Electron transport in carbon nanotubes

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**NANYANG
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**ELECTRON TRANSPORT IN CARBON
NANOTUBES**

YUAN SHAONING

SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING

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Electron Transport in Carbon Nanotubes

Yuan Shaoning

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.

Date

Yuan Shaoning

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Table of Contents

Acknowledgments.....	i
Table of Contents	iv
List of Figures	vii
List of Tables.....	xiii
Summary	xiv
Chapter 1 Introduction	1
1.1 Motivation	1
1.2 Objectives.....	3
1.3 Major contributions of this thesis	4
1.4 Organization of this thesis	6
Chapter 2 Carbon nanotubes and carbon nanotube-based devices	8
2.1 Classification of carbon nanotubes.....	8
2.2 Structure of carbon nanotubes	8
2.2.1 Structure of SWNTs	8
2.2.2 Chiral Vector $\overline{C}_h$	9
2.2.3 Translational vector $\vec{T}$	11
2.2.4 Structures of DWNTs	11
2.3 Electronic structure of CNTs.....	12
2.3.1 Electronic structure of SWNTs.....	12
2.3.2 Electronic structure of DWNTs.....	19
2.4 Observations of carbon nanotubes	20
2.5 Development of CNT-based devices with FET structure	22
2.5.1 Improvement of the contacts between CNTs and metals	23
2.5.2 Gate structures and dielectric layers.....	24
2.5.3 Switching mechanisms of CNTFETs	25
2.5.4 Conduction types of CNTFETs: p-type, n-type and ambipolar.....	27
2.5.5 DWNTs-based CNTFETs.....	31
2.5.6 Applications of CNTFETs and some practical difficulties.....	33
Chapter 3 Experimental details.....	35
3.1 The carbon nanotubes used in this project	35
3.1.1 The SWNTs.....	35
3.1.2 The DWNTs	36
3.2 Fabrication of the CNTFETs	39
3.2.1 Suspension preparation	39
3.2.2 The Substrate and electrode preparation	39
3.2.3 AC dielectrophoresis technique ⁸⁴	40

3.2.4	Electrical breakdown (burn-off process) of CNTs	42
3.3	Device characterization	44
3.3.1	Imaging and topography of devices	44
3.3.2	Electrical measurement	45
3.3.3	In situ Raman scattering	46
3.3.4	Photoluminescence of CNTs	47
Chapter 4	Hysteretic transfer characteristics of CNTFETs	49
4.1	Literature review of hysteresis in CNTFETs	49
4.2	Research status of transfer characteristics of CNTFETs	61
4.3	Effects of surfactants on hysteretic transfer characteristics of SWNTs- and DWNTs-based FETs ⁹⁵	64
4.3.1	Device fabrication and experimental flow	65
4.3.2	Experimental results	67
4.3.3	Discussions of results	73
4.4	Conclusions	77
Chapter 5	In situ Raman scattering of a DWNT-based FET	80
5.1	Literature review on Raman scattering of CNTs	80
5.1.1	Introduction of Raman Scattering Processes	81
5.1.2	Resonant and non-resonant Raman scattering Processes	83
5.1.3	The radial breathing mode	85
5.1.4	Chiral index assignment using RBM	88
5.1.5	The high-energy mode (HEM), G Mode	93
5.1.6	D band and 2D band (G' band)	100
5.1.7	Antenna effect	102
5.1.8	Research status of Raman scattering for device level CNTs	103
5.2	General information of our CNTs	105
5.3	In situ Raman scattering of DWNT-FET	110
5.4	Correlation between in situ Raman scattering and electrical conductance of DWNT-FETs ¹⁵²	118
5.4.1	Correlation between in situ Raman scattering and electrical conductance for an individual double-walled carbon nanotube	119
5.4.2	Experimental details	119
5.4.3	Results and discussion	120
5.5	Effect of Si ₃ N ₄ passivation on the Raman features	126
5.6	In situ Raman scattering of bundled DWNTs on FET geometry	128
5.7	Conclusions	137
Chapter 6	Conclusions and Future Work	140
6.1	Conclusions	140
6.1.1	Hysteretic transfer characteristics of CNTFETs	140
6.1.2	In situ Raman scattering of a DWNT-based FET	141
6.2	Future work	142
6.2.1	Chemical sensors by DWNT-FETs	142
6.2.2	Raman characterizations of CNTFETs with novel structures	143
6.2.3	Intershell interaction in DWNT	143

Author’s publications	144
References	146

List of Figures

Figure 2.1 (a) A unrolled graphene layer with honeycomb lattice. When connecting sites O to A , and B to B' , a nanotube can be constructed. $\overrightarrow{OA}$ and $\overrightarrow{OB}$ are defined as the chiral vector $\overrightarrow{C_h}$ and translation vector $\overrightarrow{T}$ of a carbon nanotube, respectively. ¹⁸ Special tube types include (b) armchair tubes (n, n) and (c) zigzag tubes $(n, 0)$. (d) All other tubes are called chiral tubes.....	10
Figure 2.2 Fragments of graphene in real space (a) and reciprocal space (b). The areas within the dashed borders are the unit cells. The unit vectors are $\overrightarrow{a_1} = (\frac{\sqrt{3}}{2}a, \frac{a}{2})$, $\overrightarrow{a_2} = (\frac{\sqrt{3}}{2}a, -\frac{a}{2})$ and $\overrightarrow{b_1} = (\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a})$, $\overrightarrow{b_2} = (\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a})$. ²¹	12
Figure 2.3 (a) The energy dispersion relations for graphene are shown throughout the whole region of the Brillouin zone. The Fermi energy E_f is reduced to six points where the bonding and antibonding bands coincide. (b) Top view of (a). The Brillouin zone of graphene is indicated by green hexagon. The Fermi level is reduced to the six corner points, indicated with black dots.*.....	15
Figure 2.4 Reciprocal space for an armchair (a), zigzag (b) and chiral (c and d) nanotube. ²¹	16
Figure 2.5 The energy band diagram (a) and density of states (c) for a metallic (5,5) nanotube. The energy band diagram (b) and density of states (d) for a semiconducting (10,0) nanotube ²¹	17
Figure 2.6 (a) Calculated band structure of (5,5)@(10,10) with intershell interaction. (b) Density of states corresponding to the band structure in (a). ¹⁹	19
Figure 2.7 Work functions for DWNTs (dots) and SWNTs (triangles) of different diameters. ²²	20
Figure 2.8 TEM images of (a) a SWNT ²³ (b) a DWNT, (c) a MWNT and (d) a SWNT bundle (cross sectional view). One hole indicates a single SWNT. ²⁴	20
Figure 2.9 STM images for SWNTs with different chiralities. ²⁵	22
Figure 2.10 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. ²⁶	23
Figure 2.11 (a) I_{ds} - V_{gs} curve for a p-type nanotube transistor. (b) I_{ds} - V_{gs} curve for an n-type nanotube transistor. ⁴⁹	27
Figure 2.12 (a) Effect of oxygen on an n-FET produced by thermal annealing open circles. ⁵⁰ (b) Variation of the characteristics of an initially p-type CNTFET as a function of increasing exposure to a potassium atom flux. ⁵¹	28
Figure 2.13 Ambipolar transfer characteristics of a CNTFET. ⁶⁰	29
Figure 2.14 Calculated conductance vs gate voltage at room temperature, varying (a) the	

work function of the metal electrode, and (b) doping of the CNT. The experimentally measured effect of (c) Oxygen adsorption and (d) potassium doping on CNTFETs. ⁴⁷ ...	31
Figure 2.15 denominating method of a DWNT*	32
Figure 2.16 I-V measurements for DWNT-FETs. (a) S@M or M@M type. (b) M@S type. (c) Temperature dependence of I-V measurement for an M@S DWNT-FET. (d) S@S type.	33
Figure 3.1 RBM peaks of SWNTs film.*	35
Figure 3.2 (a) TEM image of SWNT bundles. The scale bar is 20 nm. (b) Enlarged view of SWNT bundles. (c) AFM image of SWNT bundles.*	36
Figure 3.3 RBM peaks of DWNTs film.*	36
Figure 3.4 Diffraction pattern of DWNTs from SEM (a) and high resolution TEM (b) and (c). ⁸²	38
Figure 3.5 Inner-tube diameter distribution of DWNTs measured from HRTEM images (established from 57 individual nanotubes), which are consistent with the diameters calculated from the RBMs analysis.*	38
Figure 3.6 (a) AFM image of 4 electrodes made from a “cross” pattern mask. (b) Schematic structure of the substrate and electrodes.*	39
Figure 3.7 (a) SEM image of four Au/Ti electrodes (white parts) on a Si/SiO ₂ wafer. AC bias voltage is applied between two adjacent electrodes, as indicated in the figure. AFM images of SWNTs bridging the adjacent electrodes for a deposition time of (b) 50s and (c) 300s, respectively. The black arrows label the direction of the electric field.*	40
Figure 3.8 (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. (c) I_{ds} - V_{ds} at a series of V_{gs} of the device after burn-off process. Inset: Schematic cross section of a back-gate CNTFET. (d). I_{ds} - V_{gs} curve at $V_{ds} = -150$ mV. ⁸⁵	42
Figure 3.9 Electrical performances before and after a single-shell electrical breakdown of a DWNT. (a) A schematic drawing of current flow in a S-M DWNT after inner shell breakdown. (b) The breakdown process of (a). (c) Electrical measurement of (a) before and after breakdown. (d) A schematic drawing of current flow in a M-S DWNT after outer shell breakdown. (e) The breakdown process of (d). (f) Electrical measurement of (d) before and after breakdown. ⁶⁵	43
Figure 3.10 (a) A bundle of CNTs are observed by FESEM. (b) AFM image of a CNT device. (c) The height profile at the position of white line in (b).*	44
Figure 3.11 Schematic drawing of electrode connection during electrical measurements.*	45
Figure 3.12 Schematic diagram of the in situ Raman scattering setup.*	46
Figure 4.1 (a) AFM image of the CNTFET. The scale bar is 1 μ m. (b) I_{ds} - V_{gs} curve of the CNTFET. (c) Four read/ write cycles of the CNTFET memory at room temperature. ⁶⁷	49
Figure 4.2 (a)-(c) I_{ds} - V_{gs} curves in high vacuum with $V_{ds} = 0.5$ mV. The sweeping range of V_{gs} is increased from (a) to (c). (d) Diagram of avalanche injection of electrons into bulk SiO ₂ from CNTFET channel. (e) Data of a nonvolatile molecular memory cell. ⁶⁸	52
Figure 4.3 Memory effects in an annealed SWNT FET bundle at low temperatures (84 and 12 K). ⁷⁰	52
Figure 4.4 (a) Hysteresis recorded for non-suspended SWNT FET exposed to ambient air at $V_{ds} = 10$ mV (b) Hysteresis recorded in a vacuum chamber of the device in (a). (c)	

Hysteresis recorded for suspended SWNT FET exposed to ambient air at $V_{ds} = 10$ mV. Inset: A SEM image and a schematic structure of the device. (d) Vanished hysteresis recorded with the same device immediately after placing it in vacuum. (e) Schematic drawing depicting water molecules hydrogen bonding to the surface Si-OH groups. ⁹²	54
Figure 4.5 I_{ds} - V_{gs} curves recorded for a SWNT FET under two V_{gs} sweep rates (as indicated) in ambient air. ⁹²	55
Figure 4.6 (a) Schematic structure of CNT-based NVM with an ONO charge trap. (b) AFM image of the SWNT attached between two metal electrodes. (c) I_{ds} - V_{gs} at $V_{ds} = -0.9$ V. Two loops correspond to V_{gs} sweeping range of ± 8 V (inner loop) and ± 20 V (outer loop). d) I_{ds} - V_{gs} after charging the ONO storage node with different pulse amplitudes. ⁹³	56
Figure 4.7 (a) SEM image of PmPV/CNT composite deposited on Si wafer with patterned Au electrodes. (b) Current measured during UV illumination cycles in air. The shadowed and unshadowed regions are the UV-on and -off periods, respectively. Inset: schematic device geometry. ⁹⁴	57
Figure 4.8 Response of PmPV polymer-coated CVD-grown CNTFETs to UV light ($\lambda = 365$ nm). (a) I_{ds} - V_{gs} in air with $V_{ds} = 1$ V at UV-off (blue curves) and UV-on (red curves) conditions. Inset: schematic device geometry. (b) Memory operation in air at room temperature. ⁹⁴	58
Figure 4.9 Threshold voltage versus V_{gs} calculated over a full cycle of V_{gs} for different gate voltage ranges. SR = 1 V/s. Inset: width of the hysteresis as a function of V_{gs}^{Max} . ⁸⁵	59
Figure 4.10 Threshold voltage versus V_{gs} calculated over a full cycle of V_{gs} for different SR. $V_{gs}^{Max} = 10$ V. Inset: semilog plot of the width of the hysteresis as a function of SR. ⁸⁵	60
Figure 4.11 Conductance versus V_{gs} curves of a DWNT-FET under different conditions. ⁶⁶	61
Figure 4.12 Transfer characteristics of a SWNT-FET. (a) as-prepared. (b) after annealing at 270°C for 30 minutes in air. (c) after introducing Triton X-100/D ₂ O for 20 minutes and drying off. ⁶⁰	63
Figure 4.13 Molecular formulas of SDS, SDBS and Triton X-100, respectively.*	66
Figure 4.14 The flow of the experiments.*	67
Figure 4.15 Schematic drawings of p-type and ambipolar hysteresis loops with (a) 'anti-clockwise' hysteresis. (b) 'clockwise' hysteresis.*	68
Figure 4.16 The observed transfer characteristics for SWNT-FETs: (a) P-type 'anticlockwise'. (b) P-type 'clockwise'. (c) Ambipolar 'anticlockwise' (d) Ambipolar 'clockwise'.*	68
Figure 4.17 The observed transfer characteristics for DWNT-FETs: (a) P-type 'anticlockwise'. (b) P-type 'clockwise'. (c) No ambipolar 'anticlockwise' observed. (d) Ambipolar 'clockwise'.*	69
Figure 4.18 Transfer characteristics of CNTFETs. (a) CNTFETs after annealing and soaking. (b) SWNT-FETs after 10wt% SDBS treatment. (c) SWNT-FETs after pure Triton X-100 treatment. (d) DWNT-FETs after 10wt% SDS treatment.*	73
Figure 4.19 Schematic diagrams of the cross section for the channel of DWNT-FET treated with 10 wt% SDBS. (a) $V_{gs} < 0$ V. (b) $V_{gs} > 0$ V.*	74
Figure 5.1 Raman spectrum from one nanotube taken over a broad frequency range using $E_L = 1.58$ eV (785 nm) excitation laser, and showing the radial breathing mode (RBM), the D band, the G band and the G' band. Second-order modes are also observed. The features	

marked with ‘*’ at 303, 521 and 963 cm^{-1} are from the Si /SiO ₂ substrate. ⁹⁸	80
Figure 5.2 Schematic of (a) non-resonant (Stokes) scattering and (b) a single (incident) resonance. GS (ES) refer to the ground (excited) state of the material investigated and ω_{ph} to the phonon (or other elementary excitation) emitted in the process. The corresponding relative strengths in a Raman spectrum are indicated on the bottom. ¹⁰⁰	83
Figure 5.3 Band structure and density of states of a zigzag nanotube. ¹⁰⁰	84
Figure 5.4 Linear fit of the observed RBM frequencies as a function of inverse tube diameter $1/d$. The diameter of the assigned nanotubes is calculated from Eq. (5.3) with lattice constant $a = 0.246 \text{ nm}$. ⁸¹	86
Figure 5.5 Frequency of coupled RBM in DWNTs. Open symbols belong to uncoupled tubes of the same diameter, solid symbols to double-walled nanotubes. ¹¹⁷	88
Figure 5.6 (a) First Kataura Plot calculated in 1999. ¹²⁰ (b) Theoretical calculation calculated by the first-neighbor tight binding method, with the transfer integral $\gamma_0 = 2.9 \text{ eV}$. ⁹⁹	89
Figure 5.7 Empirical Kataura plot generated from equations (5.6) and (5.7).*	92
Figure 5.8 Frequency vs. $1/d$ for the two most intense G peaks. ¹²¹	94
Figure 5.9 The G-band for highly oriented pyrolytic graphite (HOPG), one semiconducting SWNT and one metallic SWNT. ¹⁰⁴	95
Figure 5.10 (a) The G band energy (squares) and G band width (circles) respond to gate voltage or, in an equivalent way, to the charge density. (b) The G band linewidth respond to E_F . (c) The G band energy respond to E_F . (d) and (e) schematic diagrams for explanations of (b). (f) and (g) schematic diagrams for explanations of (c). ¹³⁴	97
Figure 5.11 (a) Schematic diagram of the experimental setup for doping SWNTs by electrochemical method. The excitation laser shines through the PEO/LiClO ₄ polymer electrolyte. (b) G band intensity map vs applied gate voltage for an individual m-SWNT. ^{135,136}	98
Figure 5.12 Frequency renormalization and broadening of the CNT G-phonon mode by the electron–phonon interaction. (a) to (c) Scattering mechanisms for a metallic tube where the G mode can excite electron–hole pairs (a), a doped metallic tube where the phonon can only excite virtual electron–hole pairs (b) and a semiconducting tube where the bandgap is larger than the phonon energy, and no real electron–hole pairs can be created by the phonon (c). d–f, Calculations of the Raman width in an m-SWNT ($d=2.0 \text{ nm}$) as a function of the charge carrier density per carbon atom at different temperature (d), corresponding G-mode Raman shifts (e) and Raman shift of the LO mode (solid lines) and TO modes (dashed lines) in an s-SWNT at temperatures $T=300 \text{ K}$ for different tube diameters d as a function of carrier density (f). Black dashed lines in d and e are Raman width and shift, respectively, of graphene at 300 K. ¹³⁷	100
Figure 5.13 Raman spectra of the same isolated S@S DWNT for five closely spaced E_L values. The intensity of the higher frequency 2D peak is directly related to the intensity of the RBM peak corresponding to the outer layer. ²⁰	101
Figure 5.14 The depolarization effect in bundles of single-walled nanotubes recorded on an area of $15 \times 15 \mu\text{m}$. ¹⁵⁰	103
Figure 5.15 Morphology of SWNT observed by FESEM. (a) SWNT from water solution. (b)	

SWNT from 1wt% SDS. (c) SWNT from 4 wt% SDBS. (d) SWNT from 50 wt% SDBS.*	105
Figure 5.16 Raman spectra of (a) SWNTs from different solutions. (b) DWNTs from different solutions.*	106
Figure 5.17 (a) Schematic density of the electronic states for a SWNT. Solid arrows depict the optical excitation and emission transitions of interest; dashed arrows denote nonradiative relaxation of the electron (in the conduction band) and hole (in the valence band) before emission. (b) Contour plot of the photoluminescence intensity versus excitation and emission wavelengths for a sample of SWNTs suspended in SDS and deuterium oxide. ⁹⁰	107
Figure 5.18 Contour plot of photoluminescence intensity versus excitation and emission wavelengths for (a) SWNT. (b) DWNT in SDBS, respectively.*	107
Figure 5.19 (a) AFM image of the DWNT-FET. (b) Height profile along the dashed line indicated by arrow in (a). (c) Map of sum of Raman spectrum intensity between 1500 to 1600 cm^{-1} . (d) The RBM of the DWNT. Peak positions are labeled and the linewidths are shown in the brackets.*	110
Figure 5.20 Transfer characteristics of the device. Filled- and opened- circle curves represent I_{ds} measured before and during Raman measurement, respectively. The star is I_{ds} after all measurements when V_{gs} is swept back to -20 V.*	111
Figure 5.21 (a) G mode change during V_{gs} sweeping from -20 V to 20 V. The arrows are indicating change direction. (b) Two Lorentzian peaks (blue line) are used to fit original data (green opened circles) and the fitted curve is indicated by red line.*	112
Figure 5.22 The frequency (a), linewidth (b), intensity (c) and intensity ratio $I_{\text{G}}/I_{\text{G}^+}$ (d) for G mode as a function of V_{gs} . Red open circles represent results for G^+ and blue open triangles represent results of G^- , and open squares represent results for intensity ratio $I_{\text{G}}/I_{\text{G}^+}$. The stars are the results after all measurements when V_{gs} is swept back to -20 V.*	113
Figure 5.23 The energy band diagram of the CNTFET.*	114
Figure 5.24 Scattering mechanism for a semiconducting double-walled carbon nanotube where the G phonon can excite electron-hole pair between the top valence bands of the inner and outer shells. Dash line represents the Fermi level. The energy band pairs of the inner shell and outer shells are indicated by the arrows.*	117
Figure 5.25 (a) Transfer characteristics ($I_{\text{ds}}-V_{\text{gs}}$ curve) of the DWNT-FET obtained during Raman scattering measurement. The frequency (b), linewidth (c) and $I_{\text{G}}/I_{\text{G}^+}$ (d) for G^+ and G^- modes as a function of V_{gs} .*	120
Figure 5.26 (a) Band structure of the DWNT. Dot lines and solid lines represent band structures of outer shell (chiral index (19,0)) and inner shell (chiral index (7,5)), respectively. Dash line represents the Fermi level, ϵ_{f} . The process that the G phonons excite electron-hole pairs between the top valence bands of the inner and outer shells is illustrated. Correlation between transfer characteristics (b), frequency of G^- (c), linewidth of G^- (d) and $I_{\text{G}}/I_{\text{G}^+}$ (e) are obtained by joining the minimal I_{ds} valley on the forward and backward characteristics in Figure 5.25(a).*	122
Figure 5.27 (a) AFM image of the DWNTs-based FET. (b) Height profile along the dashed line indicated by arrow in (a). (c) Map of sum of Raman spectrum intensity between	

1500 to 1600 cm^{-1} . (d) The RBM of the DWNTs. Peak positions are labeled and the linewidths are shown in the brackets.*	128
Figure 5.28 The comparison of the G bands of the device before and after Si_3N_4 passivation. The intensity of G^+ is normalized in order to see the relative intensity change more clearly.*	129
Figure 5.29 Results of the device before Si_3N_4 passivation. The $I_{\text{ds}}-V_{\text{gs}}$ curves (a) and the frequency (b), linewidth (c), and intensity ratio $I_{\text{G}}/I_{\text{G}^+}$ (d) for G mode as a function of V_{gs} . Red symbols represent results of G^+ and blue symbols represent results of G^- , filled symbols represent the results of forward sweeping and open symbols represent results of backward sweeping.*	131
Figure 5.30 Results of the device after Si_3N_4 passivation. The $I_{\text{ds}}-V_{\text{gs}}$ curves (a) and the frequency (b), linewidth (c), and intensity ratio $I_{\text{G}}/I_{\text{G}^+}$ (d) for G mode as a function of V_{gs} . Red symbols represent results of G^+ and blue symbols represent results of G^- , filled symbols represent the results of forward sweeping and open symbols represent results of backward sweeping.*	132
Figure 5.31 Schematic mechanism of contact change caused by Si_3N_4 deposition.*	136

List of Tables

Table 3.1 Spectral data and assignments for SWNTs using photoluminescence.	48
Table 4.1 Research status of transfer characteristics of CNTFETs. (* no efforts yet)*.....	64
Table 4.2 The matrix of transfer characteristics measure at 78 V/s sweeping rate of gate voltage.*.....	71
Table 5.1 Parameters for metallic and semiconducting nanotubes used in Eq. (5.4).	87
Table 5.2 Summary of all observed RBM frequencies and transition energies of semiconducting tubes and their assignments. ⁸¹	90
Table 5.3 Summary of all observed RBM frequencies and transition energies of metallic tubes and their assignment. ⁸¹	91
Table 5.4 Research status of Raman scattering for CNTs. (* no efforts yet) *	103

Summary

This thesis presents the main findings in my PhD project on the electron transport properties of carbon nanotubes (CNTs) and CNT-based field-effect transistors (FETs). The hysteretic transfer characteristics of CNTFETs are firstly discussed with main focus on surfactant effects on the transfer curves. Afterwards, in-situ Raman scattering of an individual double-walled CNT-based CNTFET is conducted and the mechanism of the intershell interaction of the double-walled CNTs (DWNTs) are studied. The correlations between the in-situ Raman scattering and hysteretic transfer characteristics of the DWNT-FET are then presented. Through these correlations, the inferences of the Si_3N_4 passivation and the effects of bundled DWNTs on the electron transport properties are investigated.

Significant hysteretic transfer characteristics have been found in our CNTFETs based on both single-walled (SW-) and double-walled CNTs. In our experiments, ‘clockwise’ and ‘anticlockwise’ hysteresis loops in the transfer curves are observed for both DWNT-FETs and SWNT-FETs. The findings suggest that the surfactants may suppress the effects of water molecules and oxygen, and cause a change in the transfer characteristics of the CNTFETs. The competition between the surfactants and water molecules/ oxygen defines the output performance of the transfer characteristics of the CNTFETs. Furthermore, the effects of different surfactants used are compared and discussed. The ‘clockwise’ hysteresis can be well interpreted in terms of mobile ions or charge groups in SDS (sodium dodecylsulfate), SDBS (sodium dodecylbenzenesulfonate) and Triton X-100 layer around the CNTs channels. Compared with SDS, SDBS and Triton X-100 are more

easily adhere to the surface of the CNTs, which may result from the benzene rings in the molecules. Third, from the comparisons between the SWNT-FETs and DWNT-FETs, the DWNTs are suggested to have superior adsorption of surfactants.

Through the study on in situ Raman scattering from a single semiconducting DWNT in an FET geometry, we have observed the frequency shift and linewidth change of the G^- band in response to the gate voltages. We suggest the frequency shift in G^- peak is due to the change of charge density in the DWNT channel induced by the gate voltages. The unique linewidth change of the G^- peak as a function of the gate voltages is interpreted as interband electron-phonon coupling between the bands of the two concentric shells in the DWNT. In addition, relative intensity of G band (I_{G^-}/I_{G^+}) is found to be increased with the local charge density in the DWNT channel.

A close correlation between the in situ Raman scattering and transfer characteristics from a semiconducting DWNT-based FET under real-time operations has been established. The G^- peak frequency and I_{G^-}/I_{G^+} respond to the forward and backward sweeping of the gate voltage V_{gs} in a similar manner as the hysteretic transfer characteristics of the DWNT-FET. Through the correlation, the mechanism of the changes of Raman scattering with V_{gs} variation are proposed.

In our experiments, the electrical properties and Raman scattering of DWNT-FETs are changed after a Si_3N_4 layer is coated. The change in electrical properties can be attributed to the contribution from metallic tubes in the bundle. However, the changes in the Raman scattering can be attributed to several factors, the compression caused by passivation, the shift of the Fermi level and the change of the conductance of the device. Furthermore, in the bundle, the screening effect of metallic tubes to the semiconducting tubes is confirmed through the in situ Raman study.

Chapter 1 Introduction

1.1 Motivation

During the past 40 years, microelectronics based on Si has experienced an inconceivable development. Microelectronic industry has followed Gordon Moore's law that the transistor's performance and density doubles every 3 years.¹ However, such a scaling is approaching its limits due to physical and economic constraints. When the devices are scaled down to a sub-50 nm range, several serious physical problems will appear which constrain the further developments of silicon microelectronics. For examples, current leakage through the gate oxide layers and short channel effect (SCE), etc. become more significant after scaling down. Moreover, control over the density and location of dopants in the channel and source/drain region become more and more difficult. Besides, critical requirements in lithography increase the cost of fabrication. It is now generally accepted that the productivity development of silicon technology must slow down². This perspective has sparked an intensive study on alternative technology within nanometer scale. Many efforts have been put into the developments of the advanced technologies and new materials. For instance, high- κ dielectric materials has been used to solve the gate leakage problems,³ Fin-FET structure has been employed to enhance gate efficiency;⁴ strained-silicon is introduced to improve the carrier mobility;⁵ carbon nanotubes,⁶ organic films,⁷ and DNA based molecular devices⁸ are investigated as the alternatives for next developments of microelectronics.

Carbon nanotubes (CNTs), an ideal material for molecular/nano electronic devices, are one of the most promising candidates for nanoelectronic applications. The inherent advantages of

CNTs over other candidates are as following^{6,9}:

- Carrier transport in CNTs is one-dimensional (1-D);
 - ✧ Backscattering is strongly suppressed and consequently the carrier mobility is increased.
This opens up a possibility of ballistic transport.
 - ✧ Confinement of charge inside the CNTs allows ideal control of the electrostatics, resulting in a good suppression of short channel effect.
- All chemical bonds of the C atoms of CNTs are satisfied and there is no need for chemical passivation of the dangling bonds as in silicon. This implies that CNT-based electronics will not be bound to use SiO₂ as the gate oxide.
- The strong covalent bonding makes CNTs high mechanical stability (Young's modulus about ten times higher than that of steel) and high thermal stability. Thus, CNTs have immunity to electromigration and their current handling capability can be as high as 10⁹ A/cm².
- CNTs can be semiconducting (s-) or metallic (m-), *i.e.* they can be used for CNT transistors and interconnects.

However, the applications of CNTs are still at a preliminary stage. Two major bottlenecks need to break through: (1) large-scale integration of CNTs, and (2) controllable electronic performances of CNT-based devices. Therefore, study of carrier transport in CNTs is crucial for fabricating reliable and reproducible CNT-based devices. Thus, in my PhD project, I have investigated electron transport properties, mainly focusing on hysteretic transfer characteristics of the field-effect transistors (FETs) based on either single-walled (SW-) or (DW-) CNTs. In addition, confocal Raman system is used to investigate real time response of our CNTFETs under their operation condition. This may deepen our understanding on inter-shell interaction during carrier

transport in double-walled carbon nanotubes (DWNTs). In addition, after introducing a Si_3N_4 passivation to stabilize the hysteretic transfer curves, I examine the hysteretic characteristics for a DWNT-FET with a confocal Raman microscopy under real-time I-V measurements. A close correlation between the in situ Raman scattering and transfer characteristics from the semiconducting DWNT-based FET under real-time operations has been established. This correlation offers a better understanding on the carrier transport in s-DWNT when the DWNT-FET is operating.

1.2 Objectives

The main objectives of my PhD project are as follows:

- ◆ To study the electron transport properties of both SW- and DW- CNTs with FET geometries.
- ◆ To compare their hysteretic transfer characteristics of fabricated SW- and DW- CNTFETs using alternate current dielectrophoresis (ACDEP) technique. The differences between SWNTs and DWNTs are investigated.
- ◆ To investigate the mechanisms of the hysteretic transfer characteristics for the CNTFETs. A systematic investigation on the surfactant effect on the hysteresis phenomenon is carried out for the purpose of a clear physical picture of the phenomenon.
- ◆ To investigate inter shell interactions of DWNTs. With in situ Raman scattering, the phonon response of an operating device is obtained. The important parameters, such as peak frequency, peak linewidth and peak intensity ratio as a function of the gate voltage are investigated. Electron-phonon coupling is used to explain the observed phenomena.
- ◆ To understand the mechanism of electron transport in the DWNT-FET. A correlation between

in situ Raman scattering and hysteretic electrical measurements has been established for a passivated DWNT-FET. The hysteretic loops of Raman characteristics are studied.

1.3 Major contributions of this thesis

The main contributions of this PhD project are listed as follows:

1. Surfactant effects on hysteretic transfer characteristics in Schottky-barrier (SB) CNTFETs have been systematically studied. In general, the change in conduction type from p-type to ambipolar or even n-type is attributed to oxygen adsorbed at the interface between the CNT channel and electrodes while the hysteresis is widely accepted to be caused by charge trapping. In both DWNT-FETs and SWNT-FETs, “clockwise” hysteretic transfer characteristics are observed. These characteristics can be attributed to mobile ions or charged clusters in surfactant layers around the tube channels. The phenomena are well interpreted in terms of mobile ions or charge groups in SDS, SDBS, and Triton X-100 layer around the CNT channels. Competition between surfactants and water molecules determines the features of the observed hysteresis loops. Compared to SWNT-FETs, more significant surfactant influences on the transfer characteristics are observed in DWNT-FETs due to their superior surfactant adsorption properties. Our findings suggest that not only water molecules but also the surfactants play critical roles in dominating the hystereses, especially for DWNTs. This work deepens the understandings of environmental conditions on the transfer characteristics of CNTFETs.
2. The intershell coupling of DWNTs has been investigated in CNTFETs geometry using in situ Raman scattering system when the devices are in operation. Our results show that the G⁻ band of the Raman spectra has both frequency shift and linewidth change in response to the gate voltages

V_{gs} . Electron-phonon coupling is used to explain the observed phenomena. Analogous to the case of an s-SWNT, we attribute the frequency shift to the change in the charge density induced by the gate voltages. The unique linewidth change is interpreted through interband electron-phonon coupling between the valence bands of two concentric shells of the DWNT. In addition, the intensity ratio of G^- to G^+ is found to increase with increasing charge density in the DWNT channel. This work provides experimental evidences on intershell coupling in a DWNT and offers a possibility to investigate electron transport in DWNT using in situ Raman scattering.

3. The electron transport properties have been investigated through correlations between electrical measurement and in situ Raman scattering. We observed hysteresis loops in the curves of G^- peak frequency and the intensity ratio of G^- to G^+ (I_{G^-}/I_{G^+}) as a function of V_{gs} . These loops correlate very well with the hysteretic transfer characteristics of the device. The clear correlations suggest that G^- peak linewidth and I_{G^-}/I_{G^+} increase with the carrier concentration in the DWNT induced by V_{gs} . In addition, unique G^- peak linewidth variation with V_{gs} can be attributed to interband electron transition between the energy bands of two concentric shells of the DWNT excited by G phonons. This work offers a further understanding of the electronic transport properties in DWNTFET.

4. The effects of Si_3N_4 passivation are investigated using the in situ Raman scattering on an individual or bundled DWNTs based CNTFETs. For the individual semiconducting DWNT-based FET, the changes observed after Si_3N_4 passivation are attributed by neither H_2O nor O_2 desorption but the effect of compression. However, the effects in DWNT-FET with bundled DWNTs are more complicated. The first one is compression caused by passivation, which results in the upshift and the linewidth broadening for G^+ peak. The second one is the shift of the Fermi level caused by

passivation, which causes the upshift and linewidth narrowing for G^- peak. Last, the increase of I_{G^-}/I_{G^+} in magnitude after passivation is attributed to the conductance increase of the device. This work is one application of the in situ Raman scattering and offers a further understanding of the effects of Si_3N_4 passivation, one of the most common passivation used in CNTs based devices.

1.4 Organization of this thesis

Chapter 1 introduces the motivations, objectives and major contributions of this thesis.

Chapter 2 reviews the unique electronic properties of carbon nanotubes, including their classifications, electronic structure, density of electronic state, and energy gap. In addition, several carbon-nanotube-based devices are introduced.

Chapter 3 describes the device fabrication methods and the basic properties of the CNTs used in our experiments.

Chapter 4 discusses a systematic investigation of surfactant effects on hysteretic transfer characteristics of SW- and DW- CNTFETs, including a description on various surfactants introduced to control the hysteresis and the mechanism of hysteresis in the CNTFETs .

Chapter 5 reviews the Raman scattering of CNTs and describes in situ Raman scattering of an individual s-DWNT on a FET platform. Electron-phonon coupling is used to explain the results of the Raman scattering. Moreover, experimental evidence of intershell interaction using Raman scattering is discussed. The correlations between the Raman scattering and transfer characteristics of an individual s-DWNT and bundled DWNTs on FET geometry are also presented. Hysteretic loops in the Raman results are presented and explained using inter shell

coupling of the DWNT. The results suggest an electron-phonon coupling (EPC) mechanism in the DWNT when the device is under operating. Besides, the effect of Si_3N_4 passivation on the Raman features and in situ Raman scattering of bundled DWNTs on FET geometry have been interpreted using the EPC mechanism.

Chapter 6 summarizes the major contributions and conclusions from the entire project and gives recommendations for future work.

In order to differentiate our results from the quoted works from others, a symbol ‘*’ will be added to all the figure/table captions from our own work.

Chapter 2 Carbon nanotubes and carbon nanotube-based devices

2.1 Classification of carbon nanotubes

Distinct from the most common diamond and graphite forms, carbon has crystalline molecular forms such as fullerenes and CNTs. CNTs were firstly observed by Oberlin *et al.* in 1976¹⁰. However, CNTs did not attract much attention until Iijima's work in 1991¹¹. CNTs can be obtained from rolling up one or more layers of graphene, forming seamless hollow cylinders. A single CNT may consist of up to several tens of cylinders with adjacent shell separation of ~ 0.34 nm, which is called a multi-walled carbon nanotube (MWNT). In contrast, single-walled carbon nanotube (SWNT) which contains only one graphene layer, firstly synthesized by Iijima & Ichihashi¹², and Bethune *et al.* in 1993¹³. Recently, the simplest MWNTs, defined as double-walled carbon nanotubes (DWNTs), have also attracted much research attentions due to their unique double-layer structure which offer a good platform to investigate the interaction between their concentric carbon shells¹⁴⁻¹⁷.

2.2 Structure of carbon nanotubes

2.2.1 Structure of SWNTs

When examining the structure of an SWNT, an important factor, *i.e.* how the graphene

sheet is rolled up has to be taken into account. The way to roll up the graphene sheet gives dramatically different axial symmetry to the formed SWNT. The axial symmetry of SWNT is called chirality. In the following parts, the important parameters to identify the chirality of an SWNT are addressed.

2.2.2 Chiral Vector $\vec{C}_h$

A honeycomb lattice of the graphene sheet is shown in Figure 2.1(a)¹⁸. When forming an SWNT with a graphene sheet, any two sites of the lattice can be arbitrarily chosen to be connected. The description of forming an SWNT is shown through the following example. If points O and A are selected to be connected, an SWNT is constructed by rolling up the honeycomb sheet with points O and A coinciding to each other (and points B and B' overlap). Then $\vec{OB}$ is the direction of the nanotube axis, $\vec{OA}$ indicates the circumference of the nanotube. The vector $\vec{OA}$ and $\vec{OB}$ are defined as the chiral vector $\vec{C}_h$ and translation vector $\vec{T}$ of the SWNT, respectively. $\vec{C}_h$ can be expressed by two real space unit vectors $\vec{a}_1$ and $\vec{a}_2$ (see Figure 2.1(a)) of the hexagonal lattice:

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

(n, m) is also known as chiral index and the SWNTs can be classified according to different chiral index (n, m) as following:

1. If $n = m$, i.e., $\vec{C}_h = (n, n)$, it corresponds to an armchair nanotube, as shown in Figure 2.1(b).
2. In the case of $m = 0$, or $\vec{C}_h = (n, 0)$, a zigzag nanotube is formed (Figure 2.1(c)).
3. All the other (n, m) chiral vectors correspond to chiral nanotubes (Figure 2.1(d)).

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

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

where $a = 0.246$ nm which is the magnitude of the lattice constant of the honeycomb lattice.

Figure 2.1 (a) A unrolled graphene layer with honeycomb lattice. When connecting sites O to A , and B to B' , a nanotube can be constructed. $\overline{OA}$ and $\overline{OB}$ are defined as the chiral vector $\overline{C}_h$ and translation vector $\overline{T}$ of a carbon nanotube, respectively.¹⁸ Special tube types include (b) armchair tubes (n, n) and (c) zigzag tubes $(n, 0)$. (d) All other tubes are called chiral tubes.

The chiral angle θ is defined as the angle between the vectors $\overline{C}_h$ and $\overline{a}_1$ (or $\overline{a}_2$).

Due to the hexagonal symmetry of the honeycomb lattice, the chiral angle is within a range of $0 \leq \theta \leq 30^\circ$.¹⁸ As shown in Figure 2.1(a), θ represents the tilt angle of the carbon hexagons with respect to the direction of the nanotube axis and specifies the spiral symmetry¹⁸,

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

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

2.2.3 Translational vector $\vec{T}$

The translation vector $\vec{T}$ is parallel to the nanotube axis and is normal to the chiral vector $\vec{C}_h$, as shown in Figure 2.1(a). $\vec{T}$ can be expressed in terms of the unit vector of SWNT $\vec{a}_1$ and $\vec{a}_2$ as¹⁸:

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

and

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

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

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

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

The magnitude of the translation vector $\vec{T}$, representing the unit length of SWNT along tube axis, is given by

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

2.2.4 Structures of DWNTs

Double-walled carbon nanotubes, an intermediate state between SWNTs and MWNTs, consist of two cylindrical layers of carbon atoms. Each layer may have specific chiral index and the distance between two layers is $\sim 0.34 \text{ nm}$ ¹⁹. This distance is close to the average interlayer distance in graphite, which is 0.335 nm ²⁰. As we know, the van der Waals potential is stable and almost

constant when the interlayer distance of DWNTs is from 0.33 to 0.35 nm²⁰. Thus, it is possible to synthesize DWNTs with intershell distance in this range. However, due to their double-layer structure, the symmetry of DWNTs is lower than that of SWNTs and there may be interaction between these two layers, probably leading to some changes in the electronic structure of the DWNTs¹⁹. The classification of DWNTs is different from the classification of SWNTs. The chiralities of the two concentric layers are used to denote the DWNTs in the form of $(n_i, m_i)@(n_o, m_o)$ ¹⁹, where the subscripted i and o indicate the inner and outer shell, respectively. In addition, a simpler denotation of DWNTs is also used such as $M@S$ ²⁰, describing that the inner shell of DWNT is metallic while the outer shell is semiconducting.

2.3 Electronic structure of CNTs

2.3.1 Electronic structure of SWNTs

Figure 2.2 Fragments of graphene in real space (a) and reciprocal space (b). The areas within the

dashed borders are the unit cells. The unit vectors are $\vec{a}_1 = (\frac{\sqrt{3}}{2}a, \frac{a}{2})$, $\vec{a}_2 = (\frac{\sqrt{3}}{2}a, -\frac{a}{2})$ and

$$\vec{b}_1 = (\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a}), \quad \vec{b}_2 = (\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a}).^{21}$$

Similar to the way how the molecular structures of CNTs are constructed, the electronic structure of CNTs may also be calculated from that of graphene. Figure 2.2 shows the fragments of the real and reciprocal space for a graphene sheet²¹. In the hexagonal carbon lattice, there are two inequivalent sites, points A and B, in one unit cell (indicated using dashed diamond in Figure 2.2(a)) and all other lattice sites can be mapped using the displacements of $\vec{a}_1$ and $\vec{a}_2$. In a tight binding approximation, the energy dispersion of the π -electrons forming a bonding (-) and an antibonding (+) band which can be expressed as²¹:

$$E(k_x, k_y) = \pm \gamma_0 \left[1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right) \right]^{\frac{1}{2}} \quad (2.8)$$

where $\gamma_0 \sim 2.9$ eV is the integral of the energy overlap between the nearest carbon atoms. Figure 2.3(a) is a three-dimensional diagram of the energy dispersion $E(k_x, k_y)$ in Eq. (2.8). The upper half of the energy dispersion curve describes the antibonding band of π^* -energy and the lower half is the bonding band of π -energy. From this figure, one can see that the bonding and antibonding bands coincide at six points of the hexagonal Brillouin zone, which are known as Dirac points. The Fermi energy E_f is thus determined by the six points. Accordingly, graphene is classified as a zero-gap semiconductor because of the vanishing energy gap. The top view of the energy dispersion in the first Brillouin zone is shown in Figure 2.3(b), in which the gapless Fermi points are indicated at the corners with black dots. Two of these points are inequivalent, Point K and K' (also shown in Figure 2.2(b)); the others can be obtained by lattice transformations along $\vec{b}_1$ and $\vec{b}_2$. For example, as shown in Figure 2.2(b) by red arrows, point C can be obtained by transform K' with a vector $\vec{b}_1 - \vec{b}_2$.

The electronic structures of SWNTs are deduced from the energy dispersion of graphene (Figure 2.3(a)). The band structure of the SWNT is obtained by applying periodic boundary condition around the circumference of the SWNT, *i.e.*, the wave function has to be single valued:

$$e^{i\vec{k}\cdot\vec{r}} = e^{i\vec{k}\cdot(\vec{r}+\vec{C}_h)} \quad (2.9)$$

where $\vec{k}$ is a wave vector and $\vec{r}$ is a real space lattice vector of the graphene lattice. Thus, the following condition can be obtained²¹:

$$\vec{k} \cdot \vec{C}_h = 2\pi j \quad (j=0, 1, 2, \dots) \quad (2.9)$$

Therefore, the electrons are free to move only along the direction of the tube. Due to this quantization, a discrete number of parallel lines that represent the allowed modes of $\vec{k}$ values appear in the reciprocal space of graphene. The examples of armchair, zigzag and chiral nanotubes are shown in Figure 2.4(a) to (c), respectively. The interline spacing Δk depends only on the diameter d ²¹:

$$\Delta k = \frac{2\pi}{|\vec{C}_h|} = \frac{2}{d} \quad (2.10)$$

Figure 2.3 (a) The energy dispersion relations for graphene are shown throughout the whole region of the Brillouin zone. The Fermi energy E_f is reduced to six points where the bonding and antibonding bands coincide. (b) Top view of (a). The Brillouin zone of graphene is indicated by green hexagon. The Fermi level is reduced to the six corner points, indicated with black dots.*

In Figure 2.4(a) to (c), the parallel lines represent the allowed values for the wavevector $\vec{k}$. Each line corresponds to a one-dimensional channel for conduction along the nanotube. Since the allowed $\vec{k}$ lines are perpendicular to $\vec{C}_h$ (see Eq. (2.9)), the tube axis ($\vec{T}$ direction) is parallel to the $\vec{k}$ lines for all cases. In the case of armchair nanotubes, the quantization condition is:

$$n\sqrt{3}k_x a = 2\pi j \quad (j=0, 1, 2, 3, \dots, n) \quad (2.11)$$

and the allowed $\vec{k}$ lines are in k_y direction, as shown in Figure 2.4(a). The length of the first Brillouin zone for each allowed line is $2\pi/a$. There are discrete numbers of lines between the center and the edge of the hexagon. In the case of zigzag nanotubes (Figure 2.4(b)), the length of the first Brillouin zone for each allowed $\vec{k}$ lines is $2\pi/\sqrt{3}a$ and all $\vec{k}$ lines are parallel to

k_x . The quantization condition for zigzag nanotubes is:

$$nk_y a = 2\pi j \quad (j=0, 1, 2, 3, \dots, n) \quad (2.12)$$

The circle in Figure 2.4(c) encloses a region of states near the Fermi level for a chiral nanotube and is enlarged and shown in panel Figure 2.4(d). The points K_1 and K_2 are the closest points approaching to the Fermi level at K in the two nearest allowed $\vec{k}$ lines.

Figure 2.4 Reciprocal space for an armchair (a), zigzag (b) and chiral (c and d) nanotube.²¹

Substitute Eq. (2.11) or (2.12) into Eq. (2.8), the dispersion relations for armchair or zigzag nanotubes can be obtained respectively as²¹:

$$E_{armchair(n,n)} = \pm \gamma_0 \left[1 + 4 \cos\left(\frac{m\pi}{n}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right) \right]^{\frac{1}{2}}$$

$$E_{zigzag(n,0)} = \pm \gamma_0 \left[1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{m\pi}{n}\right) + 4 \cos^2\left(\frac{m\pi}{n}\right) \right]^{\frac{1}{2}} \quad (2.13)$$

Figure 2.5 The energy band diagram (a) and density of states (c) for a metallic (5,5) nanotube. The energy band diagram (b) and density of states (d) for a semiconducting (10,0) nanotube²¹.

As shown in Figure 2.4(a), armchair nanotubes have $\vec{k}$ lines cross the corner points of the Brillouin zone, thus they have zero energy gaps. In particular, the energy band diagram for a (5,5) nanotube shows that the bands crossing point is located at $k_y = 2\pi/3a$ and the distance between the allowed k-lines for armchair nanotubes is $\Delta k_x = \frac{2\pi}{n\sqrt{3}a} = \frac{2\pi}{5\sqrt{3}a}$. Therefore, within the range from 0 to $\frac{2\pi}{\sqrt{3}a}$ (between the center and the edge of the hexagon), there are six (*i.e.* $n+1$) discrete lines. The (5,5) tube is metallic since the $\vec{k}$ lines are crossing the Fermi points

(Dirac points). The energy band diagram of (5,5) nanotube is drawn in Figure 2.5(a).

However, for zigzag and chiral nanotubes, the allowed $\vec{k}$ lines do not congenitally cross the Fermi points. They may be metallic or semiconducting depending on whether the $\vec{k}$ lines cross the Fermi point. An energy band diagram of (10,0) nanotube is shown in Figure 2.5(b) as an example for the case of a semiconducting tube.

Derived from the energy dispersion diagrams shown in Figure 2.5(a) and (b), the density of states (DOS) are schematically drawn in Figure 2.5(c) and (d). For the armchair nanotube (Figure 2.5(c)), a small constant DOS near the Fermi level results from the linear crossing bands as shown in Figure 2.5(a). At energies away from the Fermi energy, Van Hove singularities (spikes-like DOS profile shown in Figure 2.5(c)) are seen at the onset of the next subbands. The Van Hove singularities are caused by the nature of the one-dimensional subbands. The energy separation between the first singularities above and below the Fermi level is denoted as ΔE_{sub} in Figure 2.5(c).

However, in the case of a semiconducting nanotube (10,0), since $\vec{k}$ lines do not cross the Fermi points, there is an energy gap E_g , as shown in Figure 2.5(d). The energy gap E_g for a semiconducting nanotube is not only dependent of its chiral angle but is dependent of the inverse nanotube radius R or diameter d ,¹³

$$E_g = \frac{\gamma_0 a_{C-C}}{R} = \frac{0.412}{R(nm)}(eV) = \frac{0.824}{d(nm)}(eV), \quad (2.14)$$

where $a_{C-C} = \frac{a}{\sqrt{3}}$ is the nearest-neighboring C-C distance on a graphene sheet.

2.3.2 Electronic structure of DWNTs

Figure 2.6 (a) Calculated band structure of (5,5)@(10,10) with intershell interaction. (b) Density of states corresponding to the band structure in (a).¹⁹

Double-walled CNTs have many unique electronic properties in comparison with SWNTs.

It is an ideal model to investigate intershell interaction. The intershell interaction is reported to be influential on the band structure of DWNT by theoretical calculation. As shown in Figure 2.6, the calculated band structure and DOS of an (5,5)@(10,10) (both shell are metallic tubes) has a small band gap, which is suggested to be caused by intershell interaction. With the first-principles study on work functions of double-walled carbon nanotubes, one can see that, for those DWNTs with ultra small zigzag SWNTs, e.g. (4,0), as their inner shells, their work functions are expected to be 0.2-0.5 eV higher than larger diameter DWNTs²². As the DWNT diameter gets larger, e.g. for a (8,0)@(17,0) DWNT, the work functions of the inner and outer tube become more comparable and their individual electronic structure become less perturbed, as shown in Figure 2.7²². In the (8,0)@(17,0) DWNT, the band gap of the semiconducting outer tube is largely retained despite the intershell interaction, *i.e.* the intershell interaction does not disturb the electronic structure of the

two individual shells when the tube diameter is relatively large, $\sim 1.35\text{nm}$ in this case²². Besides this basic understanding on the electronic structure of DWNTs, there are still many issues without clear interpretations. More experimental results, theoretical calculation and modeling are needed for in-depth understanding on the physics of DWNTs.

Figure 2.7 Work functions for DWNTs (dots) and SWNTs (triangles) of different diameters.²²

2.4 Observations of carbon nanotubes

Figure 2.8 TEM images of (a) a SWNT²³ (b) a DWNT, (c) a MWNT and (d) a SWNT bundle (cross sectional view). One hole indicates a single SWNT.²⁴

A single CNT can be observed using different types of microscopes, such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning tunneling microscopy (STM) and atomic force microscopy (AFM), etc..

The TEM images can be used to differentiate SWNT²³, DWNT and MWNT²⁴, as shown in Figure 2.8(a) to (c), respectively. The shell of SWNTs can also be visualized clearly by TEM, *i.e.*, a cross section of a SWNT bundle is shown in Figure 2.8(d), in which one hole represents an individual SWNT. The STM images are used to visualize the atomic structure of CNTs. As shown in Figure 2.9²⁵, the atomic structure of CNTs and the hexagonal structure of a 6-carbon ring could be visualized clearly. The black arrows indicate the directions of the transition vectors. From the STM images, the chiral vector and lattice constant can be obtained. Although STM images provide evidences on the atomic structure of CNTs, they are not commonly used to obtain images of the CNTs in the CNT devices due to their operational difficulties. In the STM measurements, CNTs must be laid on a conducting surface in order to obtain good images. However, CNTs are situated on insulating layers in most of the CNT-based devices in contrast. AFM and SEM have relatively lower requirements for sample preparation and higher capability of viewing relatively large scale of topography. AFM and SEM are more widely used for imaging of CNTs in CNT devices even though they provide relatively poor resolutions. We will discuss the AFM and SEM images in the following chapters.

Figure 2.9 STM images for SWNTs with different chiralities.²⁵

2.5 Development of CNT-based devices with FET structure

Field-effect transistor (FET) is one of the basic device geometry in microelectronics and it is the most common structure for CNT-based devices. The first batch of CNTFETs is reported in 1998^{26,27}, which were fabricated by connecting a semiconducting nanotube between two metal-electrodes, as shown in Figure 2.10. In the transistor, the CNTs play the role of a conducting “channel” while the two metal-electrodes function as the “source” and “drain” electrodes. A heavily doped silicon wafer is typically used as the gate electrode, so-called “back-gate”. The devices show the characteristics of a field-effect transistor when applying voltage to a gate electrode (Si substrate). The nanotube can be switched from a conducting to an insulating state, *i.e.*, the channel current decreases with increasing gate voltage, indicating that the conductance through s-SWNTs is dominated by holes. The hole current becomes saturated when the gate voltages is swept to a large negative value. Generally, these CNTFETs behave as p-type FETs and has an ON/OFF current ratio up to $\sim 10^5$. 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, etc..

Figure 2.10 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.²⁶

2.5.1 Improvement of the contacts between CNTs and metals

The aforementioned transistors have a high parasitic contact resistance ($\geq 1 \text{ M}\Omega$), low transconductance $g_m \sim 1 \text{ nS}$, and high subthreshold swing $S \sim 1\text{-}2 \text{ V/dec}$ although they are functional.⁶ These unsatisfactory characteristics are, to a large extent, due to poor contacts⁶. Two common methods are used to improve the contacts. The first method is thermal annealing which was initially reported by a group from International Business Machines (IBM)²⁸. In their transistors, s-SWNTs were placed on top of the SiO_2 film, 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 gas led to a stronger coupling between the metal and the CNTs and thus a small contact resistance was obtained. The second method is to choose an appropriate metal as electrodes. Javey *et al.* selected palladium (Pd)²⁹, 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 $\frac{4e^2}{h}$. The contact improvement

was suggested to be caused by the reduced or eliminated barriers for holes.

2.5.2 Gate structures and dielectric layers

The most widely used gate structure for CNTFETs in the past years is the doped silicon substrate as back gates and thermally grown SiO_2 as gate dielectric layer^{26,27,30}. However, since local gates can address different nanotube transistors separately on a common chip, they 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,³¹ bottom tungsten gates with SiO_2 ,³² top-gate with 2~20-nm-thick SiO_2 dielectrics.^{33,34} In addition to the local address ability, these gate structure show progressively improved characteristics of CNTFETs. For instance, the subthreshold swing S is approaching the theoretical value $\sim 60\text{mV/Dec}$ ^{33,35} due to the decrease of oxide thickness³³ and the use of high- κ dielectrics³⁵. CNTFETs with electrolyte gate³⁶ or polymer gate^{37,38} demonstrate strong gate-channel coupling with improved device characteristics. An electrolyte gate with a dielectric constant of about 80 can lead to an extremely high transconductance of $\sim 20\ \mu\text{S}$.³⁶

The performances of CNTFETs can also be improved by decreasing the gate oxide thickness. Wind *et al.*³³ compared the characteristics of a top-gated (15 to 20-nm-thick SiO_2) and a back-gated (120-nm-thick SiO_2) CNTFET fabricated on the same SWNT and found that those top-gate devices exhibited excellent electrical characteristics. The threshold voltage of the top-gated CNTFET is only -0.5 V, significantly lower than that under 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.*³⁹ concluded the scaling rule of the subthreshold swing 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 $\propto t_{\text{ox}}^{-1/2}$, which well explains the performance improvement of CNTFETs due to the decreasing of oxide thickness.

On the other hand, high- κ dielectrics have been actively pursued to replace SiO_2 as the gate insulator for silicon devices.⁶ The relatively low κ of SiO_2 (3.9) limits its applications in transistors as the gate length scales down to tens of nanometers. High- κ gate insulators afford high capacitance without relying on ultra-small film thickness, which can enhance the efficiency of charge injection into the transistor channels and meanwhile reduce direct-tunneling leakage currents.³⁵ Experimental results show that ZrO_2 ,³⁵ HfO_2 ,^{40,41} Al_2O_3 ³¹ and SrTiO_3 ⁴² have been successfully used as the gate insulators in CNTFETs.

2.5.3 Switching mechanisms of CNTFETs

So far, the switching mechanisms of CNTFETs have been studied by many groups. Generally speaking, the proposed mechanisms can be grouped into three categories. The first is conventional metal oxide semiconductor field-effect transistor (MOSFET)-like operation, in which the currents for these devices are mainly controlled by the potential barriers at the contacts. It is reported that, for the CNTFETs which consist of large diameter carbon nanotubes (3-5 nm), MOSFET-like behavior has been used to interpret the operation mechanism.^{29,43} This is because the rather small energy gap of the CNT channels allows carriers injection from the metal contacts into the valence band of the CNTs without any substantial Schottky barrier. Furthermore,

CNTFETs with extremely long channel length ($> 300 \mu\text{m}$) also exhibit MOSFET-like behavior.^{44,45} In this case, the contact resistance is insignificant and the resistance of the channel is dominated by bulk-CNT resistance. In addition, CNTFETs with Ohmic contacts can also be operated as the conventional MOSFET-like device. This type of contact can be achieved by engineering the work function of the contact metals, e.g., choose a specific metal such as Pd as electrodes for CNTFETs.

Schottky barrier (SB)-FETs is the second proposed mechanism. The CNTFETs fabricated from larger band gap CNTs behave as SB-FETs.^{40,46,47} In this case, the gate field controls the thickness of the Schottky barriers at the metal-CNT interface. Consequently, whether or not the carriers can tunnel from the source or drain electrodes into the CNT channels is dependent on the thickness of the SB. Several observations support SB-FET mechanism rather than conventional MOSFET model. First, the CNTFETs show different characteristics if the source and drain are swapped. This cannot be explained with the conventional MOSFET mechanism where the saturation currents under large positive and negative V_D are comparable since both sets of curves are symmetrical with respect to $V_D = 0$. Another evidence for this model is that the subthreshold swing S is independent of channel length⁴⁶ but oxide thickness. Furthermore, S is temperature dependent only when the temperature is above 200K. S levels off at temperatures below about 200 K, suggesting a mechanism of carrier tunneling.⁴⁰ The SB model can also provide a reasonable explanation to the effects of O_2 on the performance of CNTFETs.⁴⁷

The third operation model is the band-to-band (BTB) tunneling process reported by Appenzeller *et al.*⁴⁸ 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 current flow of

a BTB CNTFET is controlled in this mode by the valence and conduction band edges in a bandpass-filter-like arrangement. This is different from a conventional device where the Fermi distribution ultimately limits the gate voltage range from switching the device on or off. A small S value of ~ 40 mV/dec has been obtained for a BTB CNTFET at room temperature, beyond the theoretical limit value of 60 mV/dec for conventional CNTFETs.

Based on the discussion above, one must carefully interpret the switching mechanism of CNT-based devices, especially for those complicated structures. For most of the CNTFETs used in this thesis, the SB behavior would be the major mechanism to switch the devices because of the choice of the tubes and the materials of the electrodes.

2.5.4 Conduction types of CNTFETs: p-type, n-type and ambipolar

Figure 2.11 (a) I_{ds} - V_{gs} curve for a p-type nanotube transistor. (b) I_{ds} - V_{gs} curve for an n-type nanotube transistor.⁴⁹

Figure 2.12 (a) Effect of oxygen on an n-FET produced by thermal annealing open circles.⁵⁰ (b) Variation of the characteristics of an initially p-type CNTFET as a function of increasing exposure to a potassium atom flux.⁵¹

Till date, CNTFETs can be fabricated to show p-type, n-type and ambipolar conduction types.^{26,27,29,35,36,42,52,53} Typically, the intrinsic CNTFETs fabricated in ambient air exhibit p-type characteristics, as shown in Figure 2.11(a). However, this is not sufficient for future nanotube-based electronics. The ability to “dope” nanotubes purposely to achieve different conducting types is highly desired. Several methods have been developed to achieve n-type CNTFETs (Figure 2.11(b)). It is found that CNTFETs can be converted from p- to n-type simply by annealing the devices in vacuum,^{49,54} or in inert gases²⁸ or hydrogen³⁵. Figure 2.12(a)⁵⁰ shows the conversion of the transfer characteristics of a CNTFET by placing the device into a vacuum chamber. This conversion can also be reversed back to the original curve by gradually introducing oxygen in to the vacuum chamber. An alternative way to convert CNTFETs from p-type to n-type is to dope the p-type CNTFET with electron donors such as potassium^{49,50,55,56} or specific polymer complex. Potassium doping has been used to construct CNT p-n diodes⁵⁷ and complementary logic gates^{31,49}. In this method, potassium atoms in evaporated vapor are adsorbed on the surface

of SWNTs and the tubes are doped simultaneously (Figure 2.12(b)).⁵⁵ Besides, several types of polymer complex have been used as n- doping materials for CNTFETs. In particular, an n-type doping for CNTFETs can be realized by coating PEI (polyethylenimine) on the top of SWNTs.^{58,59} Recent results also suggest that p- and n- type behaviors can be controlled easily using polymer electrolyte gate. Lu *et al.*³⁷ show that, based on a lithium percolate/PEO (poly(ethylene oxide)) mixture, both p- and n-type CNTFETs can be achieved by varying the concentrations of additives DDQ (2,3-dichloro-5,6-dicyanobenzoquinone). Similarly, by varying the electron donating and accepting abilities of the chemical groups of the host polymer, unipolar p- or n-type devices that are stable at room temperature in air can be fabricated.³⁸

Figure 2.13 Ambipolar transfer characteristics of a CNTFET.⁶⁰

Besides, ambipolar characteristics of CNTFETs (Figure 2.13),⁶⁰ the intermediate state between conversions from p- to n- type characteristics have also been investigated intensively. Devices with ambipolar characteristics can operate as switches for electrons and holes depending on the signs of the gate voltage. An ambipolar characteristic can be obtained using polymer gates. Alternately, the ambipolar characteristics can also be found during annealing a p-type CNTFET

covered with SiO_2 in vacuum or in ambient atmosphere.²⁸ The CNTFETs fabricated with large-diameter (3-5 nm) SWNTs (small band gap ~ 0.3 eV) typically exhibit ambipolar characteristics.^{61,62} For small-diameter (1.4 nm) SWNTs, ambipolar behavior is observed in air with very thin gate oxide (10 nm).⁶³ In addition, these ambipolar CNTFETs can be converted to p-type with an asymmetric gate structure.⁶³

The mechanisms of conduction type conversion have been clearly clarified by Heinze *et al.*⁴⁷ through comparing theoretical calculation and experimental data of CNTFETs. For a common back-gated CNTFET with tube diameter less than 3 nm and channel length less than 10 μm , Schottky barrier behavior will be the major mechanism of switching the devices. The Schottky barrier is sensitive to the work function of the metal electrodes and the work function is sensitive to the adsorbed gases. Figure 2.14 (a) and (b) show the calculated conductance vs gate voltage with various work functions of metal electrodes and various doping level in the CNTs, respectively. There is a qualitative difference in the characteristics of the devices with changes in the work function and doping level. The change in the work function leads to a conductance lowering for one sign of V_{gs} and an increase for the opposite sign of V_{gs} without change in threshold voltage (Figure 2.14(a)). In contrast, the change in doping level to the CNTs results in curve shifting (Figure 2.14(b)). In particular, a curve shift to negative V_{gs} side is a result of n-doping and a shift to positive V_{gs} direction is a result of p-doping. As shown in Figure 2.14 (c) and (d), the experimental results are qualitatively consistent with the calculated data. The oxygen adsorption may change the conductance without shifting the threshold voltage while the potassium doping shifts the transfer curves towards negative V_{gs} side. Thus, the main effect of oxygen exposure is not on the doping of CNTs, but rather on changing the work function of the metal electrodes.

Figure 2.14 Calculated conductance vs gate voltage at room temperature, varying (a) the work function of the metal electrode, and (b) doping of the CNT. The experimentally measured effect of (c) Oxygen adsorption and (d) potassium doping on CNTFETs.⁴⁷

2.5.5 DWNTs-based CNTFETs

The first DWNTs-based CNTFETs is reported by Shimada *et al.* in 2004.⁶⁴ They found that all semiconducting DWNTs-based (diameter $\sim 1.6\text{-}2.0\text{nm}$) FETs exhibit ambipolar characteristics. The ambipolar characteristics can be explained using a small bandgap caused by large diameter, similar to SWNT-FETs. More detailed researches have been carried out by Wang *et al.* in 2005 and

2007.^{17,65} They suggest that the conductance of an individual DWNT-FET is determined by the conductivity of the outer-shell with influences from inner shell. For S@M (inner shell is semiconducting and outer shell is metallic, the denominating method is shown in Figure 2.15) or M@M DWNT-based FETs, the devices show metallic behavior because the outer shells are metallic (Figure 2.16(a)). However, for an M@S DWNT-FET, the device shows a semiconducting characteristic with weak gate dependence, *i.e.*, a small $I_{\text{on}}/I_{\text{off}}$ (Figure 2.16(b)). The $I_{\text{on}}/I_{\text{off}}$ will increase with decreasing temperature implying that the influence of metallic inner shell on the conductance becomes smaller at lower temperature (Figure 2.16 (c)). In other words, the interaction between the inner and outer shell is weaker at lower temperature. Last, for an S@S DWNT-based FET, the transfer characteristic is a p-type characteristic with high $I_{\text{on}}/I_{\text{off}}$ (Figure 2.16 (d)). Interestingly, all these three types of $I_{\text{ds}}-V_{\text{gs}}$ characteristics have been also observed in CNTFETs based on SWNTs bundle and it is not easy to differentiate these characteristics between SWNT-FETs and DWNT-FETs without employment of newer technology. New techniques such as in situ Raman scattering has been used to investigate electron transport properties of DWNTs on a FETs platform. The details of this work will be discussed in Chapter 5 and 6.

Denominating method of DWNT $(n_i, m_i)@(n_o, m_o)$

Figure 2.15 denominating method of a DWNT*

Besides, other studies have highlighted that the performances of DWNT-FETs can be more easily affected by humidity or attached functionalized groups than SWNT-FETs.⁶⁶ Nevertheless, how the adsorbed molecules affect the electrical properties of DWNT-FETs is still under argument. In Chapter 4, we pay our attention to the electrical properties of DWNTs through comparing the hysteretic behaviors of DWNT-FETs and SWNT-FETs.

Figure 2.16 I-V measurements for DWNT-FETs. (a) S@M or M@M type. (b) M@S type. (c) Temperature dependence of I-V measurement for an M@S DWNT-FET. (d) S@S type.

2.5.6 Applications of CNTFETs and some practical difficulties

Although the study on CNTFETs is still in the research stage, the CNTFETs have shown

amazing performances such as high drive current, high transconductance and high mobility.⁶ Several applications, including logic circuits,^{31,32,35,36} memories,⁶⁷⁻⁷⁰ chemical sensors,⁷¹⁻⁷³ p-n junction diodes⁷⁴ and light emission devices⁷⁵⁻⁷⁷ have demonstrated promising performances. However, many challenges remain before these molecular electronic devices become useful nano devices. Most challenges stem from the material itself. So far, no technique is able to produce a single type of uniform CNT with only one chirality. Therefore, separation techniques and breakdown process have to be used in fabricating CNTFETs.^{78,79} Usually, the separation is carried out by combination of ultrasonication and centrifuge from CNTs suspension.⁸⁰ With the process, the CNTs with different diameters are suspended well in different layers of the solution. From the supernatant of the solution after centrifuge, CNTs suspension with narrow diameter distribution can be obtained. Consequently, the devices fabricated from this kind of suspension may have small bundles of semiconducting and metallic tubes. Subsequently, the electrical breakdown process can be applied to burn off the metallic tubes in a CNTs bundle. Both techniques are used in our experiments and will be elaborated in details in Chapter 3.

On the other hand, manipulation of CNTs to desired locations is also difficult. Spin-coating CNT suspension onto structured wafers is a simple and commonly used process aiming at distributing CNTs onto sample surface.^{26,27,31,33} However, the inabilities to control the distribution, orientation of CNTs and the contamination on the entire sample surface are major drawbacks of this technique. Direct growth of CNTs from one electrode to another is a relatively controllable process.^{49,61} Unfortunately, this approach causes the catalyst contamination and poor selectivity of CNTs.

Chapter 3 Experimental details

3.1 The carbon nanotubes used in this project

3.1.1 The SWNTs

Figure 3.1 RBM peaks of SWNTs film.*

The high-purity SWNTs (95%) used in these experiments are purchased from Materials and Electrochemical Research Corporation. The SWNTs are grown using arc-discharge method. The as-prepared SWNTs have average diameter of 1.4 nm and length up to a few tens of microns. The diameter is obtained from Raman spectrum Figure 3.1, the method of retrieving tube diameter⁸¹ from Raman spectrum will be discussed in more details in chapter 5. The SWNTs are in form of bundles. Figure 3.2 shows the transmission electron microscopy (TEM) images and the

atomic force microscopy (AFM) image of the tubes. Commonly, the bundle is big and wrapping around each other. Therefore, further treatment to the suspension is necessary before device fabrication.

Figure 3.2 (a) TEM image of SWNT bundles. The scale bar is 20 nm. (b) Enlarged view of SWNT bundles. (c) AFM image of SWNT bundles.*

3.1.2 The DWNTs

Figure 3.3 RBM peaks of DWNTs film.*

The high quality DWNTs used in this project are offered by Prof. Morinobu Endo of

Shinshu University, Japan. Typical outer- and inner-shell diameters of the DWNTs are ~ 1.4 and ~ 0.8 nm (obtained from Raman spectrum Figure 3.3), respectively. The DWNTs are obtained using optimized catalytic chemical vapor deposition method and efficient purification process described in following part.⁸² Two types of catalysts are used in the growing process, i.e. conditioning catalyst and tube growth catalyst. The conditioning catalyst can cause more DWNTs growth than SWNTs due to possible increase in the amount of active carbon species. The preparation of the conditioning catalyst is described as follows. An ethanol solution containing Al_2O_3 powder and hexaammonium heptamolybdate tetrahydrate (5 wt.%) is prepared under sonication for 10 minutes; subsequent evaporation of the solvent occurred at 100°C for 1 hour, followed by baking of the products under vacuum at 110°C for 12 hours. The dry material is then grounded into fine powder using a mortar and a pestle. For the preparation of the DWNT catalyst, same procedure is applied except for the use of ammonium iron citrate (3 wt. %) and MgO powder (Wako Chemical). The synthesis of carbon nanotubes is carried out using a horizontal reactor. The Fe/MgO powder (nanotube catalyst) is placed at the center of the reactor, whereas the Mo/ Al_2O_3 (conditioning catalyst) is placed at the furnace entrance. The reactor is heated up to 875°C in an Ar atmosphere. Subsequently, the hydrocarbon feedstock ($\text{CH}_4 + \text{Ar}$ mixture, 1:1) is fed into the reactor (200 cc/min) for 10 minutes. The catalyst and the nanotube material are then extracted after allowing the furnace to cool down to room temperature. A two-step purification process is applied to purify the products. First, hydrochloric acid (18 wt. % HCl at 100°C for 10 hours) is used to remove the iron catalyst and supporting material. Second, the products are oxidized in air at 500°C for 30 minutes in order to remove amorphous carbon and chemically active SWNTs. After purification, TEM reveals that the yield of DWNTs is extremely high (more than 95%) and

that they are arranged in bundles (Figure 3.4 (a) to (c)).

Figure 3.4 Diffraction pattern of DWNTs from SEM (a) and high resolution TEM (b) and (c).⁸²

Figure 3.5 Inner-tube diameter distribution of DWNTs measured from HRTEM images (established from 57 individual nanotubes), which are consistent with the diameters calculated from the RBMs analysis.*

From the high resolution TEM image of 57 individual DWNTs, the distribution of inner shell diameter is plotted in Figure 3.5. As shown in the figure, the inner shell diameters are around 0.9 nm which are consistent with the results retrieved from RBM bands in Raman scattering (Figure 3.3).

3.2 Fabrication of the CNTFETs

3.2.1 Suspension preparation

As shown in Fig. 3.2 and Fig. 3.4, the CNT bundles are very big and wrapping around each other. Therefore, further treatments to the suspension are necessary before the device fabrication. The treatments are implemented in two steps. First, surfactants are added into the CNTs/DI water suspension. Sodium dodecylsulfate (SDS), sodium dodecylbenzenesulfonate (SDBS) or Triton X-100 are used as the surfactants, respectively.⁸³ Second, the suspension is placed into the ultrasonicator for agitation. The CNT bundles become much thinner, but unfortunately shorter, after the treatment. The dispersion of the CNTs in the suspension depends on the surfactants and the duration of ultrasonic agitation. A detailed comparison of the dispersion effects of the different surfactants will be discussed in Chapter 4.

3.2.2 The Substrate and electrode preparation

Figure 3.6 (a) AFM image of 4 electrodes made from a “cross” pattern mask. (b) Schematic structure of the substrate and electrodes.*

Silicon wafers capped with a thermally grown SiO_2 layer are used as the substrates. The metal electrodes on the substrate are deposited using standard photo lithography, electron-beam evaporation and lift-off processes. A typical electrode is made of an Au layer on top of a Ti layer, which enhances the adhesion between the Au layer and SiO_2 surface. AFM images of the electrodes obtained from a “cross” patterns and the schematic structure of the substrate with electrodes are shown in Figure 3.6 (a), and the device structure is illustrated in Figure 3.6(b). Adjacent pair of electrodes can be used as the “source” and “drain” electrodes. The distance between the two electrodes varies from 1 to 5 μm .

3.2.3 AC dielectrophoresis technique⁸⁴

Figure 3.7 (a) SEM image of four Au/Ti electrodes (white parts) on a Si/ SiO_2 wafer. AC bias voltage is applied between two adjacent electrodes, as indicated in the figure. AFM images of SWNTs bridging the adjacent electrodes for a deposition time of (b) 50s and (c) 300s, respectively. The black arrows label the direction of the electric field.*

With the CNTs suspension and the patterned electrodes, we now proceed to the manipulation of the CNTs. Take the “cross” electrodes as an example. The set up of the ac

dielectrophoresis method is shown in Figure 3.7(a). An ac bias voltage is applied between two electrodes. A drop of the well prepared CNTs suspension is introduced onto the structured substrates, on which an ac bias is applied. The peak-to-peak value of the ac source (sinusoidal wave) is within 16 V and the frequency used is 2~8 MHz. The resistance between the two electrodes is typically decreased to several K Ω to tens of M Ω after CNTs bridged the electrodes, depending on the characteristics of the contacts and the bridged CNTs. Once the resistance is decreased, the AC bias is turned off immediately. Then the wafer is rinsed with DI water to cleanse the wafer surface. The number of CNTs between the electrodes depends on the deposition time and CNT concentration of the suspensions.

The mechanism for the ac-dielectrophoresis technique is as follows. Upon applying the ac electric field, the CNTs will experience two forces. One is the electrophoretic force from the charge in the CNTs; the other is the dielectrophoretic force from the dielectric constant difference between CNTs and the solvent medium. The time-averaged dielectrophoretic force can be expressed approximately as follows:

$$\vec{F} \propto \epsilon_m \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \nabla E_{\text{rms}}^2 \quad (3.1)$$

where ϵ_m and ϵ_p are the dielectric constant of the solvent medium and the CNTs, respectively, E_{rms} is the average electric field strength. $\epsilon_m = 18.3\epsilon_0$ for IPA as solvent and $\epsilon_p = 2000\epsilon_0$, $2\sim 5\epsilon_0$, $15\epsilon_0$ for m-CNTs, s-CNTs and graphite, respectively. Since the high frequency ac bias is used here, the electrophoretic force does not affect the motion of the CNTs because of a time averaging effect. Contamination is rarely found between the two electrodes under the high frequency bias as the permittivity of the CNTs is larger than that of the other contaminants (for example, amorphous carbon) in the suspensions.

3.2.4 Electrical breakdown (burn-off process) of CNTs

Figure 3.8 (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. (c) I_{ds} - V_{ds} at a series of V_{gs} of the device after burn-off process. Inset: Schematic cross section of a back-gate CNTFET. (d). I_{ds} - V_{gs} curve at $V_{ds} = -150$ mV.⁸⁵

Most of the bridged CNTs bundles between two electrodes contain m- and s- CNTs. Since the conductance of s-CNTs displays strong dependence on the gate voltage, we can switch off them by adjusting the gate voltage V_{gs} . Thus, the source-drain current I_{ds} will only pass through m-SWNTs after the s-SWNTs are switched off. With a sufficiently high V_{ds} , a large source-drain current passing through the m-SWNTs, enough heat is generated and the metallic CNTs can be burnt off, leaving the s-SWNTs behind. I_{ds} - V_{ds} curves at different V_{gs} before and after the electrical breakdown are shown in Figure 3.8 (a) and (c), respectively.⁸⁵ Figure 3.8 (b) shows the I_{ds} - V_{ds} curves during the breakdown process. The apparent current drops in curve 1 and 3 indicate breakdown of m-SWNTs in two sweep of V_{ds} . Curve 2 is the I_{ds} - V_{ds} after the first breakdown shown in Curve 1. During the breakdown process, $V_{gs} > 14$ V is maintained to completely deplete the s-SWNTs; while V_{ds} is swept from 0 to a larger value gradually. The on/off ratio (I_{on}/I_{off}) increases from 2 up to 10^6

after breakdown as shown in Figure 3.8 (d). A high on/off ratio indicates that the current flows through s-SWNTs and majority of the m-SWNTs are indeed burnt off.

The mechanism of the electrical breakdown is as follows. CNTs have strong C-C bonds with current carrying capacities exceed $10 \mu\text{A}/\text{nm}^2$. Therefore, oxidation at the defect sites or the dangling bonds on the CNTs where local heat will be generated by the current. The m-CNTs may not be burnt off together at one time. It is possible that the outmost m-CNTs in the bundle are burnt off first as they are fully exposed to oxygen.

Figure 3.9 Electrical performances before and after a single-shell electrical breakdown of a DWNT. (a) A schematic drawing of current flow in a S-M DWNT after inner shell breakdown. (b) The breakdown process of (a). (c) Electrical measurement of (a) before and after breakdown. (d) A schematic drawing of current flow in a M-S DWNT after outer shell breakdown. (e) The breakdown process of (d). (f) Electrical measurement of (d) before and after breakdown.⁶⁵

The burn-off process of DWNTs has been investigated in details by Wang *et al.* in 2007. The breakdown of the outer or inner shell of a DWNT results in different electrical performance. As shown in Figure 3.9 (a) to (f),⁶⁵ electrical performance before and after a single-shell electrical breakdown of a DWNT are very different for the various types of DWNTs. In our experiments, breakdown of different layer in a DWNT is uncontrollable. In order to avoid this uncertainty, no breakdown process is applied to any DWNTs-based devices used in this project.

3.3 Device characterization

3.3.1 Imaging and topography of devices

Figure 3.10 (a) A bundle of CNTs are observed by FESEM. (b) AFM image of a CNT device. (c) The height profile at the position of white line in (b).*

The device topography can be observed using field emission SEM (FESEM) or AFM. From SEM image (Figure 3.10(a) as an example), a bundle of CNTs are seen between two metal

electrodes and the details of the bundle are clear. However, SEM cannot offer information such as bundle size and electrode height. Most importantly, the device may be destroyed by the high-energy electron beam after electron scanning in SEM. In contrast, AFM technique can offer accurate ($\sim 0.1\text{nm}$ or even higher) height profile of the device without damage it. The height profile (Figure 3.10(c)) at the position of white line in Figure 3.10(b) indicates that the tube diameter is around 1.48nm .

3.3.2 Electrical measurement

Figure 3.11 Schematic drawing of electrode connection during electrical measurements.*

Figure 3.11 shows a schematic drawing of electrode connection for our electrical measurements such as transfer characteristics (I_{ds} - V_{gs} curve). Hysteresis loops in the transfer characteristics of the CNTFETs are measured by sweeping gate voltage V_{gs} from -20 V to $+20\text{ V}$ (called forward sweeping) and vice versa (backward sweeping). For a typical measurement, a

sweeping speed is 78V/s, while a slow sweeping speed of 2.5 V/s is used for the purpose of comparison. The analysis of hysteresis loops will be discussed in details in the next chapter. The system used in this project is 4-probe manual probing station connected with HP 4156B semiconductor parametric analyzer, which has a current resolution of 1 pA.

3.3.3 In situ Raman scattering

Figure 3.12 Schematic diagram of the in situ Raman scattering setup.*

The in situ Raman microscopy setup is based on the WITec CRM200 confocal Raman microscopy system (50 μm pinhole) with OLYMPUS microscope objective (100 $\times$ NA=0.95). A double-frequency Nd:YAG laser (532 nm, CNI Laser) is used as the excitation laser. The laser is

coupled into a 3.5 μm -core diameter single mode fiber. As shown in Figure 3.12, the sample is placed on a translation stage, which can be moved coarsely along x- and y- axes. It also can be finely moved with a piezostage. The piezostage has 100 μm of travel distance along x- and y- directions and 20 μm in the z-direction. The Raman scattered light is directed to either 1800 grooves/mm or 600 grooves/mm grating and detected using a TE cooled charge-coupled-device (CCD) cooled to -64 °C. The direct spectral resolution is 1 cm^{-1} from the spectrometer and the spectral difference of 0.02 cm^{-1} can be resolved after curve fitting. The stage movement and data acquisition are controlled using ScanCtrl Spectroscopy Plus software from WITec GmbH, Germany. Fitting of single spectrum is performed using Renishaw WiRE2.0 software. Data analysis for Raman images is conducted using WITec Project software. As shown in the inset of Figure 3.12, the electrical measurement and Raman spectra are acquired simultaneously. The details will be discussed in Chapter 5 and 6.

3.3.4 Photoluminescence of CNTs

Photoluminescence (PL) is an important technique for measuring the electronic structure of a substance, which can be used to determine the purity and crystalline quality.^{80,86-90}

The photoluminescence of CNTs can be measured using Nanolog modular spectrofluorometer equipped with InGaAs multi channel array detector. The incident light is tuned to a single wavelength using a monochromator in the range from 400 to 850 nm with 2nm/step. The detector can detect the signal from 800nm to 1500nm. From the results of photoluminescence, the information of optical absorption and subsequent emission can be directly observed. The electronic structures of the sample can be retrieved from the PL results. In a reverse way, the any

purposely induced modification on the electronic structure may be revealed in the PL results. As shown in Table 3.1, the set of transition wavelengths observed in photoluminescence of SWNTs are corresponding to different (n,m) assignments and RBM frequencies,⁹⁰ which may be further discussed in Chapter 5.2.

λ_{11} (nm)	λ_{22} (nm)	$h\nu_{11}$ (eV)	$h\nu_{22}$ (eV)	Assignment	Predicted $\bar{\nu}_{\text{RBM}}$ (cm ⁻¹)*	Observed $\bar{\nu}_{\text{RBM}}$ (cm ⁻¹)
833	483	1.488	2.567	(5,4)	372.7	373†
873	581	1.420	2.134	(6,4)	335.2	
912	693	1.359	1.789	(9,1)	307.4	
952	663	1.302	1.870	(8,3)	298.1	297‡
975	567	1.272	2.187	(6,5)	307.4	
1023	644	1.212	1.925	(7,5)	281.9	283‡
1053	734	1.177	1.689	(10,2)	265.1	264§
1101	720	1.126	1.722	(9,4)	256.4	
1113	587	1.114	2.112	(8,4)	278.3	
1122	647	1.105	1.916	(7,6)	262.1	264‡
1139	551	1.088	2.250	(9,2)	289.7	
1171	797	1.059	1.556	(12,1)	237.0	236
1172	716	1.058	1.732	(8,6)	243.7	
1197	792	1.036	1.565	(11,3)	232.8	233¶
1244	671	0.997	1.848	(9,5)	241.4	
1250	633	0.992	1.959	(10,3)	251.1	251‡
1250	786	0.992	1.577	(10,5)	225.1	225¶
1263	611	0.982	2.029	(11,1)	256.4	
1267	728	0.979	1.703	(8,7)	228.9	
1307	859	0.949	1.443	(13,2)	211.9	
1323	790	0.937	1.569	(9,7)	214.9	215¶
1342	857	0.924	1.447	(12,4)	207.5	
1372	714	0.904	1.736	(11,4)	221.5	
1376	685	0.901	1.810	(12,2)	227.0	
1380	756	0.898	1.640	(10,6)	213.4	
1397	858	0.887	1.445	(11,6)	200.8	
1414	809	0.877	1.533	(9,8)	203.4	
1425	927	0.870	1.337	(15,1)	193.6	
1474	868	0.841	1.428	(10,8)	192.5	
1485	928	0.835	1.336	(13,5)	187.2	
1496	795	0.829	1.559	(12,5)	198.3	
1497	760	0.828	1.631	(13,3)	203.4	
1555	892	0.797	1.390	(10,9)	183.3	

*Using the expression $\bar{\nu}_{\text{RBM}} = \frac{223.5}{d_t \text{ (nm)}} + 12.5$ and assuming a C-C bond distance of 0.144 nm. †Raman

excitation wavelength 830 nm. ‡Raman excitation wavelengths 633 nm and 636 to 672 nm. §Raman excitation wavelength 1064 nm. ||Raman excitation wavelength 782 nm. ¶Raman excitation wavelength 785 nm.

Table 3.1 Spectral data and assignments for SWNTs using photoluminescence.

Chapter 4 Hysteretic transfer characteristics of CNTFETs

4.1 Literature review of hysteresis in CNTFETs

Figure 4.1 (a) AFM image of the CNTFET. The scale bar is 1 μm . (b) I_{ds} - V_{gs} curve of the CNTFET. (c) Four read/ write cycles of the CNTFET memory at room temperature.⁶⁷

Hysteretic transfer characteristic is one of the most important features of CNTFETs, which enables the applications of CNTFETs on memory. The first CNTFET memory (Figure 4.1(a)) based on the hysteresis effects was reported by Fuhrer *et al.* in 2002.⁶⁷ As shown in Figure 4.1(b), when the gate voltage V_{gs} is swept from -10 to +10 V (called forward sweeping) and vice versa (called backward sweeping), the direction of sweeping led to a difference in the threshold voltage (V_{th}) of the CNTFET. Simultaneously, the hysteresis loop was formed by a shift in V_{th} and a pronounced hysteretic window (~ 6 V) was observed. The arrows in Figure 4.1(b) indicate the sweeping directions of the gate voltage.

Figure 4.1(c) illustrates the memory operation based on the hysteresis loop of the CNTFET.

The state of the device was read at the source-drain voltage $V_{sd} = 0.5\text{V}$ and gate voltage $V_{gs} = -1\text{ V}$.

The writing and erasing operations were performed with +8 V and -8V pulses of gate voltage, respectively. A current (I_{sd}) of $> 1\text{ }\mu\text{A}$ may be observed as 'on' state, as shown in Figure 4.1(c). After ~ 50 seconds initial decay, I_{sd} remains constant and the holding time of this state exceeds 5000 seconds. The authors explained the memory effect by the charge storage in the dielectric layer right below the SWNT channel. The electric field at the SWNT/SiO₂ interface can be estimated as⁹¹

$$E = \frac{V_{gs}}{KR_t \ln(R_g / R)} \sim \frac{V_{gs}}{23R} \quad (4.1)$$

where $K = 3.9$ is the dielectric constant of SiO₂, $R = 1.35\text{ nm}$ is the SWNT radius, and $R_g = 500\text{ nm}$ is the dielectric thickness. Thus $E > 0.3\text{ V/nm}$ for gate voltage $V_{gs} = 10\text{ V}$ is obtained, which is comparable to the breakdown field for SiO₂ ($\sim 0.25\text{ V/nm}$). Moreover, at $E = 0.3\text{ V/nm}$, the movement of charges in the dielectric is reasonable. Therefore, electrons attracted by positive V_{gs} are easily injected into the dielectric from the SWNT channel and are able to remain trapped in metastable states until the polarity of V_{gs} is reversed. Another possible reason is that the gas molecules around the SWNT channel may experience corona discharge in such high electrical fields ($\sim 0.3\text{ V/nm}$), leading to ionizing of the gas molecules. The ionized gas molecules may transfer the charges to the dielectric surface. In addition, it is also possible that the high electric field causes a rearrangement of adsorbents on the SWNT, such as oxygen.

The amount of charges stored ΔQ can be expressed in terms of the threshold voltage shift as

$$\Delta Q = C_g * \Delta V_{th} \quad (4.2)$$

where $C_g = 54\text{ aF}$ is the gate capacitance and may be determined directly from low-temperature Coulomb blockade measurements, and $\Delta V_{th} = 6\text{ V}$ is the width of the hysteretic window (the shift in the threshold voltage V_{th}). Hence, $\Delta Q = 3.24 \times 10^{-16}\text{ C}$ is obtained. Accordingly, there are around

2000 electrons being trapped. The carrier mobility μ can also be determined from Figure 4.1 (b) as

$$\mu = \frac{L^2}{C_g} \frac{dG}{dV_{gs}} \quad (4.3)$$

where L is the channel length, C_g is the gate capacitance, and $\frac{dG}{dV_{gs}}$ can be obtained from the linear

portion of Figure 4.1 (b). Thus, μ is calculated for holes as $\sim 9000 \text{ cm}^2/\text{V}\cdot\text{s}$ ($\mu \sim 450 \text{ cm}^2/\text{V}\cdot\text{s}$ in pure

silicon). As a summary, one can see CNTFETs have following merits:

- ✧ Extremely high carrier mobility ($\mu \approx 9000 \text{ cm}^2/\text{V}\cdot\text{s}$ for hole).
- ✧ Small geometrical capacitance ($C_g \approx 54 \text{ aF}$).
- ✧ Enhanced electric field due to cylindrical geometry ($E \sim 0.3 \text{ V/nm}$).

These merits guarantee the local charge density effect on the conductance, as well as high charge injection capability. Therefore, the CNTFET is an ideal charge-detecting device. This is an inherent advantage of CNTFET in nanoscale memory device application.

Figure 4.2 (a)-(c) I_{ds} - V_{gs} curves in high vacuum with $V_{ds} = 0.5$ mV. The sweeping range of V_{gs} is increased from (a) to (c). (d) Diagram of avalanche injection of electrons into bulk SiO_2 from CNTFET channel. (e) Data of a nonvolatile molecular memory cell.⁶⁸

Figure 4.3 Memory effects in an annealed SWNT FET bundle at low temperatures (84 and 12 K).⁷⁰

Radosavljević and co-workers reported the nonvolatile memory (NVM) based on an n-type

CNTFET⁶⁸. The device was investigated in high vacuum to study the charge traps in bulk SiO₂. As shown in Figure 4.2 (a) to (c), the hysteresis increases steadily as the sweeping range of gate voltage is increased. This indicates that the hysteresis originates from avalanching injection into the bulk oxide traps. Take Figure 4.2(c) as an example, after a sweep from -20 to $+20$ V, the shift in threshold voltage from -7 to 2 V indicates an injection of electrons into oxide traps. The electrons are injected from the CNTFET channel, where the electric field is highest due to the cylindrical device geometry. Figure 4.2(d) illustrates the process of electrons injecting from the CNTFET channel. Based on the device, a memory cell consists of an n-CNTFET and a $1\text{ M}\Omega$ load resistor, as shown in inset of Figure 4.2(e). Read ($V_{\text{in}} = 0$) and write/erase ($V_{\text{in}} = -20\text{ V}/+20$) are applied to the input terminal (gate). Logical state “1” (“0”) is defined as $V_{\text{out}} = 1\text{ V}$ (0 V). To write (erase) a “1” (“0”) to the memory cell, V_{in} is switched rapidly to -20 V ($+20\text{ V}$) and back to 0 , so that the CNTFET is “on” (“off”) at the read voltage ($V_{\text{gs}} = 0$). As shown in Figure 4.2(e), the outputs V_{out} as a function of time are recorded, in which a series of data writing/erasing processes are performed.

The charge storage stability in CNTFET has been investigated by Cui *et al.*⁷⁰ They found that the charges stored in the CNTFETs are stable for more than 12 days at room temperature. Figure 4.3 shows the transfer characteristics at 84 and 12 K . It is noted that the curve measured at 12 K shows numerous sharp peaks originated from single-electron charging of the tube. They also found that the reproducible switching can still be detected when the temperature decreases to 5 K . The persistence of the hysteresis at low temperatures is not caused by the mobile ions within the dielectric since ion hopping is frozen out at liquid-helium temperature ($\sim 4\text{ K}$) due to the high associated activation energy. Therefore, they conclude that the mechanism for charge storage in dielectric is not enough to explain the memory effect observed in CNTFETs.

Figure 4.4 (a) Hysteresis recorded for non-suspended SWNT FET exposed to ambient air at $V_{ds} = 10$ mV (b) Hysteresis recorded in a vacuum chamber of the device in (a). (c) Hysteresis recorded for suspended SWNT FET exposed to ambient air at $V_{ds} = 10$ mV. Inset: A SEM image and a schematic structure of the device. (d) Vanished hysteresis recorded with the same device immediately after placing it in vacuum. (e) Schematic drawing depicting water molecules hydrogen bonding to the surface Si-OH groups.⁹²

In contrast, Kim and co-worker suggested that the hysteresis in CNTFETs may be dominated by charges trapped by water molecules around the nanotubes, including SiO₂ surface-bound water proximal to the nanotubes.⁹² For a common CNTFET, the CNTs channel is laid on a Si substrate capped with SiO₂ and the hysteresis loop at $V_{ds} = 10$ mV in ambient air for the device is shown in Figure 4.4 (a). When the device is put into a vacuum chamber, the hysteresis becomes smaller gradually, but it is not totally eliminated, as shown in Figure 4.4 (b). For comparison, another CNTFET was fabricated, which comprised fully suspended SWNTs over the gate by 2 μm , as shown in the inset of Figure 4.4 (c). The hysteresis loop at $V_{ds} = 10$ mV in ambient

air for the device is shown in Figure 4.4(c). Interestingly, when the device was placed into the vacuum, the hysteresis was almost eliminated, as displayed in Figure 4.4(b). The observations above suggest the charges trapped by water molecules play very important roles in the hystereses of CNTFETs and there are two types of water charge traps. Type one consists of water molecules that are weakly adsorbed on the SWNT surface, and these water molecules can be easily removed by putting the device in a vacuum environment as the case in Figure 4.4(a). Type two involves SiO₂ surface-bound water molecules in close proximity to the nanotubes, as shown in Figure 4.4(c). Hysteresis caused by this type of trapping is almost eliminated when the SWNTs are suspended, as shown in inset of Figure 4.4 (c)). In the suspended structure, the SiO₂ removed was around CNTs bulk but not near the contacts. Thus, one can conclude that, instead of the SiO₂ near contacts, SiO₂ around the channel plays the dominant roles in bounding with water molecules, resulting in the hysteresis of CNTFETs in vacuum.

Figure 4.5 I_{ds} - V_{gs} curves recorded for a SWNT FET under two V_{gs} sweep rates (as indicated) in ambient air.⁹²

In addition to the results presented above, Kim and co-workers reported how the sweeping speed of V_{gs} affected the hysteresis in CNTFET.⁹² As shown in Figure 4.5, when sweep V_{gs} in a slower speed, the constructed hysteretic window became bigger than that of fast sweeping. Bigger

hysteretic window indicates that more charges are trapped in the process of slow sweeping. The results suggest that the adsorbed water molecules can function as deep energy charge traps with slow trapping or detrapping rates.

Figure 4.6 (a) Schematic structure of CNT-based NVM with an ONO charge trap. (b) AFM image of the SWNT attached between two metal electrodes. (c) I_{ds} - V_{gs} at $V_{ds} = -0.9$ V. Two loops correspond to V_{gs} sweeping range of ± 8 V (inner loop) and ± 20 V (outer loop). d) I_{ds} - V_{gs} after charging the ONO storage node with different pulse amplitudes.⁹³

Choi *et al.* demonstrated an SWNT-based nonvolatile memory device using SiO_2 - Si_3N_4 - SiO_2 (ONO) stacks as storage hosts.⁹³ The schematic drawing of the structure of the CNT-based flash memory device is shown in Figure 4.6 (a). The device had a top gate structure with a channel width of a few nanometers and an ONO layer (14 nm) was embedded between the SWNT and gate electrode. Figure 4.6 (b) shows a device consisted of a SWNT with diameter of 3 nm and the length of 1 μm attached between two Au/Ti electrodes. The SWNT channel was completely covered by the ONO film so that atmosphere does not influence the electrical transport property of the SWNT. Two small hysteresis loops were observed at 5 K with different sweeping ranges of gate voltage (Figure 4.6 (c)). The hysteresis loops were suggested to be caused by charges trapped in

ONO layer. Figure 4.6 (d) shows a quantized increment of threshold voltage of 60 mV when the magnitude of charging voltage was increased continuously. The authors suggested that each trap site containing charge in the ONO layer of the memory device acts as a quasi-quantized energy state for the flash memory.

Figure 4.7 (a) SEM image of PmPV/CNT composite deposited on Si wafer with patterned Au electrodes. (b) Current measured during UV illumination cycles in air. The shadowed and unshadowed regions are the UV-on and -off periods, respectively. Inset: schematic device geometry.⁹⁴

Star and co-workers combined CNTFETs with a photosensitive polymer to fabricate optoelectronic memory devices.⁹⁴ Two types of photosensitive CNTFET devices were fabricated. For the first type of the devices, a composite of polymer and nanotubes was deposited onto Si wafers with pre-patterned electrical contacts. The structure and performance of the first type devices are shown in Figure 4.7. The UV illumination modulated the conductivity of the devices. However, the modulation ($\frac{\Delta I_{SD}}{I_{SD}}$) was not efficient. This may be caused by the fact that the contact resistance was very high and the channel of the device consisted of both m- and s- CNTs.

For the second type of the devices, the CNTs were firstly covered with electrodes. Then, a

polymer layer was deposited over the contacts and SWNTs by drop-casting of 0.05 μL of PmPV (0.1 wt %) solution in CHCl_3 from a micropipette. The structure and performances of the device are shown in Figure 4.8. The polymer itself did not significantly modify the device properties. However, when the device was illuminated with 365-nm light, the transfer characteristic shifted toward positive gate voltage. The change of the threshold voltage was 2 V. When the light was turned off, the threshold voltage shift of the device recovered slowly, taking hours to reach their original conductance. The memory operation of the devices in air at room temperature is shown in Figure 4.8(b). The source-drain current versus time response to UV illumination was measured under alternating gate voltage V_{gs} . The offset of V_{gs} is 1 V, amplitude = 4 V and frequency = 1 KHz. As the first type of CNTFETs (solution-coated) showed no optoelectronic memory behavior but the second type of CNTFETs (polymer-coated) showed clear optoelectronic memory behavior, the authors concluded that the proximity of nanotubes to the silicon oxide substrate is necessary for fabrication of CNTs-based long-term memory devices.

Figure 4.8 Response of PmPV polymer-coated CVD-grown CNTFETs to UV light ($\lambda = 365 \text{ nm}$). (a) $I_{\text{ds}}-V_{\text{gs}}$ in air with $V_{\text{ds}} = 1 \text{ V}$ at UV-off (blue curves) and UV-on (red curves) conditions. Inset: schematic device geometry. (b) Memory operation in air at room temperature.⁹⁴

One more noteworthy publication is the modeling of hysteresis presented by Robert-Peillard *et al.*⁸⁵ In their model, a CNT was laid on a SiO₂ layer and contacted to side electrodes. Instead of a planar model, a model with full axial symmetry is used. The only difference between the solutions for these two models is the contacts. In their works demonstrating full axial symmetry model, the carriers are injected and trapped/detrapped in the SiO₂ located within 3 nm around the CNT, leading to the shift of the threshold voltage. These trapped electrons create an additive potential to the external potential felt by the CNT charge carriers. The electrical potential on the CNT can be expressed as the sum of the potential caused by gate voltage and the potential created by trapped charges in the oxide.

Figure 4.9 Threshold voltage versus V_{gs} calculated over a full cycle of V_{gs} for different gate voltage ranges. SR = 1 V/s. Inset: width of the hysteresis as a function of V_{gs}^{Max} .⁸⁵

Figure 4.10 Threshold voltage versus V_{gs} calculated over a full cycle of V_{gs} for different SR. $V_{gs}^{Max} = 10$ V. Inset: semilog plot of the width of the hysteresis as a function of SR.⁸⁵

The influences of the parameters, such as sweeping rate (SR) and the range of the gate voltage ($-V_{gs}^{Max}$, $+V_{gs}^{Max}$), on the hysteresis (H) have also been investigated in details. As shown in Figure 4.9, when V_{gs}^{Max} is higher than a threshold value, H starts to increase linearly with the increase of V_{gs}^{Max} . The increment of H will saturate at certain value, indicating full consumption of the available traps. Furthermore, as shown in Figure 4.10, it is obvious that the slower the V_{gs} is swept, the more electrons are injected. Although the simulated curves are not exactly similar to experimental observation, the simulated trends are as expected.

From the literature review on hysteresis in CNTFETs, the following progresses in CNTFETs can be identified. First, clear hysteretic transfer characteristics have been observed in CNTFETs. Second, based on the hysteretic transfer characteristics, memory operations have been demonstrated and some novel designs have been implemented. Third, the memory effect in CNTFETs may be caused by charge trapping/detrapping in the devices. However, the origins, distributions and influences of the trapping centers on electrical properties of CNTs are still under argument. In this thesis, we have paid our attentions to the hysteretic transfer characteristics whenever we investigate the electron transport in CNTs.

4.2 Research status of transfer characteristics of CNTFETs

Since the transfer characteristics are the most important electron transport features for CNTFETs, the origins and control methods of the characteristics should be clarified. The transfer characteristics reflect two major aspects, i.e., conduction type and hysteresis. Influential factors on these two aspects of transfer curves are identified and discussed below.

During the fabrication of our devices, several types of influential factors from environment, such as water molecules, oxygen and surfactants are potential factors that affect the transfer characteristics of our CNTFETs. We hereby discuss the effects of all these factors on CNTs-based devices individually.

Figure 4.11 Conductance versus V_{gs} curves of a DWNT-FET under different conditions.⁶⁶

The effect of the adsorbed water molecules on SWNTs-based FETs has been systematically investigated by Kim and co-workers.⁹² As mentioned in Chapter 4.1, it has been reported that the

adsorbed water molecules around the nanotubes, including SiO₂ surface-bounded water proximal to the nanotubes, trap charges, resulting in the hysteresis in the electrical characteristics of the transistors. Moreover, at room temperature, the hysteresis persists in vacuum since the SiO₂-bound water molecules do not completely desorb in vacuum. Heating under dry conditions can eliminate the hysteresis.

It has also been reported by Tang *et al.* that the effect of the water molecules on DWNTs-based FETs shows different phenomena.⁶⁶ When the density of the adsorbed water molecules is low, the hysteretic transfer characteristics observed for s-DWNTs-based FETs are similar to those characteristics for s-SWNTs-based FETs. However, when the density of adsorbed water molecules is high, the gate-dependent conductance disappears, *i.e.*, the devices show metallic-like characteristics (Figure 4.11). The phenomenon is interpreted as that the adsorbed water molecules can function as trapping centers when the density of water molecules is low and the molecules act as electron donors when the density is high. Furthermore, compared with SWNTs, DWNTs are apt to adsorb water molecules on the outer surface and the electrical transport properties are more sensitive to environment in this case, as the DWNTs are hole doped and can act as an electric dipole with the inner tube.

The effect of oxygen has been discussed in Chapter 2.5.4. It has been suggested that the oxygen adsorbed to the metal contacts could change the work function of the contacts and consequently change the conduction type of the device.⁴⁷ It is believed that this is the mechanism for the p-type conduction observed for an as-prepared CNTFET in the ambient air. Since the effect of oxygen is mainly on the metal contacts and is independent on the type of CNTs, we suggest that adsorbed oxygen may have similar effect on DWNT-based CNTFETs.

It has been reported by our group that, for SWNT-based FETs fabricated from SWNTs dispersed in Triton X-100/D₂O solution, the as-prepared devices showed an ambipolar transfer characteristic, as shown in Figure 4.12(a).⁶⁰ The characteristic of the devices changed to a unipolar p-type after annealing the CNTFETs at 270°C for 30 min in air (Figure 4.12(b)). The ambipolar characteristics can be restored by introducing Triton X-100/D₂O to the device for 20 min (Figure 4.12(c)). It was suggested that, in the as-prepared device, the surfactant at the interface can change the work function of the Au electrodes and make the Fermi level lie in the middle of the CNT band gap, leading to observed ambipolar characteristic. If there is no surfactant at the interface, as the case after annealing, oxygen will play a key role in modifying the work functions of the Au electrodes, resulting in a unipolar p-type characteristic. The reverse conversion after treating the same CNTFET with pure Triton X-100 solution provides a strong evidence for this interpretation.

Figure 4.12 Transfer characteristics of a SWNT-FET. (a) as-prepared. (b) after annealing at 270°C for 30 minutes in air. (c) after introducing Triton X-100/D₂O for 20 minutes and drying off.⁶⁰

Transfer characteristics	Affecting Factor	SWNT	DWNT
Conduction type	O ₂	Affect metal work function	should be similar with SWNTs
	Surfactant	Triton X-100*	*
Hysteresis	H ₂ O	anticlockwise	anticlockwise
	Surfactant	*	*

Table 4.1 Research status of transfer characteristics of CNTFETs. (* no efforts yet)*

Till date, there is no work reporting the surfactant effect on the conduction type of DWNTs. Furthermore, for the effect of surfactants on the hysteresis in the transfer characteristics, there is no systematic investigation on both SWNTs- and DWNTs- based FETs, as summarized in Table 4.1. Therefore, we design our experiments aiming at studying the effects of different types of surfactants on the transfer characteristics of both SWNTs- and DWNTs-based FETs. Through the experiments, we should have in-depth understanding on the effects of surfactants on CNTFETs. In addition, by comparing the observations from SWNTs and DWNTs, the interaction between inner and outer shell of DWNTs will be studied.

4.3 Effects of surfactants on hysteretic transfer characteristics of SWNTs- and DWNTs-based FETs⁹⁵

4.3.1 Device fabrication and experimental flow

Both back-gated DWNT-FETs and SWNT-FETs are fabricated on p-type silicon wafers capped with 500-nm thermally grown silicon dioxide layer. The source and drain electrodes are made of 15-nm thick Ti and 45-nm thick Au by photolithography, respectively. The p-type silicon is used as the back gate. High quality DWNTs with typical outer- and inner-shell diameters of ~ 1.4 nm and ~ 0.8 nm, respectively, are obtained using optimized catalytic chemical vapor deposition method and efficient purification process described in Chapter 3. SWNTs with a diameter of ~ 1.4 nm, are produced by arc discharge method. 1wt% sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS) and Triton X-100 are used as the surfactants to disperse two types of CNTs, respectively. The molecular formulas of these surfactants are shown in Figure 4.13. The CNTs are then connected between the source and drain electrodes using AC dielectrophoresis (ACDEP) technique.

Figure 4.13 Molecular formulas of SDS, SDBS and Triton X-100, respectively.*

Afterwards, the samples are rinsed using deionized water (DIW) and then dried using N_2 for the first round tests. The second round tests are conducted on each of the devices after annealing at 300°C for ~ 45 minutes and soaked in DIW overnight so that the surfactants can be removed and water molecules can refill the interface between the CNTs and electrodes. To demonstrate the effect of surfactants on the transfer characteristics, the third round tests are conducted after the annealed and soaked devices are immersed in 10wt% SDS, SDBS or pure Triton X-100 liquids for ~ 10 hours and are rinsed and dried using DIW and N_2 , respectively. The flow chart of the experiments is shown in Figure 4.14.

Figure 4.14 The flow of the experiments.*

4.3.2 Experimental results

Hysteresis loops in the transfer characteristics of the CNTFETs are measured by sweeping V_{gs} from -20 V to +20 V (called forward sweeping) and vice versa (backward sweeping). A typical sweeping speed of 78V/s is set, while a slow sweeping speed of 2.5 V/s is used for comparison purpose. Three characters have been scanned in the electrical transfer characteristics, *i.e.*, conduction type, hysteresis direction and change in the width of hysteresis window for different sweeping rate. The conduction type has been identified as p-type, n-type or ambipolar, as discussed in Chapter 2.5.4. For the hysteresis directions are found to be opposite for hole current and electron current in the same ambipolar transfer characteristic. Thus, for clarity purpose, we use the direction of hole current as the direction of hysteresis. As shown in Figure 4.15(a), the transfer curves are shifted to a positive gate voltage side, resulting in the ‘anti-clockwise’ hysteresis. However, if the transfer curves are shifted to a negative gate voltage side, the hysteresis directions are defined as ‘clockwise’ (Figure 4.15(b)). Last, we use the threshold voltage difference between the forward and

backward sweeping to identify the width of the hysteresis. Hence,

Figure 4.15 Schematic drawings of p-type and ambipolar hysteresis loops with (a) ‘anti-clockwise’ hysteresis. (b) ‘clockwise’ hysteresis.*

Figure 4.16 The observed transfer characteristics for SWNT-FETs: (a) P-type ‘anticlockwise’. (b) P-type ‘clockwise’. (c) Ambipolar ‘anticlockwise’ (d) Ambipolar ‘clockwise’.*

Figure 4.17 The observed transfer characteristics for DWNT-FETs: (a) P-type 'anticlockwise'. (b) P-type 'clockwise'. (c) No ambipolar 'anticlockwise' observed. (d) Ambipolar 'clockwise'.*

In order to clarify the observed phenomena, all typical transfer characteristics observed are shown in Figure 4.16 and Figure 4.17 for SWNT-FETs and DWNT-FETs, respectively. In the figures, 'P' and 'A' represent p-type and ambipolar conduction types, respectively. The symbols and represent 'anticlockwise' and 'clockwise' hysteresis directions, respectively. In each figure, the characteristics are shown in the sequence of p-type 'anticlockwise', p-type 'clockwise', ambipolar 'anticlockwise' and ambipolar 'clockwise', respectively. For DWNT-FETs, ambipolar 'anticlockwise' transfer characteristic is not observed in this series of experiments, as shown in Figure 4.17. In order to clarify the effect of different surfactants on the transfer characteristics, the transfer characteristics measured at a fixed sweeping speed of the gate voltage at

78 V/s for different types of tubes and at different conditions. They are summarized in Table 4.2.

From Table 4.2, one can see that, in the first round of tests, several hysteretic transfer characteristics of the devices fabricated from corresponding 1wt% SDS, SDBS and Triton X-100 suspensions, respectively, are observed. The transfer curves obtained in the first round test include all types of transfer characteristics observed, as shown in Figure 4.16. Interestingly, in the second round of the tests, all annealed & soaked SWNT- and DWNT-FETs show typical ‘anticlockwise’ p-type hysteretic characteristics and wider hysteresis loops under a slower sweeping speed (Figure 4.18(a)), consistent with the observations by Kim *et al.* in 2003 (Figure 4.5).⁹² These uniform transfer characteristics in the second round tests offer a possibility to analyze the effects of surfactants at the same starting point. In other words, all the devices are considered as uniform devices in regard to the conduction type and the hysteretic direction in the second round tests, where the surfactants on the SWNTs and DWNTs are removed. In the third round of the tests, introduction of the surfactants to the treated devices leads to different hysteretic directions and conduction types compared to the annealed states (the second round test). Thus, a matrix of the transfer characteristics at different conditions is obtained, from which we can analyze the different aspects of the surfactant effect.

In more details, by comparing the change in the transfer characteristics after introducing different surfactants, we can compare the effects of different surfactants on the SWNTs and DWNTs, respectively. Moreover, by comparing the results between the second and the first round tests, the effect of small amount of specific surfactants on the surface of SWNTs and DWNTs can be analyzed. Similarly, by comparing the results between the second and the third round tests, the effect of large amount of surfactants on the surface of the SWNTs and DWNTs can be studied. Besides, for

a specific surfactant at the same concentration, different phenomena from the SWNTs and DWNTs may suggest the difference between the SWNTs and DWNTs, which may provide some insights into the intershell interaction of the DWNTs.

	SWNT			DWNT		
	SDS	SDBS	Triton	SDS	SDBS	Triton
1Wt% Surfactant suspension	P	P	A	P	A	A

↓ Surfactant removal	P	P	P	P	P	P

↓ Introduce 10wt% or pure surfactant solution	P	P	A	P	A	A

Table 4.2 The matrix of transfer characteristics measure at 78 V/s sweeping rate of gate voltage.*

In the third round tests, treatment of 10wt% SDS to the SWNT-FETs does not change the devices' hysteretic direction and conduction type (not shown here). However, by treating with 10wt% SDBS, the SWNT devices show 'clockwise' p-type characteristics, see the green triangle and cyan square symbols in Figure 4.18(b). In contrast, after introduction of pure Triton X-100 to the SWNT-FETs, ambipolar transfer characteristics are observed and hole current curves form 'clockwise' hysteresis loops (refer to the green triangle and cyan square symbols in Figure 4.18(c)).

For the DWNT-FETs in the third round test, treatment with 10wt% SDS to the annealed

devices causes ‘clockwise’ p-type characteristics (green triangle and cyan square symbols in Figure 4.18(d)) while introduction of 10wt% SDBS or pure Triton X-100 can only make ‘clockwise’ ambipolar characteristics (not shown here, similar to Figure 4.18(c)).

When sweeping V_{gs} with a slow speed at 2.5 V/s, both SWNT- and DWNT- FETs treated with 10wt% SDBS or pure Triton X-100 liquid show ‘clockwise’ and narrower hysteresis loops (see red and blue lines in Figure 4.18 (b) and (c)). Whilst, the DWNT device treated with 10wt% SDS changes its ‘clockwise’ to ‘anticlockwise’ characteristic under slow sweeping (red and blue lines in Figure 4.18(d)). It is also shown in Figure 4.18(c) that the backward sweeping may lead to shallower ‘valley’ for typical V_{gs} sweeping speed.

Figure 4.18 Transfer characteristics of CNTFETs. (a) CNTFETs after annealing and soaking. (b) SWNT-FETs after 10wt% SDBS treatment. (c) SWNT-FETs after pure Triton X-100 treatment. (d) DWNT-FETs after 10wt% SDS treatment.*

4.3.3 Discussions of results

In the second round of the tests, our DWNT devices have similar behaviors as the SWNT devices. This finding suggests that our DWNTs and SWNTs probably possess similar electrical properties. In other words, for the CNTFETs based on our intrinsic SWNTs and DWNTs (both have diameter $\sim 1.4\text{nm}$), the differences of transfer characteristics are not significant. This is consistent with a simulation which suggests a DWNT with outer-shell diameter $\sim 1.35\text{nm}$ or thicker has the electrical properties mostly determined by its outer shell, while the coupling between the outer and inner shells is negligible.⁹⁶ As our DWNTs and SWNTs have comparable diameters of $\sim 1.4\text{ nm}$, it is understandable that our DWCNT devices behave similarly as those SWNT devices in the second round of the tests. From this point of view, we can, therefore, say that the ‘clockwise’ hystereses and ambipolar characteristics in third round of the tests should be caused by the surfactants.

For hysteretic direction of CNTFETs, it is widely accepted that water molecules play the most important role in the typical p-type ‘anticlockwise’ hysteresis loops.⁹² The ‘anticlockwise’ hysteresis loops can be well explained by the injecting carriers from carbon the nanotube channels to adsorbed water molecules, leading to hole trapping at a negative V_{gs} and electron trapping at a positive V_{gs} . This will induce an extra negative potential at the end of forward sweeping, causing p-type ‘anticlockwise’ hysteresis loops (Figure 4.18(a)). Our finding of ‘clockwise’ hysteresis loops shown in Figure 4.18(b) to (d) can be interpreted using the similar mechanism if an extra positive

potential is induced after forward sweeping. We suggest that an extra positive potential can be generated by mobile ions or charged clusters in the surfactants layer around CNT channels. In SDS or SDBS layer, Na^+ ions are likely to cause the extra positive potential and the observation after adding 10wt% SDBS to the annealed DWNT-FETs can serve as evidence. Na^+ ions are randomly distributed in the SDBS surfactant layer around DWNTs channel. Under negative V_{gs} , Na^+ ions in the surfactant layer are attracted to the interface between surfactant and SiO_2 (Figure 4.19(a)). When sweeping to positive V_{gs} , the electric field pushes the Na^+ to the interface between DWNTs channel and surfactant (Figure 4.19(b)). Therefore, at the end of a forward sweeping, Na^+ ions pushed around the CNT channel by the positive V_{gs} generate an extra positive potential, leading to ‘clockwise’ transfer characteristics.

As Triton X-100 has no mobile ions, flexible charged clusters in this surfactant might dominate the ‘clockwise’ hysteresis loops of the annealed CNTFET with addition of Triton X-100. Given that the flexible extra long clusters of Triton X-100 can be squeezed and stretched under external electric field, the charged group in Triton X-100 can also play the same role as Na^+ in SDS and SDBS.

Figure 4.19 Schematic diagrams of the cross section for the channel of DWNT-FET treated with

10 wt% SDBS. (a) $V_{gs} < 0V$. (b) $V_{gs} > 0V$.*

On the other hand, water molecules may form a competing effect with the surfactants used. If the surfactant coverage on the CNT surface is low, the adsorbed water molecules will dominate ‘anticlockwise’ characteristics. As water molecules are slow trapping centers, a broader ‘anticlockwise’ hysteresis loop is observed with slow sweeping speed (Figure 4.18(a)). In contrast, if the surfactant coverage on the CNT surface is high, with typical sweeping speed 78V/s, Na^+ motion in response to external electric field is much faster than water molecules. Na^+ mobile ions may dominate a ‘clockwise’ hysteresis loop. However, a slower sweeping speed will allow water molecules to respond, reducing or overcoming the effect of the mobile ions. Consequently, a narrower ‘clockwise’ (Figure 4.18(b) and (c)) or an ‘anticlockwise’ hysteresis loop (Figure 4.18(d)) are observed, respectively.

The formation of shallower ‘valley’ in Figure 4.18(c) can be explained if we hypothesize that the recombination rate of the injected electrons is increased with increase in the numbers of holes injected into the CNTs channel. The holes and electrons are injected into the channel at negative and positive V_{gs} , respectively. The position of the minimum current represents a minimum number of electrons and holes in the channel. For a forward sweeping, holes are injected in the beginning when $V_{gs} \leq 0V$, followed by electrons injection when $V_{gs} \gg 0V$. Thus, electrons can quickly recombine with large numbers of injected holes at $V_{gs} \sim 0V$, leading to deep minima (see peaks ‘A’ and ‘C’). In contrast, for a reverse sweeping with a fast (or ‘typical’) sweeping speed (78V/s), accumulation of excess electrons may be formed since only a small number of holes injected at $V_{gs} \sim 0V$ are available for recombination with electrons, resulting in an increase in the

minimum current (peak 'B'). However, for a slow backward sweeping (2.5V/s), there is sufficient time for holes to be injected and recombined with injected electrons. Thus, a deep minimum (peak 'D') can still be observed.

In our observation on the conduction type, both SDBS and Triton X-100 can change the conduction type of DWNT- and SWNT- FETs from p-type to ambipolar. This change can be attributed to high surface coverage of the surfactants at the interface between the CNTs and electrodes, preventing oxygen from accessing the interface and resulting in an ambipolar characteristic. Triton X-100 has been reported to cause this kind of change in SWNT-FETs.⁶⁰

Based on the above discussion, 'clockwise' hystereses and ambipolar characteristics, may indicate high coverage level of the surfactants on the CNT channels and the interface between CNTs and electrodes, respectively. From Table 4.2, one can see that, after being treated with 10wt% SDS, the DWNT-FETs show 'clockwise' characteristics while the SWNT-FETs show 'anticlockwise' behavior. These phenomena can be interpreted if we hypothesize that, analogous to their adsorption properties for water,⁶⁶ DWNTs have superior adsorption for SDS to SWNTs. These superior adsorption properties are due to electric dipole formed by the two shells of DWNTs.⁶⁶ After being treated of 10wt% SDBS, DWNT-FETs show ambipolar characteristics, while SWNT-FETs exhibit p-type characteristics, as there are more SDBS molecules at the interface between the DWNTs and electrodes than that between the SWNTs and electrodes. The difference shown here suggests that for the DWNTs with diameter ~1.4nm, the existence of innershell interaction may enhance the adsorption properties, so that their electrical properties are more sensitive to environmental conditions. This implies that the DWNTs may have higher sensitivity for sensor application than that of the SWNTs.

Besides, compared to the SWNT-FETs treated with 10wt% SDS, SWNT-FETs treated with 10wt% SDBS have ‘clockwise’ P-type characteristics, implying that coverage level of SDBS is higher than SDS on the SWNTs channel. Moreover, the facts that SWNTs-based devices treated with Triton X-100 have ‘clockwise’ ambipolar transfer curves suggest that Triton X-100 may have even higher surface coverage. Furthermore, in the observations for DWNT-FET, the higher surface coverage level of Triton X-100 and SDBS than SDS can also be concluded. This conclusion is also supported by the observations reported by Zhang *et al.*,⁹⁷ who also concluded that SDS had weaker interaction with CNTs surface than SDBS and Triton X-100 from their research on the surfactant solubilization of SWNTs in water. This phenomenon suggests that, compared to that of SDBS and Triton X-100, SDS has low surface coverage level on CNTs because it does not have a benzene ring.

4.4 Conclusions

Significant hysteretic transfer characteristics have been found in our CNTFETs. Influential factors such as water molecules, oxygen and surfactants have different impacts on the transfer characteristics of CNTFETs. The trapping in water molecules results in the ‘anticlockwise’ hysteresis and the oxygen may influence the work function of metal electrodes and consequently change the conduction type. However, we find that the surfactant may suppress the effects of water molecules and oxygen, leading to changes in the transfer characteristics of CNTFETs. The competition between surfactants and water molecules/ oxygen defines the output of transfer characteristics of CNTFETs. Thus, it can be concluded that water molecules, oxygen and the surfactants all have crucial effects on the hysteretic transfer characteristics of CNTFETs. Furthermore, even there are not

many differences between electrical measurements of SWNT-FETs and DWNT-FETs, it is found that DWNTs may have high adsorption property than SWNTs, implying that there may be charge transferred between inner and outer shell of DWNTs at room temperature.

The main achievements and significances of this work on the electron transport mechanism are listed below:

1. The surfactants can change both the conduction type and the hysteretic direction of the transfer characteristics of CNTFETs. The change in the conduction type could be attributed to a variation of the work function of the electrodes upon coating with surfactants. The mechanism of changing hysteretic direction could be due to the existence of mobile ions and charged clusters in the surfactants.
2. The competition between the surfactants and oxygen/water molecular defines the transfer characteristics of back-gated CNTFETs, leading to four basic types of transfer characteristics which are p-type 'anticlockwise', p-type 'clockwise', ambipolar 'anticlockwise' and ambipolar 'clockwise', respectively.
3. Three most popular surfactants are used to disperse SWNTs and DWNTs. It is found that the SDBS and Triton X-100 can have more significant effects than SDS on changing the transfer characteristics of CNTFETs. This result implies that coverage level of SDBS and Triton X-100 is higher than SDS on the CNTs channel.
4. For SWNTs and DWNTs with diameter $\sim 1.4\text{nm}$, the transfer characteristics of intrinsic CNTs based FETs are similar in regard to the conduction type and the hysteretic direction. However, after being treated with a certain type of surfactant at a fixed concentration, the changes on the transfer characteristics are different for SWNT-FETs and DWNT-FETs. The significant change

of DWNT-FETs suggests that DWNTs has higher adsorption property for surfactants than SWNTs. The mechanism can be explained by the dipole formed in DWNTs through the intershell coupling.

Chapter 5 In situ Raman scattering of a DWNT-based FET

5.1 Literature review on Raman scattering of CNTs

Figure 5.1 Raman spectrum from one nanotube taken over a broad frequency range using $E_L = 1.58$ eV (785 nm) excitation laser, and showing the radial breathing mode (RBM), the D band, the G band and the G' band. Second-order modes are also observed. The features marked with '*' at 303, 521 and 963 cm^{-1} are from the Si/SiO₂ substrate.⁹⁸

Carbon nanotubes have been proven to be the unique systems for the study of Raman

spectra in one-dimensional systems.⁹⁸⁻¹⁰⁰ On the other hand, Raman spectroscopy has provided an exceedingly powerful tool for the characterization of carbon nanotubes. As the simplest system among CNTs, SWNTs have been widely investigated using Raman spectroscopy.¹⁰¹⁻¹⁰⁹ Raman spectra of graphite and SWNTs can provide us with much information about the exceptional one-dimensional property of carbon materials. In a Raman spectrum of SWNTs on Si/SiO₂ wafer, several peaks can be observed, including the radial breathing mode (RBM) peak, D peak, G peak (high-energy mode HEM), G' peak and some other second order peaks (see Figure 5.1).⁹⁸ In this part, the investigations of remarkable structure and impressive electronic and phonon properties using Raman spectroscopy are reviewed. The various types of Raman scattering process related to CNTs are presented. The modes of the Raman spectra for CNTs are discussed and summarized, followed by a review of the interesting findings for each mode. At the end of this review, some research challenges are summarized.

5.1.1 Introduction of Raman Scattering Processes

There are many identifiable features in the Raman spectra of graphite and CNTs. Different features can be attributed to different phonon modes and each feature can be interpreted with specific Raman scattering process.⁹⁸⁻¹⁰⁰ From the Raman spectra of graphite and CNTs, much information about the exceptional one-dimensional (1D) properties of carbon materials can be obtained, such as the phonon structure, the electronic structure^{110,111} and the defects^{112,113} of the sample. The Raman spectra can also provide plenty general information about the structure^{112,114} and properties¹¹⁵ of CNTs as the mechanical properties, elastic properties and the thermal properties

of CNTs are strongly influenced by phonons.

Raman scattering is the inelastic scattering of light. In a scattering event, by absorbing a photon from the excitation laser, an electron is firstly excited from the valence energy band to the conduction energy band. The excited electron is afterwards scattered by emitting (or absorbing) phonons. After that, the electron relaxes to the valence band by emitting another photon. The emitted photon has different energy from the photon from excitation laser and the energy differences are energy of phonons involved in the scattering process. The intensity of the scattered light as a function of frequency shift (energy difference between incident and emitted photons) of the scattered light is plotted as Raman spectra. Thus, we can obtain an accurate measurement of the phonon frequencies (phonon energy) of the material. Furthermore, a model for the phonon dispersion relations (or normal mode frequencies) can be deduced by combining the phonon frequency with the original geometrical structure of a crystal (or molecule). In the Raman scattering, depending on whether the process is emitting or absorbing phonons, Stokes or anti-Stokes spectra can be obtained, respectively. Not only phonons, but also any elementary excitation (such as a magnon, plasmon etc.) can be involved in the scattering process due to inelastic scattering of light in the Raman scattering. However, the elementary excitation has to satisfy energy–momentum conservation in the scattering process.

The Raman scattering can be classified into first-order and second-order scattering depending on the number of phonons (one or two) involved in the scattering process.⁹⁹ For instance, in the Raman scattering of an SWNT, G and RBM bands are the features of the first-order Raman scattering while D and G' (2D) bands are the features of the second-order scattering.⁹⁹

5.1.2 Resonant and non-resonant Raman scattering Processes

Figure 5.2 Schematic of (a) non-resonant (Stokes) scattering and (b) a single (incident) resonance. GS (ES) refer to the ground (excited) state of the material investigated and ω_{ph} to the phonon (or other elementary excitation) emitted in the process. The corresponding relative strengths in a Raman spectrum are indicated on the bottom.¹⁰⁰

If the optical transition of the Raman scattering is started and ended at real electronic states, the electrons may oscillate with the excitation laser energy. This is a general resonance phenomenon and there are two possible resonances in the optical transitions of Raman scattering. The first one is the resonance with the incident laser photon (incidence resonance) and the second one is the resonance with the scattered photon (scattered resonance). When the resonance occurs with the incident photon, the energy of incident laser light (E_L) is the same as the energy separation between the two electronic states in resonance (ΔE) (Figure 5.2(b)),^{99,100}

$$E_L = \Delta E \quad (\text{incident resonance}) \quad (5.1)$$

When the scattered resonance occurs, the scattered photon has an additional energy $\hbar\omega$,

$$E_L = \Delta E + \hbar\omega \quad (\text{scattered resonance}) \quad (5.2)$$

Consequently, in the Stokes Raman process, the incident photon energy needed for the scattered

resonance is larger than that for the incident resonance by the phonon energy ($\hbar\omega$).

From Eqs. (5.1) and (5.2), if the laser energy E_L does not coincide with the resonant energies, the optical transition in the Raman scattering process can be considered as a transition to a virtual state. The corresponding signal in Raman scattering is called non-resonant Raman spectra (Figure 5.2(a)). The peaks in non-resonant Raman spectra are much weaker in intensity than that of the resonant ones. It is reported that the resonant Raman process can increase the signal by a factor $\sim 10^3$ in comparison to the intensity of a non-resonant Raman process.⁹⁹

Figure 5.3 Band structure and density of states of a zigzag nanotube.¹⁰⁰

As shown in Figure 5.3, in the electronic structure of CNTs, the density of states (DOS) has a maximum peak, called van Hove singularity, at each bottom (or top) of the conduction band (or valence band). When the excitation energy of the Raman scattering is comparable to the energy difference between two van Hove singularities with the same momentum, the possibility of the

electron transition is enhanced. Consequently, more electrons can be subsequently scattered by phonon after being excited to conduction band. In other words, there is a band-to-band transition for electron excitation by incident laser and the Raman signal may be much enhanced with this transition. The band-to-band transition picture predicts that the transitions between symmetrically lying pairs of the valence and conduction bands contribute mostly to the incident light absorption. The transition energies are labeled E_{ii} where i labels the bands. Thus, the Raman signal is more intense in this case and the Raman signal can be correlated with the electronic structure or the chiral index of CNT, especially SWNT. Moreover, in the Raman scattering of SWNT bundle, since the signal from non-resonant SWNTs is much weaker than that from resonant ones, the signal from a resonant single isolated SWNT may be obtained in the presence of many non-resonant SWNTs when a proper excitation laser energy is selected.⁹⁹ Indeed, the theoretical calculations of the electronic and phonon structure are needed to understand the resonant Raman scattering of CNTs.

5.1.3 The radial breathing mode

The radial breathing mode (RBM),¹¹⁶ also known as breathing-like mode (BLM),¹¹⁷ is an important mode which can be used to study the nanotube diameter or identify specific carbon nanotube, *i.e.*, identify chiral index. It is a double resonant process.

The RBM peaks in Raman spectra, normally in a range of 120 to 350 cm^{-1} , correspond to the coherent vibrations of the C atoms in the radial direction,⁸¹ as if the tube is breathing, thus, they are named radial breathing mode (or breathing-like mode).

Figure 5.4 Linear fit of the observed RBM frequencies as a function of inverse tube diameter $1/d$. The diameter of the assigned nanotubes is calculated from Eq. (5.3) with lattice constant $a = 0.246$ nm.⁸¹

The RBM features are unique properties of CNTs and the frequencies of RBM peaks are inversely dependent on the diameters of the nanotubes following the equation:

$$\omega_{\text{RBM}} = \frac{c_1}{d} + c_2 \quad (5.3)$$

where c_1 and c_2 are parameters determined experimentally, $c_1 = 215 \pm 2 \text{ cm}^{-1}$ and $c_2 = 18 \pm 2 \text{ cm}^{-1}$,⁸¹ as shown in Figure 5.4. Therefore, the RBM frequencies are used to tell the existence of CNTs in a given carbon materials. Furthermore, the RBM frequencies can be used to identify the diameter distribution of the CNTs (Eq. (5.3)). As there are too many different nanotubes with slight difference in the tube diameters, it is very difficult to find a specific chiral index from an experimentally obtained RBM frequency.

As shown in Figure 5.4, when we consider SWNTs with smaller diameters, the differences between experimental data and the theoretical calculation from Eq. (5.3) become larger. These

differences imply that we have to consider the chirality dependence for SWNTs with smaller diameters. The optimized relation has been reported:¹¹⁸

$$\omega_{RBM} = \frac{A}{d} + B + \frac{C + D(\cos 3\Theta)^2}{d^2} \quad (5.4)$$

where the parameters are determined separately for metallic and semiconducting SWNTs, which are shown in Table 5.1.

	$A \text{ (cm}^{-1} \text{ nm)}$	$B \text{ (cm}^{-1} \text{)}$	$C \text{ (cm}^{-1} \text{ nm)}$	$D \text{ (cm}^{-1} \text{)}$
Semicond.	227	7.3 ± 0.3	-1.1 ± 0.3	-0.9 ± 0.2
Metallic	227	11.8 ± 1.0	-2.7 ± 1.2	-2.7 ± 0.8

Table 5.1 Parameters for metallic and semiconducting nanotubes used in Eq. (5.4).

The RBMs of DWNTs influenced by intershell coupling is very interesting. The coupling between the inner and outer shells has two eigenmodes, i.e., inphase and out-of-phase modes. It is convenient to simplify the coupling between two shells into a spring-linked vibration model. From the calculation based on this simplified model, the coupled RBM frequencies are always higher than the uncoupled ones (Figure 5.5), the dependence of the shift in RBM frequency on the coupling is given by:¹¹⁷

$$\Delta\omega_{RBM} \approx \frac{\kappa' d_i}{2cc_1} \text{ for } d_i \leq 0.7 \text{ nm} \quad (5.5)$$

where $\kappa' = 115927 u \cdot \text{cm}^{-2} \cdot \text{\AA}^{-1}$ is the effective spring constant between inner and outer shell, d_i is the diameter of the inner shell, $c = 14.375 u \cdot \text{\AA}^{-1}$ is the linear mass density of a carbon nanotube, and c_1 is defined in Eq. (5.3). However, the modes of double-walled carbon nanotubes are still not investigated in details experimentally. One noteworthy work from Dresselhaus *et al.*²⁰

shows that the RBM peaks for DWNTs are almost at same positions as those of SWNTs when the diameters of DWNTs are $\sim 1.4\text{nm}$ at which DWNTs have weak intershell interaction at room temperature for that diameter range. Besides, several experimental findings also support the suggestion that $\Delta\omega_{RBM} \approx 0$, implying that the intershell coupling has no influences on the RBM frequencies.¹¹⁹

Figure 5.5 Frequency of coupled RBM in DWNTs. Open symbols belong to uncoupled tubes of the same diameter, solid symbols to double-walled nanotubes.¹¹⁷

5.1.4 Chiral index assignment using RBM

In 1999, Kataura and co-workers present a method to correlate optical transition energy with tube diameter into a plot, which is well known as Kataura plot (Figure 5.6(a)).¹²⁰ The optical transition energy in the Kataura plot is corresponding to the excitation energy, which is closely

related to the electronic structure of carbon nanotubes. In contrast, the diameter is inversely proportional to the RBM frequency. Thus, the RBM frequency is correlated with excitation energy (phonon energy of incident laser).

Figure 5.6 (a) First Kataura Plot calculated in 1999.¹²⁰ (b) Theoretical calculation calculated by the first-neighbor tight binding method, with the transfer integral $\gamma_0 = 2.9$ eV.⁹⁹

As shown in the Figure 5.6(b),⁹⁹ each point in the Kataura plot can be correlated to a specific chiral index of a metallic or a semiconducting SWNT. Consequently, an experimental RBM peak frequencies and the exciting laser energy can be used to locate the points in the Kataura plot and then can be used to assign the SWNTs to specific chiral indices. However, Maultzsch and co-workers find that the theoretical Kataura plot has to be stretched and shifted in order to match the experimental data.⁸¹ This finding has been explained by that, rather than band-to-band transition, an excitonic transition is suggested to be the transition process in Raman scattering of CNTs.⁸¹ This suggestion is also supported by the recent experimental results. The observed RBM frequencies and transition energies of semiconducting tubes and their assignments

are summarized in Table 5.2 while the assignments of metallic nanotubes are summarized in Table 5.3.⁸¹ One point to be noted is that, the resonant window for RBM is ~ 0.1 eV, e.g., for a excitation laser with photon energy 1.96 eV, only when the points in Kataura plot fall into the range of 1.91 eV to 2.01 eV, the tubes represented by the points would respond to the incident laser.

ν	$laola$	n_1	n_2	d (Å)	$\omega_{RBM}(\text{cm}^{-1})$	E_{ii} (eV)	$\omega_{RBM}^{\text{emp}}(\text{cm}^{-1})$	$E_{ii}^{\text{emp}}(\text{eV})$	θ	Suscept.
-1	(12,1)	12	1	9.82	236.4	1.551	237	1.54	4.0	4.1
		11	3	10.00	232.6	1.570	233	1.55	11.7	2.0
		10	5	10.36	226.1	1.578	225	1.56	19.1	2.3
		9	7	10.88	216.0	1.564	215	1.55	25.9	1.3
-1	(11,0)	11	0	8.62	266.7	1.657	267	1.68	0.0	1.7
		10	2	8.72	264.6	1.690	264	1.69	8.9	2.3
		9	4	9.03	257.5	1.72	256	1.71	17.5	2.5
		8	6	9.53	246.4	1.73	243	1.72	25.3	1.4
-1	(9,1)	9	1	7.47	306.2	1.78	305	1.83	5.2	9.1
		8	3	7.72	297.5	1.857	296	1.88	15.3	35.8
		7	5	8.18	283.3	1.915	281	1.92	24.5	18.3
-1	(8,0)	8	0	6.27	352.2	1.99	361	1.97	0.0	0.1
		7	2	6.41			353	2.03	12.2	
		6	4	6.83			333	2.15	23.4	
+1	(14,1)	14	1	11.38	205.8	1.646	207	1.66	3.4	0.3
		13	3	11.54	203.3	1.610	204	1.62	10.2	0.6
		12	5	11.85	198.5	1.554	199	1.56	16.6	0.1
		11	7	12.31			192	1.47	22.7	
		10	9	12.90			185	1.38	28.3	
+1	(13,0)	13	0	10.18	230.8	1.84	229	1.85	0.0	0.2*
		12	2	10.27	228.1	1.82	227	1.82	7.6	12.2*
		11	4	10.54	221.8	1.76	222	1.74	14.9	0.1*
		10	6	10.97			214	1.64	21.8	
		9	8	11.54	204.0	1.535	204	1.52	28.1	0.5
+1	(11,1)	11	1	9.03	256.0	2.031	256	2.06	4.3	9.8
		10	3	9.24	252.1	1.945	251	1.98	12.7	3.6
		9	5	9.63			241	1.84	20.6	
		8	7	10.18	230.4	1.710	229	1.69	27.8	0.4
+1	(10,0)	10	0	7.83	291.4	2.38	292	2.35	0.0	
		9	2	7.95			288	2.28	9.8	
		8	4	8.29	280.9	2.10	277	2.11	19.1	0.3
		7	6	8.83	264.2	1.909	261	1.91	27.5	2.6
+1	(8,1)	8	1	6.69			339	2.69	5.8	
		7	3	6.96			327	2.48	17.0	
		6	5	7.47	308.6	2.20	305	2.18	27.0	

Table 5.2 Summary of all observed RBM frequencies and transition energies of semiconducting tubes and their assignments.⁸¹

From the Table 5.2 and Table 5.3,⁸¹ one can assign their experimental RBM peaks to specific chiral indices. However, not all the possible indices of commonly used carbon nanotubes (0.7~2 nm) are listed in the tables. Alternatively, Maultzsch *et al.* have proposed empirical

equations, which fit experimental data very well.⁸¹ The equation for calculating transition energy

E_{22} of a semiconducting SWNT is given as:⁸¹

$$E_{22}^S = \gamma_0 \left(\frac{4a_{c-c}}{d} + \gamma_1 \frac{a_{c-c}^2}{d^2} \right) + v\gamma_2 \cos(3\Theta) \frac{a_{c-c}^2}{d^2} \quad (5.6)$$

where $v = (n - m) \bmod 3$ is the family index taking ± 1 for semiconducting tubes. By fitting the

experimental data in Table 5.2, $\gamma_0 = 3.53$ eV, $\gamma_1 = -4.32$ eV and $\gamma_2 = 8.81$ eV are obtained.

ν	$laola$	n_1	n_2	d (Å)	ω_{RBM} (cm ⁻¹)	E_{ii} (eV)	ω_{RBM}^{exp} (cm ⁻¹)	E_{ii}^{exp} (eV)	θ	Suscept.
0	(16,1)	16	1	12.94	182.0	1.81	184	1.81	3.0	0.5
		15	3	13.08	179.0	1.83	182	1.81	8.9	1.8
		14	5	13.36	174.5	1.83	179	1.81	14.7	1.9
0	(15,0)	15	0	11.75	200.4	1.908	201	1.93	0.0	0.7
		14	2	11.83	196.3	1.934	200	1.94	6.6	3.6
		13	4	12.06	193.5	1.944	196	1.94	13.0	2.5
		12	6	12.44	189.4	1.948	191	1.93	19.1	1.9
		11	8	12.94	183.2	1.936	184	1.92	24.8	1.9
		10	10	13.57	175.7	1.889	176	1.88	30.0	0.9
0	(13,1)	13	1	10.60	220.3	2.057	221	2.07	3.7	1.5
		12	3	10.77	217.4	2.075	217	2.07	10.9	2.6
		11	5	11.11	212.4	2.084	211	2.08	17.8	1.7
		10	7	11.59	204.0	2.067	203	2.07	24.2	0.9
		9	9	12.21	195.3	2.02	194	2.04	30.0	0.5
0	(12,0)	12	0	9.40	244.9	2.18	247	2.21	0.0	
		11	2	9.50			244	2.22	8.2	
		10	4	9.78			238	2.24	16.1	
		9	6	10.24			228	2.25	23.4	
		8	8	10.85			216	2.23	30.0	
0	(10,1)	10	1	8.25	276.3	2.38	278	2.35	4.7	
		9	3	8.47	272.7	2.43	272	2.40	13.9	
		8	5	8.90	262.7	2.47	259	2.45	22.4	
		7	7	9.50	247.8	2.45	244	2.46	30.0	
0	(9,0)	9	0	7.05			323	2.47	0.0	
		8	2	7.18	315.5	2.52	317	2.53	10.9	
		7	4	7.55	305.4	2.63	302	2.65	21.1	
		6	6	8.14			282	2.71	30.0	

Table 5.3 Summary of all observed RBM frequencies and transition energies of metallic tubes and their assignment.⁸¹

Besides, the transition energy E_{11} of a metallic SWNT can be calculated from equation:⁸¹

$$E_{11}^M = \gamma_0 \left(\frac{6a_{c-c}}{d} + \gamma_1 \frac{a_{c-c}^2}{d^2} \right) - \gamma_2 \cos(3\Theta) \frac{a_{c-c}^2}{d^2} \quad (5.7)$$

In which $\gamma_0=3.60$ eV, $\gamma_1=-9.65$ eV and $\gamma_2=11.69$ eV are obtained by fitting the experimental data listed in Table 5.3. The Kataura plot calculated from Eq. (5.6) and (5.7) is shown in Figure 5.7, other transitions such as E_{11}^s and E_{33}^s can also be estimated based on the empirical Kataura plot. .

Figure 5.7 Empirical Kataura plot generated from equations (5.6) and (5.7).*

Based on the discussion above, Thomsen and Reich have presented a practical way to identify the chiral index of a nanotube by going through the following steps:^{81,100}

First, the average diameter range of nanotubes should be identified and this will be depending on the growth method of the tubes.

Second, draw a vertical line at the average diameter in the experimental Kataura plot (Figure 5.7) generated from the empirical Eqs. (5.6) and (5.7).

Third, acquire a RBM spectrum with an excitation energy. The excitation energy runs through a branch with nanotubes that have the average diameter. This may be a branch belonging to any E_{ii} .

Fourth, look at the region of expected ω_{RBM} and identify the branch in the spectra. Several branches of tubes may appear in the spectra.

Fifth, use either Table 5.2 and Table 5.3, or Figure 5.7 to identify the maxima of RBM directly and specify the chiral index (n,m) of the tube one by one.

Last, if several tubes have similar RBM peaks at the same excitation energy, the peaks can not be identified using only one excitation laser. Thus, two excitation lasers with slightly shifted wavelength may be used. After the measurements of RBMs using the first laser, the second laser is used to measure another RBMs spectrum. For a specific frequency, the RBM peaks in these two spectra should have different intensity as the photon energy of the lasers is different. The further the excitation energy is away from the specific point in Kataura plot, the lower in the intensity of corresponding RBM peak. From the relative changes in intensity, one can find out the side of the la-ola wave of first RBM peak, which will give additional evidence in the chiral index assignment.

5.1.5 The high-energy mode (HEM), G Mode

The high-energy modes (HEMs) of carbon nanotubes, also known as G band, are originated from the vibrations along the nanotube walls, *i.e.*, the tangential vibrations of the carbon atoms.^{99,100} Similar to graphite, The HEM in SWNTs involves an optical phonon mode between the two dissimilar carbon atoms A and B in the unit cell. The G band of graphite exhibits one single

Lorentzian peak at $\sim 1582 \text{ cm}^{-1}$ while the G band of single-walled carbon nanotubes have double-peak structure. This double-peak feature of G band is another unique feature observed in the Raman scattering of carbon nanotubes.^{99, 100} However, when used to identify CNTs, this feature is more reliable than the other observed feature, for example, RBMs, as RBMs will not be visualized when the excitation laser energy is not resonant with the tubes. Typically, the most intense peak is within the high-energy range between 1585 cm^{-1} and 1600 cm^{-1} (depending on the diameter and the excitation energy). This peak is known as G^+ peak, which is always higher in frequency than the G band of graphite. The peak between 1560 cm^{-1} to 1580 cm^{-1} , known as G^- peak, changes dramatically for the resonant excitation of metallic tubes.

The G band frequency of CNTs can be used for diameter characterization, distinguishing semiconducting from metallic SWNTs, probing the charge transfer arising from doping and studying the selection rules in the various Raman scattering processes and geometries.

Figure 5.8 Frequency vs. $1/d$ for the two most intense G peaks.¹²¹

The G band from an individual SWNT shows that the G band is a first-order process and it has diameter dependence. As shown in Figure 5.8, based on the Raman SWNT scattering from an individual SWNT, the frequency of G^- is dependent on the tube diameter while the G^+ frequency is independent of the tube diameter.¹²¹

Figure 5.9 The G-band for highly oriented pyrolytic graphite (HOPG), one semiconducting SWNT and one metallic SWNT.¹⁰⁴

It is reported that the linshape of G band can be used to differentiate whether a SWNT is metallic or semiconducting. As shown in Figure 5.9, for a semiconducting SWNT, the G^- peak has

Lorentzian lineshape; while for a metallic SWNT, the G^- peak has Breit-Wigner-Fano (BWF) lineshape.^{104,122-124} The BWF lineshape of Raman scattering for m-SWNT has been interpreted by electron-phonon coupling (EPC) with empirical support.^{104,125-133}

In fact, this kind of EPC, electron coupled with G phonon for graphene has already been reported by Yan *et al.* in 2007.¹³⁴ The interaction of the G phonon with small wave vector particle-hole pairs is crucially dependent on the onset energy $\mathcal{E}_c$ (around the energy of G phonon 0.2 eV) for electron transition between valence band and conduction band. The transitions need to satisfy the the Pauli principle in which $\mathcal{E}_c$ is directly linked to the position of the Fermi surface as:

$$\mathcal{E}_c = |2E_F| \quad (5.8)$$

where $|E_F|$ is the absolute value of the Fermi energy with respect to the Dirac point (K point shown in Figure 2.3). Thus, when electronic band structure is tuned around Dirac point, the G phonon may respond to the tuning. As shown in Figure 5.10, the G band frequency ω_G (squares) and G band linewidth Γ_G (circles) respond to gate voltage or, in an equivalent way, to the charge density. This response can be viewed in terms of position of the Fermi level $\mathcal{E}_F$, as shown in Figure 5.10 (b) and (c). The remarkable reduction in the linewidth at higher carrier densities can be understood as a Landau damping of phonons in which the mode decays into particle-hole pairs. The Fermi level $\mathcal{E}_F$ changes its position when charge carriers are induced and since the Pauli principle has to be satisfied, the transition is allowed only when $|E_F| < \frac{\hbar\omega_G}{2}$. The G band frequency ω_G has a minimum point near the Dirac point and change linearly with the Fermi energy $|E_F|$.

Figure 5.10 (a) The G band energy (squares) and G band width (circles) respond to gate voltage or, in an equivalent way, to the charge density. (b) The G band linewidth respond to E_F . (c) The G band energy respond to E_F . (d) and (e) schematic diagrams for explanations of (b). (f) and (g) schematic diagrams for explanations of (c).¹³⁴

In summary, by creation and annihilation of electron-hole pairs across the gapless Dirac point, the carriers in graphene respond to the perturbation of G mode lattice vibration and in turn renormalize the G-phonon energy. The G phonon energy and linewidth can be calculated by:¹³⁴

$$\hbar\omega_G - \hbar\omega_G^0 = \lambda \left\{ |E_F| + \frac{\hbar\omega_G}{4} \ln \left| \frac{2|E_F| - \hbar\omega_G}{2|E_F| + \hbar\omega_G} \right| \right\}$$

$$\Delta\Gamma_G = \frac{A_{uc} D^2}{8M v_F^2} \quad (5.9)$$

where ω_G^0 is ω_G at Dirac point, $\lambda = \frac{A_{uc} D^2}{2\pi\hbar\omega_G M v_F^2}$, A_{uc} is the area of the graphene unit cell,

M is the carbon atom mass, and D is the electron-phonon coupling strength and Fermi velocity

$v_F = 10^6$ m/sec.

Figure 5.11 (a) Schematic diagram of the experimental setup for doping SWNTs by electrochemical method. The excitation laser shines through the PEO/LiClO₄ polymer electrolyte. (b) G band intensity map vs applied gate voltage for an individual m-SWNT.^{135,136}

Interestingly, for m-SWNTs, similar phenomena are expected to be observed because of their gapless electronic structure. Consequently, a broad BWF G^- peak is observed for a metallic SWNT as mentioned above. Indeed, by doping m-CNTs with electrochemical methods¹³⁵ (Figure 5.11(a)) or electrical-field effect (EFE), more experimental evidences support this expectation. As shown in Figure 5.11(b), both frequency and linewidth of the G^- phonon for an individual m-SWNT change with gate voltage.¹³⁵ It is shown in Figure 5.11(b) that $V_{gs}=1.1\text{V}$, rather than $V_{gs}=0\text{V}$, can shift the Fermi level to Dirac point and broaden the G^- peak simultaneously. This is because the intrinsic tubes may be doped by self-doping, chemical adsorption and charged impurities trapped in the substrate. When the Fermi level ϵ_f is located around the Dirac point, the linewidth broadening caused by the transition is easily observed in a m-SWNT, *i.e.*, electrons can be excited by G^- phonons and a broadened linewidth is observed. Moreover, when ϵ_f is shifted by doping to a higher (lower) position, the transitions are suppressed due to the electronic states for the transitions are filled (evacuated), resulting in a linewidth narrowing. At the same time, the up-shift of G^- frequency is observed because charge density ρ increases. In contrast, for s-SWNTs with diameter less than 4 nm,

the transitions caused by EPC will not occur since the bandgap is larger than 0.2 eV (the value of G phonon energy). Thus, linewidth change of G phonon will not be observed for semiconducting nanotubes.

Since Raman scattering shows different responses to metallic and semiconducting SWNTs, complications may be encountered during the investigation of a bundle of SWNTs using Raman scattering, as there may be both semiconducting and metallic tubes within the bundle. Furthermore, the work presented above is the results from random distributed SWNTs with electrochemical doping which can not be directly linked with the SWNTs in a CNTFET with the charge density changed through electric field effect (EFE). Thus, there is a demand to investigate individual nanotube in a real electronic device.

The in situ Raman scattering from an individual single-walled carbon nanotube (SWNT) with diameter ~ 2.4 nm on an FET platform has been reported by Tsang *et al.* in 2007.¹³⁷ In situ Raman scattering is a nondestructive optical technique used to study electron transport in a CNT on a FET platform while the CNT-FET is under a real-time operation. For an m-SWNT, both frequency and linewidth of its G^- are dependent of gate voltage V_{gs} , as shown in Figure 5.12 (d) and (e).¹³⁷ In contrast, for an s-SWNT, the frequency of its G^+ is a function of V_{gs} while the linewidth does not change with the change of V_{gs} , as shown in Figure 5.12(f). The frequency shifts of both G^+ and G^- have been interpreted as the change of charge density ρ in the SWNT channel while the linewidth change is associated with excitations of electron-hole pairs by G phonons (Figure 5.12 (a) to (c)).

Figure 5.12 Frequency renormalization and broadening of the CNT G-phonon mode by the electron–phonon interaction. (a) to (c) Scattering mechanisms for a metallic tube where the G mode can excite electron–hole pairs (a), a doped metallic tube where the phonon can only excite virtual electron–hole pairs (b) and a semiconducting tube where the bandgap is larger than the phonon energy, and no real electron–hole pairs can be created by the phonon (c). d–f, Calculations of the Raman width in an m-SWNT ($d=2.0$ nm) as a function of the charge carrier density per carbon atom at different temperature (d), corresponding G-mode Raman shifts (e) and Raman shift of the LO mode (solid lines) and TO modes (dashed lines) in an s-SWNT at temperatures $T=300$ K for different tube diameters d as a function of carrier density (f). Black dashed lines in d and e are Raman width and shift, respectively, of graphene at 300 K.¹³⁷

5.1.6 D band and 2D band (G' band)

In the Raman spectra of carbon materials, there is a peak observed between 1250 and 1450

cm^{-1} ,^{138,139} which is induced by lattice disorder and dependent on the excitation laser energy. It is believed that the D-band is caused by the scattering of the defects in CNTs, such as in-plane substitution, vacancies, grain boundaries and finite size effects.^{140,141} 2D band (G' band), which is the overtone of the D band is another dominant feature appearing in the range of $2500\text{--}2900\text{ cm}^{-1}$ in Raman spectrum.¹⁴²⁻¹⁴⁴ Normally, the 2D band in graphite has a single peak and the abnormal two peaks are interpreted as the effect of interlayer coupling. Interestingly, at the individual nanotube level, the 2D bands sometimes appear in the forms of unusual two-peak structures for both semiconducting and metallic SWNTs.^{145,146} This phenomenon is not due to the coupling mechanism but the asymmetric property in the electronic structure of SWNT.

The changes in the D band and 2D band of the Raman scattering can be used for monitoring the structural modifications of CNTs that come from the introduction of defects and the attachment of different chemical species, respectively.

Figure 5.13 Raman spectra of the same isolated S@S DWNT for five closely spaced E_L values. The intensity of the higher frequency 2D peak is directly related to the intensity of the RBM peak corresponding to the outer layer.²⁰

For DWNTs, the Raman scattering of an individual S@S DWNT for five closely spaced laser energies are shown in Figure 5.13.²⁰ From the figure, one can see that there are two 2D peaks with large visible difference. The intensity of the 2D peak with higher energy is directly related to the intensity of the RBM peak corresponding to the outer S layer.

However, when investigating 2D band of CNTs, it is hard to see an obvious 2D band due to its nature of second-order scattering. Thus, the works on 2D band for CNTs are still not carried out intensively. Further efforts are needed to improve the reliability and sensitivity of 2D band when using it to characterize CNTs. Besides, more theoretical calculations are needed to interpret the experimental results.

5.1.7 Antenna effect

The optical characterization of CNT is affected by the one-dimensional nature of its geometry. The optical absorption of one-dimensional CNTs has been studied and the results show that there is practically no absorption of light with polarization perpendicular to the CNTs, known as antenna effect.¹⁴⁷⁻¹⁵⁰ As shown in Figure 5.14, the Raman scattering of CNTs responds to incident light only when the polarization direction of the light is parallel to the tube direction. Thus, in our experiment, the tube axis of our CNT should be kept in the same direction with the polarization of our excitation laser.

Figure 5.14 The depolarization effect in bundles of single-walled nanotubes recorded on an area of $15 \times 15 \mu\text{m}$.¹⁵⁰

5.1.8 Research status of Raman scattering for device level CNTs

Transfer characteristics	SWNTs		DWNTs	
	metallic	semiconducting	metallic	semiconducting
Conduction type	FET device level	FET device level	*	*
Hysteresis	*	*	*	*

Table 5.4 Research status of Raman scattering for CNTs. (* no efforts yet) *

As discussed above, Raman scattering is widely used to characterize the properties of CNTs including diameter, chirality and metallic/semiconducting etc.. Besides, for G peaks which are the most dominant features of Raman scattering for both graphene and SWNTs, EPC has been

widely investigated. However, with FET device geometry, only one paper about EPC for s- and m-SWNTs has been published, as discussed in Chapter 5.1.5. Till date, there are no systematic investigations on the EPC of DWNTs. Recent work by Dresselhaus *et al.* reports that, for a DWNT with diameter ~ 1.4 nm, the RBM peaks show insignificant change with the interference between the two shells of DWNTs.²⁰ However, the G band of DWNT is shifted to lower frequency because of their double-layer structure. More important, all these results are not obtained from a device geometry.

Based on the current research gap (as shown in Table 5.4), we aim to investigate the EPC and the intershell interaction of an individual DWNT on an FET geometry through tuning V_{gs} and source-drain V_{ds} . Through this study, we may have a deep understanding on electron transport mechanism of DWNTs-based FETs.

In the following chapters, we will discuss our experimental results from double-walled carbon nanotubes in the following sequence. First, Raman scattering results from both bulk SWNTs and DWNTs are compared and the effects of the surfactants on the Raman scattering will be discussed (Chapter 5.2). Since the Raman scattering results are only from the tubes which are resonant with incident laser energy, the information offered are limited for bulk CNTs. Therefore, some photoluminescence results of CNTs are also reported because PL is more suitable to analyze s-CNTs in bulk CNTs solution. Second, we shall present the experimental results of the in situ Raman scattering from an individual double-walled carbon nanotube which is on a field-effect transistor platform under normal operation (Chapter 5.3). Third, some Raman scattering results from a bundle of CNTs are presented and discussed.

5.2 General information of our CNTs

Figure 5.15 Morphology of SWNT observed by FESEM. (a) SWNT from water solution. (b) SWNT from 1wt% SDS. (c) SWNT from 4 wt% SDBS. (d) SWNT from 50 wt% SDBS.*

In order to investigate the surfactants effects on the Raman scattering, SWNT or DWNT from different solutions have been dripped on a Si substrate with thermally grown SiO_2 . After drying up, the samples are scanned and characterized with FESEM and Raman spectroscopy, respectively. As the examples shown in Figure 5.15, the morphologies of SWNTs from different solutions have been viewed by FESEM. From the photos, more substance is found to be wrapped around the CNTs when the concentration of the surfactants increases.

All the samples are in turn characterized with Raman spectroscopy. We have confirmed that there are no obvious peaks in the Raman scattering for pure surfactants (results not shown here). Some of the results are shown in Figure 5.16. As shown in Figure 5.16(a), the Raman spectra of SWNTs from the different solutions are comparable. In details, the insignificant shifts in the peak

frequencies imply that the types and concentrations of the surfactants may not affect the Raman scattering of SWNTs. In contrast, for the DWNTs, there are significant changes in the intensities of the Raman spectra, although the shifts in the frequencies are insignificant (see Figure 5.16(b)). The RBMs of the Raman spectra for the DWNTs show differences in the peak linewidths and intensities, suggesting that the uniformity of diameter distribution for DWNTs is relatively worse than that of SWNTs. This may in turn cause the differences in other features of the Raman spectra, such as peak intensity of G bands (*i.e.*, the changes in the intensity ratio of G^- over G^+ , I_{G^-}/I_{G^+}). Therefore, we can not conclude whether the root causes of the changes are from the surfactants or the tubes themselves.

In general, we can say that the types and concentrations of surfactants do not affect the results of the Raman scattering for the SWNTs under our experimental conditions. Nevertheless, from the Raman scattering of the DWNTs, a clear conclusion is not obtained due to the relatively poor diameter distribution of DWNTs. Thus, photoluminescence (PL), which can characterize the changes in electronic structures of s-CNTs in bulk form, is used to characterize the effects of surfactants on DWNTs.

Figure 5.16 Raman spectra of (a) SWNTs from different solutions. (b) DWNTs from different solutions.*

Figure 5.17 (a) Schematic density of the electronic states for a SWNT. Solid arrows depict the optical excitation and emission transitions of interest; dashed arrows denote nonradiative relaxation of the electron (in the conduction band) and hole (in the valence band) before emission. (b) Contour plot of the photoluminescence intensity versus excitation and emission wavelengths for a sample of SWNTs suspended in SDS and deuterium oxide.⁹⁰

Figure 5.18 Contour plot of photoluminescence intensity versus excitation and emission wavelengths for (a) SWNT. (b) DWNT in SDBS, respectively.*

PL is a method used to investigate the influences of electronic structure on CNTs.¹⁵¹ As shown in Figure 5.17(a), the CNT materials may absorb the incident light only when the incident

photon energy is equal to the energy for electron transition (E_{22}) and the absorbed photon will excite an electron from valence band to conduction band.⁹⁰ The excited electron will in turn relax back to the original state with one photon emission (E_{11}). Consequently, the excitation and emission photon energies in the photoluminescence of CNTs are corresponding to the optical transition energy E_{22} and E_{11} (as shown in Figure 5.17(a)), respectively. As we discussed in Chapter 2.3.1, CNTs with different chiralities have different electronic structures, *i.e.*, different E_{22} and E_{11} . Therefore, in the contour plot of photoluminescence (the intensity versus excitation and emission wavelength, as shown in Figure 5.17(b)), each intensity island is corresponding to a CNT with specific chirality. These islands are only applicable for semiconducting tubes as there are no photoluminescences for metallic tubes. The chirality assignments for SWNTs have been accomplished by Bachilo *et al.* in 2002.⁹⁰ Since the intense islands in PL contour plot are corresponding to the electronic structures of CNTs, the plot becomes an efficient index for monitoring the change in the electronic structures of CNTs.

In the photoluminescence for our samples of SWNTs (Figure 5.18(a)) and DWNTs (Figure 5.18(b)), we have only obtained PL peaks in the sample of DWNTs. The absence of the PL peaks in Figure 5.18(a) is due to the good uniformity in the diameter distribution, ~ 1.4 nm, of the SWNTs. The SWNTs with diameter ~ 1.4 nm have band gaps (E_{11}) ~ 0.58 eV, corresponding to ~ 2140 nm in wavelength which out of the measurable range. In addition, the diameters of the SWNTs also can be determined using the RBMs of the Raman scattering for the SWNTs, as shown in Figure 3.1 and Figure 5.16(a). In contrast, there are series of peaks observed in the PL contour plot from the DWNTs. From the assignment, one can see that the diameter distribution is centered at ~ 0.8 nm, which is the typical diameter of inner shells of DWNTs. The peaks in the contour plot Figure 5.18(b)

from the inner shells of the DWNTs locate at the same positions with the peaks from the SWNTs listed in Table 3.1 and the peaks in Figure 5.18(b) can be assigned accordingly. Since the peak positions in the PL plot contain the information electronic structures of CNTs, the results in Figure 5.18(b) implies that the electronic structures of the inner shell of our DWNTs suspended in SDBS are similar to the electronic structures of SWNTs suspended in SDS. Therefore, on one hand, the effects of SDS and SDBS are not intensive enough to disturb the electronic structures of SWNT and DWNTs. This is consistent with the conclusions of Chapter 4 that the surfactants change transfer characteristics through modifying the contact rather than changing the electronic structures of tubes. On the other hand, the intershell interaction between concentric shells of DWNTs is negligible for our DWNT with diameter $\sim 1.4\text{nm}$. This conclusion is consistent with a simulation work that the intershell interaction is negligible when the outer tube diameter is $\sim 1.35\text{nm}$.⁹⁶ Moreover, in the experimental investigation from Dresselhaus *et al.*, it is also found that the intershell interaction is weak at room temperature for the DWNTs with diameter $\sim 1.4\text{nm}$,²⁰ as mentioned in the end of Chapter 5.1.3.

Base on the results and discussions above, in the experiments below, the effects of surfactants on the Raman results are neglected.

5.3 In situ Raman scattering of DWNT-FET

Figure 5.19 (a) AFM image of the DWNT-FET. (b) Height profile along the dashed line indicated by arrow in (a). (c) Map of sum of Raman spectrum intensity between 1500 to 1600 cm^{-1} . (d) The RBM of the DWNT. Peak positions are labeled and the linewidths are shown in the brackets.*

Based on the results and discussion above, we conduct in situ Raman scattering of an individual DWNT in FET platform to understand the electron transport properties in the device. Besides, we may obtain evidences to explain the mechanism of intershell coupling of the DWNT.

Back-gated DWNT-FETs are fabricated on p-type silicon wafers capped with 500 nm thick thermally grown silicon dioxide layer. Source and drain electrodes are made of Ti (15 nm)/Au (55 nm) by photolithography. The p-type silicon is used as the back gate. 1wt% Triton X-100 is used as surfactant to disperse the DWNTs. The tubes are then connected between the source and drain electrodes using AC dielectrophoresis (ACDEP) technique. Subsequently, the samples are rinsed with deionized water and then dried with N_2 . Before the current-voltage (I-V) tests, the devices are annealed at 300 °C for ~ 30 minutes in ambient air in order to remove the residual surfactant and to improve the contacts between the tubes and metal electrodes.

Figure 5.19 (a) and (b) show an AFM (atomic-force microscopy) image of the device and the cross section height-profile at the dash line indicated by the arrow, respectively. The DWNT channel is characterized using a confocal Raman microscopy system with a microscope objective (100X NA=0.95), as described in a Chapter 3.3.3. The polarization direction of the excitation laser (photon energy $E_L=2.33$ eV) is parallel to the DWNT axis. The laser spot size is ~ 350 nm in diameter and the laser intensity is tuned with caution to avoid laser heating. Raman mapping scan (Figure 5.19(c)) with 100 nm/step is conducted before fixing the laser spot at the dashed circle in Figure 5.19 (a) for collection of Raman spectra. Two RBM peaks measured at $E_L=1.96$ eV are shown in Figure 5.19 (d).

Figure 5.20 Transfer characteristics of the device. Filled- and opened- circle curves represent I_{ds} measured before and during Raman measurement, respectively. The star is I_{ds} after all measurements when V_{gs} is swept back to -20 V.*

Figure 5.21 (a) G mode change during V_{gs} sweeping from -20 V to 20 V. The arrows are indicating change direction. (b) Two Lorentzian peaks (blue line) are used to fit original data (green opened circles) and the fitted curve is indicated by red line.*

Two sharp and narrow RBM peaks at 172 and 289 cm^{-1} measured at $E_L=1.96$ eV are shown in Figure 5.19(d), which obviously result from the outer and inner shells of the DWNT, respectively. According to the method presented by Maultzsch *et al.*,⁸¹ we assign the inner shell to (7, 5) (bandgap ~ 0.85 eV) from Table 5.2 or Figure 5.7. In the Kataura plot calculated from empirical equations by Maultzsch *et al.* (Figure 5.7), the branch 38 (a sum of $2n+m$) falls into the resonant window of the excitation laser energy (between 1.91 and 2.01 eV). In addition, since the I_{ds} of the DWNT-FET shows a strong gate voltage dependence (Figure 5.20) and the diameter of the DWNT measured using AFM is 1.48 nm (Figure 5.19 (b)), we assign the outer tube to (19,0) with a bandgap of ~ 0.57 eV.

Figure 5.22 The frequency (a), linewidth (b), intensity (c) and intensity ratio I_{G^-}/I_{G^+} (d) for G mode as a function of V_{gs} . Red open circles represent results for G^+ and blue open triangles represent results of G^- , and open squares represent results for intensity ratio I_{G^-}/I_{G^+} . The stars are the results after all measurements when V_{gs} is swept back to -20 V.*

As shown in Figure 3.12, V_{gs} and V_{ds} are applied to the device during the Raman measurements. With a 30-second integration time for each spectrum, two sets of Raman spectra are obtained under $V_{ds} = 0$ V and 0.05 V, respectively. In each set, Raman spectrum is measured at a certain V_{gs} from -20 V to +20 V with 5 V/step, respectively. No differences are found between the two sets of the spectra. The original spectra under $V_{ds} = 0.05$ V are shown in Figure 5.21(a) and two Lorentzian peaks at ~ 1584 cm^{-1} and ~ 1579 cm^{-1} are used to fit the G^+ and G^- peak in the G band, respectively, see Figure 5.21(b) for example.

As shown in Figure 5.22(a) to (d), the G peak frequency, linewidth, intensity and intensity ratio of G^- to G^+ (I_{G^-}/I_{G^+}) as a function of V_{gs} at $V_{ds}=0.05$ V, respectively. After each set of the

spectra is recorded, we sweep the V_{gs} back to the starting point at -20 V and obtain another spectrum to check the repeatability of the spectra. The corresponding I_{ds} and fitting results are indicated by the stars in Figure 5.20(a) and Figure 5.22 (a) to (d), respectively.

From these figures, one can see that, the spectra are quite repeatable, indicating that our Raman system is stable during the measurements and the observed V_{gs} dependent changes are not caused by laser heating.

Figure 5.23 The energy band diagram of the CNTFET.*

The CNTFET with Au electrodes forms typically Schottky barrier device,^{40,46,47} whose energy band diagram is plotted in Figure 5.23. During the Raman measurements, when $V_{gs} < V_{th}$ ($V_{th} \sim 0V$ in our case), the V_{gs} can efficiently change the contact barrier for holes to tunnel through, *i.e.*, the Fermi level is roughly aligned to top of the valence band, see the dot line marked with 1 in Figure 5.23. The charge density is a function of V_{gs} following $\rho = |C(V_{gs} - V_{th})|$,¹³⁷ where C is the unit capacitance between the gate and tube. In contrast, when $V_{gs} > V_{th}$, the Fermi level is located in the band gap of the DWNT. Both electrons and holes cannot be injected through the contact barriers so that there is no current between the two electrodes, indicated by the solid line marked with 2 in

Figure 5.23. Therefore, the charge density is not sensitive to V_{gs} when $V_{gs} > V_{th}$. The influence of $V_{ds} = 0.05V$ on the spectra can be neglected as there is not much difference found between the spectra under $V_{ds} = 0V$ and $V_{ds} = 0.05V$.

In the Raman results from our semiconducting DWNT shown in Figure 5.22 (a) and (b), the G^+ peak does not show significant change in either peak frequency or linewidth as a function of the V_{gs} . In contrast, when V_{gs} is increased from -20 V to 0 V, the G^- peak has $\sim 4\text{ cm}^{-1}$ downshift in peak frequency and a linewidth broadening from 19 cm^{-1} to 25 cm^{-1} . When V_{gs} is increased from 0 V to +20 V, the changes in frequency and linewidth are not significant. These observations are different from those of SWNTs. Tsang *et al.* find that,¹³⁷ with a single thick SWNT (tube diameter $d \sim 2.4\text{ nm}$) on 100nm-thick SiO_2 gate oxide, when V_{gs} is changed from -25 to 0 V, G^- of a metallic SWNT has $\sim 10\text{ cm}^{-1}$ downshift in frequency and $\sim 20\text{ cm}^{-1}$ broadening in linewidth, while G^+ of a semiconducting SWNT shows $\sim 5\text{ cm}^{-1}$ downshift and negligible change in linewidth. The frequency shift is well interpreted as the change in charge density in the SWNT channel induced by V_{gs} . Based on this mechanism, for a thin s-SWNT with $dt \sim 1.5\text{ nm}$, their theoretical calculation predicts a frequency shift of G^+ and $G^- \sim 1\text{ cm}^{-1}$ and $\sim 5\text{ cm}^{-1}$, respectively. As discussed in the Chapter 5.1.5, the G^- linewidth broadening in metallic SWNT is attributed to interband EPC, *i.e.*, electrons are excited by G phonons from lower energy band to higher energy band and form electron-hole pairs. However, this explanation is not valid in semiconducting SWNT with diameter $d < 2.4\text{ nm}$ because the band gap is too big for G phonons to excite the electron-hole pairs. Hence, it is predicted that the linewidth of G band in s-SWNT will not change with V_{gs} as there is no interband transition excited by G phonons.

In our experiment, the G^+ peak for the s-DWNT does not show significant change in

either peak frequency or linewidth as a function of the V_{gs} (see open circles in Figure 5.22(a) to (b)). As the gate oxide in our FET is 500 nm, the frequency shift of G^+ will be smaller than 1 cm^{-1} according to Tsang *et al.*'s suggestion for SWNT.¹³⁷ The frequency shift may be below the observation limitation.

Interestingly, the G^- peak from the s-DWNT has $\sim 4\text{ cm}^{-1}$ downshift in peak frequency and $\sim 6\text{ cm}^{-1}$ broadening in linewidth when V_{gs} increase from -20V to 0V (see open triangles in Figure 5.22 (a) to (b)). When V_{gs} increase from = -20 V to 0 V, the frequency shift can be interpreted by the charge density change although it is apparent that the frequency shift of G^- peak from the s-DWNT is smaller than the prediction for s-SWNT by Tsang *et al.*¹³⁷ However, if we consider the DWNT-FET has smaller gate-control efficiency due to thicker gate oxide, this observation is still in line with Tsang *et al.*'s prediction.¹³⁷ When V_{gs} increase from = 0 V to +20 V, these characteristics do not change significantly. This is because, when $V_{gs} > V_{th}$ ($V_{th} \sim 0V$), the Fermi level is located in the band gap of the DWNT. The charge density may not change further with V_{gs} since both electrons and holes cannot be injected through the contact barriers. Different from Tsang *et al.*'s prediction, G^- band broadening is observed in the semiconducting DWNT when V_{gs} increase from -20V to 0V. Interpretation on the G^- band broadening can be tentatively given as follows. When the V_{gs} change from -20V to 0V, the Fermi level shifts upward and approaches the top of the valence band of the outer shell. In this V_{gs} range, some states in the outer shell valence band are empty. It is also noted that the energy difference between the inner shell valence band and the outer shell valence band is comparable with phonon energy of the G mode. Consequently, electrons can be excited by G phonons from the inner shell valence band to the outer shell valence band, forming electron-hole pairs (as shown in Figure 5.24). In the range of V_{gs}

from 0 V to 20 V, the Fermi level is located in the band gap and all states in the valence bands are filled in the s-DWNT. Therefore, no electrons are excited further by phonons, causing the observed saturation in the linewidth when $V_{gs} > 0$ V.

Figure 5.24 Scattering mechanism for a semiconducting double-walled carbon nanotube where the G phonon can excite electron-hole pair between the top valence bands of the inner and outer shells. Dash line represents the Fermi level. The energy band pairs of the inner shell and outer shells are indicated by the arrows.*

As discussed above, the frequency shift in response to the change in charge density induced by V_{gs} has different behaviors in different types of CNTs, for instance, the G^+ shifts in s-SWNT, G^- shifts in m-SWNT and both G^+ and G^- shift in our s-DWNT. Besides the changes in the frequency and linewidth, Tsang *et al.* report the G^- intensity decreases and G^+ intensity increases in response to V_{gs} changes for m-SWNT and s-SWNT, respectively.¹³⁷ Clearly, both phenomena are observable in our s-DWNT (Figure 5.22(c)). Our results shown in Figure 5.22(d) indicate that, the intensity ratio of G^- to G^+ (I_{G^-}/I_{G^+}) increases with the decreasing charge density and vice versa. Based on these experimental results, we suggest that I_{G^-}/I_{G^+} can directly reflect the

charge density in both m- and s- CNTs.

In summary, through studying in situ Raman scattering from a single semiconducting DWNT in an FET geometry, we have observed the frequency shift and linewidth change of the G^- band in response to the gate voltages. We suggest the frequency shift in G^- peak is due to the change of charge density in the DWNT channel induced by the gate voltages. The unique linewidth change of the G^- peak as a function of the gate voltages is interpreted as interband electron-phonon coupling between the bands of two concentric shells in the DWNT. In addition, relative intensity of G band (I_{G^-}/I_{G^+}) is found to be increased with the local charge density in the DWNT channel.

5.4 Correlation between in situ Raman scattering and electrical conductance of DWNT-FETs¹⁵²

Based on the results and discussion in Chapter 4, Chapter 5.2 and 5.3, we see that the hysteretic transfer characteristic is one of the most important properties to be investigated, while in situ Raman scattering is a powerful tool to study the electron transport properties in FET geometry and the intershell interaction between the two concentric shells of DWNTs. However, there is no report on studying the correlation between in situ Raman scattering and the electrical conductance of DWNT-based FETs, especially when the devices are based on an individual DWNT.

In this chapter, we shall present the correlations between in situ Raman scattering and electrical measurements of the DWNTs in FETs platform.

5.4.1 Correlation between in situ Raman scattering and electrical conductance for an individual double-walled carbon nanotube

It is well known that simply-designed SWNT-FETs and DWNT-FETs exhibit hysteretic characteristics in transfer characteristics/curves and the hysteresis loops are attributed to charge trapping/detrapping processes near the CNT channels, probably associated with the trapping centers induced by adsorbed water molecules or dielectric layers.^{92,93} The hysteresis phenomenon is an important issue because it must be eliminated for most of the electronic applications and it should be stabilized for memory applications. In this work, we examine the hysteretic characteristics for a Si_3N_4 passivated DWNT-FET with confocal Raman microscopy under real-time I-V measurements.

5.4.2 Experimental details

The device used in this work is the same as the device used in Chapter 5.3. It has an individual semiconducting DWNT with (7,5)@(19,0) as conducting channel. A 300-nm thick Si_3N_4 layer has been deposited at 300 °C in vacuum (10 mTorr) by PECVD on the device to passivate it before the in situ Raman measurements.

Similar to the procedures presented in Chapter 5.3, each spectrum is obtained with a 30-second integration time under $V_{\text{ds}} = 0.05$ V. The entire set of the Raman spectra are measured at V_{gs} from -20 to +20 V and back to -20 V with 5 V/step, respectively.

5.4.3 Results and discussion

The hysteretic transfer characteristics during the Raman scattering are shown in Figure 5.25(a). As discussed in Chapter 5.3, the influence of $V_{ds} = 0.05$ V on the spectra is negligible as no significant difference is observed between the spectra under $V_{ds} = 0$ V and $V_{ds} = 0.05$ V. Two Lorentzian peaks (G^+ and G^-) are used to fit the G band. The G peak frequency, linewidth and I_{G^-}/I_{G^+} as a function of V_{gs} at $V_{ds} = 0.05$ V are shown in Figure 5.25(b) to (d), respectively.

Figure 5.25 (a) Transfer characteristics (I_{ds} - V_{gs} curve) of the DWNT-FET obtained during Raman scattering measurement. The frequency (b), linewidth (c) and I_{G^-}/I_{G^+} (d) for G^+ and G^- modes as a function of V_{gs} .*

The G^+ peak for the s-DWNT does not show significant changes in either the peak frequency or linewidth as a function of V_{gs} (see round symbols in Figure 5.25(b) and (c)).

Interestingly, the G^- peak has $\sim 12 \text{ cm}^{-1}$ shift in the peak frequency and $\sim 6 \text{ cm}^{-1}$ change in the linewidth (see triangle symbols in Figure 5.25(b) and (c)). Moreover, I_{G^-}/I_{G^+} is observed to change with V_{gs} sweeping (see Figure 5.25(d)).

After the surface passivation with the Si_3N_4 layer, an ambipolar characteristic with a stable hysteresis loop in the transfer curve is observed for V_{gs} in a range from -20 to +20 V, as shown in Figure 5.25(a). The observed p-type to ambipolar or even n-type conversion can be attributed to the removal of adsorbed oxygen on the DWNT channel during coating Si_3N_4 . This is consistent with the findings that desorption of oxygen by dielectric layer passivation or annealing CNTFETs in vacuum or inert gas promotes a conversion from p- to ambipolar or even n-type.²⁸ In addition, it has been reported that the SiO_2 - Si_3N_4 stacks act as the trapping centers for both electrons and holes.¹⁵³ The hysteresis loop is caused by the trapping/detrapping of electrons/holes in the trapping centers and it is stable after passivation. Since our Raman spectra are collected from the center of the DWNT channel, the results of the Raman scattering should reflect the energy band shift (or, in an equivalent way, the Fermi level ϵ_f shift) in the DWNT channel rather than any influences from the source and drain contacts.

Upon applying V_{gs} and V_{ds} to the device, in situ Raman spectra and I_{ds} data are acquired. Similar to the I_{ds} - V_{gs} curves, the G^- peak frequency and I_{G^-}/I_{G^+} show hysteresis loops for the forward and backward sweeping of V_{gs} , as shown in Figure 5.25(b) and (d), respectively. One can see that, there is a clear correlation between these hysteresis loops as the G^- peak frequency and I_{G^-}/I_{G^+} loops are in ‘phase’ with the loop of the transfer curve. Since I_{ds} is proportional to ρ , during the Raman measurements under a fixed V_{ds} , the change in I_{ds} reflects the change in ρ in the DWNT channel. Thus, analogous to the case for an s-SWNT, the frequency shift can be attributed to the change in ρ

induced by V_{gs} . The charge density ρ can be determined by $\rho = |C(V_{gs} - V_{th-h/e})|$, where C is the unit capacitance between the gate and DWNT channel and V_{th-h} (V_{th-e}) is the threshold voltage for hole current (electron current).¹³⁷

Figure 5.26 (a) Band structure of the DWNT. Dot lines and solid lines represent band structures of outer shell (chiral index (19,0)) and inner shell (chiral index (7,5)), respectively. Dash line represents the Fermi level, ϵ_f . The process that the G phonons excite electron-hole pairs between the top valence bands of the inner and outer shells is illustrated. Correlation between transfer characteristics (b), frequency of G^- (c), linewidth of G^- (d) and I_{G^-}/I_{G^+} (e) are obtained by joining the minimal I_{ds} valley on the forward and backward characteristics in Figure 5.25(a).*

The calculated band structure of (7,5)@(19,0) DWNT is shown in Figure 5.26(a), where

$VB_{o,1}$ and $VB_{o,2}$ are the first and second highest valence band of the outer shell, $CB_{o,1}$ and $CB_{o,2}$ are the first and second lowest conduction band of the outer shell, $CB_{i,1}$ and $VB_{i,1}$ are the lowest conduction band and the highest valence band of the inner shell, respectively. When $V_{th-h} < V_{gs} < V_{th-e}$ or ϵ_f is located in the band gap of the DWNT, both electrons and holes are blocked by the contact barriers, thus, I_{ds} is very small. In other words, when the ϵ_f is at the center of the band gap, I_{ds} should be around its minimum value. In contrast, when $V_{gs} < V_{th-h}$ (or $V_{gs} > V_{th-e}$) or ϵ_f is roughly aligned with the top of $VB_{o,1}$ (or the bottom of $CB_{o,1}$), the V_{gs} controls small contact barriers efficiently so that holes (or electrons) can tunnel through the barrier and form hole current (or electron current).

It is seen in Figure 5.25(a) that the centers of the current valleys for the forward sweeping and backward sweeping are $\sim -10V$ and $\sim +10V$, respectively. In Figure 5.26(b) to (e), we connect the I_{ds} , G^- frequency, G^- linewidth and I_{G^-}/I_{G^+} for the forward and backward sweeping, respectively, by joining the centers of the I_{ds} valleys at which ϵ_f is located at the middle of the band gap (see the grey line in Figure 5.26). One can see that, the G^- peak frequency and I_{G^-}/I_{G^+} increase when ϵ_f shifts away from the middle of the band gap by V_{gs} (Figure 5.26(c) and (e)), in phase with I_{ds} (Figure 5.26(b)). In other words, the G^- peak frequency and I_{G^-}/I_{G^+} change with I_{ds} (or ρ). One may note that the slope for I_{G^-}/I_{G^+} against V_{gs} does not closely correlate with that for I_{ds} against V_{gs} (see Figure 5.25(d) or Figure 5.26(e) and Figure 5.25(a) or Figure 5.26 (b), respectively). This may imply additional information, more detailed experimental studies, theoretical calculations and modeling are necessary to interpret it.

Interestingly, the G^- linewidth shows a ‘W’ shape in relationship with respect to ϵ_f position (Figure 5.26(d)). It firstly decreases when ϵ_f shifts away from the middle of the band gap and then increases. The linewidth change of the G^- peak for an m-SWNT as a function of V_{gs} has been

interpreted in terms of the interband electron-phonon coupling between the valence and conduction bands, *i.e.*, G phonons can excite electrons from the valence band to conduction band and form electron-hole pairs.¹³⁷ However, in an s-DWNT used here, G phonons cannot excite electrons from its valence band to conduction band because the energy of G phonon is much smaller than the bandgap. Therefore, we suggest that the linewidth change is caused by interband electron-phonon coupling between the energy bands of two concentric shells of the DWNT. In more detail, when V_{gs} is swept from -20V to V_{th-h} in forward sweeping (e.g. Point A in Figure 5.26(b)), ϵ_f might shift from $VB_{i,1}$ toward $VB_{o,1}$, as shown in Figure 5.26(a). It is also noted that the energy difference between $VB_{o,1}$ and $VB_{i,1}$ is comparable with the phonon energy of the G mode. Thus, electrons can be excited from $VB_{i,1}$ to $VB_{o,1}$ by G phonons, resulting in electron-hole pairs and the broadening of the G^- linewidth. However, when V_{gs} is further increased so that ϵ_f is in the band gap (e.g. Point B in Figure 5.26(b)), no electrons can be further excited by G phonons because of a large energy band gap between $VB_{o,1}$ and $CB_{o,1}$, leading to a saturated G^- linewidth. Similarly, when ϵ_f is located between $CB_{o,1}$ and $CB_{i,1}$, electrons can be excited from $CB_{o,1}$ to $CB_{i,1}$. However, when ϵ_f is shifted further by V_{gs} and is located above the bottom of $CB_{i,1}$, the states in $CB_{i,1}$ can be filled and the transition between $CB_{o,1}$ to $CB_{i,1}$ is suppressed, resulting in a narrowing of linewidth. On the other hand, when more and more states in $CB_{i,1}$ are filled, electrons also can be excited by G phonons from $CB_{i,1}$ to $CB_{o,2}$, forming electron-hole pairs and resulting in the broadening of the G^- linewidth. These two opposite effects may compete and determine the G^- linewidth profile. Therefore, a minimum point of the G^- linewidth can be observed. Analogously, another minimum point of the G^- linewidth is found when ϵ_f is around $VB_{i,1}$. Thus, a ‘W’ shape of the G^- linewidth with respect to the ϵ_f position is observed (Figure 5.26(d)).

The Raman scattering from an individual s-SWNT under similar experimental conditions has been reported by Tsang *et al.*¹³⁷ Their results were obtained from an s-SWNT with diameter $\sim 2.4\text{nm}$ and the results of a thinner SWNT were given theoretically. From their experimental results, the G^+ frequency varies with ρ while other parameters such as G^- frequency, G^+ linewidth and G^- linewidth, do not change. Moreover, in the theoretical calculation, the G^- frequency is suggested to vary with ρ although it is not confirmed experimentally. In contrast, the G^- frequency, rather than the G^+ frequency, is observed to shift with ρ in the Raman scattering of our s-DWNT. The finding that the G^+ frequency does not significantly change as a function of V_{gs} (as shown in Figure 5.25(b)) can be tentatively interpreted as follows. First, the gate oxide in our DWNT-FET is thicker (500 nm) than that of theirs (100nm).¹³⁷ The thick gate dielectric layer lowers the gate efficiency and, consequently, the Raman response to V_{gs} may be too small to be observed in our experiments. Second, the diameter of our DWNT is thinner ($\sim 1.48\text{nm}$) than that of theirs ($\sim 2.4\text{nm}$), which may also result in a smaller shift of the G^+ frequency to V_{gs} according to the calculation of Tsang *et al.*¹³⁷ Thus, the frequency shift of the G^+ for the DWNT is probably smaller than 1 cm^{-1} , below the observation limit. Interestingly, the G^- linewidth change is a unique phenomenon observed in an s-DWNT, which is interpreted as the inner and outer tube interaction, as discussed in previous paragraph. However, this phenomenon has not been observed in an s-SWNT probably because the energy of G phonons is much smaller than the transition energy between the energy bands of an s-SWNT.

In summary, a close correlation between the in situ Raman scattering and transfer characteristics from a semiconducting DWNT-based FET under real-time operations has been established. The G^- peak frequency and I_{G^-}/I_{G^+} respond to the forward and backward sweeping of the

V_{gs} in a similar manner as the hysteretic transfer characteristics of the DWNT-FET. We suggest that the G^- peak frequency and I_{G^-}/I_{G^+} are monotonically determined by the carrier concentration in the DWNT channel. The observed G^- peak linewidth change as a function of V_{gs} can result from interband electron transitions between the energy bands of two concentric shells of the DWNT excited by G phonons.

5.5 Effect of Si_3N_4 passivation on the Raman features

From the results presented in Chapter 5.3 and Chapter 5.4.3, one can see that not only the transfer characteristics but also the Raman features are changed after Si_3N_4 passivation (the comparison can be conducted between the results at $V_{gs} = 0V$). After passivation, the G^+ frequency shifts from $\sim 1584\text{ cm}^{-1}$ to $\sim 1589\text{ cm}^{-1}$ and the linewidth changes from $\sim 9\text{ cm}^{-1}$ to $\sim 11\text{ cm}^{-1}$ at the same time. The G^- frequency shifts from $\sim 1564\text{ cm}^{-1}$ to $\sim 1575\text{ cm}^{-1}$ and the linewidth changes from $\sim 25.5\text{ cm}^{-1}$ to $\sim 27\text{ cm}^{-1}$. Furthermore, the intensity ratio of G^- over G^+ (I_{G^-}/I_{G^+}) only shows a small change, from ~ 0.3 to 0.35 . Interestingly, the features of in situ Raman scattering are still well correlated with the electrical measurements, i.e. following the trends of transfer characteristics (see Figure 5.22 and Figure 5.25). In other words, the deposition of Si_3N_4 changes the value of the starting points in transfer curves and Raman features at $V_{gs} = 0V$ but does not affect the correlations between electrical measurements and in situ Raman scattering. By the correlations, we can estimate the position of the Fermi level at $V_{gs} = 0V$ for both case which is useful to analyze the effect of Si_3N_4 passivation.

One may suggest that, the changes in Raman results may be caused by the desorption of H_2O or O_2 during the Si_3N_4 passivation. In our point of view, the desorption of H_2O molecules may

not have much effect since they may only affect the hysteresis through the trapping/detrapping process and the hysteresis does not correspond to any change in the electronic structure, as discussed in Chapter 4.1. Moreover, desorption of O_2 may mainly change the work function of electrode and change the Schottky barrier at the source and drain contact.⁴⁷ However, this change does not affect the electronic structure of CNT body on which we focus our laser. On the other hand, the Fermi level can be shifted by passivation. The mechanism of the Fermi level shift is still not clear but we can understand this phenomenon by self-doping caused by passivation or chemical desorption (such as O_2) in the DWNT. Through correlation, we may estimate that the Fermi level at $V_{gs}=0$ V is around the top of the valence band before passivation (as shown in Chapter 5.3) and around the bottom of the conduction band after passivation (as discussed in Chapter 5.4.3). In other words, the Fermi level may be shifted from the top of the valence band to the bottom of the conduction band after the Si_3N_4 passivation. Since this movement of the Fermi level is in the bandgap, there should be no observable change in Raman scattering. Thus, for the individual semiconducting DWNT-FET, neither H_2O nor O_2 desorption during Si_3N_4 passivation can dominate the changes in the features of Raman scattering. The observed changes caused by passivation should have other mechanisms.

It has been reported that strain on CNTs could shift down the frequency of the G band while compression can shift the G band frequency up.^{154,155} Besides, Martyniuk *et al.* have reported that the SiN_x deposited at 300°C by PECVD could induce compression with the magnitude ~ 300 MPa.¹⁵⁶ Furthermore, the broadening in the G band linewidth was also observed when applying compression to the CNTs.^{154,155,157-159} Based on these experimental evidences, we suggest that, the up-shift of the G band frequency and the broadening in the G band linewidth in our results are resulted from the

compression caused by Si_3N_4 passivation. Thus, the results presented in Chapter 5.4.3 are the experimental observations from a compressed semiconducting DWNT.

5.6 In situ Raman scattering of bundled DWNTs on FET geometry

Figure 5.27 (a) AFM image of the DWNTs-based FET. (b) Height profile along the dashed line indicated by arrow in (a). (c) Map of sum of Raman spectrum intensity between 1500 to 1600 cm^{-1} . (d) The RBM of the DWNTs. Peak positions are labeled and the linewidths are shown in the brackets.*

In Chapter 5.4.3 and 5.5, we have proposed a mechanism to explain the phenomenon of the Raman scattering for an isolated semiconducting DWNT in FET geometry. In addition, the features of the in situ Raman scattering are closely correlated with the conductance of the individual semiconducting DWNT. However, in most common cases, the devices obtained consist of bundles of CNTs between the electrodes. Consequently, there is a need to understand electron transport in bundled CNTs, especially in the case when the bundles contain both metallic and semiconducting tubes.

Back-gated DWNTs-FETs containing a small bundle of DWNTs in each of the devices are fabricated using ACDEP process. Fabrication of the device has been presented in Chapter 5.3 in details. Similarly, Figure 5.27(a) and (b) show an AFM (atomic-force microscopy) image of the device and the cross section height-profile at the dash line indicated by the arrow, respectively. The DWNT channel is characterized using the same confocal Raman microscopy system as before. After conducting a Raman mapping scan (Figure 5.27(c)), the laser spot is fixed at the position marked with dashed circle in Figure 5.27(a) for acquiring the Raman spectra before and after Si_3N_4 deposition.

Figure 5.28 The comparison of the G bands of the device before and after Si_3N_4 passivation. The intensity of G^+ is normalized in order to see the relative intensity change more clearly.*

Two RBM peaks measured at $E_L=2.33$ eV with frequencies of 159 and 267 cm^{-1} are shown in Figure 5.27(d). According to the Kataura plot (Figure 5.7) and the method presented by Maultzsch *et al.*,⁸¹ we assign the higher RBM frequency to (9, 2) (semiconducting CNT). At the lower RBM frequency in the Kataura plot, branch 34 (a sum of $2n+m$) falls into the resonant

window of the excitation laser energy (between 2.28 and 2.38 eV). Therefore, we assign the lower RBM frequency to an s-DWNT (12, 10) with a bandgap of ~ 0.56 eV. The diameters of (12,10) and (9,2) are ~ 1.5 nm and ~ 0.8 nm, respectively, which match well with the diameter difference of a DWNT. The estimated diameter of the outer shell in the DWNT is around 1.5 nm while the height of the channel measured by AFM is ~ 2.1 nm (Figure 5.27(b)). Thus, it is likely that there are more than one tubes inside the DWNT channel. Moreover, our observation shows that the linewidths of the RBM peaks of the DWNTs here are larger than that of an individual DWNT shown in Figure 5.19(d), which will also suggest that it is likely our device contains bundled DWNTs. As reported by Villalpando-Paez *et al.*,²⁰ the linewidth of the RBMs of the bundled CNTs are usually larger than that of an individual tube. Based on the discussion above, there should be more than one DWNTs (total > 4 shells) in the channel but only two RBM peaks, i.e. two shells, are observed. It is possible that some shells in the channel do not have double-resonant RBM features. As a result, the G band line shape and transfer characteristics are used to identify the type of the DWNTs in the bundle. In fact, we observe BWF line shape in the G band (Figure 5.28), implying the existence of metallic tubes.

Figure 5.29 Results of the device before Si_3N_4 passivation. The I_{ds} - V_{gs} curves (a) and the frequency (b), linewidth (c), and intensity ratio I_{G^-}/I_{G^+} (d) for G mode as a function of V_{gs} . Red symbols represent results of G^+ and blue symbols represent results of G^- , filled symbols represent the results of forward sweeping and open symbols represent results of backward sweeping.*

Similar to the procedure presented in Chapter 5.3 and Chapter 5.4.3, the V_{gs} and V_{ds} are applied to the device during the Raman measurements. The Raman spectra are obtained under $V_{ds}=0.1$ V with 30 seconds integration time for each spectrum. The p-type hysteretic transfer characteristics (I_{ds} - V_{gs} curves) during the Raman scattering are shown in Figure 5.29(a), the I_{on}/I_{off} more than 100. There are several peaks observed in the G band for the bundled DWNT in the device. Based on the Raman scattering, the fitted results of the two most dominant G peaks (one G^+ and one G^- peak) are shown in Figure 5.29(b) to (d). After the first measurements of the in situ Raman scattering, the CNTFET is passivated with 300nm-thick Si_3N_4 in vacuum at 300°C . Then the second measurements of the in situ Raman scattering of the device is conducted. The

hysteretic I_{ds} - V_{gs} curves and Raman features, such as frequency, linewidth and I_{G^-}/I_{G^+} , are shown in Figure 5.30(a) to (d), respectively.

Figure 5.30 Results of the device after Si_3N_4 passivation. The I_{ds} - V_{gs} curves (a) and the frequency (b), linewidth (c), and intensity ratio I_{G^-}/I_{G^+} (d) for G mode as a function of V_{gs} . Red symbols represent results of G^+ and blue symbols represent results of G^- , filled symbols represent the results of forward sweeping and open symbols represent results of backward sweeping.*

From Figure 5.29(b) to (d), one can see that, the G^+ peak does not show significant change in either the peak frequency or linewidth as a function of the V_{gs} . In contrast, when V_{gs} is increased from -20 V to 0 V, the G^- peak has $\sim 4 \text{ cm}^{-1}$ downshift in its peak frequency and a linewidth broadening from 95 cm^{-1} to 108 cm^{-1} . When V_{gs} is increased from 0 V to +20 V, the changes in frequency and linewidth are not significant. Furthermore, after passivation (see Figure 5.30(b) to (d)), the G^+ peak does not show significant change while the G^- peak has $\sim 4 \text{ cm}^{-1}$ downshift in peak frequency and a linewidth broadening from 30 cm^{-1} to 36 cm^{-1} as a function of

the V_{gs} . These changes in the Raman spectra induced by V_{gs} follow the hysteresis of electrical measurements, which can also be interpreted using the mechanism for an individual semiconducting DWNT presented in Chapter 5.3 and Chapter 5.4.3. That is, the G^- peak frequency and I_{G^-}/I_{G^+} are determined by the carrier concentration in the DWNT channel and the G^- peak linewidth change as a function of V_{gs} results from the interband electron transitions between the energy bands of the two concentric shells of the DWNT excited by G phonons.

However, the results from the device based on bundled DWNTs before and after Si_3N_4 passivation show several differences. At $V_{gs} = 0$ V, there are significant changes in most of the observed characters, including conduction types, conductance, current on-off ratio I_{on}/I_{off} , peak frequency, peak linewidth and relative intensity ratio I_{G^-}/I_{G^+} .

First of all, a conversion from p-type to n-type conduction for this device (see Figure 5.29(a) and Figure 5.30(a)) is observed. As we discussed in Chapter 5.4.3, the conversions caused by Si_3N_4 passivation have been attributed to the effect of desorbing the adsorbed O_2 at the interfaces of the source and drain contacts.^{28,47} In this sense, it is reasonable to suggest that the interpretation of the observed p-type to n-type conversion here is same as the interpretations before.

When compare the Raman results in Figure 5.29 and Figure 5.30, one can see that, after Si_3N_4 passivation, the frequency of G^+ has an upshift about 1 cm^{-1} and the G^- frequency shifts up about 26 cm^{-1} . The linewidth of G^+ increases slightly while the linewidth of G^- decreases from $\sim 108\text{ cm}^{-1}$ to $\sim 32\text{ cm}^{-1}$.

The frequency upshift and linewidth broadening of the G^+ peak can be explained through the compression caused by the passivation. As we discussed in Chapter 5.5, compression may increase the frequency and linewidth of both G^+ and G^- band. However, the mechanism presented in Chapter

5.5 cannot fully explain the change in the G^- peak frequency and linewidth. The first noteworthy difference is the amplitude of frequency incensement of G^- ($\sim 26 \text{ cm}^{-1}$), which is much higher than the observation from the individual DWNT presented in Chapter 5.5 ($\sim 11 \text{ cm}^{-1}$). Second, the big narrowing in the linewidth cannot be explained merely by Si_3N_4 passivation. However, it can be better explained through the component of the bundle. From Figure 5.28, it is noted that the G^- band lineshape before passivation forms a BWF peak (linewidth $\sim 108 \text{ cm}^{-1}$) while it changes to Lorentzian peak (linewidth $\sim 32 \text{ cm}^{-1}$) after passivation. This phenomenon is similar to the EPC (or Kohn Anomaly) observed in m-SWNTs,¹³⁷ where the G^- peak is shifted to high frequency with narrowing linewidth when the Fermi level is shifted away from the Dirac point, as discussed in Chapter 5.1.5. Since there are metallic tubes in the bundle and the passivation may change the Fermi levels of CNTs (see Chapter 5.5), it is reasonable to suggest that the Fermi level before passivation is around the Dirac point of the m-DWNTs and, after the passivation, the Fermi level is moved away, resulting in the upshift and the narrowing of the G^- peaks. On the other hand, the compression may only cause a small broadening of the linewidth, which may be covered up by the narrowing effect induced by the Fermi level shift, leading to the observed narrowing in the G^- linewidth after the passivation.

Moreover, the changes of I_{G^-}/I_{G^+} induced by V_{gs} shown in Figure 5.29(d) and Figure 5.30(d) still follow the trends of the hysteretic transfer characteristics but the amplitude of I_{G^-}/I_{G^+} increases after the passivation. As discussed in Chapter 5.3 and Chapter 5.4.3, the I_{G^-}/I_{G^+} is correlated with the current or the charge density in the tubes. It is reasonable to observe a bigger I_{G^-}/I_{G^+} ratio after the passivation since the conductance is significantly increased.

We observe that the conductance especially the off current increases significantly after the

passivation and the $I_{\text{on}}/I_{\text{off}}$ in turn drops from ~ 100 to ~ 3 , *i.e.*, the device has changed from semiconducting to more metallic. The increase in the the conductance is commonly explained with two possible mechanisms. First, during Si_3N_4 passivation, the oxygen is removed by the high temperature and high vacuum process. The work function of the metal electrodes is changed after oxygen desorption. Thus, after the passivation, the Schottky barriers for electron tunneling may be smaller than the barrier for holes before the passivation. The “on” conductance of the device may be enhanced and the current on-off ratio should not be affected significantly. Therefore, we suggest that the oxygen effect is not the dominating mechanism of conductance enhancement observed here. Second, it has been predicted that strain may induce a semiconductor-metal (S-M) transition for SWNT. However, based on the calculation, the strain to achieve this S-M transition is pretty high.¹⁶⁰⁻¹⁶² For example, the S-M transition is suggested to occur at a compressive uniaxial stress ~ 30 GPa for a semiconducting (31, 0) SWNT, *i.e.*, ~ 10 GPa for ~ 0.1 eV change.¹⁶⁰ Obviously, the compression introduced by Si_3N_4 passivation, at a magnitude ~ 300 MPa,¹⁵⁶ is not sufficient to close the band gap of ~ 0.6 eV.

Based on the discussion above, we propose that the changes in conductance and off-current can be explained as follows. Before the Si_3N_4 passivation, we suggest that only the semiconducting tubes are contacted to the electrodes and, consequently, the conduction is dominated by the semiconducting tubes, as shown in Figure 5.31(a). After the passivation, it is possible the metallic tubes are forced to the contacts by the passivation (see Figure 5.31(b)) and these metallic tubes are involved in the conduction of the device. Both the “on” conductance and “off” conductance are enhanced. In particular, the metallic-like characteristic with higher conductance and lower $I_{\text{on}}/I_{\text{off}}$ are observed. Accordingly, $I_{\text{G-}}/I_{\text{G+}}$ is changed as it is suggested to be

dependent of the conductance.

One more point to be clarified is that the contact between the metallic inner shells of the DWNTs and electrodes is not taken into account since the inner shells are always shielded by the outer shells.

Figure 5.31 Schematic mechanism of contact change caused by Si_3N_4 deposition.*

In order to understand the phenomenon better, we also conduct several experiments on bundled DWNT-FETs with bigger bundle sizes, for example $\sim 10\text{nm}$. The transfer characteristics are typical metallic characteristics, *i.e.*, no obvious current on-off ratio (not shown here) is observed. In those devices, there is no measurable change in all the Raman features of G band with V_{gs} , such as frequency, linewidth and intensity ratio. We suggest that, the screening effects of metallic tubes to the semiconducting ones lead to the non-gate dependence of the Raman scattering and electrical measurements. The screening effects are much weaker when the bundle size is very small ($\sim 2.1\text{nm}$ in our case). Therefore, the features of gate voltage dependences in Raman scattering can be observed in Figure 5.29 and Figure 5.30.

In summary, we have observed the gate voltage dependence of in situ Raman scattering for a DWNT-FET with thin bundled DWNTs. The device is characterized before and after Si_3N_4 passivation. In both cases, the features of the Raman scattering are closely correlated to the

hysteretic transfer characteristics, similar to the results for an individual semiconducting DWNT-based FET. By the correlations, we analyze the effect of Si_3N_4 passivation on a thin DWNTs bundle in FET geometry. The change after passivation in the electrical conductance can be attributed to the contribution from metallic tubes in the bundle. However, the changes in the results of the Raman scattering can be caused by several aspects. The first one is the compression caused by the passivation, which results in the frequency upshift and the linewidth broadening for G^+ peak. The second one is the shift of the Fermi level caused by the passivation, leading to the upshift and linewidth narrowing of G^- peak. Last, the increase in the magnitude of I_{G^-}/I_{G^+} after the passivation is attributed to the increased conductance of the device. Furthermore, the results from the FET based on a thick-bundled DWNTs show that there are almost no gate voltage dependences in both the electrical measurements and the Raman scattering. This phenomenon is suggested to be caused by the screening effect of metallic tubes in the bundle.

5.7 Conclusions

The Raman scattering is a powerful tool to characterize the structure and electronic properties of CNTs, such as diameter, chiral index and charge transport properties. Furthermore, in situ Raman has been found to be an effective tool to investigate CNTs in a device geometry such as FET platform. The results from individual SWNT have been reviewed.

In our experiments, the properties of our CNTs, including SWNTs and DWNTs with $\sim 1.5\text{nm}$ diameter, are firstly studied and compared. We find that the type and concentration of surfactants do not affect either the results of Raman scattering or the electronic structures of the SWNT and DWNTs very much. Besides, there is an evidence showing that, at room temperature,

the intershell interaction between the two concentric shells of DWNTs is negligible for our DWNT with diameter $\sim 1.4\text{nm}$.

The in situ Raman scattering of an individual semiconducting DWNT on a FET platform is discussed in Chapter 5.3. We have observed the frequency shift and linewidth change of the G^- band in response to the gate voltages. We suggest the frequency shift of G^- peak is due to the change of charge density induced by the gate voltages. The unique linewidth change of the G^- peak is interpreted as interband electron-phonon coupling between the bands of two concentric shells in the DWNT. In addition, relative intensity of G band (I_{G^-}/I_{G^+}) is found to be increased with the local charge density in the DWNT channel.

In Chapter 5.4, we found that the G^- peak frequency and I_{G^-}/I_{G^+} of the in situ Raman scattering respond to the forward and backward sweeping of the V_{gs} in a similar manner as the hysteretic transfer characteristics of the DWNT-FET. We suggest that the G^- peak frequency and I_{G^-}/I_{G^+} are monotonically determined by the carrier concentration in the DWNT channel. The observed G^- peak linewidth change as a function of V_{gs} can result from interband electron transitions between the energy bands of two concentric shells of the DWNT excited by G phonons.

Moreover, we investigate DWNT-FETs with thin ($\sim 2.1\text{nm}$) and thick ($\sim 10\text{nm}$) DWNTs bundles (containing both metallic and semiconducting tubes) as their conducting channel, respectively. We found that, the Raman scattering of the device with thin DWNTs bundle still respond to the gate voltage in the same way as the individual DWNT-based FET. The changes in the Raman scattering follow the trend of hysteretic transfer characteristics. However, for the device with thick DWNTs bundle, no Raman response is observed. The screening effects of metallic tubes to semiconducting tubes can be used to explain the observation.

We also study the effect of Si_3N_4 passivation. For the individual semiconducting DWNT-based FET, the changes observed after the Si_3N_4 passivation, such as upshift in the frequency and broadening in the linewidth for the G^+ and the G^- , are more likely to be caused by the effect of compression after the passivation. However, the effects in the DWNT-FETs with bundled DWNTs are more complicated. First, the compression caused by passivation results in an upshift and the linewidth broadening for G^+ peak. Second, the shift of the Fermi level caused by the passivation could cause an upshift and linewidth narrowing for G^- peak. Last, the increase of I_{G^-}/I_{G^+} in magnitude after the passivation can be attributed to the conductance increase of the device.

Chapter 6 Conclusions and Future Work

6.1 Conclusions

In this thesis, the electrical properties of CNTs and CNTs-based electronic devices are reviewed. The electron transport properties have been investigated using the both SWNTs and DWNTs-based CNTFETs. The findings and implications in this project are summarized in the following parts. The hysteretic transfer characteristics of CNTFETs are discussed with main focus on the surfactant effects on the transfer curves. In situ Raman scattering of an individual double-walled CNT-based CNTFET are conducted and the intershell interaction of double-walled CNTs (DWNTs) is suggested to be the main reason of the observed gate-dependent changes in the in situ Raman scattering. The correlations between in situ Raman scattering and hysteretic transfer characteristics of DWNT-FET are established. Through these correlations, the influences of Si_3N_4 passivation on the electrical properties of bundled DWNTs are investigated.

6.1.1 Hysteretic transfer characteristics of CNTFETs

Significant hysteretic transfer characteristics have been found in our single-walled (SW-) and double-walled CNTs. In our experiments, ‘clockwise’ and ‘anticlockwise’ hysteresis loops in the transfer curves are observed. The findings suggest that the surfactants may suppress the effects of water molecules and oxygen, and change the transfer characteristics of the CNTFETs. The

competition between surfactants and water molecules/ oxygen determines the output of transfer characteristics of CNTFETs. Furthermore, the effects of different types of the surfactants are compared and discussed. The ‘clockwise’ hysteresis can be well interpreted in terms of the mobile ions or charge groups in SDS, SDBS and Triton X-100 layer around the CNTs channels. Compared with SDS, SDBS and Triton X-100 are more easily adhered to the surface of CNTs, which may result from the benzene rings in the molecules. Third, from the comparisons between SWNT-FETs and DWNT-FETs, we found that there are no detectable differences in electrical measurements between these two types of the FETs. However, the DWNTs are suggested to have superior adsorption of the surfactants.

6.1.2 In situ Raman scattering of a DWNT-based FET

Through the study on the in situ Raman scattering from a single semiconducting DWNT in an FET geometry, we have observed the frequency shift and linewidth change of the G^- band in response to the gate voltages. We suggest the frequency shift in G^- peak is due to the change of charge density in the DWNT channel induced by the gate voltages. The unique linewidth change of the G^- peak as a function of the gate voltages is interpreted as interband electron-phonon coupling between the energy bands of two concentric shells in the DWNT. In addition, relative intensity of G band (I_{G^-}/I_{G^+}) is found to be increased with the local charge density in the DWNT channel.

A close correlation between the in situ Raman scattering and transfer characteristics from a semiconducting DWNT-based FET under real-time operations has been established. The G^- peak

frequency and I_G/I_{G+} respond to the forward and backward sweeping of the V_{gs} in a similar manner as the hysteretic transfer characteristics of the device. Through the correlation, the mechanism of the changes of the Raman scattering with V_{gs} variation are studied.

After coating the DWNT-FETs with Si_3N_4 passivation, we found that both the transfer characteristics and the Raman scattering are changed after the passivation. The change in the transfer curves can be attributed to the oxygen desorption and the contribution from the metallic tubes in the bundle. However, the changes in the Raman scattering can be explained by several factors, including the compression caused by passivation, the shift of the Fermi level and the change of conductance of the device.

6.2 Future work

Based on what we have achieved, we may propose several directions for future work.

6.2.1 Chemical sensors by DWNT-FETs

As shown in Chapter 4, DWNTs have superior adsorption properties when compared with SWNTs. This finding implies a possible chemical/biomedical application with DWNTs. A high adsorption property could lead to a high detecting sensitivity. Moreover, the Raman scattering can be used to correlate the response from the contact passivated or body passivated geometry, which may offer in-depth interpretation for the sensing mechanism.

6.2.2 Raman characterizations of CNTFETs with novel structures

CNT-based devices with new structures need to be explored in order to enhance their electrical performances. For instance, introduction of partial gate structure has led to superior carrier mobility which is higher than the conventional prediction.⁴⁸ The charge transport mechanisms of the devices with novel structures are still not clear and become more and more important to be understood. Since the correlation between in situ Raman scattering and electrical measurements can offer in-depth understanding on the physics about charge transport mechanisms of CNTs, it is attractive to use in situ Raman scattering to investigate the CNT-based device with novel structures, targeting in-depth understanding on the operating mechanisms.

6.2.3 Intershell interaction in DWNT

As shown in the thesis, the DWNTs have unique two-layer structure which is a perfect platform to investigate shell-shell interaction. From the experimental results, we suggest that there is intershell interaction between the concentric shells of DWNTs at room temperature. However, further study is needed to understand the mechanism of the interaction. Intershell interaction may be studied through comparing SWNT and DWNT with the same diameter, especially the same chirality. The preliminary study has been reported by Dresselhaus *et al.*²⁰ The in-depth study through the correlations between Raman scattering with electrical measurements has not been conducted yet.

Author's publications

Journal papers:

1. **Shaoning Yuan**, Qing Zhang, Daisuke Shimamoto, Hiroyuki Muramatsu, Takuya Hayashi, Yoong Ahm Kim, and Morinobu Endo, "Correlation between in Situ Raman Scattering and Electrical Conductance for an Individual Double-Walled Carbon Nanotube", *Nano Letters*, **9(1)**, 383, (2009).
2. **Shaoning Yuan**, Qing Zhang, Yumeng You, Ze-Xiang Shen, Daisuke Shimamoto, and Morinobu Endo, "Hysteretic transfer characteristics of double-walled and single-walled carbon nanotube field-effect transistors", *Applied Physics Letters*, **91**, 143118 (2007).
3. Ning Peng, Qing Zhang, **Shaoning Yuan**, Hong Li, Jingze Tian, Lap Chan, "Current instability of carbon nanotube field effect transistors", *Nanotechnology*, **18**, 424035 (2007).

Conference paper:

1. Pingqi Gao, Qing Zhang, **Shaoning Yuan**, Ning Peng and Deyan He, "RAMAN STUDIES OF ELECTROSTATIC DOPING OF A THIN SINGLE-WALLED CARBON NANOTUBE BUNDLE", ICMAT 2009, will be published in *International Journal of Nanoscience*.

Manuscripts in processing:

1. **Shaoning Yuan**, Yumeng You, Qing Zhang, Ze-Xiang Shen, Daisuke Shimamoto, and

Morinobu Endo, “In situ Raman scattering from a double-walled carbon nanotube based field-effect transistor”

2. **Shaoning Yuan**, Yumeng You, Qing Zhang, Ze-Xiang Shen, Daisuke Shimamoto, and Morinobu Endo, “In situ Raman observation of the contact passivation effects in double-walled carbon nanotubes field-effect transistors”

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