Carbon nanotube based field effect transistors

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CARBON NANOTUBE BASED FIELD EFFECT TRANSISTORS

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SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY

2006

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Carbon Nanotube Based Field Effect Transistors

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School of Electrical & Electronic Engineering

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2006

Carbon nanotube based field effect transistors

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Summary

Carbon nanotube based field effect transistors (CNTFETs) and their relevant phenomena have been studied in this project. Single-wall carbon nanotubes (SWNTs) as the channel of the CNTFETs were placed between source and drain electrodes using AC dielectrophoresis technique. The observed results show that SWNTs are placed between two cross-structured electrodes along the direction of the electric field. The number of aligned SWNTs is determined by the concentration of the SWNT suspension, the processing time and electric field distribution. These experimental phenomena are analyzed theoretically in terms of the dielectrophoresis induced torque and force on the SWNTs. The simulated results suggest that the rotation time for a bundle from a random direction to the electric field direction is much shorter than the translation time. Since both metallic SWNTs (m-SWNTs) and semiconducting SWNTs (s-SWNTs) could bridge the source and drain electrodes simultaneously, the breakdown process was used to burn off the m-SWNTs. The as-prepared CNTFETs show p-type and ambipolar characteristics, depending on the solvents used for dispersing SWNTs. The CNTFETs prepared using isopropyl alcohol (IPA) and water/ sodium dodecyl sulfate (SDS) suspension exhibit p-type behavior. The ON/OFF current ratio is up to 7×10^5 . The high inverse subthreshold slope (S) of 1700mV/dec could be due to the thick dielectric (500nm-SiO₂) used in our transistors. This value satisfies the trends of S as a function of gate capacitance in the

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Schottky barrier (SB)-FETs, indicating that SB also plays an important role in controlling the performance of our CNTFETs. An important negative differential conductance (NDC) phenomenon is observed at room temperature. The peak-to-valley current ratio is about 2. In addition, the peak voltage gradually shifts from 9.2V to 7.8V when the gate voltage is swept from 6V to -6V. We suggest that a quantum well is formed on the SWNT bundle due to local depletion of O_2 or due to locally thinning of the SWNT bundle during burning off process. The NDC could result from hole resonant tunneling the quantum well. The CNTFETs prepared using water/Triton X-100 suspension exhibit ambipolar characteristics, which could be attributed to Triton X-100 at the interface between the SWNTs and electrodes. This surfactant decreases the work function of the Au electrodes, aligning the Fermi level of the Au electrodes to the mid-gap of the SWNTs. Triton X-100 between SWNTs and SiO_2 is also found to be responsible for the hysteresis in the drain current vs gate voltage curves of these CNTFETs. The ambipolar property can be converted to unipolar one (n-type or p-type) by properly adjusting the source and drain structures.

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INTRODUCTION

1.1 Motivation

The anticipated limits to future miniaturization of microelectronics have led to intense study and development of molecular electronics. The use of single wall carbon nanotubes (SWNTs) has stipulated these efforts, because these molecules exhibit unique advanced properties for nanoelectronics. Carbon nanotubes (CNTs) are tubular structures typically of nanometer diameter and a few tens of microns in length. They are unusual because of their very small diameter, which can be as small as 0.4nm so that only 10 atoms are around the circumference [1] in a single layer. CNTs have a very large aspect (length/diameter) ratio. They are the best material for a nearly ideal one-dimensional (1-D) system, which reduces phase space for scattering the carriers and opens up a room for ballistic transport of carriers [2]. In addition, the C-C bonds in CNTs are very strong, resulting in an extremely high mechanical stability and chemical inertness. All chemical bonds of the C atoms are satisfied and there is no need for chemical passivation of dangling bonds as required in silicon, implying that a variety of insulators can be used in CNT devices and thus allowing the fabrication of 3-dimensional structures [2].

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Furthermore, the thermal conductivity of the CNTs is expected to be the highest among the known materials [3]. Their electric current carrying capability can be as high as 10^9 A/cm^2 , about 1000 times as high as that for Cu, indicating a high resistance to electromigration. These unique properties make CNTs promising building blocks for future nanoelectronic technology.

Carbon nanotube based field effect transistors (CNTFETs), one of the SWNTs' important applications, have been attracting much interest. Since the first batch of CNTFETs were fabricated in 1998 [4, 5], their performance has been significantly improved in aspects of ON-OFF current ratio [6, 7], hole mobility [8] and CNT-metal electrode contacts [7]. However, how to manipulate the CNTs to the desirable electrodes is still a big challenge. Spin-coating CNT suspension onto the structured wafers [4, 5, 9, 10] is a simple process. However, the random distribution and orientation of CNTs and CNT contamination on the entire sample surface are the major drawbacks. Directly growing SWNTs from one electrode to another is a controllable process [11, 12]. Unfortunately, this approach causes the catalyst contamination and poor selectivity of the CNTs. In contrast, DC and AC electrophoresis methods have been demonstrated to be an efficient technique to place CNTs [13-15], CNT matted sheets [16], and CNT bundles with definite orientation across pre-patterned electrodes [17]. Most recently, it has been reported that single CNT bundle could be simultaneously allocated onto an array of electrodes by this technology [18]. This thesis presents a systematical experimental and theoretical study of the placement of SWNTs by AC dielectrophoresis. The unique physical phenomena related to the fabricated CNTFETs are studied.

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1.2 Objectives

The main objectives of Ph.D. project are:

- ◆ To study the AC dielectrophoresis method for placing carbon nanotubes across two electrodes. The CNT bridging direction, CNT distribution and the alignment mechanism are the topics to be investigated.
- ◆ To optimize the fabrication processes of CNTFETs. The yields of CNTFET and the CNTFETs' properties will be studied.
- ◆ To investigate the influences of the surfactants to the characteristics of CNTFETs.
- ◆ Through the simulation of the characteristics of CNTFETs, we expect to analyze our experimental observations. We suggest that the gate voltage controls the CNT channel conduction through modulating the thickness of the Schottky barrier (SB). Semiclassical method thus could be used to simulate the carrier tunneling process.
- ◆ To study the influences of the electrode structure on the transfer characteristics of the CNTFETs that could exhibit *p*-type and ambipolar characteristics.

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1.3 Major contributions of the thesis

The following contributions have been made to the project and are stated in this thesis:

(a) Single-wall carbon nanotubes suspended in isopropyl alcohol were placed between two cross-structured electrodes using an AC dielectrophoresis technique. The SWNTs were found to attach to the electrodes along the direction of the AC external electric field. The shortest gap is always placed predominately with the SWNTs and the spacial distribution of the tubes becomes wider for a long manipulation time (say, >300 sec). The observed phenomenon is analyzed in terms of the dielectrophoresis induced torque and force on the SWNTs by the AC electric field. The time for rotating SWNTs to the direction of the electric field was found to be much smaller than that for translating SWNTs. We also find that m-SWNTs are forced along the gradient direction of the spacial distribution of the electric field strength while s-SWNTs are forced in the opposite direction.

(b) The SWNTs bridging the source and drain electrodes in CNTFETs typically consist of both m-SWNTs and s-SWNTs. Through selectively burning off the metallic SWNTs by current induced oxidation, the back-gated CNTFETs with an ON/OFF current ratio of up to 7×10^5 have been successfully fabricated. The success rate of the CNTFETs with ON/OFF ratio between 10^3 and 10^6 in 20 samples is 60%. These results suggest that AC dielectrophoresis placement method is an efficient technique to fabricate CNTFETs with certain flexibilities of controlling CNT reconnection, length and orientation.

(c) It is the first time to report a significant phenomenon of negative differential conductance (NDC) in a bundle of SWNTs in a back-gated CNTFET. The apparent NDC

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with a peak-to-valley current ratio of about 2 is observed at room temperature. The peak voltage gradually shifts from 9.2V to 7.8V with changing the gate voltage from 6V to -6V. We suggest that the NDC results from hole resonant tunneling through a quantum well formed on the *p*-type semiconducting SWNTs in the bundle.

(d) The influences of the surfactants on the transfer characteristics of CNTFETs are studied. We find that the surfactant at the interface between the CNTs and electrodes can change the work function of the electrodes and therefore convert the characteristics of the CNTFETs from *p*-type to ambipolar characteristics. The adsorbed surfactants between CNTs and SiO₂ are also responsible for a hysteresis phenomenon in the drain current versus the gate voltage characteristics of the CNTFETs.

(e) A novel method is proposed to analyze ambipolar-to-unipolar conversion of CNTFETs. Using an asymmetric oxide layer between the CNT and gate electrode, we have obtained an asymmetric transfer characteristic of the CNTFETs. Semiclassical simulation results suggest that the slope of the oxide layer and the electrode thickness play important roles in the transfer characteristics. Through optimizing them, we can convert the performance of the CNTFETs from ambipolar characteristics to unipolar (*p*-type or *n*-type) behavior with a significant drop in the OFF current or an increase in the ON/OFF current ratio.

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1.4 Organization of the thesis

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

Chapter 2 gives a review of carbon nanotube fundamental properties, including SWNT structure, density of electronic state, energy gap and SWNT classification (m-SWNT and s-SWNT). The background and development of CNTFETs are summarized.

Chapter 3 presents the experimental results of the AC dielectrophoresis placement technique. The mechanism of the CNT alignment is analyzed in terms of the dielectrophoresis induced torque and force on the SWNTs by the AC electric field using an “effective dipole” method.

Chapter 4 shows the characteristics of the CNTFETs fabricated by the AC dielectrophoresis technique and the burning-off process for destroying the m-SWNTs in the bundle.

Chapter 5 presents room-temperature negative differential conductance observed in our CNTFETs. A model of hole resonant tunneling a quantum well is proposed to interpret the observed phenomena. The formation mechanism of the quantum well is discussed.

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Chapter 6 describes the influences of the surfactants used in dispersing SWNTs on the characteristics of the CNTFETs. We find that the ambipolar characteristic and hysteresis phenomena are influenced by this surfactant. A semiclassical method is proposed to simulate the ambipolar characteristics of the CNTFETs.

In chapter 7, we propose a novel approach to convert the characteristics of CNTFETs from ambipolar to unipolar. The influences of electrode height and asymmetric structure are discussed in detail using a semiclassical model.

Chapter 8 concludes this work and gives recommendations for future work.

Chapter 2 Literature review

Chapter 2

Literature review

In this chapter, we first brief the structure of single-wall carbon nanotubes (SWNTs). The electronic structure of SWNTs is then introduced in Section 2.2, where the relation between the index (n, m) of a SWNT and its physical properties will be discussed. The energy dispersion relations for armchair and zigzag SWNTs are given based on the energy dispersion relation of 2D graphite. At the same section, the density of states and band gap of semiconducting-SWNT are introduced. Finally, in Section 3, we review the development of carbon nanotube based field effect transistors (CNTFET) and some challenges in this field.

2.1 Structure of single wall carbon nanotubes

In the family of carbon, carbon nanotubes first found by Iijima in 1991[19] have attracted much attention. The nanotubes consist of up to several tens of graphitic shells with adjacent shell separation of $\sim 0.34\text{nm}$ and large length/diameter ratio, which is called multi-walled carbon nanotubes (MWNTs). Two years later, Iijima and Ichihashi [20] and Bethune et al [21] synthesized single-walled carbon nanotubes (SWNTs). A SWNT can be described as a graphene sheet rolled into a cylinder so that the structure is one-

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dimensional with a certain axial symmetry, and in general exhibiting a spiral conformation, called chirality.

2.1.1 Chiral vector: $\vec{C}_h$

Figure 2.1(a) shows an unrolled honeycomb lattice of the nanotube. $\vec{OB}$ is the direction of the nanotube axis, $\vec{OA}$ indicates the circumference of the nanotube. By rolling the honeycomb sheets so that points O and A coincide each other (and points B and B' overlap), a carbon nanotube is constructed. The vector $\vec{OA}$ and $\vec{OB}$ define the chiral vector $\vec{C}_h$ and translation vector $\vec{T}$ of the carbon nanotube, respectively. $\vec{C}_h$ can be expressed by two real space unit vectors $\vec{a}_1 = (\frac{\sqrt{3}a}{2}, \frac{a}{2})$ and $\vec{a}_2 = (\frac{\sqrt{3}a}{2}, -\frac{a}{2})$ (see Fig. 2.1(a)) of the hexagonal lattice:

$$\vec{C}_h = n \vec{a}_1 + m \vec{a}_2 \equiv (n, m) \quad (n, m \text{ are integers, } 0 \leq |m| \leq n) \quad (2.1)$$

where $a = |\vec{a}_1| = |\vec{a}_2| = 0.246nm$ is the lattice constant of two dimensional graphite. If $n = m$, i.e., $\vec{C}_h = (n, n)$, it corresponds to an armchair nanotube, as is shown in Fig.2.1(b). In the case of $m = 0$, or $\vec{C}_h = (n, 0)$, a zigzag nanotube is formed (Fig.2.1(c)). All other (n, m) chiral vectors correspond to chiral nanotubes (Fig.2.1(d)).

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Fig.2.1 (a) An unrolled honeycomb lattice of a nanotube. When we connect sites O and A, and B and B', a nanotube can be constructed. $\vec{OA}$ and $\vec{OB}$ define the chiral vector $\vec{C}_h$ and translation vector $\vec{T}$ of a carbon nanotube, respectively. Special tube types are the achiral tubes including armchair tubes (n, n) (b) and zigzag tubes $(n, 0)$ (c). All other tubes are called chiral tubes (d).

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The diameter of the carbon nanotube, d , is given by L/π , where L is the magnitude of $\vec{C}_h$ or the circumferential length of the carbon nanotube:

$$d = L/\pi, \quad L = |\vec{C}_h| = a\sqrt{n^2 + m^2 + nm}, \quad (2.2)$$

The chiral angle θ is defined as the angle between the vectors $\vec{C}_h$ and $\vec{a}_1$, with a value range of $0 \leq |\theta| \leq 30^\circ$, because of the hexagonal symmetry of the honeycomb lattice [22].

θ denotes the tilt angle of the hexagons with respect to the direction of the nanotube axis, and specifies the spiral symmetry,

$$\cos \theta = \frac{\vec{C}_h \cdot \vec{a}_1}{|\vec{C}_h| |\vec{a}_1|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}. \quad (2.3)$$

In particular, zigzag and armchair nanotubes correspond to $\theta = 0^\circ$ and $\theta = 30^\circ$, respectively.

2.1.2 Translational vector: $\vec{T}$

The translation vector $\vec{T}$ is defined to be the unit vector of a 1D carbon nanotube. $\vec{T}$ is parallel to the nanotube axis and is normal to the chiral vector $\vec{C}_h$ as shown in Fig.2.1(a),

$\vec{T}$ can be expressed in terms of $\vec{a}_1$ and $\vec{a}_2$ as:

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$$\vec{T} = t_1 \vec{a}_1 + t_2 \vec{a}_2 \equiv (t_1, t_2), \text{ (where } t_1, t_2 \text{ are integers)} \quad (2.4)$$

and

$$t_1 = \frac{2m+n}{d_R}, t_2 = -\frac{2n+m}{d_R}, \quad (2.5)$$

where d_R is the greatest common divisor of $(2m+n)$ and $(2n+m)$ and is given by

$$d_R = \begin{cases} q & \text{if } n-m \text{ is not a multiple of } 3q \\ 3q & \text{if } n-m \text{ is a multiple of } 3q, \end{cases} \quad (2.6)$$

where q is the greatest common divisor of (n, m) .

The magnitude of the translation vector, $\vec{T}$, is given by

$$T = \sqrt{3}L / d_R \quad (2.7)$$

2.1.3 Unit cells and Brillouin zones

The unit cell for a carbon nanotube in real space is given by the rectangle generated by the $\vec{C}_h$ and $\vec{T}$, the dashed rectangle $OAB'B$ shown in Fig.2.1(a). The number of hexagons, N , in the unit cell is determined by the integers (n, m) and is given by [1]

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$$N = 2(m^2 + n^2 + nm)/d_R. \quad (2.8)$$

The addition of a single hexagon to the honeycomb structure in Fig.2.1(a) corresponds to the addition of two carbon atoms. Since there are $2N$ carbon atoms in the unit cell, there must be N pairs of bonding π and anti-bonding π^* electronic energy bands. The reciprocal lattice vectors $\vec{K}_1$ in the circumferential direction and $\vec{K}_2$ along the nanotube axis are obtained from the relation $\vec{R}_i \cdot \vec{K}_j = 2\pi\delta_{ij}$, where $\vec{R}_i$ and $\vec{K}_j$ are, respectively, the lattice vectors in real and reciprocal space. They can be expressed as

$$\vec{K}_1 = (-t_2 \vec{b}_1 + t_1 \vec{b}_2)/N, \quad \vec{K}_2 = (m \vec{b}_1 - n \vec{b}_2)/N \quad (2.9)$$

where $\vec{b}_1 = (\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a})$ and $\vec{b}_2 = (\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a})$ are the reciprocal lattice vectors of two-dimensional graphite, as shown in Fig.2.2 and Fig.2.3. The reciprocal vectors, $\vec{K}_1$ and $\vec{K}_2$ for a $\vec{C}_h = (4, 2)$ chiral nanotube are shown in Fig.2.2. The first Brillouin zone of this one-dimensional material is the line segment WW' . Since $N\vec{K}_1 = (-t_2 \vec{b}_1 + t_1 \vec{b}_2)$ corresponds to a reciprocal lattice vector of two-dimensional graphite, two wave vectors which differ by $N\vec{K}_1$ are equivalent. Because t_1 and t_2 do not have a common factor except for unity, none of the $N-1$ vectors $\mu \vec{K}_1$ (where $\mu = 1, \dots, N-1$) are reciprocal lattice vectors of two-dimensional graphite. Thus the N wave vectors $\mu \vec{K}_1$ ($\mu = 0, \dots, N-1$)

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give rise to N discrete k vectors, as indicated by the $N = 28$ parallel line segments in Fig.2.2, which arise from the quantized wave vectors associated with the periodic boundary conditions on $\vec{C}_h$. The length of all the parallel lines in Fig.2.2 is $2\pi/T$ which is the length of the one-dimensional first Brillouin zone. Because of the translational symmetry of $\vec{T}$, we have continuous wave vectors in the direction of $\vec{K}_2$ for a carbon nanotube of infinite length.

Fig.2.2: The Brillouin zone of a carbon nanotube is represented by the line segment WW' which is parallel to $\vec{K}_2$. The vectors $\vec{K}_1$ and $\vec{K}_2$ are reciprocal lattice vectors corresponding to $\vec{C}_h$ and $\vec{T}$, respectively. The figure corresponds to $\vec{C}_h = (4, 2)$, $\vec{T} = (4, -5)$, $N = 28$, $\vec{K}_1 = (5\vec{b}_1 + 4\vec{b}_2)/28$, $\vec{K}_2 = (4\vec{b}_1 - 2\vec{b}_2)/28$. [after ref.22]

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Fig.2.3. (a) The unit cell and (b) Brillouin zone of two-dimensional graphite are shown as the dotted rhombus and the shaded hexagon, respectively. $\vec{a}_i$ and $\vec{b}_i$ ($i=1,2$) are unit vectors and reciprocal lattice vectors, respectively. (c) The energy dispersion relations for 2D graphite are shown throughout the whole region of the Brillouin zone. The inset shows the energy dispersion along the high symmetry directions of the triangle Γ MK shown in (b). [after refs. 1, 22]

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2.2 Electronic structure of SWNTs

The interesting electrical properties of CNTs are due in a large part to the peculiar electronic structure of graphene. In Fig.2.3(c), the energy dispersion relations of 2D graphite are shown throughout the Brillouin zone and the inset shows the energy dispersion relation along the high symmetry axes along the perimeter of the dotted triangle ΓMK shown in Fig.2.3(b). The upper half of the energy dispersion curves describes the π^* -energy anti-bonding band, and the lower half is the π -energy bonding band. The upper π^* band and the lower π band are degenerate at the K points through which the Fermi level passes. Since the density of states at the Fermi level is zero, 2D graphite is a zero-gap semiconductor.

For the nanotube structure, there is an additional quantization arising from the confinement of electrons in the circumferential direction in the tube. When the energy dispersion relations of 2D graphite, $E_{g2D}(k)$ at line segments shifted from WW' by $\mu \vec{K}_1$ ($\mu = 0, \dots, N-1$) are folded so that the wave vectors parallel to $\vec{K}_2$ coincide with WW' as shown in Fig.2.2, N pairs of 1D energy dispersion relations $E_\mu(k)$, are obtained. These 1D energy dispersion relations are given by [22]

$$E_\mu(k) = E_{g2D}\left(k \frac{\vec{K}_2}{|\vec{K}_2|} + \mu \vec{K}_1\right), \quad (\mu = 0, \dots, N-1, \text{ and } -\frac{\pi}{T} < k < \frac{\pi}{T}), \quad (2.10)$$

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corresponding to the energy dispersion relations of a SWNT. The N pairs of energy dispersion curves correspond to the cross sections of the two-dimensional energy dispersion surface shown in Fig.2.3(c), where cuts are made on the lines of $k \vec{K}_2 / |\vec{K}_2| + \mu \vec{K}_1$. If for a particular (n, m) nanotube, the cutting lines passes through a K point of the 2D Brillouin zone, where the π and π^* energy bands of two-dimensional graphite are degenerated by symmetry, the one-dimensional energy bands have a zero energy gap. Further, the density of states at the Fermi level has a finite value for these carbon nanotubes. Such tubes therefore are metallic. If, however, the cutting line does not pass through a K point, the carbon nanotubes are expected to show semiconducting behavior, with finite energy gaps between the valence and conduction bands.

A metallic energy band is determined by the fact that the ratio of the length of the vector $\vec{YK}$ to that of $\vec{K}_1$ in Fig.2.4 is an integer. Since the vector $\vec{YK}$ can be expressed as

$$\vec{YK} = \frac{2n+m}{3} \vec{K}_1, \quad (2.11)$$

The condition for metallic nanotubes is that $(2n + m)$ or equivalent $(n - m)$ is a multiple of 3. In particular, the armchair nanotubes denoted by (n, n) are always metallic, and the zigzag nanotubes $(n, 0)$ are only metallic when n is a multiple of 3.

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2.2.1 Energy dispersion of special nanotubes

Using the tight binding calculation, the energy dispersion relations for two-dimensional graphite can be approximately expressed as [22-25]

$$E_{g2D}(k_x, k_y) = \pm \gamma_0 \left\{ 1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right) \right\}^{1/2}, \quad (2.12)$$

Fig.2.4. The condition for metallic energy bands: if the ratio of the length of the vector $\overrightarrow{YK}$ to that of $\overrightarrow{K_1}$ is an integer, metallic energy band are obtained. [After ref.22]

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where γ_0 is the nearest-neighbor transfer integral [26]. The appropriate periodic boundary conditions used to obtain the energy eigenvalues for the (n, n) armchair nanotube define the small number of allowed vector $k_{x,q}$ in the circumferential direction

$$n\sqrt{3}k_{x,q}a = 2\pi q, (q = 1, \dots, 2n). \quad (2.13)$$

Substitution of the discrete allowed values for $k_{x,q}$ given by Eq.(2.13) into Eq.(2.12) yields the energy dispersions $E_q^a(k)$ for the armchair nanotube [25], $\vec{C}_h = (n, n)$,

$$E_q^a(k) = \pm \gamma_0 \left\{ 1 \pm 4 \cos\left(\frac{q\pi}{n}\right) \cos\left(\frac{ka}{2}\right) + 4 \cos^2\left(\frac{ka}{2}\right) \right\}^{1/2}, \quad (2.14)$$

$$(-\pi < ka < \pi), (q = 1, \dots, 2n)$$

in which the superscript a refers to armchair and k is a one-dimensional vector in the direction of the vector $\vec{K}_2 = (\vec{b}_1 - \vec{b}_2)/2$. The dispersion relations $E_q^a(k)$ for the $(5, 5)$ nanotube is shown in Fig.2.5a, in which there are six dispersion relations for conduction bands and six for the valence bands. The valence and conduction bands cross at a k point that is two thirds of the distance from $k = 0$ to the zone boundary at $k = \pi / a$. The crossing takes place at the Fermi level and the energy bands are symmetric for $\pm k$ values. Because of the degeneracy point between the valence and conduction bands at the band crossing, the $(5, 5)$ armchair nanotube is thus a zero-gap semiconductor. Similar calculations indicate that all (n, n) armchair nanotubes have a band degeneracy between

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the highest valence band and the lowest conduction band at $k = \pm 2\pi/3a$, where the bands cross the the Fermi level. Therefore, all armchair nanotubes are expected to exhibit metallic conduction, similar to the behavior of 2D graphene sheets.

The energy bands for the $\vec{C}_h = (n, 0)$ zigzag nanotube $E_q^z(k)$ can be obtained likewise from Eq. (2.12) by writing the periodic boundary condition on k_y as:

$$nk_{y,q}a = 2\pi q, (q = 1, \dots, 2n), \quad (2.15)$$

to yield the 1D dispersion relations for the $4n$ states for the $(n, 0)$ zigzag nanotube (denoted by the subscript z) [25]

$$E_q^z(k) = \pm \gamma_0 \left\{ 1 \pm 4 \cos\left(\frac{\sqrt{3}ka}{2}\right) \cos\left(\frac{q\pi}{n}\right) + 4 \cos^2\left(\frac{q\pi}{n}\right) \right\}^{1/2},$$

$$\left(-\frac{\pi}{\sqrt{3}} < ka < \frac{\pi}{\sqrt{3}}\right), (q = 1, \dots, 2n). \quad (2.16)$$

The calculated 1D dispersion relations $E_q^z(k)$ for the $(9, 0)$ and $(10, 0)$ zigzag nanotubes are shown in Fig.2.5 (b) and (c), respectively. There is no energy gap for the $(9, 0)$ nanotube at $k = 0$, whereas the $(10, 0)$ nanotube indeed shows an energy gap. For a general $(n, 0)$ zigzag nanotube, when n is a multiple of 3, the energy gap at $k = 0$ becomes zero; However, when n is not a multiple of 3, an energy gap opens at $k = 0$.

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Fig.2.5: One-dimensional energy dispersion relations for (a) armchair (5, 5), (b) zigzag (9,0), and (c) zigzag (10,0) carbon nanotubes labeled by the irreducible representations of the point group D_{nd} or D_{nh} , depending on whether there are even or odd numbers or bands n at the Γ point ($k = 0$). The a -bands are nondegenerate and the e -bands are doubly degenerate at a general k -point. X points for armchair and zigzag nanotubes correspond to $k = \pm\pi/a$ and $k = \pm\pi/\sqrt{3}a$, respectively. [after ref. 22]

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2.2.2 Density of states, energy gap

For all metallic nanotubes, independent of their diameter and chirality, the density of states per unit length along the nanotube axis is a constant given by

$$N(E_F) = \frac{8}{\sqrt{3}\pi a |\gamma_0|} \quad , \quad (2.17)$$

where a is the lattice constant of the graphene layer and γ_0 is the nearest-neighbor C-C tight binding overlap energy.

Of particular interest has been the energy dependence of the nanotube density of state, as shown in Fig.2.6 which compares the density of states for metallic (5, 5) and (7, 1) and semiconducting (8, 0) zigzag nanotubes. What is important is the density of states near the Fermi level E_F located at $E = 0$. This density of states has a value of zero for semiconducting nanotubes, but is non-zero (and small) for metallic nanotubes.

The energy gap for semiconducting nanotubes depends upon the reciprocal nanotube diameter d , [22]

$$E_g = \frac{|\gamma_0| a_{C-C}}{d} \quad , \quad (2.18)$$

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Fig.2.6. Electronic densities of states for (5, 5), (7, 1) and (8, 0) nanotubes showing van Hove singularities characteristic of one-dimensional systems. The (5, 5) armchair nanotube is metallic for symmetry reasons. The (7, 1) chiral tube displays a tiny gap owing to curvature effects, but will display a metallic behavior at room temperature. The (8, 0) zigzag tube is a large gap semiconductor. [After ref.1]

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independent of chiral angle of the semiconducting nanotube, where $a_{C-C} = a/\sqrt{3}$ is the nearest-neighbor C-C distance on a graphene sheet.

2.3 Development of CNTFETs

The first carbon nanotube based field effect transistors were reported in 1998 [4,5]. A semiconducting nanotube connected to two metal electrodes showed the characteristics of a field-effect transistor. By applying voltage to a gate electrode, the nanotube could be switched from a conducting to an insulating state. The transistor structure is shown in Fig.2.7. Carbon nanotubes played the role of the “channel”, while the two metal electrodes functioned as the “source” and “drain” electrodes. The heavily doped silicon wafer was used as the “gate”, so-called back-gate. The current I decreased with increasing gate voltage V_g , indicating that the transport through semiconducting SWNTs was dominated by holes. The I - V curves saturated for $V_g < 0$. These CNTFETs behaved as p -type FETs and had an ON/OFF current ratio of $\sim 10^5$. Since then, CNTFETs have been attracting a lot of interest. Their performance has also been improved by decreasing contact resistance, shortening source and drain distance, changing gate structure, decreasing gate oxide thickness and using high-k insulator, which will be discussed in detail later.

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Fig.2.7. Schematic cross-section of CNTFETs. A single CNT bridges the gap between two gold electrodes. The silicon substrate is used as back gate. [After ref. 2]

2.3.1 Improvement of the contacts between CNTs/metals

Although functional, the aforementioned transistors had a high parasitic contact resistance ($\geq 1M\Omega$), low drive currents (a few nA), low transconductance $gm \sim 1nS$, and high inverse subthreshold slope $S \sim 1-2V/Dec$. These unsatisfactory characteristics were to a large extent due to poor contacts [2]. Two methods are used to improve the contacts. One is annealing which is adapted by IBM group. In their transistors, s-SWNTs were

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placed on top of the SiO₂ film, Ti or Co source and drain electrodes were deposited on the s-SWNTs. Thermal annealing at 400°C (for Co), or 820°C (for Ti) in an inert ambient lead to a stronger coupling between the metal and the nanotube and a reduction of the contact resistance [6,27]. The other method is to use appropriate metal electrodes. Javey et al [7] selected palladium, a noble metal with high work function and good wetting interactions with carbon nanotubes, as the electrode materials and obtained a large ON state conductance which was very close to the ballistic transport limit of $4e^2/h$ [28-30]. The contact improvement was suggested to be caused by a reduced barrier or eliminated barriers for transport through the valence band of the nanotubes.

2.3.2 Gate structures

The most widely used gate structure for CNTFETs in the past was the doped silicon substrate as back gates and thermally grown SiO₂ as gate dielectric [4,5,31]. However, local gates that could address different nanotube transistors on a common chip are required for the integration of multiple transistors. Several new gate structures of CNTFETs have been developed, including bottom aluminum gates with subnanometer-thick native Al₂O₃ dielectrics [10], bottom tungsten gates with SiO₂ [32], top-gate with 2~20nm thick SiO₂ dielectrics [9,33]. In addition to local address ability, these gate structures show progressively improving CNTFET characteristics. For instance, the inverse subthreshold slope S is approaching the theoretical value [9, 34] due to the thin oxide thickness [9] and high-k dielectrics [34]. CNTFETs fabricated with electrolyte gate

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[35] and polymer gate [36, 37] demonstrated strong gate-channel coupling with improved device characteristics. An electrolyte gate with a dielectric constant of about 80 could lead to an extremely high transconductance of about $20\mu\text{S}$ [35].

2.3.3 Dielectric materials and their thickness

The performance of CNTFETs can also be improved by decreasing the gate oxide thickness. Wind et al [9] compared the characteristics of a top-gated (15-20nm SiO_2) and a back-gated (120nm SiO_2) CNTFET fabricated on the same SWNT and found that those top-gate devices exhibited excellent electrical characteristics. The threshold voltage of the top-gate CNTFET was only -0.5V, significantly lower than under bottom-gated operation, -12V. Similarly, the drive current and the transconductance are much higher for the top-gating. Using a simple model, Heinze et al [38] concluded the scaling rule of the subthreshold slope with oxide thickness and pointed out that change in the oxide thickness is equivalent to simply rescaling the gate voltage by $V_{scal} \propto t_{ox}^{1/2}$, thus S scales as $t_{ox}^{1/2}$ and the transconductance scales as $\propto t_{ox}^{-1/2}$, well explaining the performance improvement of CNTFETs due to the decreasing of oxide thickness.

High-k dielectrics have been actively pursued to replace SiO_2 as gate insulator for silicon devices [39]. The relatively low k of SiO_2 (3.9) limits its use in transistors as gate length scale down to tens of nanometers. High k gate insulators afford high capacitance without relying on ultra-small film thickness, thus allowing for efficient charge injection into the

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transistor channels and meanwhile reducing direct-tunneling leakage currents [34]. Experimental results show that ZrO_2 [34], HfO_2 [40-42], Al_2O_3 [10], SrTiO_3 [43] have been successfully used as the gate insulator in CNTFETs.

2.3.4 Influences of the diameter, length and number of CNTs on CNTFETs

In CNTFETs, carbon nanotubes serve as the conduction channel of the transistors. Metallic CNTs are not expected to show field effect due to their zero bandgap. Multi-walled CNTs have received less attention for fabricating CNTFETs because of their complex structure; every carbon shell can have different electronic character and chirality, and the shell-shell interaction may not be ignored [44, 45]. Small diameter MWCNTs with semiconducting outer shell could show semiconducting characteristics and be possibly used to fabricate CNTFETs [46, 47]. Therefore, semiconducting SWNTs are needed for CNTFETs and have been intensively studied. In CNTFET fabrication, the diameter of SWNTs can be in the range of about 1nm to 3~5nm. The channel lengths are typically between ~200nm and ~3 μm . Extremely short (10-50nm) [48, 49] and long SWNTs (0.4cm) [50] for CNTFETs have also been reported. The conduction channels can be single SWNT [4, 7, 10, 32, 34, 35, 42, 48, 51, 52], SWNT bundle or rope [53, 54], network [55-57] and thin film [58-60] of SWNT. CNTFETs with single SWNT showed high ON/OFF current ratio, transconductance and hole mobility. However, SWNT thin film transistors only exhibited a low ON/OFF current ratio (10-10000) and relatively low mobilities [55-59].

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2.3.5 Different transfer characteristics of CNTFETs: p-type, n-type and ambipolar characteristics.

Up to date, CNTFETs have shown p-type, n-type and ambipolar characteristics. Typically, CNTFETs fabricated in ambient air exhibit p-type characteristics [4, 5, 7, 34, 35, 43, 53, 61]. However, for future nanotube-based electronics, the ability to “dope” the nanotubes selectively to achieve different conducting types is highly desired. Several methods have been developed to achieve n-type CNTFETs. It is found that CNTFETs can be converted from p-type to n-type simply by annealing the device in vacuum [12, 62], in an inert gas [27] or in hydrogen [34]. Doping p-type CNTFET with potassium [12, 62-65] is another approach which was used to build CNT p-n diodes [66] and complementary logic gates [10, 12]. In this method, evaporated potassium vapor are adsorbed on the surface of SWNTs [63]. By coating polyethylenimine (PEI) on the top of SWNTs [37, 59, 67], n-type doping can also be realized. Recent results suggest that n-type and p-type behavior can be controlled easily using polymer electrolyte gate [36, 37]. Lu et al [36] show that mixing different concentrations of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) into a lithium percolate/poly(ethylene oxide) (PEO) mixture could achieve both p-type and n-type CNTFETs. Similarly, by varying the electron donating and accepting ability of the chemical groups of the host polymer, unipolar p or n devices that are stable at room temperature in air have been fabricated by Siddens et al [37]. Using these polymer gates, one can also obtain ambipolar CNTFETs [36, 37] that can operate as switches for electrons and holes depending on the sign of the gate voltage. The ambipolar characteristics were also found in annealing a p-type CNTFET covered with SiO₂ in

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vacuum or in an ambient atmosphere [27]. The CNTFETs fabricated with large diameter (3-5nm) SWNTs or small band gap ($\sim 0.4\text{eV}$) typically exhibit ambipolar characteristics [11, 68, 69]. For small diameter (1.4nm) SWNT, ambipolar behavior are observed in air with very thin gate oxide (10nm) [70]. In addition, these ambipolar CNTFETs can be converted to p-type ones with an asymmetric gate structure with respect to the source and drain electrodes [70].

2.3.6 Switching mechanisms of CNTFETs

So far, three models have been proposed to interpret CNTFET operation. Conventional metal oxide semiconductor field-effect transistor (MOSFET)-like behavior has been reported for large diameter carbon nanotubes (3-5nm). The rather small energy gap of the CNT channels allows carriers injection from the metal contact into the valence band of the CNTs without a substantial Schottky barrier involved [7, 71]. Consequently, it is mainly the potential barriers between the contacts that control the current for these devices. CNTFETs with extremely long channel length ($>300\mu\text{m}$) [8, 50] also exhibit MOSFET-like behavior. In this case, the contact resistance is insignificant, so the resistance of the channel is dominated by bulk resistance. The CNTFETs fabricated mainly from larger gap CNTs behave with the characteristics of the Schottky barrier (SB)-FET [40, 41, 72]. In this case, the gate field determines the thickness of the Schottky barriers at the metal-CNT interface and makes them more or less transparent for tunneling from the source or drain electrodes into the CNT channels. Several

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observations support this mechanism. First, the output characteristics are observed to be strongly dependent on which side of the nanotube is connected to the source and drain. This could not be explained by conventional MOSFET mechanism where the saturation currents under large positive and negative V_d would be comparable since both sets of curves are symmetrical with respect to $V_d=0$. Another evidence for this model is that the inverse subthreshold slope S shows almost no dependence on channel length [41] but increase with oxide thickness. The related experimental data can be fitted well by the SB model but not by the conventional MOSFET model [40]. Furthermore, S is temperature dependent at high temperatures but levels off at temperatures below about 200K, suggesting a carrier tunneling process [40]. The SB model can also provide a reasonable explanation to the effect of O_2 on the performance of CNTFETs [72].

Another operation model is the band-to-band (BTB) tunneling reported most recently by Appenzeller et al [52]. BTB tunneling means gate induced tunneling from the conduction into the valence band of a s-SWNT and vice versa, as observed using a dual-gated CNTFET structure. Different from a conventional device where the Fermi distribution ultimately limits the gate voltage range for switching the device on or off, current flow is controlled in this mode by the valence and conduction band edges in a bandpass-filter-like arrangement. A small S value of $\sim 40\text{mV/dec}$ has been obtained at room temperature, much smaller than the theoretical value of 60mV/dec with conventional FETs.

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2.3.7 Applications of CNTFETs and challenges

Although CNTFETs is still in an early research stage, they have shown amazing performance parameters, for instance, drive current and transconductance [2], etc. Several applications, including logic circuits [10, 12, 32, 34, 62], memories [73-76], chemical sensors [77-79], p-n junction diodes [69] and light emission devices [80-83] have been demonstrated and shown promising performance. However, many challenges remain before these molecular electronic devices become successful nanodevices. Most challenging are the materials issues. So far, no techniques could produce a single type of CNT and separation techniques or/and breakdown process [44, 82] have to be used in fabricating CNTFETs. Controllable placement of CNT onto desired electrodes is still a big challenge. Spin-coating CNT suspension onto structured wafer [4, 5, 9, 10] is a simple process. However, the random distribution and orientation of CNTs and the CNT contamination on the entire sample surface are major drawbacks. Directly growing CNTs from one electrode to another is a relatively controllable process [11, 12]. Unfortunately, this approach causes the catalyst contamination and poor selectivity of the CNTs. Both of these two mostly used methods at present could not meet the demands of large scale integration. A more practicable CNT placement process needs to be explored.

Chapter 3 Manipulation of carbon nanotubes using AC dielectrophoresis technique

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Manipulation of carbon nanotubes using AC dielectrophoresis technique

DC and AC electrophoresis methods have been demonstrated to be an efficient technique to place CNTs [13-15], CNT matted sheets [16], and CNT bundles with definite orientation across pre-patterned electrodes [17]. Very recently, placing a single CNT bundle onto an array of electrodes [18] and fabricating CNT field effect transistors with good characteristics [18, 86, 87] using this technique have been reported. Unfortunately, the mechanism of the technique has not been studied in sufficient detail yet.

In this chapter, the process of allocating SWNTs suspended in isopropyl alcohol to the electrodes using the AC dielectrophoresis technique is discussed. The SWNTs were found to attach to the electrodes along the direction of the AC external electric field. The shortest gap is always placed predominately with the SWNTs and the spacial distribution of the tubes becomes wider for a long manipulation time (say, >300 Sec). The observed phenomenon is analyzed in terms of the dielectrophoresis induced torque and force on the SWNTs by the AC electric field. The time for rotating SWNTs to the direction of the electric field is found to be much smaller than that for translating SWNTs. We also find

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that m-SWNTs are forced along the gradient direction of spacial distribution of the electric field while s-SWNTs are forced in the opposite direction of the m-SWNT motion.

3.1. Experimental procedure and results

3.1.1. Electrode fabrication

Cross-structured electrodes were fabricated on p-type silicon wafers with 500nm thick silicon dioxide layer using the processes shown in Fig.3.1. First, negative photoresist 5214 was spin-coated on the clean Si wafers. The wafers were then baked at 110°C for 1.5min to harden the photoresist. Second, the patterns on a mask were transferred to the photoresist using UV lithography technique. Following another 110°C bake for 7min, the wafers were exposed again without mask and successively developed. Next, 20-nm Ti followed by 40-nm Au were deposited onto the patterned wafers using e-beam evaporation. Finally, the unwanted Ti/Au was lifted off by immersing the wafers in acetone. The fabricated electrode pattern is shown in Fig.3.2. One can see that four electrodes form a cross structure where the ends of the electrodes are not connected to each other. The gap between the ends of neighboring electrodes is in the range of 1~4 μ m.

3.1.2. SWNT placement using AC dielectrophoresis technique

To prepare the SWNT suspension, 1mg of highly purified SWNTs were dispersed in 500ml isopropyl alcohol (IPA) and ultrasonically dispersed for 10min. Then the

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(a) Photoresist deposition

(b) Development

(c) Metal deposition

(d) Lift-off process

Fig.3.1 Electrode fabrication process.

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suspension was further diluted until the concentration of the SWNT was about 50ng/ml. The suspension was colorless and transparent after the above treatments. During the AC dielectrophoresis process, a drop of the suspension was introduced onto the cross-structured electrodes to which an AC bias was applied by a HP 8166A pulse/function generator, as shown in Fig.3.2. The peak-to-peak AC voltage was between 4~8V, depending on the electrode distance, and the frequency was fixed at 10MHz. Monitoring the variation of the resistance between two electrodes is an easy way to confirm the attachment of SWNTs to the electrodes. The resistance was typically decreased to several hundred k Ω after SWNTs bridged the electrodes. Once the resistance drop was detected, the AC bias was turned off immediately. After the SWNTs had been deposited successfully, the wafer was rinsed using IPA and deionized water to clean the wafer surface. In this way, SWNTs could be placed across any two of the four electrodes in Fig.3.2.

3.1.3 Experimental results

Figure 3.3 shows AFM images of the four samples prepared for a manipulation time of 30s, 50s, 300s and 400s, respectively. One can see that the SWNTs bridge the electrodes along the direction of the electric field. The diameters of the bundles are typically in the range of 20~60nm. Only one bundle bridges the electrodes in a short time of 30s (Fig.3 (a)). For 50s processing, three bundles are found to be located between the two electrodes. As the deposition process goes on further, more bundles attach to the electrodes and most of them are located around the shortest gap. The length of the

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(a)

(b)

Fig.3.2 (a) SEM image of four Ti/Au electrodes on a p-type Si wafer with 500nm thick SiO₂. AC bias voltage is applied across two adjacent electrodes, as schematically shown in the figure. (b) Magnification of the center part of (a).

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shortest gap of Fig.3.3(a), (b), (c) and (d) are 3, 2.2, 2 and 1.7 μm , respectively. The shortest gaps for the four different samples are different because they were prepared using different mask patterns. From Fig.3.3 (d), one can see that the number density of the SWNT bundles counted from the image is about 20bundles/ μm between the shortest gap while it is less than 20bundles/ μm at other locations. Some short SWNTs only contact one of the electrodes. It is reasonable to conclude that for a given concentration of the CNT suspension, the longer the deposition time, the more the SWNTs are placed. Although the numbers of the SWNT bundles bridging the two electrodes are different, the alignment of the SWNTs is apparently along the direction of the electric field. The SWNT density is higher at the shortest gap because the electric field there is the strongest and the SWNTs are more easily attracted to this area.

The aligned SWNT bundles consist of both m-SWNTs and s-SWNTs, which can be identified by the output characteristics of the CNTFETs fabricated by such aligned SWNTs [86]. A typical drain current I_d as a function of drain voltage V_{ds} characteristic of as-prepared CNTFETs is shown in Fig.3.4(a). It is clear that the conductance decreases with increasing the gate voltage V_g in the range of -16 to 0V . However, I_d does not continue to decrease with V_g when $V_g > 0\text{V}$, indicating that the m-SWNTs in the bundle dominate the channel conductance as the s-SWNTs are likely to be switched off at the gate voltages. From the AFM image shown in Fig.3.4(b), one can see that there are at least two bundles bridging the two electrodes. It is therefore reasonable to say that there are both m-SWNTs and s-SWNTs between the two electrodes as indicated by the transfer characteristics in Fig.3.4(a).

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Fig.3.3. AFM images of SWNTs bridging the adjacent electrodes. The deposition time is (a) 30s, (b) 50s, (c) 300s, and (d) 400s, respectively. The direction of the electric field is indicated by the arrows.

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Fig.3.4 (a) I_d as a function of V_{ds} measured at $V_g = -16 \sim 16 \text{ V}$ in steps of 4V. (b) AFM image of the sample. The unit of the scale is μm .

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3.2 Carbon nanotube alignment mechanism

3.2.1 Force and torque applied on the SWNTs

To understand the mechanism of carbon nanotube alignment in AC dielectrophoresis process, we first considered the net force upon a small physical dipole. The dipole consists of equal and opposite charges $+q$ and $-q$ located a vector distance $\vec{d}$ apart, and it is located in an electric field of force $\vec{E}$, as shown in Fig.3.5. The dipole moment $\vec{p}$ is

$$\vec{p} = q\vec{d}, \quad (3.1)$$

Fig.3.5. Schematic of a small dipole in a uniform electric field.

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In a nonuniform electric field, the two charges ($+q$ and $-q$) will experience different electric field $\vec{E}$ and the dipole will experience a net force $\vec{F}$,

$$\vec{F} = q\vec{d} \cdot \nabla \vec{E} = \vec{p} \cdot \nabla \vec{E}. \quad (3.2)$$

The torque caused by the electric field on such a dipole is given by

$$\vec{T} = \vec{p} \times \vec{E}. \quad (3.3)$$

When a drop of carbon nanotube suspension is introduced between two adjacent electrodes applied with AC power, the electric field polarizes the SWNTs and induce effective dipole moments, $\vec{p}_{eff}$. The effective dipole moment is defined as the moment of an equivalent, free charge, point dipole that, when immersed in the same dielectric liquid and positioned at the same location as the center of the original particle, produces the same dipolar electrostatic potential [88].

From Fig.3.3(d), one can see that most of the individual SWNT bundles have a radius, r , of 20nm and length, l , of 2 μ m. Such a bundle could be approximately treated as a prolate spheroid with a longer semi-axis equaling to the half length of the SWNT, $l/2$, and two equal short semi-axes equaling to the radius, r , of the SWNT bundle. The quantity of effective dipole moment for the SWNT bundle can be obtained by solving the electrostatic boundary value problem in ellipsoidal coordinates for the induced potential term and then comparing it to the general expression for the potential due to an

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equivalent dipole source. We express the effective moment in terms of the effective excess polarization [88]

$$\vec{p}_{eff} = \pi r^2 l (\varepsilon_2 - \varepsilon_1) \vec{E}^- , \quad (3.4)$$

where ε_2 and ε_1 are the dielectric constants of the SWNT bundle and IPA, respectively.

$\vec{E}^-$ is the electric field inside the SWNT. The components of $\vec{E}^-$ are related to the imposed field $\vec{E}_0$ through a set of depolarization factors. Assume that the imposed electric field has components parallel ($\parallel$) and perpendicular ($\perp$) to the longer axis of the SWNT bundle, that is,

$$\vec{E}_0 = \vec{E}_\perp + \vec{E}_\parallel \quad (3.5)$$

If the longer axis is at angle θ with respect to $\vec{E}_0$, as shown in Fig.3.6, the components of internal electric field $\vec{E}^-$ can be expressed as [88-90]

$$E_\parallel^- = \frac{E_\parallel}{1 + \left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1}\right) L_\parallel} \quad \text{and} \quad E_\perp^- = \frac{E_\perp}{1 + \left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1}\right) L_\perp} , \quad (3.6)$$

where $L_\parallel \approx 4r^2 / l^2 [\ln(\frac{l}{r}) - 1] \ll 1$ and $L_\perp = (1 - L_\parallel) / 2 \approx \frac{1}{2}$ are the depolarization factors.

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Fig.3.6. Geometry of a SWNT bundle in the external electric field $\vec{E}_0$. θ is the angle between long semi-axis of SWNT and $\vec{E}_0$.

Using Eq.(3.6) to express the internal electric field, Eq.(3.4) can be changed to

$$\vec{p}_{eff} = \pi r^2 l (\epsilon_2 - \epsilon_1) (\vec{E}_{||}^- + \vec{E}_{\perp}^-) = \vec{p}_{||} + \vec{p}_{\perp} , \quad (3.7)$$

where $\vec{p}_{||} = \pi r^2 l (\epsilon_2 - \epsilon_1) \vec{E}_{||}^-$, $\vec{p}_{\perp} = \pi r^2 l (\epsilon_2 - \epsilon_1) \vec{E}_{\perp}^-$.

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According to Eq.(3.3), the alignment torque on the SWNT bundle can be calculated using the expression

$$\vec{T} = \vec{p}_{\parallel} \times \vec{E}_{\perp} + \vec{p}_{\perp} \times \vec{E}_{\parallel} , \quad (3.8)$$

Using Eq.(3.7) to express the components of the effective moment, the magnitude of the torque is given by

$$T = \pi r^2 l (\epsilon_2 - \epsilon_1) [E_{\parallel}^- E_{\perp} - E_{\perp}^- E_{\parallel}] , \quad (3.9)$$

or

$$T = \frac{\pi r^2 l (\epsilon_2 - \epsilon_1)^2 (L_{\perp} - L_{\parallel}) E_{\parallel} E_{\perp}}{\epsilon_1 \left[1 + \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_1} \right) L_{\parallel} \right] \left[1 + \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_1} \right) L_{\perp} \right]} . \quad (3.10)$$

As $\vec{E}_0$ is at an angle of θ with respect to the long axis of the SWNT bundle, we have $E_{\parallel} = E_0 \cos(\theta)$, $E_{\perp} = E_0 \sin(\theta)$. Equation (3.10) can be simplified to

$$T = \frac{\pi r^2 l}{2} \epsilon_1 \frac{(\epsilon_2 - \epsilon_1)^2}{[\epsilon_1 + (\epsilon_2 - \epsilon_1) L_{\parallel}](\epsilon_2 + \epsilon_1)} E_0^2 \sin 2\theta . \quad (3.11)$$

For a SWNT bundle along the axis of an axially symmetric field, the DEP force expression is [88]

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$$\vec{F}_{DEP} = \frac{\pi r^2 l}{2} \left[\frac{(\varepsilon_2 - \varepsilon_1)}{1 + \left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1}\right)L_{\parallel}} \right] \frac{\partial E_{0,z}^2}{\partial z} \hat{z}, \quad (3.12)$$

where $E_{0,z}$ is the z component of E_0 . For the sake of generality, we express the force in the following form

$$\vec{F}_{DEP} = \frac{\pi r^2 l}{2} \left[\frac{(\varepsilon_2 - \varepsilon_1)}{1 + \left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1}\right)L_{\parallel}} \right] \nabla E^2. \quad (3.13)$$

Given $\varepsilon_1 = 18.3\varepsilon_0$ and $\varepsilon_2 = (2 \sim 5)\varepsilon_0$ for s-SWNTs [91], $\varepsilon_2 - \varepsilon_1 < 0$. Eq.(3.13) suggests that the s-SWNTs are forced to the regions where the magnitude of the electric field is minimum. In contrast, metallic SWNTs have high conductivity and their dielectric constant is many orders of magnitude larger than that of IPA [91]. In other words, the dielectrophoresis (DEP) force on the m-SWNTs is in the opposite direction of that on the s-SWNTs. The different signs of the DEP force on m-SWNTs and s-SWNTs lead to an opposite motion, suggesting that AC dielectrophoresis is an efficient method to separate them if the SWNTs in the suspension are fully dispersed. Since the SWNT bundles attached to the electrodes consist of both m-SWNTs and s-SWNTs as mentioned in section 3.1.3, we take $\varepsilon_2 \approx 2000\varepsilon_0$. As a result, such a SWNT bundle should be forced to the location with a maximum electric field.

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3.2.2 Simulation of SWNT motion

To simulate the motion of the SWNTs in the AC dielectrophoresis process, one important condition is the electric field distribution in the space near the two cross-structured electrodes. The distribution obtained using FEMLAB is shown in Fig.3.7. Two electrodes with height of 60nm lie in the bottom of the rectangular parallelepiped, where the electric field is calculated. In the simulation, one of the electrodes is grounded and the other is maintained at 6V.

Fig. 3.7. Three-dimensional electric field profile simulated using FEMLAB. One unit in the x, y and z axis is equivalent to $10\mu\text{m}$. The arrow length and direction represents the strength and direction of the electric field, respectively.

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We first considered the rotation of a SWNT bundle. Once the AC electric field is supplied, the induced torque expressed in Eq.(3.11) rotates the SWNT bundle around its centroid with an angular acceleration $\vec{\alpha}$, i.e.,

$$\vec{T} = I\vec{\alpha}, \quad (3.14)$$

where $I = \frac{1}{12}ml^2$, is the moment of inertia and the mass, $m \approx 6 \times 10^{-18} \text{ kg}$, is estimated from the density of graphite. If the initial angle is known, the time for the SWNT bundle rotating from initial angle to $\theta = 0^\circ$ can be calculated using Eq.(3.11) and (3.14). The translation motion is calculated using Eq.(3.13). Supposing the initial position of a SWNT bundle is $(5, 5, 5)\mu\text{m}$ and the initial angle $\theta = 80^\circ$, the rotation time and translation time of this bundle from the initial position to the final position $(2.6, 2.7, 0)$ are $4 \times 10^{-5} \text{ s}$ and $4 \times 10^{-4} \text{ s}$, respectively, as shown in Fig.3.8. The influence of the viscous force is neglected in both calculations. We can see that the rotation time is an order of magnitude shorter than the translation time. This result is consistent to the calculation with SWNT bundles in other initial positions, indicating that the SWNT bundles are aligned to the direction of the electric field before they stop moving.

The distribution of the placed SWNTs around the electrodes is also studied. 1000 SWNTs are assumed to originally distribute in a rectangular parallelepiped of $20 \times 20 \times 10 \mu\text{m}$. The center of the bottom of the rectangular parallelepiped is on the cross point of the two electrodes. The distribution of these bundles after the AC dielectrophoresis is shown in

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Fig.3.8. (a) θ as a function of the deposition time. (b) x , y and z coordinates as a function of the deposition time for a SWNT bundle which is initially located at $(5, 5, 5)\mu\text{m}$.

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Fig.3.9. Simulated distribution of the SWNT bundles around the two cross-structured electrodes (solid lines) after the ac dielectrophoresis process. The “+” signal represents the centroids of the SWNTs. In the calculation, 1000 SWNT bundles randomly distributed in the $20 \times 20 \times 10 \mu\text{m}$ rectangular parallelepiped are deposited on the substrate. 479 of them are found to locate around the shortest gap (in the quarter circle centered at $(-1, -1)$, which is indicated by the dashed line).

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Fig.3.9. There are 479 SWNT bundles located in the quarter circle with a radius of $4\ \mu m$ centered at the cross point of the extrapolations of the two electrodes. This result suggests that about half of the SWNT bundles locate around the shortest gap of the two electrodes, in agreement with the experimental observation that the shortest gap is predominately placed with SWNTs.

The above analysis suggests that the rotational motion is a much fast process than the translational motion. Therefore, the SWNT bundles are first aligned to the electric field and then forced to the strongest field to contact the two electrodes. The calculated results are consistent with our observation; (1) the SWNT bundles are along the electric field direction and (2) the number of the SWNT bundles in the strongest electric field region is much higher than elsewhere. When the processing time is short (about 30s), this region is predominately bridged with SWNTs.

3.3 Conclusion

The manipulation of single-wall carbon nanotubes (SWNTs) using AC dielectrophoresis technique has been studied experimentally and theoretically. Experimental results show that the SWNT bundles bridge two neighboring cross-structured electrodes along the direction of the electric field. The number of the bundles is mainly determined by the processing time and the spacial distribution of the magnitude of the electric field. Based on effective dipole method, the electric field induced torque and force on SWNT bundles cause the rotation and translation of the SWNT bundles, respectively. The simulation

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results suggest that the rotation motion is a much faster process than the translation motion. Therefore, the SWNT bundle are first aligned to the electric field and then forced to the strongest field to contact the two electrodes, consistent with the observed alignment phenomena.

Chapter 4 Fabrication of CNTFETs using AC dielectrophoresis

Chapter 4

Fabrication of carbon nanotube field effect transistors using AC dielectrophoresis

Since the first batch of CNT field effect transistors (CNTFETs) [4, 5] were fabricated in 1998, their performance has been significantly improved in aspects of CNT channel current on-off ratio [6, 7], hole mobility [8] and the CNT-metal electrode contacts [7]. However, how to selectively place semiconducting SWNTs in desirable locations is a big challenge. At present, spin-coating [4, 5, 9, 10] and chemical vapor deposition (CVD) [11, 12] are widely used for CNTFET device fabrication. The former technique leads to a random distribution of SWNTs over the wafers, while the later causes the contamination of catalyst (Fe, Ni, Co, et al) which must be used in CVD growth of SWNTs [11, 12, 95, 96]. Therefore, these methods could not meet the demands of large scale fabrication of CNTFETs from the point of view of uniformity and yields. A more practical method for SWNT placement must be developed. From Chapter 3, one can see that SWNTs can be controllably placed between two electrodes using AC dielectrophoresis technique. However, except for Krupke et al's results obtained in vacuum [18], there has been no further report on the fabrication of CNTFETs using AC dielectrophoresis method.

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This chapter reports the CNTFETs fabricated by AC dielectrophoresis method at an ambient environment. Through selectively burning off the metallic SWNTs, the back-gate carbon nanotube field effect transistors (CNTFETs) with a channel current on-off ratio of up to 7×10^5 have been successfully fabricated. If a CNTFET with ON/OFF ratio $> 10^3$ is regarded as a good FET, the yield is about 60%. These results suggest that AC dielectrophoresis placement method is an efficient technique to fabricate CNTFETs with some flexibilities of controlling CNT reconnection, length and orientation.

4.1 Experimental details

4.1.1 Carbon nanotube placement

CNTFETs were fabricated on p-type silicon wafers which were thermally coated with a 500nm thick silicon dioxide layer. Source and drain electrodes were made of 20nm thick Ti and 40nm thick Au. The distance between the electrodes is in the range of 1 ~ 4 μ m. The schematic cross section of a back-gate CNTFET is shown in Fig. 4.1, the p-type silicon was used as back gate here.

SWNTs could be placed across any two of the four electrodes in Fig.3.2 using AC dielectrophoresis method. In addition, the electrodes could be connected pair by pair without influencing the CNT connection formed earlier. It is clearly that the SWNTs bridge the electrodes along the direction of the electric field, as shown in Chapter 3. If the two electrodes are parallel, the SWNT orientation is perpendicular to the parallel

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electrodes, as observed in Refs. 16-18. Therefore, the SWNT length between them is controllably close to the distance between the parallel electrodes. The number of SWNTs between the electrodes is controlled by the deposition time and SWNT concentration of the suspension. For CNTFET fabrication, we select low concentration and short deposition time in order to obtain small number of SWNTs bridging mainly in the shortest gap between the two electrodes.

Fig.4.1. Schematic cross section of a backgate CNTFET. P-doped silicon is used as back-gate. S and D represent source and drain, respectively. The thickness of SiO₂ is 500nm. SWNTs placed between source and drain electrodes act as the channel of the CNTFET.

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4.1.2 Annealing process for decreasing contact resistance

To study the annealing effects, six samples numbered S1 to S6 were prepared using AC dielectrophoresis technique as described in Section 3.1.2. The device structure was also the same as that mentioned therein. The deposition time was 1min for all the six samples. The annealing process was performed on a HP-4156B Semiconductor Analyzer probe station, which was also used to measure the I-V curves in-situ. The temperature was increased from 21°C to 300°C with steps of 25°C. At each temperature, the I-V curve was measured after the temperature was stable for 10min. After the measurement at 300°C, the temperature was decreased to room temperature, while the I-V curves were measured once every 50°C.

Table 1: Total resistances of the samples at different temperatures during the annealing process.

Group	Sample name	Resistance at room temperature (before annealing) (Ω)	Resistance at 300°C (Ω)	Resistance at room temperature (after annealing) (Ω)
1	S1	1.89×10^6	2.86×10^3	1.22×10^4
	S2	1.02×10^6	2.29×10^4	3.44×10^4
2	S3	3.48×10^5	3.19×10^4	3.00×10^4
	S4	1.83×10^5	3.45×10^3	2.99×10^4
	S5	2.50×10^5	2.54×10^4	2.07×10^4
	S6	4.42×10^5	3.72×10^4	3.95×10^4

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According to the resistance variation before and after the annealing (see Table 1), the six samples can be divided into two groups. One group has the resistance decrease of about two orders of magnitude, and the other group only one order of magnitude. The final resistance after annealing are in the range of 12~40k Ω . The total resistance R_{to} can be expressed as

$$R_{to} = R_c + R_{in} \quad (4.1)$$

where R_{in} is the intrinsic resistance of tube bundles and R_c is the contact resistance between tube bundles and two electrodes. Although the total resistances of these samples before annealing had a difference of more than one order of magnitude, they are very close after annealing. We, therefore suggest that the decrease of R_{to} is mainly due to the decrease in the contact resistance R_c . The R_{to} after annealing could be dominated by R_{in} and the difference between the samples is probably caused by the different number of SWNTs in the tube bundle bridging the two electrodes.

The resistance changes during decreasing temperature are also grouped into two types. The resistance of Sample S3 and S5 decrease with decreasing temperature, as shown in Fig4.2a. However, Sample S1, S2, S4 and S6 show an increase in their resistance as seen in Fig.4.2b. The AFM images of Sample S4 and S5 are shown in Fig.4.2c and 4.2d, respectively. From the bundle size, one can see that there are more SWNTs in S4 than in S5. Therefore, it is reasonable that the initial resistance (before annealing) of S4 is smaller than that of S5 because the contact resistance plays a key role in the total

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resistance. However, the resistance of S4 after annealing becomes larger than that of S5. We, therefore, suggest that most of the SWNTs in S4 are semiconducting ones whose resistance decrease with increasing temperature. This could be the reason why the resistance of S4 after annealing is slightly larger than that at 300°C. The low resistance at 300°C is contributed by not only the decrease of the contact resistance but also the decrease of intrinsic resistance of the s-SWNTs due to the high temperature. In contrast, the SWNTs in S5 are dominated by metallic ones. As a result, the resistance of S5 as a function of temperature is different from that of S4, as shown in Fig.4.2a and 4.2b.

Since our SWNTs were dispersed in liquid solution and the AC dielectrophoresis process was also performed in liquid environment, the interface between the SWNTs and electrodes could unavoidably remain some liquid, such as water and IPA after processing. The existence of these materials in the interface could increase the contact resistance. The influence of water in the interface of the SWNTs and SiO₂ to the transfer characteristics of the CNTFETs has been reported by Kim *et al* [116]. We suggest that the resistance reduction after annealing is caused by removing these materials from the interface between the SWNTs and the electrodes. On the one hand, the direct contact between SWNTs and electrodes eliminates the negative influence of the aforementioned interface materials. On the other hand, clean gold surface may increase the coupling by increasing the effective contact length with a small CNT-electrode separation [130]. Therefore, the contact resistance is reduced. This indicates that annealing in ambient environment is a simple and efficient way to improve the electric contact between the carbon nanotubes and Au electrodes.

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Fig.4.2. Resistance as a function of temperature during annealing for Sample S5 (a) and Sample S4 (b). (c) and (d) are the AFM images of S4 and S5, respectively. The unit of the scale is μ m.

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4.1.3 Metallic tube breakdown process

Current synthetic techniques for SWNTs produce mixtures of metallic (m) and semiconducting (s) nanotubes [97, 98]. Furthermore, individual tubes tend to adhere to each other forming “ropes” or ‘bundles’ due to substantial van der Waals attractions between them [97]. If a bundle is placed across the source and drain electrodes, the conductance of the FET channel will be the sum of a gate-dependent conductance of the s-SWNTs, G_s , and a gate independent conductance of m-SWNTs, G_m . The latter will cause a large leakage current and decrease the ON/OFF current ratio seriously. Unfortunately, no methods exist for the reliable preparation of s-SWNTs either by selective synthesis or by post-synthesis separation. To remove m-SWNTs from the channel, Collions et al [44, 82] used a breakdown process to destroy the m-SWNTs. This process makes use of the fact that G_s is gate voltage (V_g) dependent. A positive gate voltage is applied to deplete the s-SWNTs, then a drain voltage V_{ds} will lead to a current flowing through the m-SWNTs only. If the V_{ds} is sufficiently high, a selective breakdown of the m-SWNTs can be achieved.

In our experiment, the bridged SWNTs using AC dielectrophoresis technique generally consisted of both m- and s-SWNTs. The drain current I_d as a function of drain voltage V_{ds} was measured using a HP-4156B semiconductor analyzer at ambient atmosphere. A typical $I_d - V_{ds}$ characteristics of as-prepared CNTFETs are shown in Fig.4.3. It is clear that the conductance decreases with increasing V_g in the range of -10 to 14 V, and I_d almost saturates for $V_g > 14$ V. Under the condition of $-10 < V_g < 14$ V, the s-SWNTs

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Fig.4.3. I_d as a function of V_{ds} measured at $V_g = -10 \sim 30\text{V}$ in steps of 8V for a as-fabricated CNTFET. The $I_d - V_{ds}$ curves are almost overlapped for $V_g > 14\text{V}$.

dominate the total conductance. In contrast, the m-SWNTs start to dominate the channel conductance for $V_g > 14\text{V}$ because the s-SWNTs are switched off at the gate voltages. In this case, the ON/OFF current ratio can only be one or two orders of magnitude. However, for proper operation of a good transistor, an ON/OFF current ratio of about 10^4 is desirable [33]. In order to improve the performance of the CNTFETs, the m-SWNTs must be removed from the conduction channel. We used the electrical breakdown method [44] to destroy the m-SWNTs. For the above sample, the gate voltage was kept at 15V during our breakdown process, and the source-drain voltage was swept in a range from

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zero to a positive value, V_{pds} . The value of V_{pds} was increased gradually from a lower voltage, say 5V, to a higher voltage to avoid destroying the whole tube bundle. For each sweeping range ($0 \sim V_{pds}$), the sweeping process was repeated for several times. If there was no conductance variation, a higher V_{pds} was used. The breakdown process was monitored by the above mentioned HP semiconductor analyzer through observing the variation of the I - V curve which reflected the conductance of the tube bundle. The conductance did not change until the source-drain bias was increased to 10.5V, at which it decreased apparently in the two consecutive sweepings (curve 1 and 2), as shown in Fig.4.4. It can be seen that in the end of the curve 1, the conductance dropped suddenly to

Fig.4.4. I_d as a function of V_{ds} during the burn-off process. Curve 1 and 2 are two consecutive sweepings from 0 to 10.5V. Curve 3 is the final sweeping from 0 to 11V.

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the same level as that of the second sweeping (curve 2). However, the second sweeping still exhibited a large conductance, indicating that only part of the m-SWNTs in the bundle were burned off. To completely remove the m-SWNTs from the bundle, V_{pds} was increased further. Curve 3 of Fig.4.4 shows another sweeping at $V_{pds}=11\text{V}$, the conductance decreased apparently after V_{ds} is more than 10V. The burn-off process was then stopped here, because the conductance at lower V_{ds} ($\leq 1\text{V}$) was already very small (not shown here). The apparent current drops in Curve 1 and 3 indicate breakdown of the m-SWNTs.

Breakdown of the m-SWNTs results from CNT oxidation under the current-induced heat [44, 82]. However, carbon nanotubes have strong carbon-carbon bonds, and their current carrying capacities exceed $10\mu\text{A}/\text{nm}^2$ [99, 100]. Therefore, the oxidation begins from the sites of defects and dangling bonds on the CNTs. The m-SWNTs may be not burnt off together at one time. We suggest that the outmost m-SWNTs in the bundle are burnt off first due to being fully exposed to oxygen, while the inner m-SWNTs are more stable and need a higher current to burn off. Some defects may be created first by the large I_d for the defect-free m-SWNTs before they can be burnt off [44].

According to our observation, the difficulty of burning the m-SWNTs in a bundle is proportional to the diameter of the bundle. Large diameter means a large number of m-SWNTs in the bundle. In other words, a much higher V_{ds} need be applied to completely burn off those m-SWNTs in the bundle. Too high V_{ds} can also cause the burn off of the s-

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SWNTs simultaneously, especially when the m-SWNTs are surrounded by the s-SWNTs. To avoid this case, it is important to place small number of SWNTs between the two electrodes through controlling the concentration of SWNT suspension and processing time. Another method is adding surfactant to the suspension for sufficient dispersion. This will be discussed in Chapter 6.

4.2 Discussion

Figure 4.5 shows the output and transfer characteristics of a CNTFET device fabricated by combining AC dielectrophoresis placement method and the breakdown process. The device was annealed at 300⁰C for 15mins at an ambient environment to improve the contact between nanotubes and electrodes. The $I_d - V_g$ curve shows that the CNT channel is ON when $V_g < 0$. The channel conductance decreases with increasing V_g positively and becomes very small (in OFF state) for $V_g \geq +5V$, indicating a p-type channel. The ON/OFF current ratio at $V_{ds} = -150mV$ is 7×10^5 , as shown in Fig.4.5(b). This ON/OFF ratio is very close to the highest value of 10^6 reported so far [6, 7].

The p-type behavior was also reported in the early back-gate CNTFETs [4, 5] which were fabricated on thick gate oxides and exposed to air. Initially, CNTFETs were supposed to work as a conventional transistor where the gate voltage modulated the channel

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Fig.4.5. Output and transfer characteristics of a CNTFET measured at room temperature and ambient environment. P-Si acts as the back gate and the thickness of the oxide layer is 500nm. (a) $I_d - V_{ds}$ curves measured for $V_g = -10V \sim 20V$ in steps of 3V. Insert: AFM image of the SWNT bundle. The diameter of the bundle is 35nm. (b) $I_d - V_g$ curve measured at $V_{ds} = -150$ mV.

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Fig.4.6. Qualitative diagram of the lineup of the valence and conduction bands of a SWNT with Au Fermi level at the source-SWNT junction in air. V_c and V_v represent conduction band and valence band, respectively. The interface between the blank and the filled parts of the source is the Fermi level (E_F) of Au.

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conductance and there was a vanishing barrier to the valence band of the SWNT. However, the finding of ambipolar conduction in CNTFETs [10, 27], the transition from p- to n-type conduction upon gas adsorption [62, 64], and local gating of the CNTFET at the contact [101] led to an argument that Schottky barriers (SBs) could play a significant role. In a SB-FET, the conduction of the transistor results from the modulation of the contact resistance. Oxygen at the interface between the SWNTs and Au electrodes increases the work function of Au through creating an interface dipole in the same direction as that produced by the spill-out surface charge [102]. The Au Fermi level thus moves close to the SWNT valence band, resulting in a smaller SB at the source/SWNT junction and enhancing hole injection [27, 40, 62, 72, 101]. Figure 4.6 qualitatively shows the lineup of the valence and conduction bands of a SWNT with the Au Fermi level at the source-SWNT junction. One can see that holes can be injected from the source to SWNT when $V_g < 0$, while electron injection is blocked by the large barriers in the source region. However, at $V_g > 0$ V the hole injections are also prohibited because the Fermi level of Au aligns to the forbidden gap of the SWNT now. The transistor thus is at the OFF state at a positive gate voltage.

One important characteristic of a FET is the inverse subthreshold slope

$$S = dV_g / d(\log I_d) , \quad (4.2)$$

which is a measure of the switching speed of a device [103]. It only depends on the temperature in conventional FETs [103]. However, S shows a significant dependence on

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gate-to-channel coupling given by the gate capacitance and the drain voltage [40]. From Fig.4.5(b), we obtain a S value of $\sim 1700\text{mV/dec}$. Taking the thick oxide layer in our CNTFET into consideration, this value is consistent with the trends of S as a function of gate capacitance [40], indicating that SB could play an important role in our CNTFETs.

In our experiment, 20 pairs of electrodes have been bridged by SWNTs and 60% of them were successfully burned to CNTFETs with on/off current ratio of 3~6 orders of magnitude. Among them, 20% has 6 orders of magnitude. Those that failed were destroyed due to the high voltage applied in the breakdown process. This result suggests that AC dielectrophoresis is an efficient technique to fabricate CNTFETs. We also found that the 40% failed electrodes could be reloaded with CNTs by repeating AC dielectrophoresis process. This is a big advantage over the random spin-coating [4, 5, 9, 10] and direct growth [11, 12] technique. In addition, the tube length and orientation of tubes placed by AC dielectrophoresis method [16-18] are controllable, resulting in uniform device characteristics. All these advantages could make this technique a potential application in large scale fabrication of CNTFETs.

4.3 Conclusion

Single wall carbon nanotubes are placed between the source and drain electrodes using AC dielectrophoresis technique. The number of bridged SWNTs and their location are

Chapter 4 Fabrication of CNTFETs using AC dielectrophoresis

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controlled by the concentration of SWNT suspension and processing time. The contact resistance is found to be decreased by upto 2 orders of magnitude after annealing up to 300 °C in ambient environment. The bridging SWNTs in the channel are found to be a mixture of metallic SWNTs and semiconducting SWNTs. The former ones are removed from the channel using the current-induced burn-off process. The residual semiconducting SWNTs act as p-type channels of the CNTFETs, which have an ON/OFF current ratio as high as 7×10^5 . The inverse subthreshold slop is 1700mV/dec for the CNTFETs with 500nm SiO₂. AC dielectrophoresis technique provides a high success rate of fabricating CNTFETs with a flexibility of controlling the SWNT alignment direction and the SWNT length, offering a promising way for large scale fabrication of CNTFETs.

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Chapter 5

Room-temperature negative differential conductance in carbon nanotubes

The one-dimensional (1D) structure with nanometer diameter and long length (of the order of micrometer) makes carbon nanotubes an ideal material for on-tube electronic devices, especially quantum devices. Nanoscale intratube junctions and the devices on SWNTs have been prepared by chemical doping [66, 103, 104] and mechanical bending techniques [105, 106]. The fabricated devices exhibit unique characteristics, such as single electron transport [103, 105, 106], low temperature negative differential conductance (NDC) [66] and intratube rectifying characteristics [104], etc.

In this chapter, we report a significant NDC phenomenon of a bundle of SWNTs in a back-gated CNTFET. The apparent NDC with a peak-to-valley current ratio of about 2 is observed at room temperature. The peak voltage gradually shifts from 9.2V to 7.8V with sweeping the gate voltage from 6V to -6V. We suggest that the NDC results from resonant tunneling through a quantum well formed on the p-type semiconducting SWNTs in the bundle. This room temperature SWNT-NDC could be quite useful for practical applications of fast switching, oscillator and amplifying devices, etc.

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5.1 Experimental detail and results

The samples used here are back-gated CNTFETs [4, 5, 86]. P-type silicon with 500nm thick thermally grown silicon dioxide layer is used as the back gate. Source and drain electrodes are made of 20nm thick Ti followed by 40nm thick Au prepared by standard UV lithography and lift-off processes. The gap between the source and drain electrode is 2 μ m.

SWNT bundles are bridged across the source and drain electrodes using the AC dielectrophoresis method shown in Chapter 3 [86]. The drain current as a function of the drain-source voltage (I_d - V_{ds} curve) is measured using a HP-4156B semiconductor analyzer at ambient atmosphere. Figure 5.1(a) shows I_d verse V_{ds} as a function of the gate voltage V_g from -16 to 16V for the as-fabricated CNTFET. One can see that when $V_g > 0$ V, V_g has little influence on the I_d - V_{ds} curves. We suggest that I_d (for $V_g > 0$ V) is dominated by those m-SWNTs in the bundle. To burn off the metallic SWNTs [44, 86], a gate voltage of +6V is applied to deplete or protect the semiconducting SWNTs while V_{ds} is scanned from zero to a positive value, V_{pds} , which is increased gradually from a lower value, say, 5V, upto a higher one until some m-SWNTs are destroyed. Two apparent current drops at V_{pds} =10.2V (Curve 2 in Fig.5.1(b)) and 12.2V (Curve 4), respectively, suggest the breakdown of some m-SWNTs.

After the burnt-off process, the resultant I_d - V_{ds} curves show significant NDC

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Fig.5.1. (a) I_d as a function of V_{ds} measured for $V_g = -16 \sim 16V$ in steps of 4V. Insert: AFM image of the SWNT bundle. (b) I_d as a function of V_{ds} during the tube burning process. Curve 1 is the one before burning. Curves 2 and 3 are sweepings from 0 to 10.2V and 11V, respectively. Curve 4 is sweeping from 0 to 12.2V with a large conductance decrease at 11.8V. Curve 5 is the last sweeping.

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Fig.5.2. (a) I_d as a function of V_{ds} at $V_g = 6$ V. Curves 1, 2 and 3 were measured under the same conditions. For clarity, Curves 2 and 3 for the repeated measures are shifted up by 2.5×10^{-6} A and 4×10^{-6} A, respectively. (b) I_d as a function of V_{ds} at $V_g = 6, 3, 0, -3$ and -6 V.

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characteristics even at room temperature. It can be seen from Fig.5.2(a) that the current peak and valley occur at $V_{ds} = 9.2V$ and $9.8V$, respectively, under $V_g = 6V$. The peak-to-valley current ratio is ~ 2 . The NDC characteristics are repeatable at a given V_g , as shown in Fig.5.2(a) (Curves 2 and 3). Figure 5.2(b) shows the NDC two days after measuring the I_d - V_{ds} curves in Fig.5.2(a). At $V_g = 6V$, the peak voltage of the NDC is exactly at the same voltage value although the peak current changes slightly. More interestingly, the peak voltage gradually decreases from $9.2V$ to $7.8V$ with V_g decreasing from $6V$ to $-6V$.

5.2 Mechanism of the NDC

It is important to note that the NDC phenomenon was not observed at the first round of the burnt-off process even if V_{ds} was higher than $9.2V$ (the peak voltage of the NDC), see Curves 1 and 2 in Fig.5.1(b). Therefore, the bundle structure and imperfect contacts between the tube bundle and electrodes should not be responsible for the NDC. We suggest that there exist a quantum well created during the burnt-off process in the semiconducting CNT and the the NDC could be associated with hole resonant tunneling through a quantum well [107]. At $V_{ds} = 0$, holes in the well are confined to discrete energy levels, say E_n , in thermal equilibrium condition, as shown in Fig.5.3(a). As V_{ds} is increased, an accumulation region forms near the barrier by the drain side and a depletion region forms near the barrier by the source side. However, very few holes can tunnel through the energy barrier until V_{ds} reaches a value (for example $9.2V$) at which the Fermi level of the drain side is aligned with E_n in the well (Fig. 5.3(b)). When this happens, holes could tunnel through the right barrier into the well at a much high

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Fig.5.3. (a)-(c) Bias voltage dependent band diagrams for the points A, B, and C on the $I_d - V_{ds}$ curve in Fig.5.2(a). Only the valence band is shown here. The dashed lines are the Fermi level E_F . S and D represent the source and drain, respectively.

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tunneling rate and subsequently through the left barrier into unoccupied states in the valence band of the source side. As V_{ds} is increased further, the valence-band edge on the right is below E_n (Fig.5.3(c)), so that the tunneling rate of holes is significantly reduced. As a result, the current begins to decrease with increasing the voltage, resulting in an apparent NDC phenomenon.

The energy levels in the well can be approximately expressed as

$$E_n \approx \frac{\hbar^2}{2m^*} \left(\frac{n\pi}{w} \right)^2, \quad (5.1)$$

where n is the quantum number labeling the energy levels, w is the width of the well, and m^* is the effective mass of holes. When the energy difference between the levels, $E_2 - E_1$, is larger than the thermal energy $k_B T = 0.026$ eV, i.e.,

$$3 \times \frac{\hbar^2}{2m^*} \left(\frac{\pi}{w} \right)^2 \geq 0.026 \times 1.6 \times 10^{-19}, \quad (5.2)$$

the NDC phenomenon could be observed at room temperature. Using $m^* = 9.31 \times 10^{-32}$ kg [108], we have $w \approx 8$ nm. The obtained well width is consistent with the dimension of Léonard and Tersoff's simulated carbon nanotube devices which show a strong room temperature NDC [109].

The shift of the peak voltage as a function of V_g can be attributed to the variation of the conductance of the SWNT bundle and the shift of the E_n with respect to the Fermi level in the quantum well. V_{ds} should drop on the contacts between the source and drain electrodes and SWNTs (V_c), the quantum well (V_q) and the SWNTs beyond the quantum

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well (V_s), i.e., $V_{ds} = V_c + V_q + V_s$. Because of a large contact resistance [5] and large SWNT (channel) resistance, V_q could be quite small. Since the channel resistance decreases with decreasing gate voltage from 6V to -6V for a *p*-type CNTFET, more voltage will drop on the quantum well at a given V_{ds} . Therefore, V_{ds} for triggering the resonant tunneling decreases with the gate voltage changing from 6 to -6V, resulting in the down shift of the peak voltage, as observed in Fig.5.2(b). The peak current could be constrained by the tunneling process so that it may not be significantly influenced by the variation of the channel resistance or V_g . On the other hand, the up-shift of E_n with respect to the Fermi level induced by decreasing V_g [110] would also lead to a decrease in the peak voltage.

Taking the burning process into account, we suggest two possibilities for the formation of the quantum well. Local depletion of adsorbed oxygen on the s-SWNT walls could be one of the reasons. The significant drops of I_d in Fig.5.1(b) indicate burning-off of the m-SWNTs in the bundle [44,82]. We suggest that the tube-burning mainly occurs in a small area far from the source and drain so that the rest parts of the broken m-SWNTs still keep contact with the metal electrodes, as observed by Collions et al [44, 82]. At the burning sites, oxygen that initially adsorbed on s-SWNTs could react with carbon atoms during the tube burning process and some remnants [111] of the burned m-SWNTs might leave behind on the surface of s-SWNTs. The remnants prevent oxygen in air from being adsorbed again. Theoretical study [112, 113] has suggested that the chemisorption of oxygen could drastically decrease the energy band gap from 0.99 to 0.38eV for a (8, 4) SWNT. A reasonable speculation is that the band gap of a SWNT could be strongly

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associated with the amount of adsorbed oxygen on the s-SWNT wall. Therefore, the s-SWNTs covered with the remnants could form local energy barriers for hole transport. In addition, variation of the diameter of the SWNT bundle could be another reason. According to Reich *et al* [114], interaction between SWNTs in the bundle could lead to a decrease in the energy gap of the semiconducting SWNTs. At the tube-burning sites, the tube number should be small due to the burning-off of the m-SWNTs (the local bundle diameter should be thinned, as observed by Collions *et al* [44]) and the energy gap at these sites could be larger than the rest of the bundle, resulting in energy barriers for a quantum well.

5.3 Theoretical simulation

We first calculate the transmission coefficient T of a particle tunneling through a quantum well according to the continuity conditions of the wave function at the boundaries of the well. Then the current is calculated using the Landauer-Büttiker formula. Variation of the channel resistance induced by the gate voltage is considered through an equivalent resistor connected to the quantum well. The shift of discrete energy level E_n in the well induced by the gate voltage is simulated by adding small change to E_n .

5.3.1 Calculation of the transmission coefficient T

Figure 5.4 shows a schematic of double energy barriers, wave function, potential (V) and width (w) in different regions. To calculate the transmission coefficient of a hole through

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Fig.5.4. Schematic of double energy barriers.

the double barriers, we first analyze the relationship of constant a_i , b_i in the wave function of different regions. In region I and II, the wave functions are

$$\psi_1(x) = a_1 \exp(ik_1 x) + b_1 \exp(-ik_1 x) \quad (\text{for } x \leq x_1), \quad (5.3)$$

and

$$\psi_2(x) = a_2 \exp(ik_2 x) + b_2 \exp(-ik_2 x) \quad (\text{for } x \geq x_1), \quad (5.4)$$

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respectively, where $k_{1,2} = \frac{\sqrt{2m|E - V_{1,2}|}}{\hbar}$.

The matching conditions of the two wave functions at the boundary x_l are:

$$\begin{cases} \psi_1(x_l) = \psi_2(x_l) \\ d\psi_1(x_l)/dx = d\psi_2(x_l)/dx \end{cases}, \quad (5.5)$$

Or

$$\begin{cases} a_1 \exp(ik_1 x_l) + b_1 \exp(-ik_1 x_l) = a_2 \exp(ik_2 x_l) + b_2 \exp(-ik_2 x_l) \\ ik_1 a_1 \exp(ik_1 x_l) - ik_1 b_1 \exp(-ik_1 x_l) = ik_2 a_2 \exp(ik_2 x_l) - ik_2 b_2 \exp(-ik_2 x_l) \end{cases}. \quad (5.6)$$

Express a_l, b_l in terms of a_2 and b_2 ;

$$\begin{bmatrix} a_1 \\ b_1 \end{bmatrix} = R_1 \begin{bmatrix} a_2 \\ b_2 \end{bmatrix}, \quad (5.7)$$

where

$$R_1 = \frac{1}{2k_1} \begin{bmatrix} (k_1 + k_2) \exp[i(-k_1 + k_2)x_l] & (k_1 - k_2) \exp[i(-k_1 - k_2)x_l] \\ (k_1 - k_2) \exp[i(k_1 + k_2)x_l] & (k_1 + k_2) \exp[i(k_1 - k_2)x_l] \end{bmatrix}. \quad (5.8)$$

Similarly

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$$\begin{bmatrix} a_2 \\ b_2 \end{bmatrix} = R_2 \begin{bmatrix} a_3 \\ b_3 \end{bmatrix}, \quad (5.9)$$

$$R_2 = \frac{1}{2k_2} \begin{bmatrix} (k_2 + k_3) \exp[i(-k_2 + k_3)x_2] & (k_2 - k_3) \exp[i(-k_2 - k_3)x_2] \\ (k_2 - k_3) \exp[i(k_2 + k_3)x_2] & (k_2 + k_3) \exp[i(k_2 - k_3)x_2] \end{bmatrix}, \quad (5.10)$$

$$\text{where } k_3 = \frac{\sqrt{2m(E - V_3)}}{\hbar}.$$

Combining Eq.(5.7) and (5.9), we obtain

$$\begin{bmatrix} a_1 \\ b_1 \end{bmatrix} = R_1 R_2 \begin{bmatrix} a_3 \\ b_3 \end{bmatrix}. \quad (5.11)$$

In the same way, we can express a_1, b_1 in terms of a_5 and b_5 ;

$$\begin{bmatrix} a_1 \\ b_1 \end{bmatrix} = R_1 R_2 R_3 R_4 \begin{bmatrix} a_5 \\ b_5 \end{bmatrix}. \quad (5.12)$$

We assume that a charge incident from left and transmit to right. Thus, $b_5 = 0$, or

$$\begin{bmatrix} a_1 \\ b_1 \end{bmatrix} = R_1 R_2 R_3 R_4 \begin{bmatrix} a_5 \\ 0 \end{bmatrix}. \quad (5.13)$$

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Since the flux density

$$j(x) = \frac{-i\hbar}{2m} \left[\psi^* \frac{d\psi}{dx} - \psi \frac{d\psi^*}{dx} \right], \quad (5.14)$$

the transmitted probability flux density j_t and the incident probability flux density j_i are

$$j_t = \frac{\hbar k_t}{m} |a_1|^2 \quad \text{and} \quad j_i = \frac{\hbar k_s}{m} |a_5|^2, \quad (5.15)$$

respectively.

Therefore, the transmission coefficient $T(E)$ can be expressed as

$$T(E) = \frac{j_t}{j_i} = \frac{k_s |a_5|^2}{k_t |a_1|^2} \quad (5.16)$$

5.3.2 Current through the quantum well

Figure 5.5 shows the valence band of the CNT channel. Since the contact resistance and SWNT resistance change with the gate voltage for a CNTFET shown in Chapter 4, we

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add an equivalent resistor to the quantum barrier structure to simulate the influence of the resistance variation. The drain voltage then drops on the quantum barrier (V_q) and the resistor R

$$V_{ds} = V_q + IR. \quad (5.17)$$

The current through the quantum well can be calculated using the Landauer-Büttiker formula

Fig.5.5. Valence band of the CNT channel. The top of the well (W_3 region) and the bottoms of the barriers (W_2 and W_4 region) are assumed to be flat in the calculation. V_q is the applied voltage on the quantum. V_w is the height of the well.

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$$I = \frac{4e}{h} \int [F(E) - F(E + eV_q)] T(E) dE, \quad (5.18)$$

where $F(E)$ is the Fermi function.

When $w_3 = 3\text{nm}$, $w_{2,4} = 2\text{nm}$, $V_w = 0.25\text{eV}$ and $E_F = 0.12\text{eV}$, the current as a function of V_{ds} is shown in Fig.5.6 (a). One can see that the peak voltage gradually shifts from $\sim 0.28\text{V}$ to $\sim 0.15\text{V}$ as the resistance decreases from $2.2 \times 10^4 \Omega$ to $1.8 \times 10^4 \Omega$. However, the value of the peak current does not show significant change. We then considered the influence of the shift of the discrete energy level in the well caused by the gate voltage. After a small amount of shift of $+0.03\text{eV}$ with respect to E_n are introduced, the curve shifts to a higher V_{ds} and the increase of the peak current is found, as shown in Figure 5.6(b). In contrast, the curve shifts to a lower V_{ds} and the peak current decreases when an up-shift of 0.03eV of E_n is used. Since the decrease of the gate voltage should cause up-shift of E_n and a decrease in the SWNT resistance, the simulation results are consistent with the experimental ones, confirming our suggestions for the observed phenomenon in Fig.5.2. The left-right shift of the peak current is influenced by the variations of both resistance and E_n , while the up-down shift of the peak only depends on the variation of E_n .

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Fig.5.6. Simulation results of I_d as a function of V_{ds} . The resistance of the added resistor is $1.8 \times 10^4 \Omega$, $2.0 \times 10^4 \Omega$ and $2.2 \times 10^4 \Omega$ for curve 1, 2 and 3, respectively. In (a), the E_n remains constant for the three curves. In (b), it is $E_n - 0.03$, E_n and $E_n + 0.03$ for curve 1, 2 and 3, respectively.

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5.4 Conclusion

Room-temperature negative differential conductance phenomenon has been observed in a bundle of SWNTs in a CNTFET. The peak-to-valley current ratio is about 2. This phenomenon is attributed to a quantum well between two adjacent energy barriers formed on semiconducting SWNTs due to burning off metallic SWNTs in the bundle. The conductance variation of the SWNTs and the shift of the energy level in the quantum well are suggested to be responsible for the peak voltage shifts from 9.2V to 7.8V with decreasing the gate voltage from 6V to -6V. This suggestion is supported by the theoretical simulation.

Chapter 6 Influences of surfactants on the characteristics of CNTFETs

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Chapter 6

Influences of surfactants on the characteristics of CNTFETs

At present, CNTFETs have been intensively studied [4, 5]. It is found that the characteristics of the CNTFETs are very sensitive to the environmental conditions. First, the adsorbed gas molecules are observed to have great influences on the electronic properties of SWNTs. Collions et al have reported that the electrical resistance, thermoelectric power, and local density of states of the SWNTs are extremely sensitive to oxygen [115]. Oxygen at the interface between the SWNT and electrode could play a key role in determining the nature of the output characteristics of CNTFETs. With different amount of oxygen exposure, the CNTFETs are found to convert from p-type, ambipolar to n-type characteristics [72]. In addition, other gases, such as NH_3 and NO_2 , can dramatically affect the transfer characteristics of CNTFETs [77]. Second, CNTFETs are also sensitive to some liquid and solid materials. Water molecule is reported to be responsible for the observed hysteresis characteristic of the CNTFETs [116-118]. The influences of water molecules can be minimized by coating PMMA on the surface of CNTFETs. Polymer electrolyte-gated CNTFETs showed strong gate-channel coupling with the improved device characteristics compared to the back-gate CNTFETs, their

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transfer characteristics are severely affected by the doping materials in the polymer [36, 37].

Most CNTFETs are fabricated using SWNT suspension. Because of the substantial van der Waals attraction, SWNTs easily aggregate in bundles. Surfactants are usually used in order to disperse the SWNT bundles. The surfactants adsorbed on the surface of the SWNTs affect the characteristics of the CNT-based devices. In this chapter, we report the effects of a surfactant Triton X-100 [16, 119, 120] on the transfer characteristics of the CNTFETs. We find that the surfactant at the interface between the CNTs and Au electrodes can change the work function of the electrodes and therefore convert the CNTFETs from typical p-type to ambipolar characteristics. The adsorbed surfactants between the CNTs and SiO₂ also result in a significant hysteresis in the source-drain current versus the gate voltage.

6.1. Experimental detail

The samples used here are the back-gated CNTFETs [86]. The transistor structure, electrode material and thickness are the same as described in Chapters 3 and 4. The SWNTs are placed between the source and drain electrodes using AC dielectrophoresis method. However, the solution for dispersing SWNTs here are different from that in Chapter 3. Two kinds of solvents are used here. One is water with 1% Triton X-100, the other is water with 1% sodium dodecyl sulfate (SDS). In the dielectrophoresis process, a

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drop of the CNT suspension is deposited onto the structured wafers on which an AC bias is applied across the source and drain electrodes. The peak-to-peak AC voltage is between 4~8V, depending on the electrode distance, and the frequency is fixed at 10MHz. Once the connection of CNTs to the two electrodes is confirmed through monitoring the variation of the resistance between the two electrodes, the AC bias is turned off immediately. After this process, the samples are rinsed using deionized water and then dried off using N₂.

6.2. Experimental Results

Figure 6.1 shows the Raman spectra of the bridged SWNTs between the source and drain. The large G⁺ (high-frequency component around 1600cm⁻¹) to G⁻ (low-frequency component around 1565cm⁻¹) ratio and the apparent radial breathing mode (RBW) at around 182cm⁻¹ suggest that the SWNTs are dominated by semiconducting SWNTs [15, 121]. The later one also indicates a tube diameter of 1.3~1.4nm.

We find that the diameter of SWNT bundle placed using these two kinds of suspension is much smaller than that of SWNT bundle placed using IPA suspension. For the case of Triton X-100/water suspension, even single SWNT can be found to bridge the electrodes. This result suggests that this surfactant is very efficient in dispersing SWNTs, consistent with other group's report [16]. The high dispersion efficiency could be related to the chemical structure of the surfactants. The molecular formula of Triton X-100 can be expressed as

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where the average number of ethylene oxide units per molecule, N , is 9 or 10. The benzene rings in the molecule make the surfactant a strong interaction with SWNTs and the long 8-carbon alkyl chain improves surfactant energetics, leading to a good dispersion of SWNTs [120].

Fig.6.1. Raman spectroscopy of one bridging bundle between two neighboring electrodes. It is excited by 514.5nm-wavelength Ar^+ ion laser.

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The improved dispersing effect increases the yields of fabricated CNTFETs. The CNTFETs fabricated using SDS/water suspension only exhibit p-type characteristics, which has similar properties as discussed in Chapter 4. However, those fabricated using Triton X-100/water suspension show either p-type or ambipolar characteristics. Among them, 9/10 are ambipolar ones. Typical ambipolar characteristics at both positive and negative drain voltages are shown in Fig.6.2. One can see that the drain current (I_d) decreases first with increasing gate voltage (V_g), reaches a minimum value ($I_{\min}$) and then increases again until saturated. Hole current and electron current are on the left and right of $I_{\min}$, respectively. The coexistence of hole current and electron current in one transistor depending on the sign of V_g is so-called ambipolar characteristic. $I_{\min}$ depends on the drain-source voltage (V_d) and increases from $\sim 10^{-10}$ A to $\sim 10^{-8}$ A as $|V_d|$ increases from 0.25V to 0.75V. The saturated I_d on the left and right sides of the minimum I_d are almost in the same order of magnitude for the as-prepared CNTFETs. However, it is found that the saturated I_d on the right side I_{n-on} decreases gradually with time and vanishes after two months' storage in air. In contrast, the saturated I_d on the left side I_{p-on} does not show any significant changes, as shown in Fig.6.3(a). The result suggests that the as-prepared ambipolar CNTFETs are not stable and they could convert to p-type ones after a long time exposure to air. Interestingly, this converted p-type CNTFET recovers its ambipolar characteristics after some pure Triton X-100/water solution is introduced to the device and dried off by nitrogen gas 20min later, as shown in Fig.6.3(b).

The hysteresis of the CNTFETs is studied by sweeping V_g from negative to positive voltage (forward sweeping) and vice versa (backward sweeping) to check the change of

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Fig.6.2. Transfer characteristics of the fabricated CNTFETs with (a) $V_d < 0$ and (b) $V_d > 0$, respectively. Gate voltages are swept from -20 to 20V. The curves marked by square, triangle and cross represent absolute value of $V_d = 0.75$, 0.5 and 0.25 V, respectively. Insert in (a): AFM image of the SWNT bundles.

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Fig.6.3. (a) Transfer characteristics of the converted p-type CNTFET from the as-prepared ambipolar CNTFET (Fig.6.2) after two months' storage in air. (b) Transfer characteristics of the same transistor after introducing Triton X-100 for 20min.

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the transfer characteristics. Figure 6.4 shows the result obtained from another ambipolar CNTFET immediately after it was fabricated. Apparent anti-clockwise hysteresis is observed when the gate voltage is first swept forwardly and then backwardly. One can see that the I_d - V_g curves shift to negative V_g under forward sweep at both positive and negative V_d . In contrast, the curves shift to positive V_g under backward sweep.

The converted p-type CNTFET also exhibits an apparent hysteresis, as shown in Fig.6.5(a). However, the hysteresis vanishes after the CNTFET is annealed at 100°C for 10mins in ambient environment, as shown in Fig.6.5(b). We note that the threshold voltage shift (ΔV_{th}) is more than 20V for the ambipolar CNTFET (Fig.6.4), and only about 15V for the p-type one (Fig.6.5(a)).

6.3 Simulation of the ambipolar characteristics

We use a semiclassical method [38] to simulate the ambipolar characteristics of the CNTFETs. The detail of this method will be described in Chapter 7. Here, the related simulation parameters are as follows. The CNT diameter, bandgap, length between the source and drain, and the temperature are 1.4nm, 0.6eV, 200nm, and 300K, respectively. The Fermi level at the metal-CNT contact is assumed at the middle of the CNT band gap. In the calculation, the gate oxide thickness and gate voltage are scaled down to 5nm and -1~1V, respectively, according to the ‘scaling rules’ [38] of CNTFETs. The simulated results are shown in Fig. 6.6.

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Fig.6.4. Drain current as a function of gate voltage with (a) $V_d = -0.75V$ and (b) $V_d = 0.75V$, respectively. The arrows indicate the sweep direction of gate voltage.

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Fig.6.5 Drain current as a function of gate voltage (a) before and (b) after annealing at 100°C, respectively. The arrows indicate the sweep direction of gate voltage.

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Fig.6.6. Simulated transfer characteristics of the CNTFETs with (a) $V_d < 0$ and (b) $V_d > 0$, respectively.

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6.4 Discussion

6.4.1 Origin of the ambipolar characteristics

It was suggested that the ambipolar characteristics are related to large diameter SWNTs, say around 3~5nm, which possess a smaller band gap [11]. However, this is not our case, as the diameter of the CNTs used in the experiments is about 1.4nm. Both p-type and n-type SWNTs across the source and drain are unlikely to be an interpretation as our transistors were fabricated by burnt-off technique [44, 86] in which a positive gate voltage was applied to switch off the p-type SWNTs and to burn out those metallic SWNTs under a large I_{ds} . For the details, see Chapter 4. Thus, any n-type SWNTs across the electrodes should be burnt out in the process. It is well accepted that CNTFET works as a Schottky-barrier transistor in which the gate voltage modulates the barrier thickness [72]. When the Fermi level of the electrodes lies close to the mid-gap of the SWNTs, the Schottky barriers for electrons and holes are equal, and electrons and holes are injected into the SWNTs under positive and negative gate voltages, respectively. In comparison with the p-type CNTFETs fabricated using SDS/water suspension and the isopropyl alcohol (IPA) SWNT suspension [86], we suggest that the observed ambipolar behavior is caused by Triton X-100 surfactants between the SWNTs and electrodes. Since the surfactants separate the SWNTs efficiently, it is reasonable to assume that some Triton X-100 surfactants adsorb on the surface of the SWNTs. In addition, some surfactants can adsorb to the surface of the electrodes during the AC dielectrophoresis process. As a

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result, the interface between the SWNTs and electrodes could be filled with the surfactants after the process. The surfactants at the interface could change the work function of the Au electrodes and make the Fermi level lie in the middle of the CNT band gap. If there is no surfactants at the interface, oxygen will play a key role in modifying the work functions of the Au electrodes, and the Fermi level of the electrodes thus lies close to the valence band of the SWNTs [102]. Thus, the barrier for holes is reduced and hole injection is enhanced. In contrast, the barrier for electrons becomes larger. The electron current at positive V_g is thus suppressed, leading to a p-type CNT channel. Therefore, the initially observed p-type CNTFETs are due to lack of Triton X-100 at the interface while the conversion of the ambipolar to p-type characteristics could be attributed to the vanish of the surfactants. The recovery of the ambipolar (Fig.6.3(b)) from p-type characteristics (Fig. 6.3(a)) for the same CNTFET after introducing pure Triton X-100/water solution could be a strong evidence.

6.4.2. Comparison between simulation results and experimental results

In Fig.6.6, the simulated results show that at a negative V_d (Fig.6.6(a)) the curves almost overlap for the hole current while they split for the electron current, vice versa for a positive V_d (Fig.6.6(b)). Since the electron current rises monotonically with V_g , exactly the same as the hole current increases monotonically with $V_d - V_g$ [33], the minimum current occurs at $V_{g-min} = V_d / 2$, as shown in Fig.6.6(b). As a result, the minimum current increases with increasing V_d , consistent with our experimental result (Fig.6.2). The simulated curves are symmetric with respect to the gate voltage $V_{g-min} = V_d / 2$. However,

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the experimental curves are asymmetric. The inverse subthreshold slopes $S = dV_g / d(\log I_d)$ derived from the curve for $V_d = -0.25\text{V}$ are about 1800 and 760mV/dec for the hole current and electron current, respectively. This result indicates that the SB for holes is larger than that for electrons and thus the Fermi level of the electrode is located somewhat close to the conduction band of the SWNT. Comparing the simulation results with the experimental ones, we can see that when $V_d < 0\text{V}$, both simulated $V_{g-\min}$ (Fig.6.6(a)) and experimental $V_{g-\min}$ (Fig.6.2(a)) are negative. They shift to $V_g = 0$ as $|V_d|$ decreases to zero. When $V_d > 0\text{V}$, the simulated $V_{g-\min}$ are positive and gradually shift to $V_g = 0$ with decreasing V_d . In contrast, the corresponding observed $V_{g-\min}$ values are negative and do not show an apparent shifting. Since the hysteresis in the transfer characteristics of the CNTFETs has been observed, as shown in Fig.6.4 and Fig.6.5, we suggest that the discrepancy of our results is caused by the hysteresis effects of our devices. In Fig. 6.4, the I_d - V_g curves shift to negative V_g under forward sweep at both positive and negative V_d , resulting in that the $V_{g-\min}$ is at a negative V_g when $V_d > 0$.

6.4.3 Mechanism of the hysteresis

Early reported hysteresis of CNTFETs was attributed to charge transfer between the CNTs and silicon dioxide [73, 75, 76, 122]. However, the hysteresis phenomena are also found to be closely related to the environmental conditions. They occur in ambient air and vanish in vacuum [123], suggesting that the molecules adsorbed on the CNTs in the devices maybe play a key role in the hysteresis. Recent studies support this assumption. It is found that water and alcohol molecules at the interface between CNTs and SiO_2 [116,

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117] play more important roles than the traps at the interface of SiO₂/Si in the hysteresis. Furthermore, CNTFETs coated with poly(methyl methacrylate) (PMMA) exhibit nearly hysteresis-free characteristic after being baked at 150°C for ~24h [116]. Through studying the interactions of SWNTs with a series of aromatic compounds, such as aniline, phenol, anisole, toluene, chlorobenzene and nitrobenzene, Star *et al* [118] found that the shift of the I_d - V_g curves was proportional to the Hammett sigma values of the aromatic compounds or their different electron donating properties. This is another important evidence for the above assumption. In our case, the vanishing of the hysteresis after annealing at 100°C in air rules out the contribution of the traps due to SiO₂/Si and water as a higher annealing temperature, say above 400°C, is needed to eliminate the trapping centers at the interface between Si and SiO₂ [124]. According to Kim *et al*' [116] report, the elimination of the hysteresis caused by water needs to anneal the CNTFETs at 200°C in H₂ for 4.5h, but a significant hysteresis recovery immediately upon exposure of the devices to ambient air. This is fully contrary to our observation. We, therefore, suggest that the hysteresis of our CNTFETs is caused by charge transfer between the adsorbed surfactants and the SWNTs. The observed anti-clockwise hysteresis suggests that it could be caused by hole injection from the SWNT to the surfactant. The electric field at the SWNT surface can be expressed as [75]

$$E = V_g / \epsilon R \ln(t_{ox} / R) \quad (6.1)$$

where R is the average SWNT radius, t_{ox} is the gate oxide layer thickness, and ϵ is the dielectric constant of SiO₂. For $R = 0.7\text{nm}$, $t_{ox} = 500\text{nm}$, $\epsilon = 3.9$ and $V_g = 20\text{V}$,

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$E \approx 1V/nm$ is high enough for the Fowler-Nordheim-type tunneling [122], i.e. the hole transfer from SWNTs to surfactants. Triton X-100 is a kind of aromatic compounds and is sensitive to strong oxidizing agents. It is conceivable that the remaining surfactants at the interface between the SWNTs and SiO_2 are oxidized when the CNTFET is heated to $100^\circ C$ in air. As a result, the hysteresis is reduced significantly after annealing. In addition, the extent of hysteresis is related with the amount of Triton on the SWNT surface. There should be more surfactants on the SWNT surface of the as-fabricated ambipolar CNTFET than that on the converted p-type one. Consequently, ΔV_{th} for the former one (more than 20V) is much larger than that for the later one (about 15V).

6.5. Conclusion

The influences of surfactants (Triton X-100 and SDS) on the transfer characteristics of CNTFETs have been studied. The CNTFETs are fabricated using AC dielectrophoresis methods from the SWNT suspension prepared by dispersing SWNTs in water with 1% of those surfactants. The CNTFETs fabricated with SDS/water suspension only exhibit p-type characteristic. However, 90% of the CNTFETs with Triton show ambipolar characteristics, and only 10% possess p-type characteristics. Triton X-100 at the interface between the SWNTs and the electrodes could be responsible for the ambipolar characteristics. Apparent anti-clockwise hysteresis has been observed in the fabricated

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CNTFETs by sweeping the gate voltage successively in two directions (forward and backward). The hysteresis could be attributed to the charge transfer between the SWNTs and the surfactants under the SWNTs. This kind of hysteresis can be removed by annealing the CNTFETs at 100°C in ambient air, under which the surfactants should be oxidized.

Chapter 7 Simulation of ambipolar-to-unipolar conversion of CNTFETs

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Chapter 7

Simulation of ambipolar-to-unipolar conversion of CNTFETs

Switching mechanism of CNTFETs was initially assumed to be analogous with a traditional Si MOSFET. However, by comparing the transfer characteristics of the CNTFETs exposed to different oxygen levels to those doped with different amounts of potassium, Heinze *et al* [72] pointed out that the Schottky barrier (SB) at the contacts between the carbon nanotubes (CNTs) and electrodes plays a key role in controlling the performance of the devices. Therefore, CNTFETs could be operated as unconventional “Schottky barrier transistors” in which they function primarily by varying the contact resistance rather than the channel conductance. The SB model is also supported by the fact that the inverse subthreshold slope of the I_d - V_g curve is temperature dependent at high temperatures and it levels off at temperatures below 200K [2]. The performance of CNTFETs can be systematically improved by reducing the oxide thickness [10, 34, 40]. However, due to the SB contacts at the nanotube/metal interface [40, 72, 101], vertically scaled CNTFETs exhibit more pronounced ambipolar characteristics [33] and unacceptable OFF current at high drain voltage. Some methods have been taken to overcome these disadvantages [70, 125] by taking advantage of the fact that the performance of a SB field effect transistor (SB-FET) is largely controlled by the electric

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field at the contacts [72]. A sharp contact could lead to electric field focusing, or, in other words, a larger field at the contact. Therefore, the device performance can be dramatically influenced by the contact geometry in addition to the thickness of the gate oxide layer. By introducing an asymmetric gate structure with respect to the source and drain electrodes, Heinze *et al* [125] have shown a significant improvement of the performance of SB-CNTFETs and Lin *et al* [70] have demonstrated a conversion of a CNTFET from ambipolar to unipolar (p-type) characteristics.

In this chapter, we examine the influences of CNTFET structures on the characteristics of the devices. Using an asymmetric oxide layer between the CNT and gate electrode, we have obtained asymmetric transfer characteristics of the CNTFETs based on semiclassical simulation. The results suggest that the slope of the oxide layer and the electrode thickness play important roles in the transfer characteristics of such CNTFETs. Through optimizing them, we can convert the performance of the CNTFETs from ambipolar characteristics to unipolar (p-type or n-type) behavior with a significant drop in the OFF current or an increase in the ON/OFF current ratio.

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7.1. Methodology

7.1.1 Introduction of Wentzel-Kramers-Brillouin (WKB) approximation [126]

Consider the one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\psi(x). \quad (7.1)$$

Its solutions are implicit functions of $\hbar$. In the limit of $\hbar \rightarrow 0$, a good approximation to $\psi(x)$ is given by a linear combination of the functions

$$\psi_{\pm}(x) = \frac{1}{\sqrt{p(x)}} \exp\left\{\pm \frac{i}{\hbar} \int^x dx' p(x')\right\}, \quad (7.2)$$

where $p(x) = \sqrt{2m(E - V(x))}$. This is known as the basic W.K.B solutions. If $V(x) > E$, $p_1(x) \equiv \sqrt{2m(V(x) - E)}$ is used to replace of $p(x)$. The solution to the Schrödinger equation can be given by

$$\psi(x) = \frac{A}{\sqrt{p_1(x)}} \exp\left[\frac{1}{\hbar} \int_{x_0}^x dx' p_1(x')\right] + \frac{B}{\sqrt{p_1(x)}} \exp\left[-\frac{1}{\hbar} \int_{x_0}^x dx' p_1(x')\right], \quad (7.3)$$

where A and B are arbitrary constants, x_0 is between two adjacent turning points.

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In the case of $E > V(x)$, $p_2(x) \equiv \sqrt{2m(E - V(x))}$ is used, and the solution is expressed as

$$\psi(x) = \frac{A}{\sqrt{p_2(x)}} \exp \left[\frac{i}{\hbar} \int_{x_0}^x dx' p_2(x') \right] + \frac{B}{\sqrt{p_2(x)}} \exp \left[-\frac{i}{\hbar} \int_{x_0}^x dx' p_2(x') \right] \quad (7.4)$$

Fig.7.1. Potential barrier $V(x)$ with a beam of particles of energy E approaching it from $-\infty$.

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With the WKB method, one can calculate the transmission coefficient of a particle of energy E tunneling through a potential barrier. In Fig.7.1, the particles are assumed to be incident from the left, and x_1 and x_2 are the two turning points. In region III there is only a transmitted wave, and therefore in the W.K.B approximation it can be expressed as

$$\psi_{III}(x) = \frac{A}{\sqrt{p_2(x)}} \exp \left[\frac{i}{\hbar} \int_{x_2}^x dx' p_2(x') \right], \quad (7.5)$$

or equivalently

$$\begin{aligned} \psi_{III}(x) = & \frac{A}{\sqrt{p_2(x)}} \cos \left[\frac{1}{\hbar} \int_{x_2}^x dx' p_2(x') - \frac{\pi}{4} + \frac{\pi}{4} \right] \\ & + \frac{iA}{\sqrt{p_2(x)}} \cos \left[\frac{1}{\hbar} \int_{x_2}^x dx' p_2(x') - \frac{\pi}{4} - \frac{\pi}{4} \right] \end{aligned} \quad (7.6)$$

where A is a constant. Using the connection formulae [126] in the W.K.B method, we obtain

$$\begin{aligned} \psi_{II}(x) = & \frac{Ae^{-i\pi/4}}{\sqrt{p_1(x)}} \exp \left[\frac{1}{\hbar} \int_x^{x_2} dx' p_1(x') \right] \\ = & \frac{Ae^{-i\pi/4}}{\sqrt{p_1(x)}} \exp \left[\frac{1}{\hbar} \int_{x_1}^{x_2} dx' p_1(x') \right] \exp \left[-\frac{1}{\hbar} \int_{x_1}^x dx' p_1(x') \right], \end{aligned} \quad (7.7)$$

and apply these formulae once again,

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$$\psi_I(x) = \frac{2Ae^{-i\pi/4}}{\sqrt{p_2(x)}} \exp\left[\frac{1}{\hbar} \int_{x_1}^{x_2} dx' p_1(x')\right] \cos\left[\frac{1}{\hbar} \int_x^{x_1} dx' p_2(x') - \frac{\pi}{4}\right]. \quad (7.8)$$

This equation can be rewritten in the form

$$\begin{aligned} \psi_I(x) = & \frac{Ae^{-i\pi/2}}{\sqrt{p_2(x)}} \exp\left[\frac{1}{\hbar} \int_{x_1}^{x_2} dx' p_1(x')\right] \exp\left[-\frac{i}{\hbar} \int_{x_1}^x dx' p_2(x')\right] \\ & + \frac{A}{\sqrt{p_2(x)}} \exp\left[\frac{1}{\hbar} \int_{x_1}^{x_2} dx' p_1(x')\right] \exp\left[\frac{i}{\hbar} \int_{x_1}^x dx' p_2(x')\right], \end{aligned} \quad (7.9)$$

where the second term represents a wave traveling along the positive x-axis and the first term is another traveling wave in the opposite direction. The ratio of $[\psi_{III}(x)]^2$ of Eq.(7.5) to the square of the second term of Eq.(7.9) gives for the transmission coefficient the approximate expression

$$T = \exp\left[-\frac{2}{\hbar} \int_{x_1}^{x_2} dx p_1(x)\right]. \quad (7.10)$$

Using $p_1(x) = \hbar k(x)$, where $k(x)$ is the wave number, Eq. (7.10) changes to

$$T = \exp\left[-2 \int_{x_1}^{x_2} dx k(x)\right]. \quad (7.11)$$

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7.1.2 Semiclassical calculation

The structures of the CNTFETs studied here are illustrated in Fig.7.2. The thickness of the SiO₂ layer on a doped Si wafer is 5nm. Fig.7.2(a) shows a CNTFET in which a CNT is buried underneath a pair of symmetric source and drain electrodes. Another CNTFET has asymmetric source and drain, as shown in Fig.7.2(b). One terminal of the CNT is buried underneath the source electrode and the other end is placed on the top of the drain electrode through a SiO₂ prism (the raised part of the gate oxide layer) whose slanted angle α is 45°, 60° and 75°, respectively. The thickness of the source and drain electrodes is fixed at either 20 nm or 60 nm. The distance between the surface of the Si wafer and a grounded top electrode (not shown here) is 165 nm.

A semiclassical method [38] is used to calculate the transfer characteristics of the CNTFETs. Under an assumption of ballistic transport, the channel current can be expressed using the Landauer-Büttiker formula as follows

$$I = \frac{4e}{h} \int [F(E) - F(E + eV_d)] T(E) dE, \quad (7.12)$$

where V_d is the drain voltage, $F(E)$ is the Fermi function and $T(E)$ is the energy-dependent transmission through the SB between the CNTs and electrodes. $T(E)$ can be determined using Eq. (7.11) with the wave number [38, 127]

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(a)

(b)

Fig.7.2. Schematic side-view of the back-gated CNTFETs. (a) The CNTFETs with the symmetric source and drain. The CNT (dash line) is buried under the source and drain electrodes. (b) The CNTFETs with asymmetric source and drain. An oxide prism is attached to the drain. The CNT is from the bottom of the source along the prism to the top of the drain. The slanted angle α of the prism is taken as 45° , 60° , and 75° , respectively, in our calculation.

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$$k(x) = \frac{2}{3aV_0} \left\{ \left(\frac{E_g}{2} \right)^2 - [E + eV(x)]^2 \right\}^{\frac{1}{2}}, \quad (7.13)$$

where $a = 0.144\text{nm}$, $E_g = 0.6\text{eV}$, and $V_0 = 2.5\text{eV}$ are the C-C bond length, the CNT band gap and the tight-binding parameter, respectively. $V(x)$ is the electrostatic potential along the CNT and is obtained by solving the Laplace equation numerically for the device geometries, as shown in Fig. 7.2. The integration is performed between the two classical turning points x_1 and x_2 [38]. Charge on the CNT is neglected in the simulation. The CNT diameter, bandgap, length between the source and drain, and the temperature are 1.4nm , 0.6eV , 200nm , and 300K , respectively. The Fermi level at the metal-CNT contact is assumed at the middle of the CNT band gap.

7.2. Results and discussion

Figure 7.3 shows the distribution of electrostatic potential for the CNTFET with the symmetric source and drain under zero drain voltage. From the potential contour lines in Fig.7.3, one can see that the electric field is higher at Point A than Point B. Therefore, the CNT in the structure shown in Fig.7.2(a) should have different electrostatic potential distribution from that in the structure shown in Fig.7.2(b).

The effect of the slanted angle α on the SB width is illustrated in the energy band diagram of Fig.7.4 for a gate voltage of $V_g = 0.1\text{V}$ and a drain voltage of $V_d = 0.4\text{V}$. The

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Fig.7.3. Electrostatic potential contour lines for the symmetric source and drain CNTFET with $V_g = 1V$ and $V_d = 0V$. Adjacent contour lines differ by $0.2V$. The channel length and electrode length are $200nm$ and $100nm$, respectively. The bottom oxide thickness is $5nm$.

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Fig.7.4. The band diagrams for the symmetric and asymmetric structures of the CNTFETs with $V_d = 0.4V$ and $V_g = 0.1V$. E_{FS} and E_{FD} are the Fermi levels of the source and drain electrodes, respectively. The angle values indicated correspond to the slanted angle α of the prism in Fig. 7.2(b).

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band by the source side bends slightly up while it bends downward by the drain side. Electrons are injected from the source and the electron current is the same for the two structures of the CNTFETs as the SB width at the source side is not affected by the contact details at the drain. However, as shown in Fig.7.4, the width of the SB at the CNT-drain contact becomes wider with decreasing α , resulting in a lower hole tunneling probability or a low hole current at the given positive V_d . Therefore, the total current decreases with decreasing α .

The transfer characteristics of the CNTFETs with 20nm thick electrodes and $V_d = 0.4V$ are shown in Fig.7.5(a). Curve 1 for the structure of the symmetric source and drain shows a typical ambipolar characteristic, consistent with the experimental observations for the CNTFETs with a 2nm or 5nm thick gate oxide [33]. The minimum current occurs at $V_g = V_d/2$, indicating that the electron current rises monotonically with V_g exactly the same as the hole current increases monotonically with $V_d - V_g$. Curves 2 to 4 are for $\alpha = 75^\circ, 60^\circ$ and 45° , respectively. It can be seen that the curves overlap for $V_g > 0$, while they deviate from each other for $V_g < 0$, indicating that the hole current is suppressed gradually with decreasing α . When $V_d > 0$ and $V_g > 0$, electron injection at the source is insignificantly affected by the four different CNT-drain contacts. However, the hole injection depends mainly on the energy band near the CNT-drain contact. For a smaller α , the electric field at the CNT-drain contact is smaller than that for a larger α , resulting in a thicker energy barrier, as shown in Fig.7.4. The thick energy barrier decreases the hole tunneling possibility and hence decreases the hole current. As a result, the total current becomes smaller for $V_g < 0$, see Fig.7.5(a). When the drain height is increased from 20nm

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Fig.7.5. The transfer characteristics of the simulated CNTFETs with $V_d = 0.4V$. Curve 1 is for the symmetric structure in Fig.7.2(a) and Curves 2, 3 and 4 are for the asymmetric structure in Fig.7.2(b) with $\alpha = 75^\circ$, 60° and 45° , respectively. The drain electrode height for (a) and (b) are 20nm and 60nm, respectively.

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to 60nm, the electric field difference between Points B and A (in Fig.7.3) is increased significantly. Therefore, the hole current could be further suppressed for the asymmetric structure, as shown in Fig.7.5(b). For this case, the difference in electrostatic potentials on the CNT near the drain contact for the different inclination angles becomes so small that the hole current does not show an apparent difference for $\alpha = 45^\circ$ and 60° . The device characteristics are changed from the ambipolar for the symmetric CNTFET to the unipolar (n-type) for the asymmetric devices. The minimum current is decreased by more than an order of magnitude and the corresponding V_g decreases from 0.2V to about 0V. This characteristic conversion is consistent with the effect of an asymmetric CNTFET reported by Heinze *et al* [125]. In their design, the thickness of the gate oxide under the drain electrode is 100nm, much larger than that of the gate oxide under the source electrode (2nm).

When $V_d < 0$, instead of the hole current, the electron current is suppressed for the asymmetric CNTFETs. The CNTFETs are then converted from the ambipolar transistors for the symmetric structure to the unipolar (p-type) one for the asymmetric structure, as shown in Fig.7.6.

The typical output characteristics of the CNTFETs are shown in Fig.7.7(a). An interesting outcome of the thick SB at the drain side of the asymmetric CNTFETs is to suppress the drain leakage current at a higher V_d (the band diagram is shown in Fig.7.7(b)). As a result, the plateau (solid curve) in the output characteristics is very flat, as shown in Fig.7.7(a). In contrast, the plateau (dashed line) for the symmetric CNTFET

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Fig.7.6. The transfer characteristics of the simulated CNTFET used in Fig.7.5(b). However, $V_d = -0.4V$. Curve 1 is for the symmetric structure in Fig.7.2(a) and curves 2, 3 and 4 are for the asymmetric structure in Fig.7.2(b) with $\alpha = 75^\circ$, 60° and 45° , respectively.

is limited by the onset of the drain leakage current due to the very thin drain SB. At small V_d ($<0.3V$), the energy band bend upward at both the source and the drain sides (Fig.7.7(c)), the electrons injected at the source contact are significantly blocked by the thick drain SB for the asymmetric CNTFET, resulting in a reduced current and the lack of a linear regime in the I_d - V_d curve, as shown in Fig.7.7(a). Instead of the linear regime for

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Fig.7.7. (a) Simulated output characteristics of the CNTFETs at $V_g = 1V$. The dashed line is for the symmetric structure in Fig.7.2 (a). The solid line is for the asymmetric structure in Fig.7.2 (b) with $\alpha = 45^\circ$. The drain height is 60nm. (b) and (c) are the band diagrams of the above asymmetric structure at $V_g = 1V$, $V_d = 1.8V$ and $0.1V$, respectively.

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the symmetric structure, a clear exponential tail can be seen for the asymmetric one. This is a drawback of the asymmetric structure.

In practice, CNTs are placed across source and drain electrodes by spin-coating [4, 5, 9, 10], direct growth [11, 12], ac dielectrophoresis [18, 86 87], etc. Neither of the techniques are capable of precisely controlling and aligning the CNTs. Thus, they may attach to the bottom or top of the source and drain electrodes. An air gap prism (instead of the oxide prism mentioned above) between the CNTs and oxide layer may exist near the source or drain. If so, the physical picture discussed above could be used to explain why some CNTFETs prepared under similar conditions could possess different characteristics.

7.3. Conclusion

A semiclassical method is used to study the transfer characteristics of carbon nanotube based field effect transistors (CNTFETs). By introducing an oxide prism to the side wall of the drain, the distance between the CNTs and the back gate is increased near the drain, leading to a wide energy band bending. The bent energy band significantly reduces electron or hole tunneling injection rate, depending on the polarity of the gate and source-drain voltages. By adjusting the slanted angle of the prism and the drain electrode thickness, we find that the characteristics of the CNTFETs could convert from ambipolar to unipolar.

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8.1 Conclusion

(1) Manipulation of single-wall carbon nanotubes (SWNTs) using AC dielectrophoresis technique has been studied experimentally and theoretically. The SWNT bundles are found to bridge two neighboring cross-structured electrodes along the direction of the electric field. The shortest gap between the two electrodes is predominately bridged with SWNTs and the number of the SWNTs increases with the processing time. The AC dielectrophoresis process is analyzed theoretically using the “effective dipole moment” method. Using a 3-dimensional electric field, the rotation and translation motions of the SWNT bundles are simulated. The simulation results suggest that the rotation motion is a much faster process than the translation motion. In other words, the SWNT bundles are first aligned to the electric field and then forced to the strongest field to contact the two electrodes, consistent with the observed alignment phenomena. The statistic distribution of the SWNT bundles around the electrodes shows that about half of the total bundles in a drop of suspension can be attached to the smallest gap. The simulated results are in agreement with our experimental observations.

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(2) Carbon nanotube based field effect transistors are successfully fabricated by combining AC dielectrophoresis technique and metallic tube breakdown process. We find that the thicker the CNT bundle, the more difficult to burn off the metallic SWNTs in the bundle. The transistors fabricated using IPA suspension exhibit p-type characteristics with an ON/OFF current ratio of upto 7×10^5 . The inverse subthreshold slop of 1700mV/dec for the CNTFETs with 500nm SiO₂ indicates that the Schottky barrier modulation plays an important role in controlling channel conductance. This technique provides a high success rate of fabricating CNTFETs with a flexibility of controlling the SWNT alignment direction and the SWNT length, offering a promising way for large scale fabrication of CNTFETs.

(3) Room-temperature negative differential conductance phenomenon has been observed in the SWNT bundle channel in a CNTFET. The peak-to-valley current ratio is about 2. This phenomenon could be attributed to a quantum well between two adjacent energy barriers formed on semiconducting SWNTs due to the burning off metallic SWNTs in the bundle. The conductance variation of the SWNTs and the shift of the energy level in the quantum well are suggested to be responsible for the peak voltage shifts from 9.2V to 7.8V with decreasing the gate voltage from 6V to -6V. This suggestion is supported by our theoretical simulation.

(4) The influences of surfactants (Triton X-100 and SDS) on the transfer characteristics of CNTFETs have been studied. The CNTFETs fabricated with SDS/water suspension

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only exhibit p-type characteristic. While most of those prepared with Triton X-100/water suspension show ambipolar characteristics, suggesting that Triton X-100 could decrease the work function of the electrodes in contrast to the effect of oxygen. The charge transfer between the SWNTs and Triton X-100 is suggested to be responsible for the observed hysteresis in the $I_d - V_g$ curves. This kind of hysteresis could be erased by annealing the CNTFETs at 100°C in ambient air, the condition under which the surfactants are oxidized.

(5) By introducing an asymmetric oxide layer between the CNT and the gate electrode, the distance between the CNTs and the back gate is increased near the drain, leading to a wide energy band bending. The bent energy band significantly reduces electron or hole tunneling injection rate, depending on the polarity of the gate and source-drain voltages. Through adjusting the slope of the oxide layer and the drain electrode thickness, we find that the characteristics of the CNTFETs could convert from ambipolar to unipolar with a significant increase in the ON/OFF current ratio.

8.2 Future work

The study of carbon nanotube based field effect transistors in this thesis has shown some promising results. However, there are still some aspects worth further studying.

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- (1) AC dielectrophoresis technique offers a way to separate s-SWNTs and m-SWNTs, as they move to opposite directions due to different force direction induced by dielectrophoresis. Using metal grids dipped in the SWNT suspension as electrodes to adsorb m-SWNTs, we can purify the SWNT suspension. This could result in a kind of highly purified s-SWNTs dominated suspension.
- (2) The negative differential conductance in SWNTs needs further study. Although we have observed this phenomenon at room temperature, its mechanism is not very clear at present. Some factors should be considered, such as the influences of the diameter of the bundles, the burning-off position on the tube bundles, etc. In addition, low temperature investigation must provide more information for understanding the mechanism.
- (3) In Chapter 6, we show that the CNTFETs fabricated using Triton X-100/water suspension exhibit ambipolar characteristics. Although such a property can be used in light emission device, more wide application is possible for the unipolar CNTFETs. A novel method for ambipolar-to-unipolar conversion has been proposed in Chapter 7. However, this method has been only studied theoretically. Careful experiments are needed to verify the expectation.
- (4) DC performance of CNTFETs has been improved significantly in the aspects of the ON/OFF current ratio, inverse subthreshold slop, transconductance and contact resistance, etc. However, the AC electrical properties, which are

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technologically relevant for both active and passive devices, have been seldom investigated. The main reason for the lack of high-frequency data is that carbon nanotube resistance is much higher than 50Ω , the desired value for an impedance matched high-frequency measurement setup [128]. Using a non-standard amplitude calibration method, high-frequency response for single tube CNTFETs was reported with the highest frequency only up to 250MHz due to the μA current drive. When the drive current is higher, the measured frequency can be higher [129]. Using AC dielectrophoresis technique, the drive current can be improved through increasing the number of SWNTs in the channel. Therefore, CNTFETs fabricated by this method can be used to study high frequency properties of SWNTs.

- (5) The desire for light-weight, unbreakable displays has attracted a lot of attention.

The advanced mechanic property makes carbon nanotube an ideal material to be used on flexible substrates. Furthermore, CNTFETs do not have to use SiO_2 as the dielectric. Thus it would be very meaningful to build CNTFETs on materials other than Si with the AC dielectrophoresis technique at room-temperature and in air.

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Author's publication from this work

1. **Jingqi Li**, Qing Zhang, Ning Peng and Qi Zhu, "Manipulation of carbon nanotubes using AC dielectrophoresis", *Appl. Phys. Lett.*, 86(2005)153116.
2. **Jingqi Li**, Qing Zhang, Hong Li, Mary B. Chan-Park, "Influence of Triton X-100 on the characteristics of carbon nanotube field-effect transistors", *Nanotechnology*, 17(2006)668-673.
3. **Jingqi Li** and Qing Zhang, "Room-temperature negative differential conductance in carbon nanotubes", *Carbon*, 43(2005)667-670.
4. **Jingqi Li** and Qing Zhang, "Simulation of ambipolar-to-unipolar conversion of carbon nanotube based field effect transistors", *Nanotechnology*, 16(2005)1415.
5. **Jingqi Li**, Qing Zhang, Dajiang Yang, and Jingze Tian, "Fabrication of Carbon nanotube field effect transistors by ac dielectrophoresis method", *Carbon* 42 (2004) 2263-2267.
6. **Jingqi Li**, Qing Zhang, Mary B. Chan-Park, Yehai Yan, "Annealing effect on electric contacts between carbon nanotubes and electrodes", *International Journal of Nanoscience*, in press.

The following papers finished during this period are either overlap with the above papers or the subjects are outside the scope of this thesis.

7. **Jingqi Li**, Qing Zhang, S. F. Yoon, J. Ahn, Qiang Zhou, Sigen Wang, Dajiang Yang, Qiang Wang, "Erosion resistance of polycrystalline diamond films to atomic oxygen", *Carbon* 41(2003)1847-1850.

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15. S. G. Wang, Qing Zhang, R. L. Wang, S. F. Yoon, J. Ahn, D. J. Yang, J. Z. Tian, **Jingqi Li**, Q. Zhou, “Multi-walled carbon nanotubes for the immobilization of enzyme in glucose biosensors”, *Electrochemistry Communications* 5(2003)800-803.
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