hysteretic behavior can be attributed to two reasons: (1) Charge injection from carbon nanotube

(CNT) to the dielectrics. Due to the small diameter of the CNT, the localized field is high enough to produce Fowler-Nordheim tunneling. (2) Water and alcohol molecules adsorbed on the CNT and SiO₂ surface responsible for the charge rearrangement. Finally, the performance of the CNTFET memory can also be improved through optimizing the device structure.

7.2 Future Work

1. Different from traditional Si MOSFETs, CNTFETs can be treated as Schottky Barrier field effect transistors. The properties of CNT-metal contacts is critical to determine the performance of the CNTFETs. Firstly, electrical transport in CNTFETs under different temperatures and gate voltage need to be measured in order to get the Schottky barrier height between the s-SWNTs and metal electrodes. This is important to deeply understand the transport mechanisms in the CNTFETs. Secondly, further experiments are needed to investigate how to reduce CNT-metal contact resistance.
2. AFM is a powerful tool for manipulating CNTs and measuring the morphology, modulus, electrical conductance of the CNTs. Manipulation technique (Vector scan) will be employed to move the SWNTs to accurately control the contact between the metal electrodes and SWNTs, and map the distribution of current.
3. As prepared CNTFETs typically exhibit p-type characteristics probably due to the oxygen adsorption on the CNT surface. Vacuum annealing and passivation should be employed to

desorbed oxygen and obtain n-type CNTFETs. Doping of the SWNTs gives another direction to change the CNT electrical properties. One way is potassium vapor doping. Nanotube device are placed in the potassium vapor. However, the resolution and doping concentration are not easily to control. Ion implantation of the CNTs could be a powerful tool to accurately doping the CNTs.

4. Due to the tiny size, high surface-volume ratio and good mechanical capability, CNTs are excellent material for chemical sensors, such as CO, NO, N₂O, NH₃, and organic molecules. CNTFET structure can be employed to detect these chemicals. The detector structure needs to be optimized in order to reduce response time and have high reliability
5. CNTFET memory will be attractive due to its small feature size, high sensitivity, low power and high speed. However, the stability will be a main obstacle for the CNTFET memory application. Device configuration, quality of CNTs and proper annealing conditions should be investigated in detail to enhance the stability of CNTFET memory.

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