Carbon nanotube field-effect transistors and gaseous interactions

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CARBON NANOTUBE FIELD-EFFECT
TRANSISTORS AND GASEOUS INTERACTIONS**

**PENG NING
SCHOOL OF ELECTRICAL AND ELECTRONIC
ENGINEERING
2009**

Carbon nanotube field-effect transistors and gaseous interactions

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School of Electrical and Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2009

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

20-Dec-2009

Date

A handwritten signature in black ink, consisting of stylized Chinese characters, likely '彭宁' (Peng Ning).

Peng Ning

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Summary

This thesis presents the major findings achieved in my Ph.D project on carbon nanotube (CNT) field-effect transistors (FETs) and gaseous interactions. It consists of four main parts: (1) AC dielectrophoretic (DEP) manipulation of CNTs; (2) studies of gaseous interaction in CNTFETs through selective Si_3N_4 passivation; (3) real-time detection of chemical gases using CNTFETs and (4) differentiating the sensing mechanisms in CNTFET-based NH_3 detectors.

The motion of single-walled CNTs (SWNTs) in suspension under the influence of an applied electric field is analyzed in terms of induced DEP torque and force. The SWNTs are found to rotate to the field direction in a much shorter time than that needed for a translational motion along the field gradient. As a result, SWNTs are well placed normal to the electrode edges using the ac DEP technique. Due to different dielectric properties, metallic SWNTs and semiconducting SWNTs could be separated from each other by tuning the frequency of the applied ac electric field. Both theoretical and experimental results show that perpendicular electrodes have higher controllability of the SWNTs location than parallel electrodes.

Our as-prepared CNTFETs are typically p-type Schottky barrier (SB) FETs in ambient. A selective Si_3N_4 passivation technique is developed to protect the CNT/metal contacts and/or CNT channel. The devices with passivated source and drain contacts and uncovered CNT channel show n-type characteristics in air, suggesting that a dominant

influence of environmental oxygen is to modulate the SB height at the CNT/metal contacts. Moreover, by passivating only the source contact, a tunable Schottky diode involving the drain contact is obtained. A novel model is developed for CNT/metal contacts, in which the electrostatic charge balance across the contact and the dipole polarization along the CNT are appropriately taken into consideration. Using this model, the unique n-type characteristic of the CNTFET with passivated source contact is well interpreted by electron tunneling through V_{DS} -dependant drain SB. By applying the model to Schottky diodes with asymmetric metal contacts, we show that only for those CNTFETs with one of the two CNT/metal contacts protected, the dipole polarization effect can be observed and becomes important to determine the conduction type of the devices.

The CNTFETs are used as chemical gas sensors and their sensing performances are studied in terms of the applied gate voltages. The sensitivity and reversibility of the sensor is found to be significantly improved under appropriate positive gate voltages. Selective Si_3N_4 Passivation technique is employed to differentiate the sensing mechanism of CNTFET-based NH_3 gas sensors. Our results clearly show that the SB modulation at the CNT/metal contacts dominates the sensing performance at room temperature. At temperature above 150°C , NH_3 molecules start to adsorb on the CNT wall so that a charge transfer process contributes to the sensing signal. NH_3 adsorption is confirmed to be facilitated by environmental oxygen.

Chapter 1

Introduction

1.1 Motivation

The semiconductor industry has been so successful that it has changed every aspect of our life, especially in the past 40 years. Its amazing growth basically affirms Moore's law¹, which is stated as doubling of transistor performance and quadrupling of the number of devices on a chip every three years. Minimization of the devices has been achieved by shrinking Metal-Oxide-Semiconductor field effect transistor (MOSFET) and other relevant dimensions.^{2,3} However, scaling down to 20nm becomes really challenging due to fundamental physical constraints,³⁻⁶ which are often cited as: 1) tunneling of carriers through the thin gate oxide layer; 2) tunneling of carriers from the source to drain, and from the drain to the body of the MOSFET; 3) control of the density and location of dopant atoms in the MOSFET channel and source/drain region to provide a high on-off current ratio; and 4) the finite subthreshold slope. As a result, people start to study and develop new technologies and new materials. For example, high- κ dielectric materials,⁷

strained-silicon,⁸ carbon nanotubes,⁹ organic films,¹⁰ and DNA based molecular devices¹¹ have been intensively studied.

Single-walled carbon nanotube (SWNT) is considered as one of the most promising candidate for nanoelectronic applications due to its outstanding electrical and electronic properties:⁹

- Carrier transport is one-dimensional (1-D). This characteristic reduces phase space for scattering of the carriers and opens up a possibility of ballistic transport.
- All chemical bonds of the C atoms are satisfied and there is no need for chemical passivation of dangling bonds as in silicon. This implies that SWNT electronics would not be bound to use SiO₂ as gate oxide.
- The strong covalent bonding gives SWNTs high mechanical stability (their Young's modulus about ten times higher than that of steel), thermal stability and immunity to electromigration. Their current handling capability can be as high as 10⁹ A/cm².
- Both transistors and interconnects can be made out of semiconducting (s-) and metallic (m-) SWNTs, respectively.

However, current CNT based electronic devices are still far from attaining practical applications. First, it is still a challenge to manipulate SWNTs to the desirable electrodes. Spin-coating CNT suspension onto the structured wafers¹²⁻¹⁵ is simple, but the random distribution and orientation of CNTs and CNT contamination on the entire sample surface are the major drawbacks. While directional growth of SWNTs offers a controllable process,^{16,17} it can also cause catalyst contamination and poor selectivity of

CNTs. In contrast, the AC dielectrophoresis (DEP) method has been demonstrated to be an efficient technique to place CNTs,¹⁸⁻²⁰ CNT matted sheets,²¹ and CNT bundles²² with definite orientation across pre-patterned electrodes, but the mechanism is not well understood. Second, the electrical properties of CNT devices are found to be very sensitive to ambient gases, but the fundamental mechanisms for the gaseous interaction remain unclear, which has restrained the understanding of CNT devices. Taking oxygen for example, it has been claimed that oxygen molecules dope CNT²³⁻²⁵ or modulate the Schottky barrier (SB) at the metal-CNT contacts.^{26,27} Similar ambiguity existing in CNT based gas sensors greatly hampers the development towards practical gas sensing applications. Therefore during my Ph.D project, I first carry out a systematic study on AC DEP manipulation of CNTs. Using this technique, various types of CNTFET devices are fabricated, and the gaseous interactions in CNTFETs are studied in detail. From that, a novel model is developed for nanoscale contacts between CNT and metal electrodes. Moreover, the CNTFETs are applied as real-time gas sensors and the underlying sensing mechanisms are identified.

1.2 Objectives

The main objectives of my Ph.D project are as follows:

- ◆ To study the AC DEP manipulation of CNTs and to fabricate CNTFET devices using this technique.

- ◆ To investigate the influence of ambient gas molecules on the properties of CNTFETs. The influence of environmental oxygen on CNTFETs is to be identified.
- ◆ To develop a physical model addressing the nanoscale nature of CNT/metal contacts.
- ◆ To apply the CNTFETs as real-time gas sensors. The gate modulation on the sensing performance will be studied in detail.
- ◆ To investigate the sensing mechanisms in CNTFET-based gas sensors. The sensing signals from the CNT channel and metal/CNT contacts must be differentiated.

1.3 Major contributions of this dissertation

The main contributions of my Ph.D thesis are listed as following:

1. AC DEP manipulation of CNTs is systematically studied. The motions of CNTs in suspension under the influence of an applied electric field are analyzed in terms of induced DEP torque and force. The CNTs are found to rotate to the field direction in a much shorter time than that needed for a translational motion along the field gradient. As a result, CNTs are well placed normal to the electrode edges using the AC DEP technique. Due to different dielectric properties, metallic CNTs (m-CNTs) and semiconducting CNTs (s-CNTs) can be separated from each other by tuning the frequency of the applied AC electric field. By using different electrode structures to vary the electric field distribution, the location of CNTs can be well controlled. Using the AC DEP technique,

CNTFETs with various structures are successfully fabricated. We also find that the surfactants used could affect the electrical performance of the device.

2. A selective Si_3N_4 passivation technique is developed to protect the CNT/metal contacts and/or CNT channel. The devices with passivated source and drain contacts and uncovered CNT channel show n-type characteristics in air, suggesting that a dominant influence of environmental oxygen is through modulating the SB height at the CNT/metal contacts. Moreover, by passivating only the source contact, a tunable Schottky diode is obtained. The polarity and conduction type of the diode can be adjusted by the applied gate voltages (all voltages in this thesis refer to the potential difference with respect to the source).

3. A nanocontact model is developed, in which the energy band bending in the carbon nanotube near to the contact is quantitatively characterized through establishment of electrostatic charge balance between carbon nanotube and metallic pads under the influences of environmental oxygen. By applying our model to CNTFETs with asymmetric metal contacts, we show that the dipole polarization in the CNT, determined by contact configurations, is crucial for the device performance in ambient.

4. The sensing performance of CNTFET based gas sensors is studied in terms of the applied gate voltages. By applying a positive gate voltage of 8V, an extremely high NH_3 sensitivity of 178.5% per ppm is achieved at room temperature, which is 65 times greater than that under a gate voltage of -8V. The reversibility of the sensor is also found to be significantly improved under appropriate positive gate voltages. We also find that an increase in humidity weakens the gate controllability and decreases the sensor's

sensitivities to both NH_3 and NO_2 . In addition, the sensitivity diminishes significantly when the operating temperature increases from room temperature up to 150°C .

5. The sensing mechanisms for CNT based NH_3 sensors are systematically studied on a FET platform. Three CNTFET structures are employed, i.e., both the contacts and CNT channel are accessible to the detecting gas; only the channel is accessible to the gas with the contacts passivated and, in contrast, only the contacts are accessible to the gas with the channel passivated. We clearly show that the SB modulation at the CNT/metal contacts dominates the sensing performance at room temperature, and the sensor exhibits high sensitivity and good tunability under appropriate gate voltages. At higher temperatures, say 150°C or above, NH_3 molecules start to adsorb on the CNT wall so that the charge transfer process contributes to the sensing signal. NH_3 adsorption is confirmed to be facilitated by environmental oxygen.

1.4 Organization of this dissertation

Chapter 1 introduces the motivations, objectives, major contributions and organization of the dissertation.

Chapter 2 gives a review of CNT properties, including classifications of CNTs and electronic structures. The background and development of CNTFETs are summarized.

Chapter 3 shows a systematic study on AC DEP manipulation of CNTs. The motion and distribution of CNTs are modeled.

Chapter 4 describes the fabrication processes of CNTFETs. The current instability in CNTFETs under the influence of surfactant, biasing and temperatures are studied.

Chapter 5 discusses the gaseous interaction in CNTFETs by a selective passivation technique. A novel model is developed to characterize the metal/CNT contacts under the influence of environmental oxygen.

Chapter 6 reports on the performance of real-time gas sensors using CNTFETs. The sensing performance can be significantly tuned by the gate bias.

Chapter 7 presents a detailed study on the sensing mechanism of NH_3 detection. By varying device structure, sensing temperature and background, the relevant sensing mechanisms are clearly identified.

Chapter 8 concludes the entire project and gives recommendations for future work.

Chapter 2

Carbon Nanotubes and Relevant Devices

2.1 Overview of carbon nanotubes

CNTs are hollow cylinders composed of one or more concentric layers of carbon atoms in a honeycomb lattice arrangement. They were first observed by Oberlin *et al.* in 1976.²⁸ Iijima brought CNTs to the world's attention in 1991 by detailed transmission electron microscopy (TEM) studies of multi-walled CNTs (MWNTs).²⁹ Two years later, SWNTs were successfully synthesized by Iijima *et al.*³⁰ and Bethune *et al.*³¹ Due to their simple structures and unique electronic properties, SWNTs are regarded as the most promising candidate for nanoelectronic applications.

2.2 Structure of single-walled carbon nanotubes

SWNTs typically have a diameter of 1-2nm and a length of several micrometers. The large aspect ratio makes the nanotubes nearly ideal one-dimensional (1-D) objects.

SWNTs' properties are dependant on the detailed arrangement of the carbon atoms, or so-called chiral vector. Note that the below treatment below follows closely with Ref. 32.

2.2.1 Chiral Vector: $\vec{C}_h$

Fig 2.1 (a) shows an unrolled honeycomb lattice of the nanotube. By rolling the honeycomb sheet so that points O and A coincide (and points B and B' coincide), a CNT can be constructed. Therefore, the chiral vector $\vec{C}_h$ (the rolling up of honeycomb sheet) and the translation vector $\vec{T}$ ($\vec{OB}$ is translated to $\vec{AB'}$ during the rolling-up) are defined by $\vec{OA}$ and $\vec{OB}$, respectively. $\vec{C}_h$ can be expressed by two real space unit vectors $\vec{a}_1$ and $\vec{a}_2$ (see Fig 2.1 (a)) of the hexagonal lattice:

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

If $n = m$, i.e., $\vec{C}_h = (n, n)$, it corresponds to an armchair nanotube, as 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)).

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. As $n\vec{a}_1$, $m\vec{a}_2$ and $\vec{C}_h$ form a triangle with 120° between $n\vec{a}_1$ and $m\vec{a}_2$, we can have

$$|\vec{C}_h|^2 = |n\vec{a}_1|^2 + |m\vec{a}_2|^2 - 2|n\vec{a}_1||m\vec{a}_2|\cos 120^\circ, \quad (2.2)$$

Therefore,

$$d = L / \pi, \quad L = |\vec{C}_h| = a\sqrt{n^2 + m^2 + nm}, \quad (2.3)$$

where the lattice constant of the honeycomb lattice $a = |\vec{a}_1| = |\vec{a}_2| = 0.249 \text{ nm}$.

Fig 2.1 (a) An unrolled graphene layer with honeycomb lattice. When we connect sites O with A , and B with 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 include armchair tubes (n, n) (b) and zigzag tubes $(n, 0)$ (c). All other tubes are called chiral tubes (d).³²

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

$$\cos \theta = \frac{\vec{C}_h \cdot \vec{a}_1}{|\vec{C}_h| |\vec{a}_1|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}. \quad (2.4)$$

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

2.2.2 Translational vector: $\vec{T}$

The translation vector $\vec{T}$ is defined to be the unit vector of a 1-D CNT. $\vec{T}$ 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:

$$\vec{T} = t_1 \vec{a}_1 + t_2 \vec{a}_2 \equiv (t_1, t_2), \text{ (where } t_1, t_2 \text{ are integers)} \quad (2.5)$$

and

$$t_1 = \frac{2m+n}{d_R}, \quad t_2 = -\frac{2n+m}{d_R}, \quad (2.6)$$

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

$$d_R = \begin{cases} q & \text{if } n-m \text{ is not a multiple of } 3q \\ 3q & \text{if } n-m \text{ is a multiple of } 3q, \end{cases} \quad (2.7)$$

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

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

$$T = \frac{\sqrt{3}L}{d_R} \quad (2.8)$$

2.2.3 Unit cells and Brillouin zones

The unit cell of a CNT in real space is given by the rectangle generated by $\vec{C}_h$ and $\vec{T}$, i.e., 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 by³³

$$N = 2(m^2 + n^2 + nm)/d_R. \quad (2.9)$$

The addition of each 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

$$\vec{K}_1 = (-t_2 \vec{b}_1 + t_1 \vec{b}_2)/N, \quad \vec{K}_2 = (m \vec{b}_1 - n \vec{b}_2)/N \quad (2.10)$$

where $\vec{b}_1$ and $\vec{b}_2$ are the reciprocal lattice vectors of the two-dimensional graphite. 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 the two-dimensional graphite, two wave vectors that 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 $\mu\vec{K}_1$ ($\mu = 0, \dots, N-1$) 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 CNT of infinite length.

Fig 2.2 The Brillouin zone of a CNT 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 $\vec{C}_h = (4, 2)$, $\vec{T} = (4, -5)$, $N = 28$, $\vec{K}_1 = (5\vec{b}_1 + 4\vec{b}_2)/28$, $\vec{K}_2 = (4\vec{b}_1 - 2\vec{b}_2)/28$.³²

2.3 Electronic structure of SWNTs

The interesting electrical properties of CNTs are in a large part due to the peculiar electronic structure of graphene. In Fig 2.3 (a), the energy dispersion relations of 2-D graphene are shown throughout the Brillouin zone and the inset shows the energy dispersion relation along the high symmetry axes 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 degenerated at the K points through which the Fermi level passes. Since the density of states at the Fermi level is zero, 2-D graphene is a zero-gap semiconductor.

Fig 2.3(a) The energy dispersion relations for 2-D 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 ΓMK shown in (b). (b) The unit cell and (c) Brillouin zone of two-dimensional graphene 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. (d) The condition for metallic energy bands: if the ratio of the length of the vector $\overrightarrow{YK}$ (pointing from point Y to point K) to that of $\overrightarrow{K_1}$ is an integer.³²

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 2-D graphene, $E_{g2D}(\mathbf{k})$ at line segments shifted from WW' by $\mu \overrightarrow{K_1}$

$(\mu = 0, \dots, N-1)$ are folded so that the wave vectors parallel to $\vec{K}_2$ coincide with WW' as shown in Fig 2.2, N pairs of 1-D energy dispersion relations $E_\mu(k)$, are obtained. These 1-D energy dispersion relations are given by³²

$$E_\mu(k) = E_{\text{g2D}}\left(k \frac{\vec{K}_2}{|\vec{K}_2|} + \mu \vec{K}_1\right), \quad (\mu = 0, \dots, N-1, \text{ and } -\frac{\pi}{T} < k < \frac{\pi}{T}) \quad (2.11)$$

The wave vectors in the $\vec{K}_1$ direction become quantized for the electron wave function to be single-valued while for a nanotube of infinite length, $\vec{K}_2$ remains continuous. The N pairs of energy dispersion curves correspond to the cross sections of the two-dimensional energy dispersion surface shown in Fig 2.3 (d), where cuts are made on the lines of $k \vec{K}_2 / |\vec{K}_2| + \mu \vec{K}_1$, if k and μ fulfill the condition in Eqn. 2.11. Therefore, CNT simply consists of N 1D energy bands within the Brillouin zone of length $2\pi / |\mathbf{T}|$, where each band is a cut of the graphene dispersion relation on the lines $(k \vec{K}_2 / |\vec{K}_2| + \mu \vec{K}_1)$. That is, the E-k diagrams are plots of N energy bands versus the wave vector, k , in the direction of the reciprocal lattice vector, $\vec{K}_2$, with each band corresponding to one of the N quantized wave vectors in the $\vec{K}_1$ direction. One can essentially imagine N cuts of the graphene dispersion relation, each cut corresponding to a quantized wave vector in the $\vec{K}_1$ direction, folded back into the first Brillouin zone (WW') to result in an E-k plot with N discrete energy bands. If for a particular (n, m) nanotube, the cutting lines passes through a K point of the 2-D Brillouin zone, where the π and π^* energy bands of two-

dimensional graphene are degenerated by symmetry, the one-dimensional energy bands have a zero energy gap. In other words, 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 $\overrightarrow{YK}$ to that of $\overrightarrow{K_1}$ is an integer. Since the vector $\overrightarrow{YK}$ can be expressed as

$$\overrightarrow{YK} = \frac{2n+m}{3} \overrightarrow{K_1}, \quad (2.12)$$

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.

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

$$N(E_F) = \frac{8}{\sqrt{3}\pi a \gamma_0} \quad (2.13)$$

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

Fig 2.4 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.³²

Figure 2.4 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 for (8,0) tube has a value of zero. Thus, it is a semiconducting nanotubes. In contrast, (5,5) and (7,1) tubes are for metallic nanotubes.

The energy gap for semiconducting nanotubes depends upon the reciprocal nanotube diameter R ,

$$E_g = \frac{\gamma_0 a_{C-C}}{R}, \quad (2.14)$$

where $a_{\text{c-c}} = \frac{a}{\sqrt{3}}$ is the nearest-neighbor C-C distance on a graphene sheet. But it is independent of chiral angle of the semiconducting nanotube.

2.4 Development of CNT-based devices with FET structure

Making use of the unique electronic properties, high-performance CNT-based FETs can be fabricated.^{34,35-37} Semiconducting CNTs (s-SWNTs) with their appealing electrical properties are natural candidates for the fabrication of terminal nanodevices. Indeed, already in 1998 it was demonstrated that SWNTs could be used as channels for FETs.^{12,13} 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. 2.5. A CNT played the role of a “channel”, while the two metal electrodes functioned as the “source” and “drain” electrodes. A heavily doped silicon wafer was used as the “gate” electrode, so-called back-gate. The channel current decreased with increasing gate voltage, indicating that the conductance through s-SWNTs was dominated by holes. The transfer curves saturated for negative gate voltages. These CNTFETs behaved as p-type FETs and had an ON/OFF current ratio of $\sim 10^5$. Over the past decade, the performance of CNTFETs has been improved by decreasing contact resistance, shortening source and drain distance, changing gate structure, decreasing gate oxide thickness and employing high- κ insulator.

Fig 2.5 (a) A schematic cross section of CNTFETs. A single CNT bridges the gap between two gold electrodes. The silicon substrate is used as the back-gate. (b) Transfer characteristics of a CNTFET. The insert shows that the gate modulates the conductance by 5 orders of magnitude.¹³

2.4.1 Improvement of the contacts between CNTs/metals

Although functional, the aforementioned transistors had a high parasitic contact resistance ($\geq 1 \text{ M}\Omega$), low transconductance $g_m \sim 1 \text{ nS}$, and high inverse subthreshold slope $S \sim 1\text{--}2 \text{ V/dec}$. These unsatisfactory characteristics were to a large extent due to poor contacts.⁹ Two common methods are used to improve the contacts. One is annealing. In IBM's transistors³⁸, s-SWNTs were placed on top of the SiO_2 film and Co (or Ti) 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 CNTs, and hence a small contact resistance. The other method is to use appropriate metal-electrodes. Javey *et al.* selected palladium,³⁴ a noble metal with high work function and good “wetting” interactions with CNTs, as the electrode materials and obtained a large “ON” state conductance that was very close to the ballistic transport limit of $\frac{4e^2}{h}$, where e is the electronic charge and h is the Planck constant.³⁵⁻³⁷ The contact improvement was suggested to be caused by a reduced or eliminated barriers for holes. Similarly, scandium contact was reported to afford almost perfect contact with the conduction band of CNT, evidenced by the near ballistic n-type CNTFETs with Sc contacts.³⁹ However, for 1-D system like CNT, the quantum capacitance C_Q has to be considered. Only when $C_Q \ll C_G$, $4e^2/h$ can be reached, which requires low temperature and high V_{DS} .⁴⁰

2.4.2 Gate structures

The most widely used gate structure for CNTFETs in the past was the doped silicon substrate back gate and thermally grown SiO_2 as gate dielectric.^{12,13,41} 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 Al_2O_3 dielectrics,¹⁴ bottom tungsten gates with SiO_2 ,⁴² top-gate with 2~20-

nm-thick SiO₂ dielectrics.^{15,43} In addition to the local address ability, these gate structures show progressively improved CNTFET characteristics. For instance, the inverse subthreshold slope S is approaching the theoretical value of 60mV/dec, due to decreased oxide thickness¹⁵ and high- κ dielectrics⁴⁴. CNTFETs fabricated with liquid electrolyte gate⁴⁵ and poly(ethylene oxide) solid electrolyte gate^{46,47} demonstrated strong gate-channel coupling with improved device characteristics, as shown in Fig. 2.6. An electrolyte gate with a dielectric constant of about 80 could lead to an extremely high transconductance of $\sim 20 \mu\text{S}$.⁴⁵ Very recently, IBM reported a gate-all-around structure of CNTFET.⁴⁸ The subthreshold slope, however, was 250mV/dec, probably due to interface traps and short-channel effects.

Fig 2.6 Schematic of (a) liquid-electrolyte CNTFET⁴⁵ and (b) Polymer-electrolyte CNTFET⁴⁶.

2.4.3 Gate dielectric materials

The performance of CNTFETs can also be improved by decreasing the gate oxide thickness. Wind *et al.*¹⁵ compared the characteristics of a top-gated (15 to 20-nm-thick SiO₂) and a back-gated (120-nm-thick SiO₂) CNTFET fabricated on the same SWNT and

found that those top-gate devices exhibited excellent electrical characteristics. The threshold voltage of the top-gated CNTFET was only -0.5 V, significantly improved from the bottom-gated operation, -12 V. Similarly, the drive current and the transconductance were much higher for the top-gating. Using a simple model, Heinze *et al.*⁴⁹ derived the scaling rule of the subthreshold slope with oxide thickness and pointed out that the change in the oxide thickness is equivalent to simply rescaling the gate voltage by $V_{\text{scal}} \propto t_{\text{ox}}^{1/2}$, thus S scales as $t_{\text{ox}}^{1/2}$ and the transconductance scales as $\propto t_{\text{ox}}^{-1/2}$, well explaining the performance improvement of CNTFETs due to the decreasing of oxide thickness.

High- κ dielectrics have been actively pursued to replace SiO₂ as gate insulator for silicon devices.⁹ The relatively low κ of SiO₂ (3.9) limits its use in transistors as gate length scales down to tens of nanometers. High- κ gate insulators afford high capacitance without relying on ultra-small film thickness, thus allowing for efficient charge injection into the transistor channels and meanwhile reducing direct-tunneling leakage currents.⁴⁴ Experimental results show that ZrO₂,⁴⁴ HfO₂,⁵⁰⁻⁵² Al₂O₃¹⁴ and SrTiO₃⁵³ have been successfully used as the gate insulators in CNTFETs.

2.4.4 Transfer characteristics of CNTFETs: p-type, n-type and ambipolar characteristics

To date, CNTFETs have shown p-type, n-type and ambipolar characteristics. Typically, CNTFETs fabricated in ambient air exhibit p-type characteristics.^{12,13,34,44,45,53-55} However, for future nanotube-based electronics, the ability to vary the conduction type is highly desirable. Several methods have been developed to achieve n-type CNTFETs. It

is found that CNTFETs can be converted from p- to n-type simply by annealing the devices in vacuum,^{16,56} or in inert gases³⁸ or hydrogen⁴⁴. Doping p-type CNTFET with potassium^{16,26,57,58} is another approach, and has been used to build CNT p-n diodes⁵⁹ and complementary logic gates^{14,16}. In this method, evaporated potassium are adsorbed on the surface of SWNTs. By coating polyethylenimine (PEI) on the top of SWNTs,^{60,61} n-type doping can also be realized. Recent results suggest that p- and n-type behavior can be controlled easily using a polymer electrolyte gate. Lu *et al.*⁴⁶ showed 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- 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-type devices that are stable at room temperature in air were fabricated by Siddons *et al.*⁴⁷ Using these polymer gates, one can also obtain ambipolar CNTFETs as the polymer gate is so efficient to operate as switches for electrons and holes. Ambipolar characteristics are also found during annealing a p-type CNTFET covered with SiO₂ in vacuum or in an ambient atmosphere.³⁸ The CNTFETs fabricated with large-diameter (3-5 nm) SWNTs (small band gap ~ 0.4 eV) typically exhibit ambipolar characteristics.^{17,60} For small-diameter (1.4 nm) SWNTs, ambipolar behavior is observed in air with very thin gate oxide (10 nm).⁶² 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.⁶²

2.4.5 Switching mechanisms of CNTFETs

So far, three models have been proposed to interpret CNTFET operation. The first one treats CNTFETs with large diameter carbon nanotubes (3-5 nm) in analogy to conventional metal oxide semiconductor field-effect transistors (MOSFETs). The rather small energy gap of the CNT channels allows carrier injection from the metal contact into the valence band of the CNTs without a substantial Schottky barrier.^{34,63} CNTFETs with extremely long channel length ($> 300 \mu\text{m}$)^{64,65} also exhibit MOSFET-like behavior. In both cases, the contact resistance is insignificant compared to the resistance of the CNT channel.

The second one models the CNTFETs fabricated from larger band gap CNTs as Schottky barrier (SB)-FETs.^{27,50,51} Heinze and co-worker proposed the Schottky barrier model,²⁷ in which the transistor action occurs primarily by modulation of the contact resistance rather than the channel conductance. For ordinary field-effect transistors, the contacts are Ohmic contacts for the purpose of effective switching. However, there is a substantial Schottky barrier (SB) at the contacts between CNTs and metal electrodes. 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. Figure 2.7a shows the simulated electrostatic potential in a top gate CNTFET at 2V gate voltage. Figure 2.7b shows the conductance for different SB heights. When the metal Fermi level is situated in the middle of the CNTs' band gap, the conductance at zero drain voltage shows a symmetric dependence on the gate voltage.

Fig 2.7 Conductance for realistic FET geometries. a) Electrostatic potential (contour lines) for a top gate CNTFET with gate voltage of 2V. b) Corresponding conductance versus gate voltage at room temperature, for different SBs.²⁷

The current is calculated by the Landauer formula,

$$I(V) = \frac{4e}{h} \int [F(E) - F(E + eV_D)] P(E) dE \quad (2.14)$$

where V_D is the drain voltage ($V_S=0$) and $F(E) = \frac{1}{e^{(E-E_F)/K_B T} + 1}$ is the Fermi function. The

energy dependent transmission probability $P(E)$ is calculated within the Wentzel-Kramer-Brillouin (WKB) approximation using the idealized band structure (where the Fermi level at the interface falls deep in the badgap, so the barriers for both electrons and holes are substantial). $P(E)$ is given by the following formula,

$$\ln P(E) = -\frac{4}{3bV_\pi} \int_{Z_i}^{Z_f} (\Delta^2 - [E + \phi(Z)]^2)^{1/2} dz \quad (2.15)$$

where $b=0.144\text{nm}$ is C-C bond length, $\Delta=0.3\text{eV}$ is half the CNT bandgap. $V_\pi=2.5\text{eV}$ is the tight-binding parameter, and $\Phi(Z)$ is the electrostatic potential along the CNTs. Increasing the voltage difference between source and gate electrodes leads to a large electric field at the contact, reducing the width of the SB and allowing thermally assisted

tunneling. Asymmetric conductance shown in Figure 2.6b is caused by different SB height for electrons and holes. The source and drain metal Fermi level does not fall in the center of the CNT bandgap, resulting in the different SB heights for electrons and holes. It is noted that the above model neglects the reflection that would occur even in absence of a barrier and tends to overestimate the conductance. Castro *et al.* found that the above model tends to overestimate the current and transconductance for thermionically injected carriers and they improved the above model by taking into consideration of quantum mechanical reflection of thermionically injected carriers.⁶⁶ In their model, an analytical expression for quantum mechanical reflection for the thermionic case is obtained under phase-incoherent conditions.

Several observations support the above 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 $V_D = 0$. More evidence for this model is that the inverse subthreshold slope S is independent of channel length⁵¹ but increases with oxide thickness. The related experimental data can be fitted well by the SB model but not by the conventional MOSFET model.⁵⁰ Furthermore, S is temperature dependent at high temperatures but levels off at temperatures below about 200 K, suggesting a carrier tunneling process.⁵⁰ The SB model could provide a reasonable explanation to the effects of O_2 on the performance of CNTFETs,²⁷ but new conduction mechanisms are needed for complicated device structures.

The third model is the band-to-band (BTB) tunneling reported by Appenzeller *et al.*⁶⁷ BTB tunneling means tunneling from the conduction into the valence band of an s-SWNT and vice versa, as observed using a dual-gated CNTFET structure. The phenomena are likely associated with CNTFETs with doped contacts, and not with SB-CNTFETs. 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 ~ 40 mV/dec has been obtained at room temperature, much smaller than the theoretical limit value of 60 mV/dec with conventional MOSFETs. Therefore, due to the unique electrical properties of CNT, such as low dimensionality, relatively small bandgap and quasiballistic transport, careful treatment on the conduction theories must be carried out when CNT-based devices become more and more complicated.

2.4.6 Applications of CNTFETs and challenges

Although CNTFETs are still in an early research stage, they have shown amazing performance parameters, for instance, high drive current, high transconductance,⁹ etc. Many applications, including logic circuits,^{14,16,42,44,45,56} memories,⁶⁸⁻⁷⁰ chemical sensors,⁷¹⁻⁷³ p-n junction diodes⁷⁴ and light emission devices⁷⁵⁻⁷⁷ have been demonstrated and shown promising performance. However, many challenges remain before these molecular electronic devices become practically useful. Most challenges are from the materials issues. So far, no synthesis technique can produce a single type of CNT and

separation techniques and breakdown process have to be used in fabricating CNTFETs. Controllable placements of CNT onto desired locations is difficult. Spin-coating CNT suspension onto the structured wafers¹²⁻¹⁵ is a simple process. However, the random distribution and orientation of CNTs and contamination on the entire sample surface are major drawbacks. Directly growing CNTs from one electrode to another is a relatively controllable.^{16,17} Unfortunately, this approach causes catalyst contamination and poor selectivity of CNTs. A more practicable CNT placement process needs to be explored. Moreover, some fundamental issues require further investigations for a better understanding of CNT devices, for example, the CNT/metal interface.⁷⁸⁻⁸¹

Chapter 3

AC Dielectrophoretic Manipulation of CNTs

3.1 Introduction

CNTs, due to their small size and outstanding electrical and electronic properties,⁹ are considered as promising building blocks for nanoelectronic devices. SWNTs have been widely used in CNT based electronic devices such as CNTFETs,^{12,13} chemical sensors⁷¹⁻⁷³ and interconnect applications⁸²⁻⁸⁵. However, selectively and controllably patterning of SWNTs still remains a challenge. Commonly used methods include spin coating¹²⁻¹⁵ and direct growth of CNTs.^{16,17} For the spin-coating technique, CNTs are first dispersed in a solution and then spin-coated onto silicon wafers. This method has been widely applied during the early development of CNT devices due to its simplicity. But the location and orientation of disposed CNTs are random. In contrast, directly growing CNTs provides precise control of CNTs location and orientation. A Metal catalyst (Ni, Fe, etc) is first patterned and the CNTs are then grown along preferred direction (assisted by gas flow or electric field) from one catalyst islands to the other. High-temperature require for CNT growth and long growth time are the bottleneck for this technique.

Recently, AC DEP method has been demonstrated to be an efficient technique to place CNTs¹⁸⁻²⁰ and CNT bundles²². A concise model of the CNTs' motion and spatial distribution under the influence of electric field is yet to be developed.

In this chapter, the motion of CNTs in suspension under applied AC electric field are modeled by analyzing the induced DEP torque and force on the CNTs. Different behaviors of semiconducting and metallic CNTs are compared. The spatial distributions of the SWNTs between two adjacent electrodes are studied.

3.2 Theoretical modeling

In order to understand the mechanism of carbon nanotube alignment in the 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 $\vec{E}$, as shown in Fig.3.1. The dipole moment $\vec{p}$ is

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

Fig 3.1. Schematic of a small dipole in a uniform electric field.

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

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

3.2.1 Effective dipole moment

SWNTs typically have a diameter of 1-2nm and a length of several micrometers. The large aspect ratio makes the nanotubes nearly ideal one-dimensional (1-D) objects. For an SWNT in a liquid medium, the applied electric field easily polarizes the SWNT in its length direction, inducing an effective dipole moment, $\vec{p}_{eff}$. 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.⁸⁶

The quantity of effective dipole moment for the SWNT 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 equivalent dipole source as shown in Appendix A. We express the effective moment in terms of the effective excess polarization⁸⁶

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

where r and l are the radius and length of SWNT; ε_1 and ε_2 are the dielectric constants of the liquid suspension and the SWNT, 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, 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.3.2, the components of internal electric field $\vec{E}^-$ can be expressed as⁸⁶

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

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.

Fig 3.2. Geometry of a SWNT 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), Eq.(3.4) can be changed to

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

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

3.2.2 AC DEP induced torque

According to Eq.(3.3), the alignment torque on the SWNT 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

$$T = \pi r^2 l (\varepsilon_2 - \varepsilon_1) [E_{\parallel}^- E_{\perp} - E_{\perp}^- E_{\parallel}], \quad (3.9)$$

or

$$T = \frac{\pi r^2 l (\varepsilon_2 - \varepsilon_1)^2 (L_{\perp} - L_{\parallel}) E_{\parallel} E_{\perp}}{\varepsilon_1 \left[1 + \left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1} \right) L_{\parallel} \right] \left[1 + \left(\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1} \right) L_{\perp} \right]}. \quad (3.10)$$

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

$$T = \frac{\pi r^2 l}{2} \varepsilon_1 \frac{(\varepsilon_2 - \varepsilon_1)^2}{[\varepsilon_1 + (\varepsilon_2 - \varepsilon_1) L_{\parallel}](\varepsilon_2 + \varepsilon_1)} E_0^2 \sin 2\theta. \quad (3.11)$$

In the case of non-rotational AC voltage across two electrodes as in our experiments, the SWNT still rotates in a similar way to the DC case⁸⁶, as illustrated in Fig. 3.3. When the electric field changes its polarity, so does the induced dipole and the torque remains the same.

Fig 3.3 Schematic of the rotational motion of an SWNT under different polarities of electric field (front View).

3.2.3 AC DEP induced force

When the electric field is nonuniformly distributed, the dipole will experience a net force $\vec{F} = \vec{p} \cdot \nabla \vec{E}$, or

$$\vec{F}_{DEP} = \frac{\pi r^2 l}{2} \epsilon_1 \text{Re}(K) \nabla E^2, \quad (3.12)$$

where $K = \frac{(\epsilon_2^* - \epsilon_1^*)}{\epsilon_1^* + (\epsilon_2^* - \epsilon_1^*)L_{||}}$ is the complex Clausius-Mossotti function, $\epsilon_{1,2}^* = \epsilon_{1,2} + \frac{\sigma_{1,2}}{i\omega}$,

ω is the frequency of applied electric field. ϵ_1 and ϵ_2 are the permittivity of the suspension medium and CNT; σ_1 and σ_2 are the conductivity of the suspension medium and CNT, respectively. Detailed derivation is included in Appendix B.

Isopropyl alcohol (IPA) is used to suspend SWNTs, which has a conductivity σ_1 of $6\mu S/m$. The conductivity is estimated as $10^5 S/m$ and $10^8 S/m$ for s-SWNT and m-SWNT, respectively²⁵. As illustrated in Fig. 3.4, the SWNT will travel along the gradient of E^2 and the direction remains the same when the electric field changes its polarity, for the induced dipole changes polarity with the electric field. The direction and magnitude

of the force is mainly determined by $\text{Re}(K)$. If $L_{\parallel}$ is very small, we can derive that (see Appendix B)

$$\text{Re}(K) = \frac{\sigma_1(\sigma_2 - \sigma_1) + \omega^2 \varepsilon_1(\varepsilon_2 - \varepsilon_1)}{\sigma_1^2 + \omega^2 \varepsilon_1^2}. \quad (3.13)$$

At low frequency, the direction of the force is determined by the conductivity of SWNT and the medium. However, at high frequency, it is determined by the permittivity. Due to different dielectric properties ($\varepsilon_1 = 2 \sim 5 \varepsilon_0$ for s-SWNT⁸⁷ and $>2000 \varepsilon_0$ for m-SWNT⁸⁸), m-SWNT always experiences a positive DEP force (pointing to higher electric field). For s-SWNT, the DEP force becomes negative (pointing to lower electric field) as frequency increases. As the magnitude of $\text{Re}(K)$ is much larger for m-SWNT than that of s-SWNT, the DEP force on the m-SWNTs should be much larger than that on the s-SWNTs. Thus, for a bundle of SWNTs, the m-SWNTs inside will dominate the motion of the bundle. In other words, the SWNT bundle will also move towards the electrodes where the electric field is the strongest.

Fig 3.4 Schematic of the translational motion of an m-SWNT under different polarities of electric field (front View).

3.3 Simulation of CNT motion

Simulated spatial distributions of the electric field between two adjacent perpendicular and parallel electrodes are obtained by solving Poisson's equation with FEMLAB⁸⁹. Electric fields in a space of $30\mu\text{m} \times 30\mu\text{m} \times 15\mu\text{m}$ for a perpendicular structure and $10\mu\text{m} \times 10\mu\text{m} \times 10\mu\text{m}$ for a parallel structure are obtained with 2 grid points per μm , respectively. With that, AC DEP torque and force induced on a SWNT can be deduced from Eq. (3.11) and (3.12). We consider the length of CNT to be $2\mu\text{m}$ and the radius is 1.4nm for a single tube and 20nm for a CNT bundle. The motion of the CNT is divided into rotation and translation. The simulation is carried out in a series of small time intervals. The values of the electric field and its gradient along the trajectories of the CNT are interpolated from the nearest grid points.

Figure 3.5 illustrates the motion of an s-CNT which is initially located at $(5\mu\text{m}, 5\mu\text{m})$ with a 60° angle with respect to the external field, after an AC voltage of 2V with 5MHz frequency is applied to the perpendicular electrode structure. We can see that the rotation time is much smaller than that for the translation, suggesting that the CNT is first aligned with the electric field and then translated to the place where the electric field is at its maximum. This finding is consistent with our experimental observations in which the CNTs are found to be well aligned along the electric field.

Fig 3.5 Schematic of the spatial motion of an s-CNT (bold blue line) which is initially located at $(5\mu\text{m}, 5\mu\text{m}, 5\mu\text{m})$. 1 and 2 represent s-CNT before and after rotation, respectively. The light blue line shows the translational locus. The centroid position of the s-CNT for the process time of 1s , 2s and 2.6s are indicated, respectively. The regions in red represent the electrodes.

Due to different dielectric properties, the s-CNT and m-CNT could behave very differently during the AC DEP manipulation. Figures 3.6 and 3.7 compare the rotational and translational motions of both s- and m-CNTs, which are initially located at $(5\mu\text{m}, 5\mu\text{m}, 5\mu\text{m})$ with an angle $\theta = 80^\circ$ with respect to the external field, associated with an AC signal of 6V peak-to-peak value at 10MHz . One can see that, for both of them, rotational motion is much faster than translational. This implies that good alignment of

CNTs can be easily achieved. Due to the thousand-times larger permittivity, m-CNT rotates and translates faster than s-CNT. Especially for translational motion, s-CNT takes a much longer time. Therefore, the AC DEP technique could be employed to separate out s-CNTs from m-CNTs by controlling the manipulation time, provided they are well separated from each other in suspension (ideally all single tubes).

Fig 3.6 The angle θ between the electric field and the axis of (a) s-CNT and (b) m-CNT as a function of time, respectively.

Fig 3.7 Position of (a) an s-CNT's centroid and (b) an m-CNT's centroid as a function of time, respectively. X, Y, Z refer to the coordinates of the CNT when it translates during the AC DEP manipulation.

Varying the frequency of the applied AC electric field provides another way to optimize the manipulation process. Figure 3.8 shows the value of $\text{Re}(K)$ versus frequency of both m-CNT and s-CNT. Our results show that around 800MHz, the value for s-CNT will become negative, which means that the s-CNTs are repelled from electrodes, opposite to the m-CNTs motion. As discussed in Sec. 3.23, the DEP force is determined by permittivity at high frequency. m-CNT has a much larger permittivity than that of IPA, so it is polarized first by the external electric field and receives a positive DEP force, as illustrated in Fig. 3.9. However, the permittivity of s-CNT is smaller compared to IPA and now IPA is polarized first before s-CNT. As a result, s-CNT receives a negative DEP force. Therefore, it is possible to separate s-SWNTs from m-SWNT using a high frequency electric field. Even at a frequency of 13MHz, it was reported that high purity s-SWNT suspension could be obtained.⁸⁹ Since the DEP force on m-CNTs is several orders of magnitude larger than that on s-SWNTs, most m-CNTs and very few s-CNTs will be filtered out from suspension, leaving only s-CNTs in the suspension. This technique could be also employed in fabricating horizontal interconnects, where pure m-CNTs are desired to propagate the signal from one device to another.

Fig 3.8 $\text{Re}(K)$ as a function of frequency for (a) an s-CNT and (b) an m-CNT, respectively.

Fig 3.9 The DEP force on an s-CNT (upper) and an m-CNT (lower) at $f > 800$ MHz.

It is clear that, as the frequency increases, the magnitude of AC DEP force decreases and thus the time for the CNT to bridge electrodes increases. Figure 3.10 plots the translational time for both s-CNT and m-CNT initially at $(5\mu\text{m}, 5\mu\text{m}, 5\mu\text{m})$, over a frequency range of 1MHz to 200MHz. We can see that the manipulation time increases dramatically for both kinds of CNTs as the frequency increases. Actually, the distance a CNT travels in experiments could be much larger than that in our calculation, so it would take a long time to get rid of the m-CNTs from the suspension by using very high frequency DEP method. That is why in the experiments, relatively lower frequency is applied to reduce manipulation time.

Fig 3.10 Translation time as a function of frequency for (a) an s-CNT and (b) an m-CNT, respectively.

One practical problem is that, more than one CNT could bridge the electrodes in a short time, and it is not desirable for obtaining single-tube devices to study 1-D carrier transport. Figure 3.11 shows the calculated translation time for an s-CNT at different starting locations. As the initial position of s-CNT moves away from the electrodes, the

translation time becomes much longer. Thus, the time interval between the first and second CNT bridging the electrodes can be made large provided all CNTs in the suspension are well separated from each other. In that case, the chance for getting a single CNT bridging the electrodes is much greater.

Fig 3.11 Translation time for an s-CNT to bridge the electrodes as a function of its initial coordinates, which is assumed to be the same in X, Y, and Z direction.

3.4 Simulation of CNT spatial distribution

We assume that initially 1000 SWNT bundles for the perpendicular electrodes and 200 for the parallel electrodes are randomly distributed in the suspension, respectively. After an AC voltage is applied for 1 minute (which is long enough in our simulation for all CNTs reach the ground plane), the distributions of the CNTs are shown in Fig. 3.12(a) and (b). In this simulation, the interaction between the CNTs is negligible; as in

experiments, the mean separation between any two adjacent CNTs calculated is much longer as compared to the CNT length.

For the perpendicular electrodes, about 50% of the SWNT bundles are attracted into the region bounded by the green curve as shown in the Fig. 3.12(a). From Fig. 3.12(b), one can see that for the parallel electrodes, the SWNT bundles are uniformly distributed all over the area between the two adjacent electrodes, as the electric field is uniform in between them. These simulated distribution results are consistent with experimental observations in Fig. 3.13. The perpendicular structure has better spatial control of SWNT bundles, as the electric field is crowded between the two adjacent tips. In other words, the number of CNTs bridging the electrodes can be controlled through optimizing the field strength and the concentration of CNT suspension. This efficient patterning technique can also be used to align many CNTs in a large scale, which is reported recently.⁹⁰

Fig 3.12 Simulated distribution of (a) 1000 SWNT bundles for perpendicular-structured electrodes and (b) 200 bundles for parallel-structured electrodes, respectively. In both plots, the red regions represent the electrodes and the blue '+' represent the centroids of

SWNT bundles. The green dash line in (a) defines the region in which 50% SWNT bundles are captured.

Fig 3.13 AFM images of the SWNTs attached to (a) perpendicular-structured electrodes and (b) parallel-structured electrodes, respectively. The arrows indicate the external electric field (E) direction .

3.5 Conclusions

We have studied the mechanism of manipulating CNTs using the AC DEP method. We demonstrated that AC DEP is an efficient technique to control the alignment and location of the CNTs. The main conclusions obtained from this work are:

- Due to induced DEP torque and force, the CNTs will rotate to align with the applied electric field direction and translate along the gradient of electric field.
- The rotation time is much smaller than the translation time. Therefore, good alignment of CNTs can be obtained.

- By manipulation time control or frequency tuning, m-CNTs and s-CNTs can be separated from each other due to their different dielectric properties.
- A perpendicular electrodes structure has better control of SWNT's location and orientation than the parallel structure.

Our findings should hold valid not only for CNTs, but also for nano wires, nano rods or nano belts of other materials.

Chapter 4

CNTFETs Fabrication and Current Stability

4.1 Introduction

From Chapter 3, we show that CNTs can be effectively manipulated with the AC DEP method. Here, we describe the fabrication processes of CNTFETs and study the current stability of the as-prepared devices. First, the CNTs are aligned across metal electrodes, and the m-CNTs are selectively burned off, leaving the s-CNTs as the conducting channel. In this way, various structures of CNTFETs can be realized. Current stability in CNTFETs is then studied under the influences of gate voltages, surfactants and temperature, respectively.

4.2 CNTFETs fabrication

4.2.1 SWNT suspension

SWNTs used in our experiments were characterized using Raman spectroscopy. The Raman spectrum of the SWNTs on Si/SiO₂ substrate is shown in Fig. 4.1. From the

relationship between the radial breathing mode (RBM) frequency and average diameter D of the SWNT, i.e., $\omega_{RBM} \approx 248/D$,⁹¹ D is estimated to be around 1.4 nm. The large ratio of G^+ peak (at 1592 cm^{-1}) to G^- peak (at 1565 cm^{-1}) suggests that the majority of the SWNTs are semiconducting.^{92,93} 1mg of SWNTs are dispersed in 1l IPA or de-ionized (DI) water with 1% wt sodium dodecyl benzene sulfonate (SDBS), sodium dodecyl sulfate (SDS) or Triton X-100 for better dispersion of SWNTs. After ultrasonic-agitation using a tip-sonicator (MISONIX sonicator 3000) at a power of 480 w/l for 2 mins, the suspension was centrifuged (SIGMA sartorius 2-16) at 6461 g for 2 hrs, where g is the gravitational acceleration of 9.81 m/s^2 . Then, the upper 30% supernatant was carefully decanted. The suspension was then ultrasonically agitated for more than 30mins before the ac dielectrophoresis (DEP) process.

Fig 4.1. Raman spectrum of our SWNTs.

4.2.2 CNT placement

CNTFETs are fabricated on heavily doped p-type $\langle 100 \rangle$ silicon wafers (resistivity is about 0.01 to 0.02 $\Omega\text{-cm}$) coated with a thermally grown SiO_2 layer of 100nm to 500nm in thickness. The metal electrodes, consisting of an Au layer on top of a Ti layer, are deposited using standard photo lithography and E-beam evaporation technology. Optical images of the electrodes made from two different mask patterns are shown in Fig. 4.2. The distance between two electrodes varies from 1.5 to 10 μm .

Fig 4.2 Optical images of (a) 4 electrodes made from a cross mask. b) 7 electrodes made from a parallel mask.

The CNT suspension is then dropped onto the electrodes with an AC voltage across with a frequency of 2-10MHz. The peak-to-peak voltage ranged from 6V to 16V, depending on the electrodes' separation. Due to the induced DEP force, the CNTs in the suspension align with the electric field direction and move towards the electrode surface. The AC voltage was turned off immediately once SWNTs bridged the electrodes, as

confirmed by monitoring the resistance across electrodes. The number of the SWNTs between the electrodes can be controlled by adjusting the SWNT concentration and the manipulation time. For CNTFET fabrication, we select low concentration and short manipulation time in order to obtain a small number of SWNTs bridging mainly in the shortest gap between the two electrodes.

4.2.3 M-CNT burn-off process

Up to now, it is still difficult to selectively grow pure s-CNTs or m-CNTs. Furthermore, individual tubes tend to form bundles due to substantial Van der Waals attractions between them. 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-CNTs, and a gate independent conductance of m-CNTs. The latter will cause a large leakage current and decrease the ON/OFF current ratio seriously. To remove m-SWNTs from the channel, Collins *et al.* used a breakdown process to destroy the m-SWNTs.^{94,95} Since the conductance of s-CNTs displays strong dependence on the gate voltage, they can be switched off by adjusting the gate voltage V_{GS} . Most current will then pass through m-CNTs. With a sufficiently high V_{DS} , a large current passes through the m-CNTs and generates enough heat to burn them off, leaving the s-CNTs essentially intact.

In our experiment, the CNT bundles across the source and drain electrodes consisted of both m- and s-CNTs. The drain current I_{DS} as a function of drain voltage V_{DS} was measured using a HP-4156B semiconductor analyzer at ambient atmosphere. The output characteristics before and after the electrical breakdown are shown in Fig. 4.3a and

4.3c, respectively. The on/off ratio (I_{ON}/I_{OFF}) increases from 2 up to 10^4 after breakdown, as shown in Fig. 4.3d. The high on/off ratio indicates that most of the current was contributed by s-SWNTs and almost all of the m-SWNTs were burnt off. Figure 4.3b shows the I_d - V_{ds} curves during the breakdown process. The gate voltage was kept at 15V during our breakdown process, and the source-drain voltage was swept in a range from zero to a positive value, V_{PDS} . The value of V_{PDS} was increased gradually from a lower voltage, say 5 V, 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 conductance did not change until the source-drain bias was increased to 10.5 V, at which it decreased apparently in the two consecutive sweepings (curve 1 and 2). It can be seen that in the end of the curve 1, the conductance dropped suddenly to the same level as that of the second sweeping (curve 2). However, the second sweeping still exhibited a large conductance, indicating that only some of the m-CNTs in the bundle were burned off. To completely remove the m-CNTs, V_{PDS} was increased further. Curve 3 of Fig.4.3b shows another sweeping at $V_{PDS}=11$ V, the conductance decreased apparently after V_{DS} is more than 10 V. The burn-off process was then stopped here, because the conductance at lower V_{DS} (≤ 1 V) was already very small (not shown here). The apparent current drops in Curves 1 and 3 indicate breakdown of the metallic tubes.

Fig 4.3 a) I_{DS} - V_{DS} at a series of V_{GS} for an as-prepared device. b) I_{DS} as a function of V_{DS} during the burn-off process at $V_{GS}=15$ V. c) I_{DS} - V_{DS} at a series of V_{GS} of the device after burn-off process. d). I_{DS} - V_{GS} curve at $V_{DS}=-0.15$.⁹⁶

The breakdown of the m-CNTs could result from CNT oxidation under the current-induced heat.^{94,95} Although perfect carbon nanotubes have strong carbon-carbon bonds, and their current carrying capacities exceed $10\mu\text{A}/\text{nm}^2$,⁹ CNTs with defects could be oxidized when the oxidation begins from the defect. The outermost 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.

4.2.4 Various structures of CNTFETs

Using AC DEP technique, various structures of CNTFETs can be realized for different purposes. Taking bottom-gated CNTFET for example, metal gate can be first defined on the substrate. A layer of gate oxide is then deposited, followed by source/drain electrodes formation. After that, CNTs are aligned across the source drain electrodes. In this case, a bottom metal-gated CNTFET with CNTs exposed to ambient is fabricated, suitable for studying the gaseous interaction in CNT devices. Similarly, passivation materials like Si_3N_4 can be selectively deposited to protect one part of as-prepared CNTFETs, which will be discussed in details in Chapter 5. Figure 4.4 shows the AFM images of four CNTFET structures.

Fig 4.4 AFM images of (a) a CNTFET with a full bottom metal gate; (b) a CNTFET with a partial bottom metal gate; (c) a CNTFET with one side passivated with Si₃N₄; (d) a CNTFET with both contacts passivated by Si₃N₄, respectively.

4.3 Current stability in CNTFETs

Since the first demonstration of CNTFETs in 1998,^{12,13} many applications of such devices have been proposed, including gas sensors,⁷¹⁻⁷³ logic circuits,^{14,16,42,44,45,56} memories,⁶⁸⁻⁷⁰ and so on. A lot of efforts have been made to improve the performance of CNTFETs^{15,44} and the integration of such devices^{97,98}. However, as an SWNT has a very

large surface to volume ratio, its electrical and electronic properties are very sensitive to its surrounding chemical environments. It has been observed that CNT channel conductance is variable with time and the instability issue could restrain CNT-based devices from practical applications. Here, the current instability of CNTFETs is studied under different gate voltages, surfactants and temperatures, respectively. From that, techniques to improve the current stability for CNTFETs are discussed.

Three surfactants were used to disperse the CNTs, namely, SDBS, SDS, Triton X-100. For our CNTFETs prepared with SDS⁹⁹ and Triton¹⁰⁰, counterclockwise hysteresis is usually observed in the transfer characteristics, consistent with other reports of CNTFETs prepared without surfactants.^{12,13,69} However, our devices using SDBS as the surfactant usually show a clockwise hysteresis. The transfer characteristic of a typical CNTFET made with SDBS (Device 1) is shown in Fig. 4.5(a). Figure 4.5(b) shows the source-drain current I_{DS} versus time under a constant drain voltage $V_{DS}=0.01\text{ V}$ and gate voltage $V_{GS}=-4\text{ V}$, 0 V , and 4 V , respectively. One can see that I_{DS} at $V_{GS}=-4\text{ V}$ (referred to as I_{ON}) increased with time, while I_{DS} at $V_{GS}=4\text{ V}$ (referred to as I_{OFF}) decreased with time. To rule out the influence from the electrical heating caused by I_{DS} , intermittent pulses of $V_{DS}=0.01\text{ V}$ were applied. Since I_{DS} only flowed through the CNT channel in the duration of the V_{DS} pulse (5 s), the heat generated can be negligible, as shown in Fig. 4.5(c). The similar trends of I_{DS} in Fig. 4.5(b) and (c) suggest that the I_{DS} variation was not caused by the electrical heating. When both V_{GS} (-4 V , 0 V and 4 V) and V_{DS} (0.01 V) were applied intermittently as shown in Fig. 4.5(d), the first data point in each pulse window showed a similar current value. However, even within the short duration of the gate voltage pulse,

I_{DS} showed a significant decrease, so that the current decays in Fig. 4.5(b), (c) and (d) were more likely to originate from a charging effect induced by the applied gate voltage.

Fig 4.5. (a) Transfer characteristic of as-prepared CNTFET (Device 1) with SDBS and Triton X-100; (b) I_{DS} as a function of time biased at constant V_{GS} and V_{DS} ; (c) I_{DS} as a function of time biased at constant V_{GS} and intermittent V_{DS} (the solid line connecting the pulse is only a guide to show the trend of I_{DS} . There is no data when V_{DS} is off); (d) I_{DS} as a function of time biased at intermittent V_{GS} and intermittent V_{DS} . For intermittent V_{DS} and V_{GS} bias, the pulse waveform is shown as dotted window in the figures.

It was reported that mobile ions may influence the characteristics of CNT devices.^{101,102} Moreover, considering the fact that our CNTFETs prepared with Triton X-

100 and sodium dodecyl sulfate (SDS) usually show counterclockwise hysteresis, we speculate that the clockwise hysteresis and observed current instability could arise from the SDBS used. The chemical properties of the three surfactants are listed in Table 4.1. The binding between SDBS and CNT surface is strong due to π -like stacking of benzene rings so that high surface coverage can be achieved.^{103,104} As illustrated in Fig. 4.6, mobile sodium ions can be attracted in the SDBS layer surrounding the small CNT bundle. When a positive gate voltage was applied, sodium ions were likely to be repelled from their neutral positions to the CNT surface. As they moved towards the channel, a higher potential induced by the ions assists further depletion of holes in the CNT, leading to a drop in the channel conductance. In contrast, when a negative gate field was applied, the ions moved away from CNT surface. The channel became less influenced by the electric potential of the ions, and I_{DS} showed slight increase. For transfer characteristic, when forward gate sweeping started from -4V, all positive ions move away from CNT towards the gate and the channel was not much affected. In contrast, as backward sweeping started at +4V, sodium ions should stay close to CNT surface and further deplete the channel. In other words, the threshold gate voltage for the backward sweeping was shifted to a more negative value compared to the forward sweeping, resulting in clockwise hysteresis loop. Moreover, this feature was only observed in the devices prepared with SDBS. Poor surface coverage of SDS and lack of mobile ions in Triton X-100 may not promote a clockwise hysteresis loop.

Table 4.1. Summary of chemical properties of SDBS, SDS and Triton X-100. “++”, “+” and “-” indicates very strong, strong and weak surface coverage, respectively.

	SDBS	SDS	Triton X-100
Chemical structure	$C_{12}H_{25}-\text{C}_6\text{H}_4-\text{SO}_3^-\text{Na}^+$	$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$	$\text{O}(\text{CH}_2\text{CH}_2\text{O})_N-\text{H}-\text{C}_6\text{H}_4-\text{C}_8\text{H}_{17}$
Sodium ion	Yes	Yes	No
Benzene ring	Yes	No	Yes
Surface coverage	++	-	+

Fig 4.6 Schematics of a small CNT bundle with SDBS encapsulation layer.

Reliability problems arising from mobile ions in Si devices usually occur under high-temperature and high-voltage operations due to small ion mobility in SiO₂ (usually

in order of $10^{-12} \text{cm}^2/\text{Vs}$). However, due to the small size of a CNT, the electric field around its surface becomes very high. By cylindrical geometry approximation, $E = V_G / \kappa_t \ln(h/r_t)$, where $r_t=0.7\text{nm}$ is the radius of CNT, $\kappa=3.9$ and $h=100\text{nm}$ are the dielectric constant and thickness of gate oxide layer, respectively. For a gate bias of 4 V, the electric field in the surfactant layer is about 0.3 V/nm. Compared to 0.25 V/nm of SiO_2 breakdown, this sufficiently high electric field could allow the movement of Na^+ even at room temperature.

The degree of the hysteresis loop can be characterized by the V_{TH} shift as in Fig. 4.5(a), which depends on experimental conditions like the range and the rate of gate voltage sweep.¹⁰⁵ For consistency, $\pm 4 \text{ V}$ and 1 V/s were used throughout the experiments. By assuming that all the Na^+ ions are able to follow the gate sweep, we can roughly estimate the concentration of Na^+ ions. The unit length capacitance of the SDBS layer can be expressed as $C_s \approx 2\pi\kappa_s\epsilon_0 / \cosh^{-1}(h_s/r_t) = 2.44\text{aF/nm}$, where $\kappa_s=75$ ⁹² and $h_s=2\text{nm}$ ¹⁰⁶ are the dielectric constant and thickness of the SDBS encapsulation layer, respectively. The total charge of Na^+ ions $Q_s = C_s \Delta V_{\text{TH}} \approx 23 |e|/\text{nm}$, which gives a Na^+ concentration of 8 atomic percent, similar to Zhang *et al.*'s results by XPS studies.¹⁰⁷

The mobility of Na^+ ions in the SDBS encapsulation layer can be estimated from the transient behaviors of I_{DS} in Fig. 4.5(b). Under $V_{\text{GS}}=4 \text{ V}$, Na^+ ions were pushed closer to CNT and I_{DS} quickly decayed to a stable value after 20s. By exponentially fitting this decay to $I = I_0 - I' \exp(-t/\tau)$, where I_0 is pre-exposure current level and I' is the magnitude of change in current, we obtain $\tau=2.63 \text{ s}$, which can be regarded as the

characteristic time for Na^+ movement. Through the ion velocity $V_{\text{Na}} = h_s / \tau = \mu_{\text{Na}} E$, the mobility of Na^+ μ_{Na} is calculated to be $2.5 \times 10^{-14} \text{ cm}^2/\text{Vs}$. Though this value is very small, large electric field around the CNT makes the influence of Na^+ ions prominent even at room temperature.

Figure 4.7(a) compares the transfer characteristics of another CNTFET (Device 2) prepared using SDBS at $T=20^\circ\text{C}$, 50°C and 100°C , respectively. The hysteresis loops changed from clockwise at 20°C to counterclockwise at 50°C , at which SDBS began to decompose. The transient behavior of I_{DS} at these three temperatures in Fig. 4.7 (b)-(d) further elaborated this process. I_{OFF} decreased with time at $T=20^\circ\text{C}$, but began to increase after 40s at $T=50^\circ\text{C}$, as a result of SDBS decomposition. When temperature reached 100°C , I_{OFF} increased with time significantly. These observations could be attributed to carrier trapping in adsorbed gas molecules and will be further explained.

Fig 4.7 (a) V_{TH} shift of Device 2 at 20°C , 50°C and 100°C , respectively. The corresponding I_{DS} versus time at $T=20^\circ\text{C}$, $T=50^\circ\text{C}$ and $T=100^\circ\text{C}$ is shown in (b), (c) and (d), respectively.

To eliminate the influence of mobile ions, we removed SDBS by the following treatments.¹⁰⁷ As-prepared CNTFETs were soaked in DI water overnight, followed by 350°C annealing for a few hours. It is noted that the CNTFETs made with high SDBS concentration may require long soaking and annealing processes. After the treatments, the devices showed a typical p-type characteristic with a counterclockwise hysteresis loop, as shown in Fig. 4.8 (a) for Device 1. The hysteresis loop became counterclockwise, similar to those devices made via direct CNT growth without involving any surfactants. Vijayaraghavan *et al.* pointed out that the counterclockwise hysteresis is caused by

charge trapping in surrounding secondary dielectrics formed by a water layer, or other adsorbed gas molecules.^{105,108} Our observations are consistent with their suggestions. When constant gate voltages were applied, carriers could be injected from the CNT channel to surrounding dielectrics and counteract with applied gate electric field. As a result, the induced screening effect could lead to a lower effective gate field on CNT channel, so that I_{ON} and I_{OFF} approached each other, as shown in Fig. 4.8(b).

Fig 4.8 (a) The transfer characteristics of Device 1 after SDBS removal and (b) its I_{DS} vs time under $V_{GS} = -4V$, $0V$ and $4V$, respectively.

We have discussed two kinds of instability origins in CNTFETs. Mobile ions may lead to an increase in I_{ON} and thus high consumption of active power; whereas carrier trapping can cause low current drive and high standby power. To improve the stability of CNTFETs, we suggest that: (1) mobile ion contaminations should be avoided during the fabrication processes. For example, Triton-X100 could be used to disperse CNTs; (2) heat treatment and passivation layers are required to eliminate the trapping centers induced by adsorbed molecules.

4.4 Conclusions

With AC DEP and selective burn-off methods, CNTFETs with on/off ratio of up to 10^4 have been successfully fabricated. These results suggest that AC dielectrophoresis placement method is an efficient technique to fabricate CNTFETs with some flexibilities of controlling CNTs orientation and location. The channel current instability of as prepared CNTFETs is studied. We suggest that sodium ions in the adsorbed SDBS layer on the CNT walls respond to the applied gate electric field, leading to an increase in I_{ON} and a decrease in I_{OFF} with time, as well as a clockwise hysteresis loop in the transfer characteristics. After the removal of the adsorbed SDBS, the devices show a decrease in I_{ON} and an increase in I_{OFF} with time, with a counterclockwise hysteresis loop. Charges injected from the CNT channel to the surrounding dielectrics could be responsible for the findings.

Chapter 5

Studies of Gaseous Interaction in CNTFETs through Selective Si_3N_4 passivation

In this chapter, we will first review some important literature works, mainly regarding the influence of ambient oxygen on the performance of CNT devices. Next, we develop a selective passivation technique to investigate the gaseous interaction in our CNTFET. Using this technique, we are able to differentiate channel/contact effects and identify the underlying mechanism. A novel model is developed for the nanoscale contacts between CNT and metallic pads.

5.1 Literature review on gaseous interaction in CNT devices

Without any intentional doping, early CNTFETs exhibited p-type conduction in air, i.e. the transistors could be turned “ON” at negative gate voltages and switched “OFF” by positive gate voltages.^{12,13} It was later found that the electrical properties of

SWNT were extremely sensitive to its chemical environment. Collins *et al.* found that, exposure to air could cause a dramatic influence on the CNT's resistance.²³ Identical results were obtained if pure dry oxygen was used rather than air, indicating that oxygen could be the source of the effect. As shown in Fig. 5.1 (a), stepwise change in the resistance of CNT was observed when switching the measurement environment between vacuum and air, and the I-V characteristics in Ar and O₂ are clearly different, Fig. 5.1 (b). A first-principle calculation later suggested that oxygen could dope CNT with a binding energy of 0.25eV and about 0.1 electron from carbon nanotube to every oxygen molecule was predicted.²⁴ Under these circumstance, the operating mechanism of CNT could follow that of MOSFET with a p-type CNT as the conduction channel, or bulk switching in short.

Fig 5.1 (a) Sensitivity of the electrical resistance R of SWNT films to gas exposure. (b) I-V characteristics for an isolated CNT in inert Ar gas and after exposure to O_2 . The I-V curve acquired over bare Au substrate is included as a reference.²³

To construct a CMOS-like device, n-type CNTFETs are needed. Alkali metal doping^{16,26,57,58} and vacuum annealing^{16,56} were found effective to convert p-type CNTFETs to n-type. After a careful comparison of these two methods shown in Fig. 5.2,

Derycke *et al.* challenged the hypothesis of oxygen doping with the following arguments:²⁶ (1) oxygen hole doping could not explain the absence of electron conduction for large positive gate voltages; (2) assuming that the CNTs were p-doped by oxygen, its removal should lead to intrinsic CNTs, rather than the observed n-type behavior; (3) during the gradual n-to-p conversion when the vacuum annealed device was re-exposed to air, no significant change in the threshold voltage was observed, unlike the potassium doping process. Therefore, they proposed that the main effect of oxygen is to modify the barriers at the CNT/metal contacts, as illustrated in Fig. 5.2 (c) and (d).

Fig 5.2 (a) Effect of oxygen on an n-FET produced by thermal annealing. The O_2 exposures are: 2min at $P=10^{-4}$ Torr (black triangles), $P=5 \times 10^{-4}$ Torr (Open squares), $P=5 \times 10^{-3}$ Torr (gray diamonds), $P=10^{-1}$ Torr (open triangles) and exposure to the ambient

(black circles). (b) Effect of potassium doping on a CNTFET. The FET is initially p-type (curve 1-7). After seven doping cycles, no more current can be detected (open circles 8,9). At higher doping levels, the device becomes n-type (curve 10-12). (c) Schematic energy band diagram in the region of CNT/metal contact at $V_{DS}=0$ of starting p-type device in air and (d) the device after annealing in vacuum.²⁶

With the above findings, IBM Research Division raised the concept of SB transistor for CNTFET, where the transistor action occurs primarily by varying the contact resistance rather than the channel conductance.²⁷ They calculated the transport behavior of a top-gated CNTFET, as illustrated in Fig. 5.3(a). From Fig. 5.3(b), we can see that when the metal Fermi level falls in the middle of CNT bandgap ($\Phi_B=0.3\text{eV}$), the conductance shows a symmetric dependence on the gate voltage. If not, the SB height becomes different for electrons and holes, resulting in an asymmetric conductance curve. Whenever the SB is large enough to efficiently control current, the device operates as a SB-FET. The underlying mechanism for the transistor action is illustrated in Fig. 5.3(c). Already at 4V there is substantial carrier density in the channel, but the current is blocked by the SB. Increasing the voltage difference between source and gate electrodes leads to a large electric field at the contact, reducing the width of the SB and allowing thermally assisted tunneling.

Fig 5.3 Conductance for realistic FET geometries. (a) Device geometry, with metal contacts on the left and right, a ground plane and a top gate. Contour lines show the electrostatic potential for a top gate voltage of 2V. (b) Corresponding conductance versus gate voltage at the room temperature, for different SBs. The SB height for electrons is indicated for each curve. (c) CNT conduction band energy near the contact for gate voltage of 4 and 10V.²⁷

It is now generally believed that the work function of metal could be increased by adsorbed oxygen through charge transfer or surface dipole interaction,^{27,50,51,109,110} and therefore the SB for holes at the CNT/metal contact is reduced, leading to p-type conduction. However, this explanation treats the metal and CNT separately and does not consider the nanoscale nature of the contact. Yamada proposed a novel model for CNT/Au interface.¹¹⁰ As illustrated in Fig. 5.4, negatively charged oxygen molecules adsorbed in the nanoscale gap between Au and CNT could disturb the electrostatic balance of the system. A potential drop across the gap and a surface bending at the CNT are induced; as a result, the SB at the contact is modulated. Using a graphical solution for

the charge neutrality equation, he showed that when oxygen adsorbs on the CNT/Au contact interface, the SB for holes is reduced, no matter whether the CNT is p-doped or n-doped. The SB modulation effect is found to be most significant when the CNT is in depletion mode, while it is negligible when a CNT accumulation mode is involved. An oxygen coverage of 0.1% to 1% on gold surface is enough to observe the SB modulation of more than 0.1eV.

Fig 5.4 Band structures for a Schottky junction between the metallic electrode and s-CNT (a) in vacuum and (b) in air, showing a potential drop ΔU in the transition region. Here a is the transition width, ϵ_{tr} is the dielectric constant, Φ_s is the CNT electron affinity, ζ is the CNT Fermi level, χ_m is the metallic work function, Φ_{bh} is the hole SB and σ_{ox} is the negative charge due to oxygen molecules.¹¹⁰

5.2 Motivation

It is well accepted that environmental oxygen could greatly influence the performance of CNTFETs, but the exact role of oxygen requires further investigation. On one hand, adsorbed oxygen on the CNT channels could induce charge-transfer and make

the CNTs hole rich. On the other hand, adsorbed oxygen at the CNT/metal interfaces may alter the Fermi level of the electrode metals at the contacts and result in a smaller SB for holes and, in turn, easier hole injection. It has been under discussion, both theoretically and experimentally, whether the charge transfer²³⁻²⁵ or the SB modulation^{26,27} dominates the properties of CNTFETs in ambient. In addition to oxygen, the performance of CNTFETs is found to be affected by other adsorbents like H_2O ¹¹¹ and surfactants¹⁰⁰, etc. In order to passivate the CNT devices to avoid being affected in various chemical environments, several passivation materials have been employed. For example, polymethylmethacrylate (PMMA) was widely used to protect a CNT device in sensing applications.¹¹²⁻¹¹⁴ However, mechanical and thermal instabilities of polymers restrict the devices from further processing. Dielectric layers such as SiO_2 layer¹¹⁵ or Si_3N_4 layer¹¹⁶ were reported to insulate the CNT devices from the ambient, but the electrical performance of passivated CNTFETs has not been studied in details. More importantly, the influences of ambient gases on the CNT channel and CNT/metal contacts should be differentiated. Therefore in our work, we purposely passivate one part of the CNTFETs and study the mechanisms of gaseous interaction in CNTFETs.

5.3 Fabrication of CNTFETs with selective Si_3N_4 passivation

Fabrication process of CNTFET is described in Chapter 4. Here, Au was selected to form a Schottky contact with the SWNTs. Note that the CNTs are on top of Au electrodes and the contact regions are fully accessible to the ambient. After fabrication,

90% of CNTFETs showed p-type transfer characteristics and symmetric output characteristics in air, the rest being ambipolar with stronger hole conduction. The devices were checked using AFM for exact location and orientation before lithography and Si_3N_4 deposition. Next, photoresist was spin-coated onto the devices and openings at either the CNT channel or CNT/Au contacts were defined by optical lithography. The devices were then placed in the plasma enhanced chemical vapor deposition (PECVD) chamber at 7 Torr overnight for gas desorption. A 500 nm thick Si_3N_4 layer was deposited using a mixed flow of gases with 100 sccm 4% diluted silane gas, 20 sccm ammonia gas and 600 sccm nitrogen gas at 50°C with 40 W rf power, followed by a liftoff process to create the desired passivation patterns. To our experience, an rf power of 60W or below does not cause damage to the CNTFET devices. In order to verify the passivation properties of Si_3N_4 , we also fabricated a reference sample fully covered with 200nm Si_3N_4 . Figure 5.5 shows that the reference sample is not affected by measurement pressure and NH_3 gas, which validates the passivation property of Si_3N_4 thin film.

Fig 5.5 The ON current (at $V_{GS}=8V$) and OFF current (at $V_{GS}=-8V$) of the reference sample in response to (a) measurement pressure and (b) various concentration of NH_3 gas.

5.4 CNTFETs with both contacts passivated

We first passivated the source and drain contacts of an as-prepared p-type CNTFET (D1) and the output characteristic of the device is shown in Fig. 5.6. The device showed an excellent n-type performance in ambient with no degradation in its saturation conductance. If the exposed CNT channel were hole doped due to oxygen adsorption, Device D1 would mimic an i-p-i or n-p-n structure, which has been used for studying single electron transistors¹¹⁷ or band-to-band (BTB) tunneling phenomenon⁶⁷. A long CNT channel $\sim 7\ \mu\text{m}$ and a thick gate oxide $\sim 200\ \text{nm}$ in Device D1 should not satisfy the requirements for BTB tunneling. Also, two p-n junctions connected back-to-back should not lead to high conductance or good on/off ratio. Thus, we suggest that, environmental hole doping does not cause a measurable effect in our devices. Actually, our results can be well interpreted through a hypothesis of SB modulation. As oxygen adsorbs at the CNT/Au contacts, the work function of the Au electrode increases¹⁰⁹ and/or the electrostatic charge balance at the CNT/Au interface could be disturbed¹¹⁰, leading to a smaller SB for hole injection. However once the passivation is in place, the Fermi level of the Au electrodes, in a simple way, moves relatively towards the conduction band edge of the CNT, as illustrated shown in Fig. 5.7. Combining scanning Kelvin probe microscopy and electrostatic force microscopy, Cui *et al.* experimentally confirmed that the energy level alignments at CNT/Au contacts were modulated by oxygen adsorption due to occupancy of surface states and suppress of surface dipoles.⁸⁰ The conduction type of the devices after passivation depends on the intrinsic energy-level alignment at the CNT/Au

contacts. All our devices in this structure showed enhanced n-type performance after the contact passivation. It is noted that, for studying sensing properties of CNTs, Su-8¹¹³, SiO_2 ¹¹⁵ and PMMA¹¹² have been employed to passivate the contacts of CNTFETs. However, none of those measures could convert the CNTFETs from p-type to n-type, implying that those protected contacts in the previous work were not completely isolated from oxygen. In contrast, our results suggest that Si_3N_4 thin film is an excellent passivation material to prevent gas molecules from diffusing in. Besides, Si_3N_4 is much superior to polymers in terms of thermal and mechanical stabilities.

Fig 5.6 (a) Transfer characteristics of Device D1 before and after the source and drain contacts were passivated with Si_3N_4 ; (b) atomic force microscope (AFM) image (upper) and schematic (lower) of Device D1 after passivation.

Fig 5.7 Illustration of Au electrode work function reduction due to Si_3N_4 passivation. In this case, Au's Fermi level is aligned near CNT's valence band edge and hole transport is favored. After Si_3N_4 is in place to passivate the CNT-Au contact, the work function of Au is reduced and aligned near to the conduction band edge of CNT. As a result, electron conduction becomes dominant.

5.5 Nanoscale contacts between CNT and metallic pads

From above results, we understand that the role of oxygen is to modulate the CNT/metal contacts. In the following, we carried out a detailed study on the nanoscale contacts between CNT and metallic pads.

Metal/semiconductor contacts play a crucial role in many electronic devices, such as Schottky diodes, metal-semiconductor field-effect transistors (MESFETs), photodetectors, solar cells, etc. In the simplest picture, a Schottky barrier (SB) exists at the contact interface between a semiconductor and metal, and the energy barrier height is mainly determined by the difference between the metal work function and semiconductor electron affinity. However, much more complexity and uncertainty could arise at a nanoscale contact junction, where only a few metal atoms could form the contact and the

actual SB height can no longer be inferred from the traditional contact properties of the metals and semiconductors. To study the properties of nano contacts, carbon nanotube field-effect transistors (CNTFETs) provide a good platform. The nanometer-scaled contacts in CNTFETs do dominate the electrical properties of the devices. Most CNTFETs exhibit p-type characteristics in ambient without any intentional doping. While early studies suggested hole doping from oxygen,²³⁻²⁵ it is now generally believed that the CNT/metal contacts play a dominant role. If the Fermi-levels of the electrode metals lie below the mid-energy gap of the CNT, a small SB for holes should form and p-type conduction must be observed. Interestingly, the work function of the electrode metals is found to be strongly affected by adsorbed oxygen. By annealing the CNTFETs in vacuum or desorbing O_2 from the electrodes, the work function of the metal pads decreases so that a p-type to n-type conversion has been achieved.^{26,27} Although well accepted, the above picture is from a common concept for bulk semiconductor/metal contact. It is insufficient to interpret the nature of the nanoscale contacts, especially when the contact area becomes so small that interface adsorbents could affect the contact properties significantly. For this purpose, Yamada first proposed a non-intimate Schottky model in which an interface layer of charged or polarizable molecules formed at an CNT/Au contact could disturb the charge balance across the contact and modulate the SB.^{118,119} Yamada's model presents a physical picture for an individual CNT/metal contact or CNTFETs with symmetric contacts under the influence of environmental oxygen. However, for CNTFETs with asymmetric contacts, especially for CNT based Schottky diodes, the two different contacts both play roles in determining the device performance.

While most importantly, they must interact each other. Here, we propose a concept of “dipole polarization” along the CNT channels. With this concept, the electrostatic charge balance in the entire CNT channel and two contacts can be established and thus, the energy band bending near the two CNT/metal contacts can be obtained quantitatively. By considering the dipole polarization along the CNTs, we are able to link the contact properties with the device performance and interpret our unique observations from CNTFETs with asymmetric contact configurations.

In Device D2, the source side is passivated with a 500nm Si_3N_4 layer, as illustrated in Fig. 5.8. After the passivation, the device shows diode-like behavior. The asymmetric output characteristics of the device in air are shown in Fig. 5.9. At $V_{\text{GS}} = -4$ V, the device shows a higher channel conductance at a positive V_{DS} than that at $-|V_{\text{DS}}|$, and the maximum current rectification ratio is more than 10^2 . When $V_{\text{GS}} = 4$ V is applied, the polarity of the device is flipped. These observations suggest that the device functions as a tunable diode through the gate voltages. More interestingly, the conduction type of the device under $V_{\text{DS}} < 0$ is dependant of V_{DS} . As shown in the inset of Fig. 5.9, a clear p-type to n-type conversion is observed when V_{DS} is varied from -0.2 V to -0.75 V. Surprisingly, after the device is placed in vacuum, the n-type behavior, instead of being enhanced, is weakened and the output characteristic became more symmetric (see Fig. 5.10a). From common understandings, the environmental oxygen could cause hole doping to the CNT or increase the electrode metal work function. When the oxygen molecules desorb from the CNT device in vacuum, we would have observed n-type, instead of p-type conduction. In this sense, the role of oxygen needs to be reconsidered.

Yamada suggested that the electrostatic charge balance at a non-intimate CNT/Au contact can be dominated by adsorbed oxygen.¹¹⁸ In our devices, the CNTs are manipulated onto predefined Au electrodes. Due to the surface roughness of the electrodes, a small gap L ($\sim 1\text{nm}$ from AFM measurement of Au electrode surface roughness) between the Au and CNT could exist, such that a non-intimate Schottky contact is likely to form and the contact SB is susceptible to adsorbed oxygen. More importantly, dipole polarization along the CNT channel must be considered to establish the electrostatic charge balance of the whole device, from one contact to CNT, and to the other contact. The main purpose here is to study the charge redistribution in the device upon oxygen adsorption. The energy band of the CNT near to the contacts must adjust accordingly to restore the charge balance.

Fig 5.8 Atomic force microscope image of the CNTFET with source side passivated by Si_3N_4 . Inset: A schematic of the device structure. Positive charges (blue) and negative charges (red) are illustrated at the drain and source end of CNT, respectively.

Fig 5.9 Output characteristic of the CNTFET in atmospheric air. Inset: Transfer characteristic of the device under three V_{DS} , respectively.

Fig 5.10 (a) Output and (b) transfer characteristics of Device 2 at $P = 2.2 \times 10^{-6}$ Torr.

In the following, a detailed picture is obtained by analyzing the energy band bending (EBB) under the influence of the adsorbed oxygen molecules. Note that even for top contact configuration with CNT underneath metal electrodes, the charge balance could be still affected by oxygen molecules adsorbed along the contact interface, of course, in a less significant way as compared to the bottom contact configurations.

The single-walled CNT used in this work has a typical diameter of 1.4 nm. Therefore, the CNT with Fermi level of 4.7 eV and a bandgap E_g of 0.6 eV is considered in our model. The potential drop across the nano gap ΔU , the CNT electron affinity ϕ_0 , Fermi level position ζ (measured from the conduction band edge to the Fermi level of CNT), surface band bending and depletion width at the source and drain, $\phi_{S,S}$, $\phi_{S,D}$, W_S , W_D , are marked in Fig. 5.11, respectively. Our devices showed an ambipolar characteristic with higher hole conduction under high vacuum (see Fig. 5.10b), implying that the Fermi level of the Au should align slightly below the midgap of the CNT. Therefore, the effective work function of Au $\chi_m = 4.75$ eV is assigned under vacuum conditions in our model.

Fig 5.11 Schematic energy band diagrams of the CNTFET at $V_{DS}=0$ and $V_{GS}=0$ (a) under vacuum and (b) in air.

For the unpassivated drain contact, environmental oxygen molecules adsorbed on the Au surface could easily become negatively charged.¹²⁰ Thus, positive charges are induced in Au electrode (σ_m) and CNT (σ_{NT}) to balance these negative oxygen charges (σ_{ox}) in C/m². The charge neutrality condition can be expressed as follows:

$$\sigma_m + \sigma_{NT} + \sigma_{OX} = 0 \quad (5.1)$$

In Eqn. (5.1), $\sigma_m = \frac{\Delta U \epsilon_g}{qL}$, where q is the unit charge and ϵ_g is the permittivity of the gap (since the dielectric constant of gases are close to unity, $\epsilon_g \approx \epsilon_0$) and $\Delta U = \phi_s + \phi_0 + \zeta - \chi_m$ is as shown in Fig. 5.10a. The charge supplied by the CNT σ_{NT} can be modeled as $\sigma_{NT} = \pm \sqrt{2\epsilon_{NT} |\phi_s| N_B}$, where the permittivity of semiconducting SWNT (s-CNT) $\epsilon_{NT} \sim 3\epsilon_0$.⁸⁷ The effective doping level N_B can be determined by $N_i \exp \frac{|\zeta - \frac{1}{2}E_g + \phi_s|}{kT}$, where k is the Boltzmann constant, T is the absolute temperature and N_i is the intrinsic carrier density in the CNT ($\sim 10^{22} \text{ m}^{-3}$).¹²¹ The influence of the gate modulation on the Fermi level can be modeled as $\zeta = \zeta_0 - \alpha V_G$, where ζ_0 is the Fermi level position at $V_{GS}=0$ V and the gate efficiency α measures how much gate voltage can move the CNT Fermi level, which is usually less than 0.1 in experiments.^{1,2} Considering our back gate structure and thick gate oxide (200 nm SiO₂), we assign $\alpha \sim 0.025$, corresponding to the CNT Fermi level moving from 0.1 eV below mid-gap to 0.1 eV above, when the gate voltage is swept from -4 V to 4 V. Oxygen charge σ_{OX} is given by $\sigma_{OX} = -\frac{qP_{O_2}N_A L}{22.4 \times 10^{-3}}$, where P_{O_2} is the partial pressure of oxygen in atm and N_A is the Avogadro constant.

Solving Eqn. (5.1) by iteration for ϕ_s , we are now able to depict the detailed EBB. As shown in Fig. 5.10b, a surface band bending at the drain $\phi_{s,D} \approx 0.1$ eV (bending

upwards from the CNT to Au) with a depletion width $W_D = \sqrt{\frac{2\varepsilon_{NT}\phi_S}{q^2N_B}} \approx 9.3$ nm occurs

under $V_{GS} = 0$ V. The Schottky barrier for holes $\phi_{Bh,D} = \frac{1}{2}E_g - \phi_S = 0.20$ eV is thus obtained. Equivalently, the effective work function of the drain electrode is increased by 0.05 eV under the influence of adsorbed oxygen.

At the source side, the contact is passivated with a dense Si₃N₄ layer so that environmental oxygen is not able to reach the CNT-Au contact. Once positive charges are induced at the drain end, the CNT is easily polarized and an electrical dipole should form. According to the first-principle calculations, for an s-CNT in our experiment, typically about 95% of the charges are balanced in the longitudinal direction and only 5% are along the radial direction.¹⁷ In other words, nearly the same amount of negative charges should be induced at the source end. Therefore, static charges are separated at the two ends of CNT, and we name this effect as “dipole polarization”, with a quantity determined by the product of electrical charges at the two contacts and the distance of them. Using this concept, the electrostatic charge balance of the whole system (drain contact-CNT-source contact) is established and the device performance can be predicted. In this case, $\phi_{S,S} \approx -0.10$ eV (bending downwards from CNT to Au), $W_S \approx 9.6$ nm, $\phi_{Bh,S} = 0.40$ eV and $\phi_{Be,S} = 0.20$ eV can be obtained for the source contact under $V_{GS} = 0$ V and $V_{DS} = 0$ V.

Now the p-to-n conversion can be understood through the picture of EBBs. Under negative V_{DS} , or $V_D - V_S < 0$, the conduction type is mainly determined by hole current

from the source contact and electron current from the drain contact. The highest hole current occurs when holes are injected from the source contact at $V_{GS} = -4$ V, and the hole barrier $\phi_{Bh,S}$ is calculated to be 0.35 eV with a length $W_S \approx 26.0$ nm. Similarly, at maximum electron current ($V_{GS} = 4$ V), the electron barrier $\phi_{Be,D} \approx 0.38$ eV and $W_D \approx 15.9$ nm are obtained at the drain. Obviously, electrons from the drain encounter a higher but narrower barrier as compared to holes from the source. When the applied $|V_{DS}|$ is small, hole injection at the source contact is favored (see Fig. 5.12(i) and (ii)) and the device exhibited p-type behavior. As the magnitude of V_{DS} increases, the effective electron barrier width would become even narrower ($W_{eff} < W_D$). As illustrated in Fig. 5.12(iii) and (iv), when electron tunneling through the drain barrier dominates the current, the transfer characteristic becomes n-type. Our results suggest that both V_{DS} and V_{GS} could affect the EBB which controls the carrier transport through the contact.

Fig 5.12 Schematic energy band diagrams in air. (i) $V_{GS} = -4$ V and $|V_{DS}| < 0.2$ V and (ii) $V_{GS} = 4$ V and $|V_{DS}| < 0.2$ V, (iii) $V_{GS} = -4$ V and $|V_{DS}| > 0.5$ V and (iv) $V_{GS} = 4$ V and $|V_{DS}| > 0.5$ V, respectively.

As discussed above, the rectification effect mainly arises due to the difference in the SB heights at the source and drain contacts. Therefore, we are able to study how the CNT/metal contact is affected by investigating the pressure dependence of the rectification. The current rectification ratio (CRR), defined as the relative change in I_{DS} when V_{DS} is reversed, i.e., $I_{DS}(-V_{DS})/I_{DS}(V_{DS})$, is often used as a gauge of the rectification effect. In another CNTFET with asymmetric passivation (Device D3), the saturation CRR (at $V_{GS} = -4$ V and $|V_{DS}| = 1$ V) are monitored as a function of chamber pressure, as shown in Fig. 5.13. We find that the onset of rectification occurred at 100

Torr, and the calculated critical oxygen surface density is $\sim 10^{11} \text{ cm}^{-2}$, two orders of magnitude smaller than the value given by Yamada's model. This discrepancy could result from the structural difference, i.e., our CNT was placed on top of the Au electrode, instead of being buried underneath the metal pad. Oxygen may modulate the SB easily for CNT situated on top of electrodes as in our devices, rather than underneath. The adsorption time constant τ can be extracted from the inset of Fig. 5.13, where the saturation CRR is plotted as a function of time when Device D3 was abruptly re-exposed from 10^{-3} Torr to atmospheric air. According to transition state theory,¹²² $\tau = \nu_0 e^{-(E_B / K_B T)}$, where ν_0 is the attempt frequency for oxygen ($\sim 10^{12} \text{ s}^{-1}$), we can estimate the oxygen adsorption energy E_B to be about 0.6 eV. This value is comparable to the oxygen binding energy at gold surface¹²⁰, but twice that of at CNT walls²⁴.

Fig 5.13 Saturation CRR versus air pressure at $|V_{DS}|=1\text{V}$ and $V_{GS}=-4\text{V}$. Inset: saturation CRR versus time when Device D3 is exposed to atmosphere. An exponential fitting is given.

5.6 CNT Schottky diodes with asymmetric metal contacts

In our device discussed above, oxygen induces an upward bending at the unpassivated drain contact, which allows electron tunneling at largely negative V_{DS} . Meanwhile, the polarization along the CNT increases the SB height for holes in the passivated source contact. As a result, n-type conduction is observed in air. Once the adsorbed oxygen is removed from the drain contact in vacuum, the polarization effect fades away and the hole injection from the source contact is no longer suppressed. Thus, the device exhibits an ambipolar characteristic with stronger hole conduction. In contrast, for CNTFETs with Au and Ti¹²³ or Pd and Al¹²⁴ top contacts in air, as oxygen molecules adsorb at both the source and drain contacts, no polarization along CNT would occur. Due to the negative charges from oxygen molecules, the hole SBs are lowered at both contacts, leading to enhancement of hole conduction. As a result, n-type characteristics were not observed in air. For comparison, we fabricated a Schottky diode with Au and Al contacts (Device D4), in which the CNT was placed on top of the Au electrode on one side and embedded inside Al contact on the other side.¹²⁵ As illustrated in Fig. 5.14, a CNT is embedded underneath the Al drain contact but on top of Au source contact. It is reasonable to assume that the drain CNT/Al contact is much less influenced by oxygen as compared to the source CNT/Au contact, and the dipole polarization along the CNT could still occur once positive charge induced at the source end of CNT by oxygen.

Fig 5.14 Schematic of our Au/Al Schottky diode.

In vacuum, Device D4 showed n-type characteristic (See Fig. 5.15a), implying that the electron barrier at the Al drain contact is smaller than the hole barrier at the Au source contact for $V_{DS} < 0$. At $V_{DS} > 0$, electrons from the source ($I_{e,s}$) could tunnel through the thin barrier and the device would still be n-type, of course, with much smaller current. After Device D4 was placed in air, oxygen could reduce the SB height for holes at the Au contact. However, since the CNT/Al intimate contact is less affected by oxygen in comparison with the CNT/Au contact, the dipole polarization could still occur along the CNT and reduce the SB height for electron at the Al contact. As a result, the n-type performance remained in ambient. The decrease in the magnitude of electron current could be explained by the unfavorable bending at the drain contact. As illustrated in Fig. 5.15b, the increase of Au work function, however, decreases the electron current from the source, and the device becomes insulating at $V_{DS} > 0$.

Fig 5.15 Output characteristics of Device D4 (a) at $P=7\text{mTorr}$ and (b) in air. Insets: schematic energy band diagrams at $V_{GS}=20\text{V}$, $V_{DS}=0\text{V}$.

5.7 Conclusions

In this chapter, we have investigated the gaseous interactions in CNTFETs with a selective Si_3N_4 passivation technique and the findings are as summarized as followings:

1. Air stable n-type CNTFETs is prepared by coating the source and drain CNT/Au contacts with Si_3N_4 thin film, suggesting that the dominant mechanism for environmental oxygen effect is to modulate SB in our devices.
2. A tunable Schottky diode is fabricated by passivating only the source contact of a CNTFET with Si_3N_4 thin film. Interestingly, the device shows n-type characteristic in air but p-type in vacuum, which is not expected from conventional understanding of CNT/metal contacts.
3. A novel model is therefore developed for the CNT/metal contacts, in which the electrostatic charge balance across the contact and the dipole polarization along the CNT are appropriately taken into consideration. Our model shows that under the influence of the negative charges from adsorbed oxygen molecules at the interface, an upward band bending is induced in the CNT, and the work function of the metal electrodes is effectively increased.
4. We show that our model can be applied to Schottky diodes with asymmetric metal contacts. We found that only for those CNTFETs with one of the two CNT/metal contacts protected, the dipole polarization effect can be observed and becomes important to determine the conduction type of the devices.

Chapter 6

Real-time Gas Sensors using CNTFETs

6.1 Introduction

Although much attention has been paid to integration of CNT devices^{97,98}, it is well agreed that at current stage, a possible application is individual electronic devices containing CNTs as their key element for sensing purpose.¹²⁶⁻¹²⁹ In addition to a small diameter, an extremely large surface to volume ratio makes CNT a suitable material for nanoscale chemical sensing. The advantages of miniaturized chemical or biological sensors using CNT includes:¹²⁶ (1) great adsorptive capacity due to a large surface area to volume ratio; (2) great modulation of electrical properties upon exposure to analytes due to strong interaction over the CNT walls; (3) easy configuration as chemiresistor and FETs and potential integration with low-power microelectronics to form a complete system with microprocessor and wireless communication units. While commercial metal-oxide sensors usually operate at temperatures above 200°C, CNT sensors show the ability of room temperature detection. In 2000, Kong *et al.* demonstrated the first CNT based gas sensors, in which the conductance change of CNT in response to detecting

gases was used as a gauge.⁷¹ Since then, many types of CNT-based chemical sensors have been demonstrated. CNT networks,¹³⁰ functionalized CNTs,⁷³ CNT and polymer composites,¹³¹ etc. are used as sensing elements. These sensors are typically operated under 2-terminal conditions and thus their performances are not tunable, so that further flexible and reliable applications of the CNT sensors are constrained. In this chapter, we demonstrate that our CNTFETs-based NH_3 sensors under 3-terminal conditions have excellent sensing performance and their sensitivity and reversibility can be modulated through gate biases.

6.2 Experimental details

The fabrication processes of our CNTFETs are as described in Chapter 4. As shown in Fig. 6.1, a CNT was laid on top of Au source and drain electrodes at the contact areas. Such CNTFETs have top-contact and bottom-gated configurations, which is very suitable for gas sensing purpose. The as-prepared CNTFETs showed p-type characteristic with a hysteresis window (see Fig. 6.2). It is well accepted that this p-type feature could result from the SB at the Au-CNT contacts. As the contacts are exposed to air, the barrier is easily influenced by adsorbates,^{100,132,133} so that the characteristics of CNTFETs are greatly affected. To remove remaining surfactants for a clean channel,¹⁰⁷ the device was first soaked in DI water overnight and then annealed at 200°C for 2 h in dry air environment to desorb water molecules. These treatments can effectively reduce the resistance of the CNT/Au contacts and to eliminate humidity effect, so that I_{DS} (at $V_{\text{GS}}=-$

8V) was increased by 33% and the hysteresis was significantly reduced, as shown in Fig. 6.2.

Fig 6.1 Schematic (upper) and AFM image (lower) of a CNTFET.

Fig 6.2 Transfer characteristics of the CNTFET before and after soaking and annealing treatment. The arrows indicate the sweeping direction of gate voltage.

After the device fabrication, it was placed in a gas testing chamber with 0.5L capacity. Figure 6.3 shows the setup of our gas sensor system. Dry air or pure N_2 are used as background gas. The total flow rate into the chamber was fixed at 500sccm, and the detection range of the chemical gases was 10-500ppm. The sensing temperature was set through a temperature controller with a thermocouple near the sample surface. The humidity level was adjusted through the ratio between dry and wet air (passing the dry air through a water tank). In the following experiments, the CNTFETs were first stabilized in dry air environment, followed by exposure to chemical gas. After that, the samples were purged with dry air to monitor the recovery process, before they were annealed at 200°C for full recovery. NH_3 and NO_2 , being typical reducing and oxidizing gases, respectively, were chosen for this study.

Fig 6.3 Schematic of our gas sensor system

6.3 Results and Discussion

6.3.1 Current stabilization

It was observed that I_{DS} took a long time to be stabilized in dry air environment and changes in I_{DS} showed opposite trends under positive and negative gate biases, as shown in Fig. 6.4(a). A careful comparison suggests that this time-scale instability of I_{DS} is associated with gate-induced trapping process¹³⁴, rather than electrical heating¹³⁵ at the contacts. To confirm this, we first kept a constant $V_{GS}=+8V$ and compared I_{DS} under a constant $V_{DS}=0.2V$ and an intermittent V_{DS} with a pulsed waveform shown with the dotted windows in Fig. 6.4(b). Negligible heating was generated under the intermittent

V_{DS} , in comparison with the case of the constant V_{DS} . The values of I_{DS} for both cases were found comparable. Moreover, quite stable values of I_{DS} were observed when intermittent V_{GS} of +8V was applied. Therefore, the instability of I_{DS} should not be attributed to the electrical heating at the contacts. It could be resulted from the carrier trapping-induced screening effect.¹⁰⁸ Carriers injected from the channel to surrounding dielectrics are likely to screen the channel from the gate potential, resulting in the observed instability in the conductance.

Fig 6.4 (a) Stabilization processes of I_{DS} at $V_{GS} = +8V$ and $V_{GS} = -8V$; (b) influences of constant and intermittent biases on I_{DS} .

6.3.2 Gate modulated sensitivity

Upon introduction of 500ppm NH_3 , I_{DS} decayed over the sensing interval marked in Fig. 6.5. Under $V_{GS} = -8V$, I_{DS} dropped from 48.5nA to 3.3nA, yielding a sensitivity of

$\Delta R/R = 2.74\%$ per ppm. In contrast, a much higher sensitivity of 178.5% per ppm was obtained under $V_{GS}=+8V$.

Fig 6.5 Responses of I_{DS} to NH_3 exposure and recovery process at $V_{GS}=+8V$ and $V_{GS}=-8V$.

The interaction of NH_3 and CNTFET could be direct and/or indirect. On one hand, NH_3 may donate electrons to the CNT channel and decrease hole concentration in the channel. However, this charge transfer is generally believed to be very weak,^{71,136,137} which fails to explain the high sensitivity obtained in our experiment. On the other hand, our CNTFETs are essentially the Schottky barrier FETs with exposed CNT/Au contacts. Carriers injected into the CNT channel have to overcome the Schottky barrier formed at the Au-CNT interface, by means of thermionic emission and/or tunneling.¹³⁸ As

illustrated in Fig.6.6, a negative gate bias bends the energy band of the CNT upwards. Due to a thin barrier width, holes could tunnel through the barrier and enter the CNT channel easily. Thus, tunneling current would dominate I_{DS} . When a positive gate bias is applied, the CNT's energy band is bent downwards and hole tunneling is suppressed. I_{DS} would mainly consist of the thermionic emission current, which depends exponentially on the barrier height at the contact interface. When NH_3 gas molecules were adsorbed at the Au-CNT contacts, the work function of the Au electrodes was found to reduce.¹³⁹ Under $V_{GS}=-8\text{V}$ (at which I_{DS} saturates, see Fig. 6.2), this reduction may not increase the hole tunneling barrier width very much. However, at $V_{GS}=+8\text{V}$, a small increase in the barrier height could greatly block the thermionic emission process and lead to an exponential drop in I_{DS} . In this case, a very high sensitivity was obtained.

Fig 6.6 Energy band diagrams at the Au-CNT contacts for (a) $V_{GS}=+8\text{V}$ and (b) $V_{GS}=-8\text{V}$, respectively. In both cases, NH_3 reduces the work function of Au so that the Fermi level of Au shifts upward from solid lines to dashed ones, correspondingly.

Figure 6.7 shows in detail that at $V_{GS}=+8V$, the current decayed exponentially within the first 200s after NH_3 introduction. If we attribute this quick decay to barrier modulation and fit it as $I_{DS} = I_0 \exp(-t/\tau)$, we can obtain the $\tau=32.8s$ for $V_{GS}=+8V$, which can be considered as the response time of the Schottky barrier modulation in our experiments. At the same time, the thermionic emission current can be expressed as $I_{DS} \sim T^2 \exp(-q\phi_B/K_B T)$, where T is the temperature in Kelvin, ϕ_B is the Schottky barrier height and K_B is Boltzmann's constant. The barrier change $\Delta\phi_B$ due to NH_3 adsorption is found to be 154.2meV. For $V_{GS}=-8V$, a larger $\tau=58.6s$ and a smaller $\Delta\phi_B=86.3meV$ are obtained, due to the existence of tunneling current.

Fig 6.7 Exponential fitting of current decays during the sensing interval.

From $S = \Delta R / R_0 \approx \exp(q\Delta\phi_B / K_B T) - 1$, we predict that the sensitivity would degrade as the temperature rises. Table 6.1 summarizes the response of the CNTFET to

NH₃ at three temperatures under the conditions of $V_{DS}=0.1V$ and $V_{GS}=+8V$. The change in Schottky barrier height ($\Delta\phi_B$) is estimated to be 154.2meV, 45.5meV and 43.3meV at 20°C, 100°C and 150°C, respectively. The decreasing $\Delta\phi_B$ can be attributed to less ammonia adsorption at higher temperatures. Since thermally assisted tunneling probably occurs at elevated temperatures, we may underestimate the $\Delta\Phi_B$ for the cases of $T=100^\circ C$ and $T=150^\circ C$.

Temperature (°C)	20	100	150
Pre-exposure I_0 (nA)	13.4	24.3	85.2
Post-exposure I_{DS} (nA)	0.015	5.91	26.0
S (% per ppm)	178.5	0.62	0.46
Extracted $\Delta\Phi_B$ (meV)	154.2	45.5	43.3

Table 6.1 Performance of CNTFET NH₃ gas sensor at various temperatures. The CNTFET is biased at $V_{DS}=0.1V$ and $V_{GS}=+8V$.

6.3.3 Gate modulated reversibility

Another interesting phenomenon is the gate induced recovery processes, as shown in Fig. 6.5. After terminating the introduction of NH₃, the NH₃ concentration was decreased immediately due to pumping out. I_{DS} at $V_{GS}=-8V$ showed no apparent recovery within 5 h. This is consistent with other reports, in which it usually takes more than 12 h for CNT-based gas sensors to recover at room temperature. In contrast, I_{DS} at $V_{GS}=+8V$

recovered quickly. This indicates that, the reversibility of our CNTFET sensors can be significantly enhanced by electrical means at room temperature.

The different recovery rate can be interpreted in terms of the desorption energy barrier of NH_3 molecules. Novak and co-workers reported that a positive gate bias could sufficiently lower the desorption energy barrier for dimethyl methylphosphonate on SWNT networks.¹⁴⁰ Our observation of I_{DS} recovery is consistent with their suggestions. The binding energy between NH_3 and the gold surface is strongly related to the adsorption geometry. With nitrogen facing the gold surface, the binding energy is found to be -0.32eV , in comparison with -0.09eV in the flipped case with hydrogen facing the gold surface, as illustrated in Fig. 6.8.¹³⁹ From our experimental results, it is possible that the gate electric field may alter the orientation of adsorbed NH_3 molecules and the binding energy could be reduced under positive gate voltages. Slow recovery is always a practical problem for real-time CNT sensors. To obtain quick recovery, high temperature annealing⁷¹ or UV exposure⁷³ are typically employed. The fact that a positive gate bias can promote a fast recovery suggests that room temperature reversible CNT NH_3 sensors are feasible.

Fig 6.8 Illustration of NH_3 orientations in favored and flipped case with different binding energy to Au surface.

6.3.4 Humidity effect

Water molecules play an important role in affecting the performance of CNTFETs. On one hand, it was found to be the main cause of hysteretic behavior of the transfer characteristic for CNTFETs.^{69,111} Vijayaraghaven *et al.* investigated the temperature dependence of the hysteresis and suggested that water molecules could trap carriers injected from CNTs. The carrier trapping process in the surrounding dielectrics formed by adsorbed water and other gas molecules could screen the applied gate electric field.¹⁰⁸ On the other hand, water molecule was also suggested to enhance the adsorption of NH_3 on CNTs. It is believed that NH_3 could be first dissolved in the water layer adsorbed on the CNTs and then charge the CNTs.¹⁴¹

In order to fully understand the effects of humidity, we first investigated the current stabilization process at different humidity levels. Another CNTFET was used in this experiment, which was biased at $V_{\text{DS}}=10\text{mV}$ under two gate voltages of 20V and -20V, respectively. Consistent with previous studies in Chapter 4, I_{DS} typically increased with time at a positive V_{GS} , while it decreased at a negative V_{GS} , see Fig.6.9. These observed I_{DS} – humidity relations can be attributed to the charge trapping process.¹⁰⁸ When charges were trapped in the adsorbed water molecule layer surrounding the CNTs, they could partially screen the applied gate electric field so that the CNTFETs became less depleted or less accumulated for gate voltages of 20V and -20V, respectively. In other words, the charge-injection-induced screening could lower the effective gate electric field and this is reflected in the change of I_{DS} . As shown in Fig. 6.9, larger changes in I_{DS} were observed at higher humidity levels. Water molecules are known

significant charge traps in CNT devices.^{69,111} Increase of humidity leads to the enhanced trapping process and weaker gate control so that the temporal change in I_{DS} becomes more severe.

Fig 6.9 Transient behavior of I_{DS} in background gas with different humidity levels for (a) $V_{GS}=20V$ and (b) $V_{GS}=-20V$, respectively.

We have shown in previous sections that proper positive gate voltages could increase the sensitivity of CNTFET-based NH_3 gas sensors. In the following humidity test, a 20 V gate voltage was applied to the CNTFETs. The sample was firstly allowed to stabilize in the background gas for 5000s, and was then exposed to 200ppm NH_3 or 50ppm NO_2 for 1000s, respectively. After an annealing process for full recovery, the measurement was repeated at different humidity levels. Fig. 6.10 shows the response to 200ppm NH_3 at three humidity levels. The sensitivity $S = \Delta R / R_0$ was 223%, 22% and 9.7% for humidity levels at 0%, 20% and 40%, respectively. The degradation of the sensitivity due to humidity can be attributed to the weakening of the gate modulation. In our devices, the metal-CNT contacts were fully exposed to NH_3 gas molecules and the influences could mainly result from the Schottky barrier modulation at the contacts. Yamada predicted that the barrier modulation is significant when the CNT channel is depleted.¹¹⁰ This is consistent with our experimental observations. Actually, when positive gate voltages were applied, the tunneling current through the contact was greatly reduced, leaving the device in depletion mode. A small Schottky barrier modulation by the gas molecules could lead to a large variation in the sensitivity. As increase in humidity level weakens the gate control, a decrease in sensitivity is expected. In addition, it is also possible that at higher humidity levels, water molecules occupy most of the adsorption sites in the CNT device, making it difficult for NH_3 to adsorb. In this sense, humidity would also decrease the sensitivity of NH_3 detection. More importantly, our experiments showed that the indirect interaction of NH_3 and CNTs was not enhanced by water molecules. Instead, the CNTFET was less influenced by NH_3 under higher

humidity. A similar sensitivity-humidity relationship was also observed for NO_2 detection. For instance, the sensitivity of the sample to 50ppm NO_2 was 282%, 200% and 184% at humidity levels of 0%, 40% and 80%, respectively. As humidity was increased, the decrease in NO_2 sensitivity was not as significant as that for NH_3 , suggesting that NO_2 adsorption is more stable than NH_3 at high humidity levels.

Fig 6.10 Sensitivity of CNTFET biased at $V_{GS}=20\text{V}$ to 200 ppm NH_3 at the three humidity levels.

6.3.5 Temperature effect

Commercially available metal-oxide sensors typically operate at elevated temperatures above 200°C . Our CNTFET-based NH_3 sensors are of excellent sensitivity even at room temperature. Fig. 6.11a shows the response of one CNTFET to 50ppm NO_2 at 4 different temperatures from 20°C to 150°C . The sensitivity decreases with increasing

temperatures. It has been recently reported that no NO₂ adsorption was observed on CNTs for $T > 200\text{K}$ using high-energy resolution core level photoemission spectroscopy.¹⁴² The mechanism of NO₂ sensing could be attributed to the contact barrier modulation,¹¹³ especially for the devices with unpassivated metal/CNT contacts. The work function of Au was increased due to NO₂ adsorption and a smaller Schottky barrier was obtained for hole injection. In this context, a large positive gate voltage of 20V could suppress the tunneling current and I_{DS} should be dominated by thermionic current, $I_{DS} \sim T^2 \exp(-q\phi_B / K_B T)$, as $S = (I'_{DS} - I_{DS}) / I_{DS0} = \exp(-q\Delta\phi_B / K_B T) - 1$. From the inset of Fig. 6.11a, $\Delta\phi_B$ is reduced by a factor of 2.6 from 20°C to 150°C. This phenomenon is understandable since adsorption of NO₂ on Au involves an activation process and it becomes significantly small at high temperatures within the same testing period, in comparison with that at room temperature, leading to a small $\Delta\phi_B$. In other words, the decrease in the sensitivity with temperature should arise from two aspects, namely, the exponential dependence of sensitivity on $1/T$ and a declining $\Delta\phi_B$. From Fig. 6.11b, the current during NO₂ exposure fits well with: $I_{DS} = I_{DS-SAT} - \Delta I_{DS} \exp(-t/\tau)$, where I_{DS-SAT} is the saturation current, ΔI_{DS} is the total current change and τ defines the current response time. Table 6.2 summarizes the values obtained at various temperatures. Although the exposure time was fixed at 1000s in the experiments, I_{DS-SAT} allows us to predict the current level for a long time exposure and the maximum sensitivity S_{MAX} to 50ppm NO₂ can be calculated by $\Delta I_{DS} / (I_{DS-SAT} - \Delta I_{DS})$ (See Table 6.2). The response time τ depicts the gas adsorption rate at the metal-CNT contacts, which is an intrinsic property

of the device to a specific gas at a given temperature. An increasing τ with temperature is probably due to fast desorption of NO_2 at higher temperatures.

Fig 6.11 (a) Response of I_{DS} to 50ppm NO_2 at various temperatures. Inset: $\Delta\phi_B$ as a function of temperature; (b) Exponential fittings of I_{DS} during 1000s NO_2 exposure at

various temperatures. Open symbols are the experimental data and solid lines are fitted curves.

T (°C)	20	50	100
I_{DS-SAT} (nA)	60.2	67.1	81.7
ΔI_{DS} (nA)	51.92	42.92	45.83
τ (s)	210.4	238.4	396.0
S_{MAX} (%)	627.1	177.5	127.8

Table. 6.2. The constants extracted by fitting current $I_{DS} = I_{DS-SAT} - \Delta I_{DS} \exp(-t/\tau)$ at different temperatures.

6.4 Conclusions

We have systematically studied the sensing performance of CNTFET-based real-time gas sensors. The conclusions include:

- a proper positive gate voltage could enhance the sensitivity of CNTFET gas sensors, and also significantly accelerate the recovery process at room temperature. Our results suggest that tunable CNT gas sensors can be realized by adjusting the gate voltage;
- the temporal responses of I_{DS} suggest that an increase of humidity level could weaken the gate control and reduce the sensitivities to NH_3 and NO_2 . A larger

gate voltage is required to operate the CNTFET gas sensors in a more humid environment;

- the sensitivity of CNTFET gas sensor decreases significantly as temperature increases from room temperature to below 150°C.

Chapter 7

Sensing Mechanisms of Carbon Nanotube based NH₃ Detection

7.1 Introduction

Although tremendous progress has been made in CNT based gas sensing applications, the underlying sensing mechanism still remains unclear. Previously proposed mechanisms include the indirect interaction through the hydroxyl group on SiO₂ substrate⁷¹ or pre-adsorbed water layer,¹⁴¹ adsorption of gas molecules at the interstitial sites in the CNT bundle,¹⁴³ direct charge transfer from the adsorbed gas molecules to CNT,¹⁴⁴ and modulation of the SB at CNT/metal contacts,¹¹⁹ etc. Until now, there has been no unifying work able to identify the mechanisms. Furthermore, in order to optimize the CNT sensor for practical applications, it is important to understand whether the sensing signals are from the CNT channel and/or the CNT/metal contacts. Using a short-

channel device with passivated CNT/metal contacts by thermally evaporated SiO_2 , Bradley *et al.* found a good sensitivity to NH_3 and suggested that NH_3 mainly interacts with the CNT channel.¹¹⁵ Zhang *et al.* argued that when the passivation length was comparable to the depletion length in the CNT, the contacts could be indirectly affected. In their work, polymethylmethacrylate (PMMA) was applied to protect the CNT/metal contacts from NO_2 exposure and their devices became insensitive after contact passivation.¹¹³ Interestingly, Liu *et al.* also employed PMMA as a passivation layer. They observed changes in the transfer characteristics upon exposure to NH_3 and NO_2 for both contact-passivated device and channel-passivated devices, suggesting that both the CNT channel and the CNT/metal contacts play a role in the detection process.¹¹² The obvious ambiguity in those reports could arise from the permeable passivation materials used. Moreover, as the experiments were carried out at room temperature and air ambient only, exclusive identification of the sensing mechanisms is not possible.

In this chapter, we differentiate the sensing mechanisms using a selective Si_3N_4 passivation technique. The sensing signals from the CNT channel and CNT/metal contacts are truly distinguished. Strikingly distinct sensing performance at various testing conditions is observed. From our results, a clear understanding of gaseous interactions in a CNT sensor FET geometry is obtained.

7.2 Experimental details

SWNTs were aligned between Ti/Au source and drain electrodes predefined on a p-type silicon wafer using an ac DEP technique, which is simple and cost effective, and suitable for CNT sensor fabrications. Note that the CNTs in this work are on top of Au electrodes and the contact regions are fully accessible to the ambient. A heavily doped Si wafer with a 200 nm thick thermally grown SiO_2 layer on top was used as the gate. These devices are typically SB-CNTFETs. As illustrated in Figure 7.1, three device structures were employed in our experiments: (1) an as-prepared CNTFET with the exposed CNT channel and CNT/Au contacts; (2) only the contacts passivated with 500nm Si_3N_4 layer and (3) only the channel passivated with 500nm Si_3N_4 layer. Dry air was used as the background gas with a flow rate of 500sccm in the following experiments unless otherwise stated. NH_3 gas was selected as the detecting species to study the sensing mechanisms of the CNT sensors. The total channel length, passivation length at both contacts and the CNT length are 6 μm , 1.5 μm and 3 μm , respectively.

Fig 7.1 Schematics for (a) Device 1: As-prepared CNTFET; (b) Device 1A: the contacts passivated by Si_3N_4 and (c) Device 2: the central CNT channel passivated by Si_3N_4 .

7.3 Results and Discussion

7.3.1 NH_3 sensing at room temperature

An as-prepared CNTFET (Device 1) showed a sensitive response to small concentrations of NH_3 at room temperature (see Figure 7.2a). It is seen that, under a positive gate voltage, both the sensitivity and reversibility were much higher than those under a negative one, consistent with our previous findings in Chapter 6.

Fig 7.2 Real-time detection of NH_3 at room temperature under various gate voltages (a) before (Device 1) and (b) after the contacts passivation (Device 1A), respectively. Inset: an atomic force microscope (AFM) image of Device 1A after the passivation.

In order to experimentally differentiate whether the sensing responses are from the CNT channel and/or the CNT/Au contacts, we passivated the CNT/Au contacts of Device 1 with a Si_3N_4 thin film, leaving the CNT channel open. After the passivation, we found that the device (Device 1A) did not respond to NH_3 at room temperature, even at a concentration up to 500ppm, as shown in Fig. 7.2b. For comparison, we only passivated the CNT channel with Si_3N_4 thin film in another CNTFET (Device 2), but uncovering the CNT/Au contacts. Interestingly, Device 2 showed a high sensitivity at room temperature (see Fig. 7.3). Therefore, we can unambiguously conclude that NH_3 gas induced SB modulation is a dominant mechanism for our CNT gas sensors at room temperature.

Fig 7.3 Sensing response of Device 2 at room temperature. Inset: AFM image of Device 2 with central channel passivated.

Actually, PMMA was widely employed as a passivation material to protect the CNT/metal contact regions for gas^{112,113} and protein sensing¹¹⁴. However, two major problems exist due to the polymer nature of PMMA. Firstly, PMMA is not dense enough

to fully passivate the contacts. For example, NO_2 was found to penetrate the $2.2\mu\text{m}$ thick SU-8/PMMA layer in 30mins.¹¹³ Thus, the CNT/metal contacts are inevitably affected by the gradual diffusion of the detecting species through the PMMA layer, so that the role of the contact in the detection could not be eliminated. Secondly, PMMA is thermally unstable above 100°C . This is a critical limitation as the adsorptions of some biomolecules and gas molecules on CNTs are enhanced at high temperatures. In contrast, Si_3N_4 is much denser and it can completely insulate the contacts from chemical environment.¹¹⁶ Meanwhile, its thermal stability allows for high temperature sensing experiments, as shown later.

7.3.2 NH_3 sensing at elevated temperature

The transfer curves of Device 1A before and after exposure to 500ppm NH_3 for 1000s are monitored at $T=25^\circ\text{C}$, $T=50^\circ\text{C}$ and $T=100^\circ\text{C}$ in Fig. 7.4 (a), (b) and (c), respectively. No significant change in gate characteristics was observed. We suggest that, the adsorption of NH_3 on the CNT is not favored at this temperature range.

Fig 7.4 Transfer characteristics of Device 1A with contacts passivated before and after exposure to NH₃ at (a) T=25°C, (b) T=50°C and (c) T=100°C respectively.

The transfer curve started to shift towards negative gate voltage after NH₃ exposure at 150°C and above, see Fig. 7.5a. Since the contacts were fully isolated from NH₃, this parallel shift in the transfer curve suggests that NH₃ could adsorb on the CNT wall and donate electrons to the CNT. Consequently, the Fermi level of the CNT moves towards the conduction band edge so that the threshold voltage V_{TH} becomes more negative. When the testing temperature reached 200°C, this phenomenon became more prominent. Progressive shift of the transfer curve in accordance with NH₃ concentrations is shown in Fig. 7.5b. Under a first order estimation, the total charge transferred $\Delta Q = C_G \Delta V_{TH}$, where the gate capacitance $C_G = \frac{2\pi\epsilon\epsilon_0 L}{\cosh^{-1}(h/r)}$,⁹⁶ the SiO₂ dielectric constant $\epsilon=3.9$ and thickness $h=200\text{nm}$. For a SWNT bundle with a length $L\sim 5\mu\text{m}$ and a radius $r\sim 5\text{nm}$, $C_G\approx 0.25\text{ fF}$. Thus, ΔQ is approximately 0.625fC or about

4000 electrons, at 200°C with $\Delta V_{TH} = 2.5V$ for 500ppm NH₃. If the cross-sectional area of NH₃ $A \sim 0.13\text{nm}^2$, the length of the exposed CNT channel $L' \sim 3\mu\text{m}$, the coverage $\theta \sim 0.07$ (interpolated from the Langmuir plot for 500ppm NH₃ on CNT¹¹), the charge transfer rate $f \approx \Delta QA / q\theta\pi L'$ is about 0.02 electron per adsorbed NH₃ molecule. This value is reasonably consistent with typical theoretical predictions.^{121,122}

Fig 7.5 The transfer characteristics for Device 1A with the contacts passivated before and after exposure to NH₃ at (a) T=150°C and (b) T=200°C, respectively.

The extracted sensitivity $S = \Delta R / R_0$ of Device 1 and Device 1A under three gate voltages at T=25°C are shown in Fig. 7.6a. For Device 1, a very high sensitivity and significant gate modulation were observed. When the gate voltage is varied from negative to positive, the dominant carrier injection process changes from tunneling to thermionic emission, and the source-drain current becomes very sensitive to the SB height. A small change in the contact SB height due to NH₃ adsorption will be prominently reflected in the source-drain current. Our device structure with a CNT on top of metal electrodes could also enhance the SB modulation effect. Once the contacts passivation is carried out in Device 1A, it essentially does not respond to NH₃, implying that the CNT channel is not active to NH₃ at room temperature. Figure 7.6b compares the sensitivities for Device 1A and Device 2 at T=150°C. At small NH₃ concentrations, a low coverage of NH₃ on the CNT channel and poor charge transfer efficiency result in a small sensitivity in Device 1A. When the NH₃ concentration is increased, the sensitivity for Device 2 becomes saturated, probably due to limited interaction area in the CNT/Au contacts.

Fig 7.6 Extracted sensitivities for (a) Device 1 and Device 1A at $T=25^\circ\text{C}$; (b) Device 2 and Device 1A at $T=150^\circ\text{C}$, respectively.

7.3.3 Effect of oxygen on NH_3 sensing

Theoretical studies suggest that, NH_3 interacts weakly with pristine CNTs with little charge transfer.^{71,137,145} Existence of a large activation barrier prevents adsorption of NH_3 on perfect CNTs even at high temperatures. However, the adsorption of the gas molecules on defective CNTs could be much easier.^{146,147} In addition, the adsorption barrier of NH_3 on a defective CNT can be further lowered by pre-dissociated oxygen atoms, leading to an enhanced charge transfer rate, as pointed out by Andzelm *et al.*¹⁴⁸ In order to study the influences of oxygen on NH_3 adsorption onto the CNT wall, we changed the background gas from dry air to N_2 . Device 1A was first annealed in N_2 environment at 350°C for 2 hrs to degas the adsorbed oxygen. Note that during the high-temperature annealing, remaining oxygen molecules at the contacts were further desorbed and the device became more n-type. The transfer curves before and after exposure to 500ppm NH_3 for 1000s from $T=25^\circ\text{C}$ to $T=150^\circ\text{C}$ are shown in Fig. 7.7, and real-time sensing results at $T=200^\circ\text{C}$ are shown in Fig. 7.8. No detectable changes due to NH_3 exposure were observed. Comparing with the sensing response observed in dry air environment, we can confirm that the adsorption of NH_3 is facilitated by environmental oxygen. It was also found that the sensitivity was restored after the background was changed to dry air again. Our results are consistent with Andzelm *et al.*'s predictions. NH_3 could preferentially attach to the defect sites on CNT with pre-dissociated oxygen, as illustrated in Fig. 7.9.

Fig 7.7 Transfer characteristics of Device 1A in N_2 before and after exposure to NH_3 at (a) $T=25^\circ\text{C}$, (b) $T=50^\circ\text{C}$, (c) $T=100^\circ\text{C}$ and (d) $T=150^\circ\text{C}$ respectively.

Fig 7.8 Response of I_{SD} to various concentrations of NH_3 in N_2 at $T=200^\circ\text{C}$ for Device 1A.

Fig 7.9 Schematic of NH_3 adsorption on Device 1A. Here, we illustrate a NH_3 molecule adsorbs on a CNT with Stone-Wales defect with pre-dissociated oxygen atoms, as suggested in Ref. 148.

7.3.4 Comparisons of the sensing mechanisms in CNT based gas sensors

From our results, we are able to rule out several possibilities of indirect interactions between NH_3 and CNT. Firstly, as the testing environment was totally dry, NH_3 adsorption through a water layer is not applicable here. Secondly, if NH_3 could interact through the SiO_2 substrate or adsorb inside the CNT bundles, a reduced sensitivity should have been observed after the contacts passivation. However, as Device 1A is totally insensitive to NH_3 at room temperature, this hypothesis is not consistent

with our observation. Therefore, we suggest that charge transfer and the SB modulation are the two mechanisms in our CNT sensors.

At room temperature, the weak adsorption of NH₃ on the CNT wall does not induce any measurable effect on the source-drain current. The sensing signal mainly arises from the contacts, where NH₃ adsorption could reduced the work function of the Au electrode, leading to an increased SB for hole injection.. As illustrated in Figure 7.10b, when a negative gate voltage bends the energy band of the CNT upwards, the SB width becomes very narrow and holes could tunnel through the barrier, even when the SB height is increased by NH₃. In contrast, at a positive gate voltage, the SB width is too thick for hole tunneling. Thus, hole injection is only through thermionic emission over the SB height. The source-drain current is then expressed as:¹³⁸ $I_{DS} \sim T^2 \exp(-q\phi_B / K_B T)$, where ϕ_B is the Schottky barrier height, K_B is the Boltzmann's constant and T is the temperature in Kelvin. In this case, the sensitivity for the SB modulation is $S = \Delta R / R_0 \approx \exp(q\Delta\phi_B / K_B T) - 1$. Owing to the exponential dependence on the SB height change $\Delta\phi_B$, extremely high sensitivity can be achieved. Our results are consistent with Yamada's theoretical prediction that the SB modulation is most significant when the CNTFET is operating in the depletion mode.¹¹⁹

One disadvantage of the SB dominated sensors is a typical long recovery process at room temperature. Once the operating temperature is increased, the sensitivity degrades significantly due to its exponential dependence with $1/T$, as we discussed previously in Chapter 5. The nanoscale CNT/metal contacts could also be prone to subtle

environmental noises, causing fluctuations during detection. In contrast, using the CNT channel as a sensing element can avoid the problems. In addition, the large surface to volume ratio of CNT offers another merit. At $T > 150^\circ\text{C}$, when the adsorption barrier is further lowered by oxygen, NH_3 adsorption on the defect sites of the CNT becomes favored. Upon the consequent charge transfer, the Fermi level of the exposed central CNT channel moves upwards and the energy band shifts downwards with respect to those passivated parts, a potential barrier is therefore created and impedes the current flow, see Figure 7.10d.³¹ Here, we would like to emphasize that, the charge transfer effect can be studied only when the contacts are fully protected. Otherwise, as temperature increases, the sensitivity enhancement from the charge transfer effect and the degradation due to SB modulation counteract each other.

Fig 7.10 Schematic energy band diagram for: Device 1 (a) before and (b) after the NH_3 exposure (An intrinsic CNT is considered. The work function of the source/drain electrodes is initially near the valence band edge of the CNT and is reduced after NH_3 exposure); Device 1A (c) before and (d) after the NH_3 exposure (After passivation, the work function of electrodes aligns near the midgap of CNT. The Fermi level of the exposed central CNT channel shifts upwards due to electron-doping from NH_3). Legend: Red dotted for $V_{GS} < 0$; Green solid for $V_{GS} = 0$; Blue dashed for $V_{GS} > 0$.

Table 7.1 compares the SB modulation and charge transfer mechanisms. The sensors with the SB modulation usually demonstrate a high sensitivity at room temperature. Their sensing performance can be adjusted through the gate voltages. In contrast, the sensors under the charge transfer mechanism require high working

temperatures, showing a good reversibility. Functionalization techniques^{73,146} could be applied in order to enhance the sensitivity for this type of sensors.

Mechanism	SB modulation	Charge transfer
Sensitivity	Extremely high in depletion mode	Low
Gate dependence	Strong	Weak
Operating Temperature	Room temperature	T>150°C
Reversibility	Low, can be improved at positive gate voltage	Good

Table 7.1 Comparisons between sensors operated by SB modulation and charge transfer.

7.4 Conclusions

In summary, sensing mechanisms for CNT based NH₃ sensors have been systematically studied on a FET platform. We clearly show that the SB modulation at the CNT/metal contacts dominates the sensing performance at room temperature, and the sensor exhibits high sensitivity and good tunability under appropriate gate voltages. At higher temperatures, say 150°C or above, NH₃ molecules start to adsorb on the CNT wall and the charge transfer process from the adsorbed NH₃ molecules to the CNTs contributes to the sensing signal. NH₃ adsorption is confirmed to be facilitated by environmental oxygen.

Chapter 8

Conclusions and Future Work

8.1 Conclusions

In my Ph.D project, I began with analyzing AC DEP manipulation of CNTs and using this method to fabricate CNT devices with various structures. After that, I studied the gaseous interaction in CNTFETs with a selective passivation technique. I developed real-time gas sensors using CNTFETs and clearly identified the underlying sensing mechanisms. The main findings and conclusions can be summarized as followings:

8.1.1 AC DEP manipulation of CNTs

Manipulation of CNTs using AC DEP has been studied theoretically and experimentally. The motions of CNTs are analyzed in terms of AC DEP induced torque and force. Upon applying an external electric field, the CNTs in suspension will rotate to align with the electric field direction and translate along the gradient of electric field. Simulation results suggest that the time required for the rotational motion is much shorter

than that for the translational motion. This result is consistent with experimental observations, where good alignment of CNTs can be easily achieved in our devices. Owing to different dielectric properties, m-CNTs and s-CNTs could experience opposite DEP forces, and therefore can be separated from each other during the manipulation process. By varying electrode structures to adjust the electric field distribution, the location of CNTs can be controlled. Most of the CNTs will bridge the shortest gap across the electrodes.

8.1.2 Gaseous interactions in CNTFETs

Gaseous interactions in CNTFETs have been studied with a selective Si_3N_4 passivation technique. The CNTFETs with passivated source/drain contacts and uncovered CNT channel show stable n-type characteristics in air, suggesting that a dominant influence of environmental oxygen is to modulate the SB height at the CNT/metal contacts, rather than doping holes to the CNT channel. By passivating only the source contact of as-prepared CNTFETs, tunable Schottky diodes are achieved. The polarity and conduction type of the diode can be switched by applied gate voltages.

8.1.3 Novel model for nanoscale contacts between CNT and metallic pads

A novel model is developed for CNT/metal contacts, in which the electrostatic charge balance across the contact and the dipole polarization along the CNT are appropriately taken into consideration. Our model shows that under the influence of the negative charges from adsorbed oxygen molecules at the interface, an upward band

bending is induced in the CNT, and the work function of the metal electrodes is effectively increased. Using this model, the unique n-type characteristic of the CNTFET with passivated source contact is well interpreted by electron tunneling through V_{DS} -dependant drain SB. By applying the model to Schottky diodes with asymmetric metal contacts, we show that only for those CNTFETs with one of the two CNT/metal contacts protected, the dipole polarization effect can be observed and becomes important to determine the conduction type of the devices.

8.1.4 Real-time gas sensors using CNTFETs

The performance of CNTFETs based gas sensors has been systematically studied. A proper positive gate voltage could enhance the sensitivity of the CNTFET based NH_3 sensors by more than 50 times. It is also found that positive gate voltages could significantly accelerate the recovery process at room temperature. Our results suggest that tunable CNT gas sensors can be realized by adjusting the gate voltages. Increase of humidity level is found to weaken the gate controllability and reduce the sensitivities to both NH_3 and NO_2 . The sensing mechanisms for CNT-based NH_3 sensors have been distinguished by the selective passivation technique. We unambiguously show that the SB modulation at the CNT/metal contacts dominates the sensing performance at room temperature, and that the sensor exhibits high sensitivity and good tunability under appropriate gate voltages. At higher temperatures, say 150°C or above, NH_3 molecules start to adsorb on the CNT wall so that the charge transfer process contributes to the sensing signal. NH_3 adsorption is confirmed to be facilitated by environmental oxygen.

8.2 Future work

My Ph.D work focuses on fabricating individual CNTFET devices and studying the physics of gas sensors. Further development could investigate large-scale fabrication of CNTFETs and practical applications of CNT devices.

8.2.1 Improving the performance of CNTFETs

The performance of our current CNTFETs is still behind the state-of-art silicon devices due to following reasons: (1) the gate oxide is very thick ($>200\text{nm}$); (2) the CNT-metal contacts are non-ohmic; (3) the channel length is long ($>1.5\mu\text{m}$, limited by our optical lithography system). Thin gate oxide, or high- κ dielectrics could increase the gate efficiency and reduce the gate voltage required to operate the CNTFETs, making them more suitable for practical sensing applications. Another way is to employ advanced gate structures, for example, double-gate or surrounding-gate configurations. Ohmic contact could be achieved by embedding CNTs underneath metal electrodes and careful selection of metals. For example, Pd³⁴ and Sc³⁹ were reported to form ohmic contact with CNTs. E-beam lithography or “shadow evaporation” method can be used to fabricate CNTFETs with very short channel length.

8.2.2 Large-scale fabrication of CNTFETs using AC DEP technique

The location of CNTs across the electrodes by AC DEP technique is mainly determined by the electric field distribution. Therefore, through proper design of an

appropriate electrode pattern, alignment of CNTs across many paired electrodes can be achieved in one manipulation process. The concept is recently proven where CNT devices with an integration density of several million devices per square centimeter are obtained using AC DEP manipulation.¹⁴⁹ This greatly enhances the yield for CNT devices, suitable for low-cost CNT sensor fabrication.

8.2.3 Compact model incorporating the SB calculation

Our model for CNT-Au contact mainly focuses on the treatment of SB under the influence of oxygen and is not able to quantitatively estimate the channel current. Therefore, a compact model incorporating our SB-calculation into the calculation of total channel current is desirable. In order to achieve that, the mid-length CNT channel needs to be considered in the Landauer expression for a complete and self-consistent evaluation of the current, as suggested in Ref. 150

8.2.4 Metal nanoparticle decoration for sensitivity and selectivity enhancement

Our current CNT gas sensors have poor selectivity to different gases and are insensitive to hydrogen gas. Metal nanoparticle decoration¹⁵¹⁻¹⁵³ could be a promising way solving the problem. Our preliminary results showed that, after Au nanoparticle decoration, CNTFETs can detect 1000ppm H₂ easily at room temperature. The possibility

of combining several kinds of metal nanoparticle in one CNTFET or using array of CNTFETs to differentiate gas molecules can be further explored.

8.2.5 CNTFET based biological sensors

The CNTFET can also be employed to detect biological analytes. The findings we have obtained should be meaningful to biological sensors as well. The device structures can be readily applied, for example, we can passivate the source/drain contacts of CNTFETs and study the influence of gate voltages on the detection of certain biological stimuli.

Appendices

Appendix A: Induced effective moment of dielectric ellipsoid

The induced effective moment of a dielectric ellipsoid can be obtained by examining the limit of the electrostatic potential at a point far from the ellipsoid, where ellipsoidal coordinates degenerate into spherical conditions. Consider an ellipsoid with semi-axes a , b , c and dielectric permittivity ε_2 suspended in a fluid of permittivity ε_1 . The axis a is aligned with imposed electric field component E_x . The general solution for the electrostatic potential can be expressed as:

$$\phi_1 = \phi_0 + \frac{Z_2}{Z_1} \phi_0 \int_0^\infty \frac{ds}{(s+a^2)R_s} \quad (\text{A1})$$

Where $\phi_0 = -E_x r \cos \theta$, r and θ are, respectively, the polar angle and radial position in spherical coordinates, ξ is an elliptical coordinate, and $R_s = \sqrt{(s+a^2)(s+b^2)(s+c^2)}$.

Application of the boundary conditions provides a relationship between the coefficients Z_1 and Z_2 :

$$Z_2 = \frac{-\frac{abc}{2}(\varepsilon_2 - \varepsilon_1)Z_1}{\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)\frac{abc}{2}\int_0^\infty \frac{ds}{(s+a^2)R_s}} \quad (\text{A2})$$

Using Eqn. A1 and A2 with the depolarization factor L_x , and then taking the limit $\xi \gg a^2, b^2, c^2$ to reduce the elliptic integral, we obtain a simplified expression for the second term in Eqn. A1, the induced component of the electrostatic potential.

$$\phi_1^+ \approx \frac{\frac{abc}{2}(\varepsilon_2 - \varepsilon_1)(-E_x r \cos \theta) \int_\xi^\infty \frac{ds}{s^{5/2}}}{\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)L_x}$$

Far from the ellipsoid, $\xi = r^2$ and the induced potential reduces to:

$$\phi_1^+ \approx -\frac{\frac{abc}{3}(\varepsilon_2 - \varepsilon_1)E_x \cos \theta}{\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)L_x} \frac{1}{r^2} \quad (\text{A3})$$

As $\phi_1 = \frac{p_{eff} \cos \theta}{4\pi\varepsilon_1 r^2}$, we may now identify the x component of the effective dipole moment

due to the dielectric ellipsoid:

$$(p_{eff})_x \approx \frac{4\pi abc}{3}\varepsilon_1 \left[\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + (\varepsilon_2 - \varepsilon_1)L_x} \right] E_x \quad (\text{A4})$$

The other components of the effective moment, $(p_{eff})_y$ and $(p_{eff})_z$ are of similar form.

Appendix B: Detailed derivations for AC DEP torque and force on a CNT

For a prolate spheroid ($a \gg b=c$, which simulates the case of a CNT), we can decompose the electric field into paralleled and perpendicular direction with respect the a-axis.

Therefore we have

$$\vec{E}_0 = \vec{E}_{\parallel} + \vec{E}_{\perp}$$

Similarly, we can also decompose the effective moment into two components. Now the torque is expressed as:

$$\vec{T} = \vec{p}_{\parallel} \times \vec{E}_{\perp} + \vec{p}_{\perp} \times \vec{E}_{\parallel}.$$

$$\text{As } \vec{p}_{\text{eff}} = \frac{4\pi abc}{3}(\varepsilon_2 - \varepsilon_1)\vec{E}^-,$$

$$E_x^- = \frac{E_{0,x}}{1 + \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1} L_x}, \text{ where } L_x = \frac{r^2 l}{4} \int_0^{\infty} \frac{ds}{(s + \frac{a^2}{4})^{\frac{3}{2}} (s + r^2)}$$

We obtain

$$T = \frac{4\pi abc}{3}(\varepsilon_2 - \varepsilon_1) [E_{\parallel}^- E_{\perp} - E_{\perp}^- E_{\parallel}] \quad (\text{B1})$$

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

For a CNT in an external electric field, we decompose the effective momentum and electric field into parallel ($\vec{a}$) and perpendicular direction ($\vec{b}$), with respect to CNT's length. So we have:

$$\vec{p}_{eff} \approx \frac{\pi r^2 l}{2} \epsilon_1 K (E_{\parallel} \vec{a} + E_{\perp} \vec{b}) \quad , \quad \text{where} \quad K = \frac{(\epsilon_2^* - \epsilon_1^*)}{\epsilon_1^* + (\epsilon_2^* - \epsilon_1^*) L_{\parallel}} \quad \text{is the complex Clausius-}$$

Mossotti function, and $\epsilon_{1,2}^* = \epsilon_{1,2} + \frac{\sigma_{1,2}}{j\omega}$, ω is the frequency of applied electric field. ϵ_1 and ϵ_2 are the permittivity of the suspension medium and CNT; σ_1 and σ_2 are the conductivity of the suspension medium and CNT, respectively

$$\text{As } \vec{F} = \vec{p}_{eff} \bullet \nabla \vec{E} = \frac{\pi r^2 l}{2} \epsilon_1 K (E_{\parallel} \vec{a} + E_{\perp} \vec{b}) \bullet \left(\frac{\partial E_{\parallel}}{\partial x} \vec{a} + \frac{\partial E_{\perp}}{\partial y} \vec{b} \right) = \frac{\pi r^2 l}{2} \epsilon_1 K \nabla E^2$$

Now the time-dependant form of DEP force is expressed as:

$$\vec{F}(t) = \vec{p}_{eff}(t) \bullet \nabla \vec{E}(t) = \text{Re}[\vec{p}_{eff} \exp(j\omega t)] \bullet \text{Re}[\vec{E} \exp(j\omega t)]$$

The above equation indicate that the DEP force on a CNT in an AC electric field will consist of two components: a constant (average) term and a time-varying term. However, any motion due to the time-varying term is usually damped heavily by the viscosity of the suspension term, so that only the time-average term is important. Then we can have the time-average DEP force as:

$$\vec{F}_{DEP} = \frac{\pi r^2 l}{2} \epsilon_1 \text{Re}(K) \nabla E^2 \quad (3.12)$$

As the CNT length $l \gg$ radius r , $L_{\parallel} \sim 0$. $K = \frac{(\varepsilon_2^* - \varepsilon_1^*)}{\varepsilon_1^* + (\varepsilon_2^* - \varepsilon_1^*)L_{\parallel}} \approx \frac{\varepsilon_2^* - \varepsilon_1^*}{\varepsilon_1^*}$. If we

substitute $\varepsilon_{1,2}^* = \varepsilon_{1,2} + \frac{\sigma_{1,2}}{j\omega}$,

we have

$$\begin{aligned}
 K &= \frac{\varepsilon_2 + \frac{\sigma_2}{j\omega} - (\varepsilon_1 + \frac{\sigma_1}{j\omega})}{\varepsilon_1 + \frac{\sigma_1}{j\omega}} = \frac{j\omega(\varepsilon_2 - \varepsilon_1) + \sigma_2 - \sigma_1}{j\omega\varepsilon_1 + \sigma_1} = \frac{j\omega(\varepsilon_2 - \varepsilon_1) + \sigma_2 - \sigma_1}{\varepsilon_1^2 + \sigma_1^2} \\
 &= \frac{\sigma_1(\sigma_2 - \sigma_1) + \omega^2\varepsilon_1(\varepsilon_2 - \varepsilon_1)}{\varepsilon_1^2 + \sigma_1^2} + j\omega \frac{\sigma_1(\varepsilon_2 - \varepsilon_1) - \varepsilon_1(\sigma_2 - \sigma_1)}{\varepsilon_1^2 + \sigma_1^2}
 \end{aligned} \tag{3.13}$$

Author's Publications

1. **Ning Peng**, Hong Li and Qing Zhang, "Nanoscale contacts between carbon nanotube and metallic pads", *ACS Nano*, Accepted
2. **Ning Peng**, Qing Zhang, Chee Lap Chow, Ooi Kiang Tan and Nicola Marzari, "Sensing mechanisms for carbon nanotube based NH₃ gas detection", *Nano Lett.*, **9** 1626 (2009)
3. **Ning Peng**, Qing Zhang, Ooi Kiang Tan and Nicola Marzari, "Study of gaseous interactions in carbon nanotube field-effect transistors through selective Si₃N₄ passivation", *Nanotechnology*, **19** 465201 (2008)
4. **Ning Peng**, Qing Zhang, Yi Chau Lee, Hui Huang, Ooi Kiang Tan, Jingze Tian and Lap Chan, "Humidity and temperature effects on carbon nanotube field-effect transistor-based gas sensors", *Sensor Lett.*, **6** 796 (2008)
5. **Ning Peng**, Qing Zhang and Yongshun Sun, "Motion of carbon nanotubes in suspension under AC electric field", *Int. J. Nanomanufacturing*, **2** 50 (2008)
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