Controllable synthesis and rapid identification of carbon nanotube intramolecular junctions

An, Jianing

2014

An, J. (2014). Controllable synthesis and rapid identification of carbon nanotube intramolecular junctions. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/59860>

<https://doi.org/10.32657/10356/59860>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**CONTROLLABLE SYNTHESIS AND RAPID IDENTIFICATION OF
CARBON NANOTUBE INTRAMOLECULAR JUNCTIONS**

AN JIANING

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2014

CONTROLLABLE SYNTHESIS AND RAPID IDENTIFICATION OF CARBON NANOTUBE INTRAMOLECULAR JUNCTIONS

AN JIANING

AN JIANING

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University

in partial fulfillment of the requirement for the degree of

Doctor of Philosophy

2014

Acknowledgement

If you ask me what the biggest challenge is in my life, I would definitely say it is my Ph.D, with no doubt. During the past four years, I have put my hard work and my talent and my heart into this study program, because I always believe, in research you get back what you put into it. Now this thesis has finally been completed, and I know nothing could have been possible without the help of many people.

First of all, I would like to express my deepest appreciation to my supervisor, Professor Zheng Lianxi, a sophisticated, mature, and gracious gentleman. You have such a surprisingly kind heart. When I joined your group, I knew nothing about research. You gave me your dedication and encouragement, your time and patience, your nurture and support. I look up to you like the perfect role model, your attitude towards life, work, and family has greatly impressed me. I am forever grateful for you.

I would like to thank Zhan Zhaoyao, my dear senior. You are one of the most talented and generous people I have ever met. You taught me a lot about how to do research. Thank you so much for your help and guidance all the way. Also, many thanks are due to my colleagues, Sun Gengzhi, Zhou Jinyuan, Hari Krishna, and Reinack Hansen. To all the staffs in MMC lab, CMMS lab, and Materials lab, thank you for your helps on my experiments. At NTU I met some of my best friends, Zhang He, Tang Cheng, Wang Xiaoyan, Wei Caiyi, Zhu Guiping, and Wu Fang. I am so glad to have shared this journey with you.

Thank you to Qiu Zhiliang, my big brother. You are always so brave and fearless. When I think about “courage”, I think about you. You are the reason that I never give up pursuing my dreams. Thank you to Hou Jie for those happy memories. I feel so blessed that I met you. The things you taught me about life and love are priceless. Thank you to Sun Xueting, you are the most loyal and reliable friend in my life. You had such respect for me that I started learning to respect myself. I will never forget that or stop being thankful. Thank you to Chen Xingkuan, you came into my life at a time when I was trying to figure out who I really was. You are so warm and sweet, you made me feel so well taken care of. Thank you for accompanying me and putting up with me.

I owe my special thanks to my parents. I know how hard it was for you to raise me and get me well educated, the sacrifices you made were uncountable. Thank you for your unconditional support. I have nothing in return but my endless love. I love you.

Table of Contents

Acknowledgement	I
Table of Contents.....	III
List of Figures	VIII
List of Tables	XIX
Abstract.....	XX
Chapter 1 Introduction	1
Chapter 2 Literature Review	7
2.1 Introduction to CNTs	7
2.1.1 Structure and properties of CNTs	8
2.1.2 Synthesis of CNTs	20
2.1.3 Applications of CNTs in nanoelectronics	25
2.2 Introduction to CNT IMJs	28
2.2.1 Concept of CNT IMJs	28

2.2.2	Types, properties and applications of CNT IMJs.....	28
2.3	Preparation of CNT IMJs.....	33
2.3.1	Generation of defects onto CNTs	34
2.3.2	Synthesis via CVD method	35
2.3.3	Doping of CNTs.....	37
2.3.4	Mechanical deformation.....	39
2.3.5	Modulation of SWNTs via interaction.....	41
2.3.6	Welding of CNTs.....	46
2.4	Identification of CNT IMJs	47
2.4.1	Morphology identification	47
2.4.2	Atomic structure identification.....	49
2.4.3	Resonance Raman spectroscopy	51
2.5	Summary	56
Chapter 3	Experimental Details	57
3.1	Synthesis of Ultralong, Horizontally Aligned SWNTs	58

3.2	Preparation of CNT IMJs.....	60
3.2.1	Fabrication of trenched structures on flat substrates.....	60
3.2.2	Growth of SWNTs across trenches	61
3.3	General Characterization Methods.....	62
3.3.1	Scanning electron microscopy	62
3.3.2	Atomic force microscopy	63
3.4	Resonance Raman Spectroscopy	63
3.5	Electrical Measurements.....	64
Chapter 4	Synthesis of Ultralong, Horizontally Aligned Single-Walled Carbon Nanotubes....	66
4.1	Introduction	66
4.2	Synthesis of Ultralong and Dense SWNT Arrays	68
4.3	Density and Length Control.....	70
4.3.1	Influence of growth parameters on CNTs morphology	70
4.3.2	Growth condition mediated catalysts effects.....	77
4.3.3	Alignment difference with respect to CNTs density	79

4.4	Electrical Measurements.....	82
4.4.1	Electrical characterization of isolated SWNTs	82
4.4.2	Performance of SWNT FETs	83
4.5	Conclusions.....	88
Chapter 5	Carbon Nanotube Intramolecular Junctions Induced by Strain	90
5.1	Introduction.....	90
5.2	Preparation of SWNT IMJs	91
5.3	Identification and Characterization of SWNT IMJs Using Raman Spectroscopy.....	92
5.3.1	Raman Characterization of individual SWNTs	93
5.3.2	Chiral and dimensional uniformity	96
5.3.3	Identification and characterization of SWNT IMJs	97
5.4	Formation Mechanism	104
5.5	Electrical Measurements on SWNT IMJs.....	106
5.6	Conclusions.....	108
Chapter 6	Carbon Nanotube Intramolecular Junctions Induced by Interactions	109

6.1	Introduction	109
6.2	IMJs Induced by Tube-Substrate Interaction	112
6.3	IMJs Induced by Tube-Tube Interaction.....	117
6.4	Conclusions	121
Chapter 7	Conclusions	123
Chapter 8	Recommendation for future Work	126
	Publications.....	127
	References	129

List of Figures

Figure 1.1. Typical current-voltage ($I - V$) characteristics of a Schottky junction and an Ohmic junction.	2
Figure 2.1. Schematic diagrams showing (a) a single-walled carbon nanotube (SWNT), and (b) a multi-walled carbon nanotube (MWNT).	7
Figure 2.2. (a) Conceptual diagram showing a layer of graphene rolling up into a SWNT. (b) The unrolled graphene honeycomb lattice, indicating the chiral vector $\mathbf{c}_h$ along the circumferential direction and chiral angle θ . (c) The resulting (5, 3) nanotube. Adapted from ref. [37].	9
Figure 2.3. Atomic structure of (a) an armchair nanotube, (b) a zigzag nanotube, and (c) a chiral nanotube. Adapted from ref. [38].	10
Figure 2.4. (a) The 3D band structure of a graphene sheet. (b) Zoom-in energy dispersion at one of the $\mathbf{K}$ points near the Fermi energy. Adapted from ref. [41]. (c) The wave vectors associated with a nanotube, as indicated, along the nanotube axis and along the circumference of the nanotube, respectively. (d) Schematic illustration of zone-folding graphene sheet to form the 1D band structure of CNTs. (e) The resulting 1D energy dispersions for a metallic nanotube and a semiconducting nanotube. Adapted from ref. [40]. (f) DOS for a metallic nanotube (upper panel) and a semiconducting nanotube (lower panel), displaying vHSs due to 1D confinement. Adapted from ref. [38].	12

Figure 2.5. (a) Phonon dispersion relations of 2D graphene. (b) The corresponding phonon DOS for the graphene sheet. (c) Phonon dispersion for a (10, 10) armchair carbon nanotube, obtained with the zone-folding approach. (d) The corresponding phonon DOS for the (10, 10) nanotube. Adapted from ref. [45]. 14

Figure 2.6. (a) A typical FET setup for electrical transport measurements on SWNTs. Conductance versus gate voltage of (b) a metallic and (c) a semiconducting SWNT at room temperature. Insets: schematic drawing of the expected energy dispersion near the Fermi energy for (b) a metallic and (c) a semiconducting SWNT. Adapted from ref. [51]. 17

Figure 2.7. (a) SEM image of SWNTs prepared using a “fast-heating” technique. Adapted from ref. [31]. (b) One ultralong SWNT with growth length of 4 cm. Adapted from ref. [56]. (c) Dense SWNT arrays were obtained by annealing Fe in air. Adapted from ref. [58]. (d) Under extremely low feeding flow condition, SWNT arrays appear super straight. Adapted from ref. [59]. 22

Figure 2.8. (a) High-performance FETs fabricated with densely packed SWNT arrays as conduction channel. Adapted from ref. [68]. (b) A 5-stage ring oscillator assembled on one individual nanotube and its output characteristic. Adapted from ref. [70]. (c) Optical image of CNT-based ICs on flexible plastic substrates. Adapted from ref. [71]. (d) SEM image of small hysteresis CNT-based ICs by exploiting monolayer graphene as electrodes. Adapted from ref. [72]. 26

Figure 2.9. (a) Atomic structure of an (8, 0)/(7, 1) tube. The red balls denote the atoms forming

a 5-7 defect pair on the nanotube. Adapted from ref. [82]. (b) $I - V$ characteristics across an M-S IMJ as shown in the inset, showing rectifying behavior. (c) Plot of conductances obtained from two straight metallic nanotube segments and the kink M-M junction as a function of temperature, respectively. (b) and (c) are adapted from ref. [84]. (d) $I - V$ curves of three SWNT segments, the inset show the rectifying behavior of the S-S junction. Adapted from ref. [86]. . 30

Figure 2.10. (a) Schematic of a split-gate p-n junction photodiode under focused optical illumination. (b) A spatially resolved photocurrent map with continuous wave laser excitation. Scale bar, 1 μm . (a) and (b) are adapted from ref. [92]. (c) An SEM image of the overall configuration to probe the switching behavior of a Y-junction. (d) Observation of abrupt modulation of the electrical current through terminal 2 when ~ 4.6 V DC voltage was applied onto the stem (terminal 1). (c) and (d) are adapted from ref. [93]..... 32

Figure 2.11. TEM images of an isolated SWNT before (a) and after (b) extensive electron irradiation at 100 keV, showing drastically dimensional change. Scale bar, 10 nm. Adapted from ref. [24]..... 35

Figure 2.12. (a) An AFM image and a schematic illustration of an S-S junction formed by changing the diameters of different segments via a temperature-mediated approach. Scale bar, 4 μm . Adapted from ref. [86]. (b) The ascending temperature-time curve and (c) corresponding Raman result of an ultralong SWNT grown under the temperature-time process, showing diameter decrease along the length. Adapted from ref. [114]. 36

Figure 2.13. (a) Schematic structure of a p-n junction fabricated by doping half of a semiconducting SWNT with potassium. The area highlighted by dashed lines in the corresponding AFM image shows the PMMA-covered region. The bottom is the band diagram for the p-n junction. Adapted from ref. [88]. (b) $I - V$ characteristics of a p-type FET (black line), a p-n junction (red line) and an n-p junction (blue line) by applying different voltages onto the two split gates. Adapted from ref. [89]. 38

Figure 2.14. (a) Schematic configuration of the setup for manipulating a suspended SWNT with an AFM tip. The tip was moved in the z direction to push the nanotube towards the bottom of the trench. (b) Experimental result of conductance versus strain. Inset, conductance versus bending angle. (c) Simulated atom configurations of the nanotube pushed to 7° and 15°, respectively. (a), (b), and (c) are adapted from ref. [117]. (d) Evolution of the band gap of a strained nanotube as V_{tip} is increased. The nanotube transferred from a p-type semiconductor to a p-n-p junction. Adapted from ref. [118]. (e) Formation of junctions by AFM manipulation. A sharp buckle (upper two images) and nanotube crossing (bottom two images) can be observed from the AFM image. Adapted from ref. [120]. (f) Change of Raman spectra as a result of increasing strain to an individual CNT. Adapted from ref. [121]. 40

Figure 2.15. (a) A model of the tube-quartz interaction. Left image: real space representation of the electronic states at the Fermi level for a (19, 0) SWNT sitting on the (001) surface of a quartz substrate. Middle image: average bond length along the tube axis (open circles) and along the tube circumference (filled circles). Right image: average density of electrons per carbon atom.

Adapted from ref. [136]. (b) Raman spectra of one individual SWNT with the laser spot moving from the SOS segment to the SUS segment, showing downshift in frequency for both RBM and G band. Inset is RBM evolution when the laser beam was moved from SUS to SOS on the right side. Adapted from ref. [137]. 44

Figure 2.16. (a) A HR-SEM image of a bridging nanotube adhered to the pillar edge, showing bending morphology. (b) A TEM image of a SWNT following the contour of a pillar, creating a buckled pattern at the edge of the 2 μm hole. (a) and (b) are adapted from ref. [138]. (c) A top-down TEM image of a SWNT deformed in the radial direction due to tube-tube interactions. Scale bar, 5 nm. (d) A TEM image showing a CNT buckling junction. Scale bar, 5 nm. (c) and (d) are adapted from ref. [139]. 45

Figure 2.17. (a) TEM and AFM (inset) images of bent SWNT IMJs produced using a CVD method. Three typical bending angles are: a) 34°, b) 26°, and c) 18°. Adapted from ref. [98]. (b) A tri-potential electrochemical setup for selectively depositing metal nanoparticles along tube length. WE, working electrode. CE, counter electrode. RE, reference electrode. (c) AFM images showing a 2 μm nanotube segment before (left image) and after (right image) decorated with Ni nanoparticles. (d) Curved segment of the nanotube incorporate a higher density of defects. Scale bar, 15 nm. (b)-(d) are adapted from ref. [145]. 48

Figure 2.18. (a) A STM image of an M-S junction formed between a (21, -2) upper portion and a (22, -5) lower portion. (b) Tunneling conductance recorded at the upper and lower locations indicated in (a), exhibiting a semiconducting profile for the upper portion and a metallic profile

for the lower portion. (c) A detailed STS spectra evolution of the IMJ. The black arrows and red arrows respectively highlight the first vHS of the semiconducting and metallic structure. Scale bar, 1 nm. (a)-(c) are apapted from ref. [28]. (d) HRTEM image of a 5-7 defect found in an SWNT. (e) An enlarged image showing the 5-7-7-5 defects. (d) and (e) are adapted from ref. [29]. 50

Figure 2.19. (a) Kataura plot showing transition energies for all possible (n, m) SWNTs with diameters in the range $0 < d_t < 3.0$ nm, using a tight-binding method. Schematic picture showing atom vibrations for (b) the RBM and (c) the G band. Adapted from ref. [149]. 52

Figure 2.20. (a) The G band acquired for highly oriented pyrolytic graphite (HOPG), one semiconducting SWNT and one metallic SWNT. (b) RBM and G band features for three isolated SWNTs of the indicated (n, m) values. (c) Plot of G band frequencies as a function of $1/d_t$, for both semiconducting SWNTs (solid circles) and metallic SWNTs (open circles). The lines are fit to the experimental points. Adapted from [154]. 54

Figure 3.1. A schematic diagram of ethanol CVD setup for the synthesis of ultralong CNTs. 59

Figure 3.2. Schematic of photographic fabrication of trenched structures for CNT growing on, (a) thermally grown SiO_2 layer, and (b) PECVD grown SiO_2 layer, respectively..... 61

Figure 3.3. Schematic representation of the preparation of CNT IMJs. The trenched structures were pre-fabricated on Si/ SiO_2 substrates, using standard photolithography technique. The CVD process was then carried out to grow SWNT arrays across the trenches..... 62

Figure 3.4. (a) Typical FET geometry for electrical measurements on individual SWNTs. (b) FET setup to probe the electrical properties of SWNT-based IMJs and the impact of IMJs on the parent nanotube. 65

Figure 4.1. (a) SEM image of as-synthesized CNT arrays. (b) A typical Raman spectrum obtained from the sample shown in (a), the frequencies of RBM and G band are indicated, the peak at $\sim 304\text{ cm}^{-1}$ is associated with the Si/SiO₂ substrate. (c) Diameter distribution of 38 individual CNTs that exhibited RBM in their Raman spectra. (d) The catalyst region after being pretreated for 20 min but before CNT growth, where uniform nanoparticles can be observed at the edge. 69

Figure 4.2. SEM images of CNT arrays grown using CVD method, with different catalyst concentrations: (a) 0.005 M, (b) 0.01M, (c) 0.05M, and (d) 0.1 M. (e) Comparison of the number distribution of CNTs along their axial direction for the four as-prepared samples..... 71

Figure 4.3. SEM images of the catalyst region from samples prepared with 0.005 M (a), 0.01 M (b), 0.05 M (c), and 0.1 M (d) FeCl₃ ethanol solution, respectively. 72

Figure 4.4. SEM observations of CNT arrays and their corresponding catalyst regions with the pretreatment time of 10 min (a and d), 20 min (b and e), and 30 min (c and f), respectively. (g) Density of CNTs as a function of length obtained from samples with different pretreatment time. 74

Figure 4.5. SEM images showing the morphology of CNT arrays grown at 975 °C (a), 950 °C (b),

and 925 °C (c), respectively. The samples were prepared with 0.005 M FeCl₃ ethanol solution. (d)

Length distribution of CNTs, showing temperature dependence. 75

Figure 4.6. SEM images from the sample grown with 0.1 M catalyst solution at different temperatures: (a) 975 °C, (b) 950 °C, and (c) 925 °C. The corresponding comparison of length distribution is shown in (d). 76

Figure 4.7. (a) Merged SEM image shows horizontally aligned CNT arrays grown from the catalyst region on Si/SiO₂ substrates. (b) Length distribution of CNTs grown on the whole sample (1.5 cm long, 1 cm wide). (c) SEM observation of CNT arrays taken near the catalyst edge and (d) SEM observation of CNT arrays taken far away from the catalyst edge. (e) A CNT bundle is formed with the attachment of the two neighboring nanotubes, due to the strong tube-tube interaction. (f) SEM image of one representative CNT from the sample acquired at a lower temperature, showing super straight morphology. 80

Figure 4.8. Measured $I_{ds} - V_{ds}$ curves for (a) an individual metallic SWNT and (c) an individual semiconducting SWNT under seven different gate voltages. Their corresponding electrical behavior of the room-temperature current (I_{ds}) versus gate voltage (V_G) is exhibited in (b) and (d), respectively, under a bias voltage $V_{ds} = 2$ V. 83

Figure 4.9. Variation in FET parameters with nanotube diameter. All the FETs were made of one isolated SWNT. (a) on-current (I_{on}), (b) off-current (I_{off}), (c) current on/off ratio (I_{on} / I_{off}), (d) threshold voltage (V_{th}), (e) transconductance (g_m), and (f) hysteresis (ΔV_{th} , black square) and the

estimation of charge traps in the SWNT FETs (using number of charges trapped per unit length, blue circle). The error bar given in the plots are related to estimates in the measurements. 86

Figure 5.1. (a) An SEM image showing oriented SWNTs grown on a trenched Si/SiO₂ substrate. (b) A zoom-in SEM observation at one edge of a 20 μm wide, 2 μm deep trench, showing that the nanotube is well suspended over the trench. 92

Figure 5.2. A typical G band mapping image (inset) of the SOS segment of one isolated as-grown SWNT, with 514 nm excitation wavelength. A representative Raman spectrum acquired from one single point of the SOS segment, exhibiting strong Raman features of RBM, D band, G band, and G' band. 94

Figure 5.3. (a) Tapping mode AFM mapping of an SOS segment in a 30 × 30 μm² area. (b) An enlarged AFM image of the area enclosed by the blue dashed square in (a), showing the isolated nanotube. (c) A typical height profile of the nanotube indicated in (b), showing the diameter is around 1.9 nm. 95

Figure 5.4. (a) A sketch of the 1 cm-long isolated nanotube lying on Si/SiO₂ substrate, spanning over 20/50 μm trenches. (b) Evolution of Raman features along the nanotube length. The series of Raman spectra were acquired as the 514 nm laser beam moving along the nanotube. The labels (#A-#D) indicate different locations on the Si/SiO₂ substrate, referring to (a). 96

Figure 5.5. A 2D G band map of the (22, 5) nanotube partially suspended on a 20 μm wide trench, its confocal optical image shows the geometric configuration of the trench. The three

regions can be clearly differentiated from the mapping image, as indicated as “SOS”, “trans”, and “SUS”. Its corresponding SEM image provides spatial information about the nanotube lying suspended over the trench..... 98

Figure 5.6. Comparison of Raman features obtained from SOS, trans, and SUS segments respectively, showing evolutions through the three regions. ($E_{\text{laser}} = 2.41 \text{ eV}$)..... 99

Figure 5.7. A specific analysis of the G band taken from the trans segment, using Lorentzian function fitting. The experimental profile (blue line), each fitting Lorentzian profile (green line), and calculated total profile (red line) are displayed respectively. 102

Figure 5.8. $I_{\text{D}} / I_{\text{G}}$ and ω_{G} versus position along the axis of the nanotube. The Raman mapping image of the nanotube across the trench is used as a reference indicating the relative positions, where the middle of the trench is set as “0”. Similar trend of the $I_{\text{D}} / I_{\text{G}}$ variation (b) and G band frequency shift (c) can be also observed in other trenches. 103

Figure 5.9. (a) SEM image of an individual SWNT growing across a 100 μm wide, 5 μm deep trench. A portion of the SUS segment is stuck to the lower substrate. (b) SEM image showing the nanotube with curve morphology, which is induced by local turbulence because of the trenched structure. 105

Figure 5.10. $I - V$ characteristics of the SWNT (SOS segment) and the IMJ (SUS segment), respectively. 107

Figure 6.1. (a) SEM image of on isolated SWNT lying across a 10 μm wide, 10 μm deep trench. The SOS segment is wider and brighter than the SUS segment. The SiO_2 layer of the substrate was grown using PECVD. (b) Comparison of Raman spectra obtained from SUS and SOS segments, respectively. The nanotube was on PECVD grown SiO_2 layer. (c) Lorentzian fitting of the G band from the SOS segment, referring to (b). (d) Another set of SOS vs SUS Raman spectra, which were acquired from SWNT lying on amorphous SiO_2 layer. 113

Figure 6.2. AFM images of one SWNT on the surface of (a) PECVD grown SiO_2 layer, and (b) thermally grown SiO_2 layer. The color scale bar indicates the height of the features..... 116

Figure 6.3. (a) SEM image of a pair of suspended CNTs adhering to each other and ending in Y-junctions. (b) A zoom-in SEM image of the Y-junction at the edge of the trench..... 118

Figure 6.4. (a) A Raman mapping image of the Y-junction, where CNT A, CNT B, and the junction are indicated. (b) G band spectra for CNT A and CNT B, respectively. (c) Raman spectrum acquired from the joint region. (d) The spectrum obtained by simply summing up the G peaks of CNT A and CNT B. 119

Figure 6.5. (a) Geometry optimization without hydrostatic stress. (b) Geometry optimization with hydrostatic stress..... 120

List of Tables

Table 3.1. A typical list shows variation on the growth parameters.	60
Table 4.1. Parameters for Reynolds number calculation (at 1248 K).....	81
Table 4.2. Lists of nanotube diameters for each SWNT FET, obtained from the corresponding RBM frequencies.....	85

Abstract

The nanoscale dimensions, together with the unique electronic structures of carbon nanotubes (CNTs), make these one-dimensional (1D) molecular systems attractive building blocks for future electronics. Since CNTs could be either metallic or semiconducting depending on their diameter and chirality, joining two different CNTs could form so called intramolecular junctions (IMJs). These CNT IMJs are at molecular size level, and possess unique electronic properties, and thus, could be used as active components in next generation electronic circuits or used to foster innovative nanodevice applications.

The successful implementation of advanced functions into CNT IMJs critically depends on the availability of methods that allow us to controllably prepare and rapidly identify the CNT IMJs, which are still rather challenging up till now. Moreover, the exotic properties of CNT IMJs have not been probed adequately, due to the existing lack of in situ characterization techniques. Herein, we present a strategically smart method to accomplish these goals. Ultralong, horizontally aligned, and defect-free single-walled carbon nanotubes (SWNTs), with tunable length and density have been firstly synthesized in an ultralow gas flow chemical vapor deposition (CVD) system using ethanol as the carbon source. The as-grown SWNTs are of high quality, with narrow diameter distribution. Raman characterization on specific individual SWNTs indicates that the SWNTs are structurally and chiral uniform along their lengths. These could eliminate the influence of random defects on our characterization, offering perfect structural carriers of IMJs, and paving the way for the controllable fabrication of IMJs.

The trenched structures were then employed into the synthesis processes to induce the formation of IMJs. In essence, the pre-fabricated trenches on Si/SiO₂ surfaces were used to introduce uniaxial strain and bending deformation onto the ultralong SWNTs that lie suspended across them. As a result, the nanotube lattice and electronic structures could be altered and topological defects could be generated, leading to the formation of IMJs. Due to their geometric configuration, the trenched structures could also define the formation location in the vicinity of their edges, which facilitates the rapid identification of the as-prepared IMJs. The presence of SWNT IMJs has been verified via in situ Raman spectroscopy and electrical transport measurements. Elaborate characterizations on the IMJs classified them as S-S junctions, exhibiting rectifying behaviors. The amount of the induced strain was also well controlled by adjusting the trench profile, to prepare IMJs with various types.

These trenched structures were also exploited as an unperturbed platform to study the intrinsic signatures of other types of SWNT IMJs induced by tube-substrate interaction and tube-tube interaction. On one hand, because SWNTs are capable of being fully suspended across the trenches without getting in contact with the substrate, it is quite feasible to probe the peculiarities of IMJs induced by tube-substrate interaction, by comparing the sitting-on-substrate (SOS) segment and suspended (SUS) segment of the same individual nanotube. On the other hand, IMJs induced by tube-tube interaction are more discernible owing to the suspended morphology. The effect of the tube-tube interaction on the IMJ was discovered using Raman characterization and explained by performing first principle calculations.

Chapter 1 Introduction

A junction, which occurs at the interface of two materials, is one of the necessary elements in electronic circuits. There are many types of junctions. The one exists between two different materials, for example semiconducting materials with unequal band gaps, is called heterojunction. By engineering the electronic energy bands, heterojunctions can be applied in many electrical devices, such as semiconductor lasers, solar cells, and transistors. On the other hand, a homojunction occurs between two similar materials, for example two semiconducting materials that have equal band gaps but different doping. In most practical cases, homojunctions refer to as p-n junctions, which are manufactured at the boundary of p-type (acceptor doped) and n-type (donor doped) semiconductor materials. Moreover, a metal-semiconductor junction is always created when a metal and a semiconductor are in contact. It can be either a Schottky junction or an Ohmic junction depending on the current-voltage ($I-V$) characteristics: a Schottky junction exhibits a rectifying behavior, while an Ohmic junction has a linear and symmetric $I-V$ characteristic, as depicted in Figure 1.1. All these junctions are desired in electronic circuits to serve as key components, by providing reliable connections or acting as functional building blocks, such as diodes, bipolar transistors, rectifiers, switches, amplifiers, and photovoltaic devices, *etc.*

Figure 1.1. Typical current-voltage ($I - V$) characteristics of a Schottky junction and an Ohmic junction.

However, in traditional circuits, these junctions are in micrometer scale, which limits the device density and hinders a higher level of electronic circuits' miniaturization. As a consequence, the inevitable trend for the development of electronic circuits is to utilize individual molecules as functional elements. Intramolecular junctions (IMJs), the junctions exist in single molecules or are formed by chemical bonds, are then of great value in providing a broad perspective to accomplish this goal. Among all forms of IMJs, the ones based on carbon nanotubes (CNTs) have been most widely and intensely studied by scientists globally. CNTs are one-dimensional (1D) macromolecular systems that possess superior electronic, physical, chemical, and mechanical properties [1]. In particular, their unique high carrier mobility [2], high on-off ratio [3], and high current carry capacity [4] make them attractive candidates for achieving high-performance nanoelectronics. Substantially, a wide range of electronic applications have been proposed, including field-effect transistors (FETs) [5-7], interconnects

[8-10], field emission sources [11-13], ultra-sensitive chemical sensors [14-16] and biosensors [17], and transparent conductive membranes [18, 19], *etc.* Depending on the diameter and chirality, CNTs can be classified as either metallic or semiconducting [20], showing distinct electrical transport behavior. Metallic CNTs possess high carrier mobility, which is equivalent to that of good metals, suggesting that they would make ideal interconnects in nanoelectronics. At the same time, the intrinsic characteristics of the semiconducting CNTs, as controlled by their topology, allow us to build functional devices at the nanometer scale and are predicted as a replacement of current silicon-based complementary metal-oxide-semiconductor (CMOS) devices in future nanoelectronics [21, 22]. In this regard, there is great interest in fabricating CNT-based junctions with different structures and properties, by seamlessly joining two or more CNT segments together. Because on one hand, the CNT IMJs can provide stable interconnections for constructing CNT-based integrated circuit (IC). While on the other hand, they exhibit novel properties that pristine CNTs lack, enabling new potential nanodevices and fostering innovative applications in nanoelectronics.

In spite of the potential applications of the IMJs based on CNTs being so proactive and fascinating, there still remain tremendous challenges that may hamper the IMJs wide applications in ICs. In essence, intrinsic topological defects can occur naturally in the conventional CNT production, and have a significant impact on the nanotubes properties. Unfortunately, those topological defects locate randomly in CNTs. It can be rather hard to identify them, let alone to monitor their effects on the nanotubes properties. Therefore, such kind of topological defects is useless in practical nanoelectronics. In order to prepare useful CNT

IMJs, a large amount of synthesis methods have been proposed, including electron or ion irradiation [23-25], e-beam welding [26], and current annealing [27] *etc.* However, most of those IMJs were obtained by chance. It is still rather difficult to fabricate stable CNT IMJs in a controlled and high-yield manner. In addition, how to detect and characterize the as-obtained IMJs in an accessible way has become a leading problem in the CNT IMJs research field. Traditional characterization tools, such as scanning electron spectroscopy (SEM) and atomic force microscopy (AFM), relatively lack a high resolution to identify the topological defects in CNTs. Up till now, the atomic structure of the CNT IMJs have been directly imaged by the scanning tunneling microscopy (STM) [28] and high-resolution transmission electron microscopy (HRTEM) [29]. However, the low mass elements severely limit the availability of these two instruments of rapidly identifying CNT IMJs over large length scales. Most recently, resonance Raman spectroscopy, a technique related to the nanotubes vibrational properties, has been proven to be powerful in the CNT research [30]. It is more convenient compared to STM and HRTEM, because it is non-contact and non-destructive, and can be operated at room temperature and in the air. Furthermore, Raman spectra can provide valuable insights into the dimension and chirality of a single nanotube. However, when Raman spectroscopy is performed on isolated CNTs, especially used to characterize the CNT IMJs, it is prone to be time-consuming due to the narrow resonance window, which makes it less efficient.

In summary, to realize the full potential of IMJs in realistic electronic systems, there are two obstacles to overcome: controllably synthesizing and rapidly locating and identifying the CNT IMJs. Technically, a controllable synthesis of IMJs is a fundamental step to produce a large

amount of IMJs with designed structure, location, size and orientation. A rapid identification will not only make nanometer scale characterization much more efficient, but also open a door to systematically study the properties of IMJs and their impacts on parent CNTs. Therefore, the objectives in this study will cover both aspects:

- 1) To develop advanced methods to prepare CNT IMJs in a controlled way, on the basis of a chemical vapor deposition (CVD) process. A sequence of fundamental researches will also be conducted on exploring optimized conditions for the controllable synthesis of IMJs.
- 2) To propose a unique technique that can rapidly and precisely locate, identify, and characterize CNT IMJs. The technique should be related to a combination of SEM, AFM, Raman spectroscopy and other necessary characterization instruments. Some other measurements will also be carried out to study the unique properties of IMJs, and their potential influences on CNTs.

The unique merit of these approaches is to fabricate trenched structures in the synthesis processes. According to well-accepted “floating growth” mechanism [31], the ultralong CNTs are capable of flying over the substrate and eventually lying suspended across a series of trenches. For the segments that are supported by the substrate, the electronic and optical properties of which are inevitably affected by the tube-substrate interaction derived from van der Waals force [32]. While the suspended segments, that are free from any effect from the surrounding environment, could retain their intrinsic structure and properties. For this

reason, IMJs can be formed between the supported segments and the suspended segments. In addition, as a direct result of the trench configuration, the partially suspended CNTs are subject to mechanical deformations, such as uniaxial strain and bending deformation, which will influence the nanotubes lattice and electronic structures, leading to the formation of CNT IMJs. The trenches are not only employed to regularly generate IMJs to the CNTs, but also exploited as markers for rapidly and accurately identifying the as-produced IMJs. Because the IMJs are intentionally prepared in the vicinity of the trench edge, with the help of SEM images, it is feasible to utilize Raman spectroscopy to precisely identify and intensively characterize the IMJs. Most prominently, the trenched structures on Si/SiO₂ substrates provide a platform to directly investigate the exotic electrical transport properties of the IMJs by means of electrical measurements on the partially suspended CNTs.

We expect our work to contribute to a comprehensive and systematic study of the CNT-based IMJs, and subsequently, pave the way for leading these remarkable molecular devices into real applications.

Chapter 2 Literature Review

2.1 Introduction to CNTs

Carbon nanotubes (CNT), a member of the fullerene structural family, have a cylindrical structure formed by one or more concentric, crystalline layers of carbon atoms. Depending on the number of the concentric layers, CNTs can be categorized into two species: single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs), as shown in Figure 2.1. The first discovery and characterization of the MWNTs by Iijima *et al.* in 1991 [33] and the following synthesis of SWNTs in abundance in 1993 [34, 35] have stimulated great academic and industrial interest in exploring their fundamental properties and exploiting a wide range of realistic applications. Tremendous advances have been accomplished in the study of CNTs during the past two decades. Due to their unique structures and exotic physical, chemical, mechanical, electrical, thermal and optical properties, CNTs have been regarded as ideal models for studying the nature of one-dimensional (1D) systems.

Figure 2.1. Schematic diagrams showing (a) a single-walled carbon nanotube (SWNT), and (b) a multi-walled carbon nanotube (MWNT).

2.1.1 Structure and properties of CNTs

2.1.1.1 Atomic structure

For simplicity, we take SWNTs as a model to introduce the structure of CNTs. A SWNT can be described as a single layer of graphene lattice rolled up into a seamless hollow cylinder with nano-metric diameter, as sketched in Figure 2.2 (a). The way the 2D graphene sheet is wrapped can be mathematically defined in terms of the chiral vector $\mathbf{C}_h$, such that

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n, m) \quad (2.1)$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the unit vectors of the graphene honeycomb lattice, and n and m are a pair of integers denoting the number of unit vectors along two directions in the hexagonal network contained in the chiral vector $\mathbf{C}_h$ [36]. For example, as shown in Figure 2.2 (b), the chiral vector is labeled as $\mathbf{C}_h = 5\mathbf{a}_1 + 3\mathbf{a}_2$. Geometrically, by wrapping the single graphene layer in the way of joining the two ends of the chiral vector (point A and A') together, a (5, 3) SWNT can be constructed, as illustrated in Figure 2.2 (c). Apparently, the chiral vector determines the circumference of the tube, thus the diameter d_t of the nanotube can be calculated from its indices (n, m) as follows,

$$d_t = \frac{|\mathbf{C}_h|}{\pi} = \frac{a}{\pi} \sqrt{n^2 + nm + m^2} \quad (2.2)$$

where $a = \sqrt{3} \times a_{cc}$ ($a_{cc} = 1.42 \text{ \AA}$, the C-C bond length) is the lattice constant of the honeycomb

sheet.

Figure 2.2. (a) Conceptual diagram showing a layer of graphene rolling up into a SWNT. (b) The unrolled graphene honeycomb lattice, indicating the chiral vector $\vec{C}_h$ along the circumferential direction and chiral angle θ . (c) The resulting (5, 3) nanotube. Adapted from ref. [37].

As shown in Figure 2.2 (b), the angle between the chiral vector $\vec{C}_h$ and the lattice vector $\vec{a}_1$ is defined as the chiral angle θ , the value of which varies in the range $0 \leq |\theta| \leq 30^\circ$, owing to the hexagonal symmetry of the graphene lattice. Depending on different chiral angle value, the pattern of the carbon hexagons on the sidewall of the SWNTs arranges differently. Three categories of SWNTs are now defined: the armchair tubes (n,n) , with the chiral angle of $\theta = 30^\circ$, display C-C bonds perpendicular to the tube axis. The zigzag tubes $(n,0)$, with the chiral angle of $\theta = 0^\circ$, display C-C bonds parallel to the tube axis. These two types of nanotubes are classified as achiral tubes, the names of armchair and zigzag arise from the shape of the cross-section ring, as shown in Figure 2.3 (a) and (b) respectively. All remaining nanotubes are known as chiral tubes (n,m) , corresponding to chiral angles of $0 < |\theta| < 30^\circ$ (see Figure 2.3 (c)) [37].

Figure 2.3. Atomic structure of (a) an armchair nanotube, (b) a zigzag nanotube, and (c) a chiral nanotube. Adapted from ref. [38].

2.1.1.2 Band structure and electronic properties

As stated in the previous section, a SWNT is geometrically a rolled up graphene lattice, substantially the band structure of a SWNT can be deduced based on the band structure of a graphene sheet. For the 2D graphene sheet, carbon atoms are arranged in the hexagonal lattice with sp^2 bonding configuration. Among the four valence orbitals of the carbon atom, three orbitals ($2s$, $2p_x$ and $2p_y$) are hybridized to form the in-plane σ and σ^* bonds, the remaining $2p_z$ orbital results in delocalized π and π^* bonds by overlapping with other $2p_z$ orbitals. The energy levels associated with the π orbitals are known to be near the Fermi energy (E_F), which determines the band structure of graphene [37]. Figure 2.4 (a) shows a calculated 3D band

structure of graphene derived from the π orbitals, according to the tight-binding approximations [39]. Close to the Fermi energy, the π and π^* bands have linear dispersion (see Figure 2.4 (b)) and meet each other at six points, which are the six corners (K points) of the Brillouin zone (BZ) in graphene. The band structure of SWNTs can be obtained from the energy dispersion of graphene using the zone-folding approximation. There are two wave vectors, $\mathbf{K}_{\parallel}$ (along the nanotube axis) and $\mathbf{K}_{\perp}$ (along the circumferential direction), associated with a SWNT, as illustrated in Figure 2.4 (c). The wave vector $\mathbf{K}_{\parallel}$ is continuous if we assume a SWNT as infinitely long, however, owing to the confinement of electrons around the tube circumference, $\mathbf{K}_{\perp}$ should be quantized satisfying the boundary condition,

$$\mathbf{K}_{\perp} \cdot \mathbf{C}_h = 2\pi p \quad (2.3)$$

where p is an integer. This boundary restriction implies that only a certain set of $\mathbf{K}_{\perp}$ states is allowed when forming SWNTs from graphene. The 1D band structure of SWNTs can be generated by cross-sectional cutting of the energy dispersions of the graphene with the allowed $\mathbf{K}_{\perp}$ states, as displayed in Figure 2.4 (d). The zone-folding method gives rise to two possibilities in the band structures of SWNTs, as compared in Figure 2.4 (e). If the allowed $\mathbf{K}_{\perp}$ states pass through the K points, the points where the valence (π) band and the conduction (π^*) band get into touch, the resulting 1D band structure of the nanotube shows linear energy dispersion near the Fermi level with zero band gap, and thus the nanotube is metallic. Alternatively, if the allowed $\mathbf{K}_{\perp}$ states miss the K points, the nanotube has two parabolic 1D bands with an energy

band gap and exhibit semiconducting behavior [40].

Figure 2.4. (a) The 3D band structure of a graphene sheet. (b) Zoom-in energy dispersion at one of the K points near the Fermi energy. Adapted from ref. [41]. (c) The wave vectors associated with a nanotube, as indicated, along the nanotube axis and along the circumference of the nanotube, respectively. (d) Schematic illustration of zone-folding graphene sheet to form the 1D band structure of CNTs. (e) The resulting 1D energy dispersions for a metallic nanotube and a semiconducting nanotube. Adapted from ref. [40]. (f) DOS for a metallic nanotube (upper panel) and a semiconducting nanotube (lower panel), displaying vHSs due to 1D confinement. Adapted from ref. [38].

Due to the 1D confinement properties, SWNTs produce a series of subbands, exhibited as peaks or spikes in their density of states (DOS), which are called van Hove singularities (vHSs).

The DOS, $g(E)$, with 1D subbands can be given by:

$$g(E) = \sum_i g_i(E) \quad (2.4)$$

$$g_i(E) = \frac{8}{hv_F} [1 - (E_g^i / 2E)^2]^{-1/2} \quad (2.5)$$

where h is the Planck constant, $v_F \approx 8 \times 10^5$ m/s is the Fermi velocity, and E_g^i are the individual energy gaps. At the Fermi energy ($E = 0$), the DOS is constant for metallic nanotubes (Figure 2.4 (f) upper panel), in contrast, the DOS is zero for semiconducting nanotubes because of the existence of band gap (Figure 2.4 (f) lower panel) [37].

In accordance with the band structure, SWNTs fall into three distinct electronic classes [20]. The armchair (n,n) tubes are always metallic. For the (n,m) tubes with $n - m = 3j$, where j is a nonzero integer, the band structure is slightly modified due to the tube curvature effects [42], therefore a small band gap would open up and turn the tubes into small band gap semiconductors. Finally, all the (n,m) tubes with $n - m = 3j \pm 1$, where j is a nonzero integer, are semiconductors with large band gap, which shows tube diameter dependence as $E_g \sim 1/d_t$ [43].

2.1.1.3 Phonon structure

The 1D nature of CNTs is manifest not only in their electronic band structure, but also in their phonon properties. In analogy with the deduction of the electronic structures of SWNTs from graphene, their parent materials, the phonon dispersion relations and phonon DOS for

SWNTs can be calculated by zone folding the graphene Brillouin zone. In Figure 2.5 (a) and (b), the phonon dispersion of 2D graphene and the corresponding phonon DOS are shown. The six phonon branches are labeled as: out-of-plane transverse acoustic (oTA), in-plane transverse acoustic (iTA), longitudinal acoustic (LA), out-of-plane transverse optic (oTO), in-plane transverse optic (iTO), and longitudinal optic (LO), respectively [44]. By slicing the phonon dispersion relations with cutting lines, the phonon dispersion for a (10, 10) armchair SWNT can be obtained, as illustrated in Figure 2.5 (c). The quantum confinement of the 1D structure leads to vHSs exhibiting in the corresponding phonon DOS of the (10, 10) nanotube (see Figure 2.5 (d)) [45].

Figure 2.5. (a) Phonon dispersion relations of 2D graphene. (b) The corresponding phonon DOS for the graphene sheet. (c) Phonon dispersion for a (10, 10) armchair carbon nanotube, obtained with the zone-folding approach. (d) The corresponding phonon DOS for the (10, 10) nanotube. Adapted from ref. [45].

2.1.1.4 Transport properties

Due to the satisfied and strong C-C covalent bonding in the sp^2 configuration, CNTs are able to transport large amount of electric current. The transport properties of CNTs can be described using the Landauer's formula [46], for a given quasi-1D system, the conductance can be stated as:

$$G = \frac{4e^2}{h} \sum_i \int_{-\infty}^{\infty} \frac{df[(E - E_F)/k_B T]}{dE} \xi_i(E) dE \quad (2.6)$$

where k_B is the Boltzmann constant, T is the absolute temperature, $\xi_i(E)$ is the transmission of the i th 1D subband state at the energy E , and df/dE is the energy derivative of the Fermi function. For isolated SWNTs, their small diameter and long length lead to very large aspect ratios, in addition to the lack of boundaries in the perfect and hollow cylinder structure. All these features result in reduced carrier scattering and possible ballistic transport in CNTs [21]. In the ideal case where the transport inside the CNT is ballistic (electrons travel the length of the channel without being scattered) and the tube has perfect contacts, equation (2.6) predicts a quantized conductance of $G_Q = 4e^2/h$. In the non-ideal case, the total resistance ($R = 1/G$) can be divided into the contact resistance and the residual scatter's resistance as $R = R_{\text{contacts}} + R_{\text{tube}}$. For a uniform CNT with diffusive scattering, by assuming the tube length is L and the electron mean free path for momentum relaxation is l_0 , we thus have $R_{\text{tube}} = (h/4e^2)(L/l_0)$. Apart from this quantum mechanical resistance, there are other sources

of resistance, such as that produced by poor coupling between the CNT and the contact leads, or Schottky barriers at metal-semiconducting-CNT junctions [47, 48]. At or near room temperature, the two contributions to the resistance add incoherently, leading to the classical transport in CNTs.

Carrier mobility is another important parameter for characterizing the transport properties of semiconducting CNTs, which measures how fast the charge carriers respond to the external electronic field. It can be defined as the ratio of the drift velocity to the applied electronic field:

$$\mu = \frac{v}{E} = \frac{e\tau}{m^*} = \frac{\sigma}{ne} \quad (2.7)$$

where v is the drift velocity of charge carriers, E is the magnitude of the applied electronic field, σ is the conductivity, and ne is the charge density. For the 1D structure, $\sigma = GL$, where G is the conductance and L is the channel length [49].

Electrical transport measurements on individual CNTs can be performed on Si/SiO₂ substrate with a three terminal device configuration [50]. A schematic diagram is shown in Figure 2.6 (a), two metal electrodes designated as “source” and “drain” directly contact the individual CNT, which plays the role of a “channel”. A third electrode, the “gate”, is coupled to the nanotube through the insulating dielectric layer. The gate and the tube act like two plates of a capacitor, and the gate can electrostatically induce carriers onto the tube. It was found that SWNTs exhibited two different types of behavior of conductance versus gate voltage at room

temperature, depending strongly on their chirality. As seen in Figure 2.6 (b), the conductance in metallic SWNT is independent of the applied gate voltage, because the crossing of the conduction and valence bands at E_F provides electrons independently of the gate voltage. In contrast, the conductance in semiconducting SWNTs varies by orders of magnitude when changing the gate voltage, as shown in Figure 2.6 (c). The asymmetry between the turn-on gate voltage below and above the Fermi level enables the semiconducting SWNTs behave as field-effect transistors (FETs) [51].

Figure 2.6. (a) A typical FET setup for electrical transport measurements on SWNTs. Conductance versus gate voltage of (b) a metallic and (c) a semiconducting SWNT at room temperature. Insets: schematic drawing of the expected energy dispersion near the Fermi energy for (b) a metallic and (c) a semiconducting SWNT. Adapted from ref. [51].

2.1.1.5 Theory of CNT-based field-effect transistors

In the previous section, we have introduced the use of semiconducting CNTs as the active ingredient of FETs. In order to fulfill the analysis of transistor operation, herein we will derive the transport characteristics of CNTFETs on the basis of a diffusive metal-oxide-semiconductor (MOSFET) model. The configuration of a typical CNTFET is shown in Figure 2.6

(a), when a voltage V_G is applied to the gate electrode, charge carriers will be induced in the nanotube that can contribute to a current passing the nanotube. CNTFETs show a p-type behavior, a threshold voltage (V_{th}) separates the operation mode. At $V_G \leq V_{th}$, the device behaves like a conductor, the total charge per unit length is:

$$q = ne = \frac{C}{L}(V_G - V_{th}) \quad (2.8)$$

where n is the charge density per unit length, C/L is the capacitance per unit length of nanotube. According to Ohm's law for this device in the diffusive regime ($j = \sigma \varepsilon$, j is the current density, σ is the conductivity, and ε is the electric field), we can calculate the actual current flow from source to drain (I_{ds}):

$$I_{ds} \equiv j = \mu \frac{C}{L^2} [(V_G - V_{th})V_{ds} - \frac{V_{ds}^2}{2}] \quad (2.9)$$

where μ is the effective constant mobility and V_{ds} is the source-drain bias. At small bias ($V_{ds} \ll V_G - V_{th}$), equation (2.9) reduces to:

$$I_{ds} \equiv j = \mu \frac{C}{L^2} [(V_G - V_{th})V_{ds}] \quad (2.10)$$

Specifically, the capacitance per unit length of nanotube can be modeled by a cylinder on a planar substrate and given as:

$$\frac{C}{L} = \frac{2\pi\epsilon_0\epsilon_r}{\ln\left(\frac{2t_{ox}}{r}\right)} \quad (2.11)$$

where ϵ_0 is the permittivity of free space (8.8542×10^{-12} F/m), $\epsilon_r \approx 3.9$ is the dielectric constant of SiO₂ gate insulator, t_{ox} is the SiO₂ thickness and r is the radius of the nanotube.

The conductance of the device can be obtained from its definition:

$$G \equiv \frac{I_{ds}}{V_{ds}} = \mu \frac{C}{L^2} (V_G - V_{th}) \quad (2.12)$$

Therefore, we can get the expression for the mobility that is the intrinsic mobility of the nanotube excluding any device attributes as [52]:

$$\mu_{eff} = \frac{L^2}{C} \frac{1}{(V_G - V_{th})} G \quad (2.13)$$

Another term used to present the device mobility is the field-effect transistor mobility μ_{FET} , which also includes the device attributes like contact resistance, parasitic resistance, surface effect, etc. The μ_{FET} obtained from the output characteristics can be given by:

$$\mu_{FET} = \frac{L^2}{C} \frac{\partial G}{\partial V_G} \quad (2.14)$$

With the definition of experimentally-relevant transconductance $g_m = \left. \frac{\partial I_{ds}}{\partial V_G} \right|_{V_{ds}=const.}$, the field-

effect transistor mobility can be related to transconductance as:

$$\mu_{FET} = g_m \frac{L^2}{C} V_{ds} \quad (2.15)$$

2.1.2 Synthesis of CNTs

Since the first report of the discovery of MWNTs by Iijima [33], the past decades have witnessed significant research efforts in efficient and high-yield nanotube synthetic methods. The success in nanotube growth has led a wide variety of availability for specific scientific studies or realistic applications. Generally, there exist three main techniques for the synthesis of CNTs, which are arc discharge method, laser ablation method and chemical vapor deposition (CVD) method. CVD is known as irreversible deposition of a solid from a gas through a heterogeneous chemical reaction. Compared to arc discharge and laser ablation methods, CVD is a simple and economic approach for preparing CNTs at low temperature and ambient pressure. It not only beats the arc and laser methods in yield and purity, but also provides structure control and architecture control. CVD allows direct CNT growth in a wide morphology, such as networks, films, and aligned or entangled nanotubes on the substrates, providing a broad perspective on the applications of CNTs.

2.1.2.1 Synthesis of ultralong, horizontally aligned SWNTs

It has been demonstrated that horizontally aligned SWNTs are suitable for a diverse range of applications, however, the performance of SWNT-based devices are greatly limited

due to the lack of control over the tubes structure, chirality, morphology and orientation. One effective approach to orient SWNTs is to use the feeding gas to align SWNTs along the flow direction. This gas-flow-directed growth method was originally discovered by Huang *et al.* by developing a “fast-heating” technique, which results in millimeter-long, well aligned SWNT arrays grown on substrates, as shown in Figure 2.7 (a) [31, 53, 54]. Different from the conventional CVD procedure, they quickly transferred the catalyst-contained substrate into the center hot zone of the furnace. The generated convection flow would lift up the catalyst particles and the growing nanotubes from the substrate surface and direct the growth orientation of the floating nanotubes.

Following this technique, many improved CVD strategies have been reported, devoting to improving the length, density and alignment of the SWNT arrays. To avoid the interaction with the substrate, catalysts were elevated using a metal underlayer [55] by Yu *et al.*, where they obtained millimeter long and oriented SWNTs. A breakthrough has been made in the growth length by Zheng *et al.* by employing ethanol as the carbon source [56]. At the growth temperature of 900 °C, 4 cm long SWNT arrays were successfully grown on flat Si/SiO₂ substrate, without the formation of amorphous carbon (see Figure 2.7 (b)). The growth rate could be as high as 11 μm s⁻¹, attributed to the high reactivity and dissociation property of the ethanol molecules. In another subsequent work, over 18.5 cm long SWNTs were obtained using a super-aligned CNT film as the catalyst supporting frame [57].

Figure 2.7. (a) SEM image of SWNTs prepared using a “fast-heating” technique. Adapted from ref. [31]. (b) One ultralong SWNT with growth length of 4 cm. Adapted from ref. [56]. (c) Dense SWNT arrays were obtained by annealing Fe in air. Adapted from ref. [58]. (d) Under extremely low feeding flow condition, SWNT arrays appear super straight. Adapted from ref. [59].

The structure and quality of the produced CNTs are highly dependent on the catalysts used in the CVD system. Various catalysts were employed, including Fe, Co, Pb, Cu, and Ni, to facilitate the growth of ultralong and dense CNTs on substrates. Using Cu as the catalyst precursor, Zhou *et al.* obtained aligned SWNT arrays with a density of 2–3 SWNTs/10 μm [60]. Compared with Fe, Cu has a smaller solubility of carbon, indicating that carbon could precipitate more easily to form CNTs. Furthermore, the lower catalytic activity of Cu for carbon decomposition could avoid amorphous carbon formation and elongate the lifetime of the catalysts [60]. On the other hand, the activity of Fe catalysts can be greatly enhanced by

annealing in air. By employing the annealed Fe as catalyst and optimizing the growth conditions, Liu *et al.* increased the density of long SWNT arrays to 60 nanotubes per 100 μm , as shown in Figure 2.7 (c) [58].

Apparently, the flow dynamics of feeding gas is a key component of controlling the alignment of SWNTs. A tube-in-tube setup was designed to generate laminar flow, resulting in better alignment of SWNTs growth [61]. It has been demonstrated that high flow rate of feeding gas would induce turbulence to the growing nanotube, degrading the alignment. Therefore, low feeding gas flow was preferred to obtain straight nanotubes. Under extremely low feeding flow of 1.5 sccm, Jin *et al.* obtained super straight, ultralong SWNT arrays, as shown in Figure 2.7 (d) [59].

2.1.2.2 Growth mechanism

From the reaction point of view, the growth of a nanotube involves the carbon feedstock going through a dissociation-diffusion-precipitation process over the catalyst nanoparticles, according to the well-accepted vapor-liquid-solid (VLS) growth mechanism [62]. CNTs can be nucleated and extruded from saturated catalyst nanoparticles, depending on the location of the nanoparticles on the growing nanotubes, the growth mechanism can be described as “base growth” and “tip growth” [63]. In the base growth model, the catalyst nanoparticles are stationed on substrates, while the nanotubes are growing on top of the nanoparticles. Normally, short and random CNTs are grown via this mechanism, because the strong interaction between the nanotube and substrate hinders the elongation and the control

of orientation of the produced nanotubes. Ultralong CNTs are expected to follow the tip growth mechanism, as indicated, the catalyst nanoparticles are located at the tip of the growing nanotubes. Once the catalyst nanoparticles are lifted up, they will generate floating nanotubes in their wake [64].

As the pioneer in growing ultralong SWNTs, the “fast-heating” technique exploited the convection flow, which was generated by the sudden exposure of the cool growth substrate to high growth temperature, to lift up the catalyst nanoparticles together with the growing nanotubes. A “kite-mechanism” was proposed to describe the growth scenario: just like a flying kite, the active end of the nanotube, with the catalyst nanoparticle attached, will be kept floating and aligned by the feeding gas, while leaving the rest portions of the nanotube lying on the substrates. This mechanism was supported by successfully growing CNTs over trenches and vertical barriers on the substrate surface [31]. Since the nanotube was “partially floating” during the growth, the van der Waals interaction between the nanotube and the substrate may terminate the growth, reflected by the wavy and tangled observation at the end of nanotubes [56]. In contradiction with the “partially floating” mechanism, Hofmann *et al.* suggested that the entire nanotube was kept floating during growth, because no matter how they rotated the substrate, the nanotube would always follow the gas flow direction [65]. Although the “tip growth” mechanism is more reasonable for the horizontal synthesis of ultralong CNTs, it is also possible that a flying nanotube is base-grown [66]. Specifically, the observation of “U-turn” structure implies that the nanotube tip was rapidly pinned to the substrate at the early growth stage due to local turbulent, while the growth was continued through the base of the nanotube

[53, 67].

2.1.3 Applications of CNTs in nanoelectronics

2.1.3.1 High-performance field-effect transistors

A main application of CNTs in nanoelectronics is to fabricate FETs based on semiconducting SWNTs. The first CNT-based FETs were fabricated by Tans *et al.* in 1998 [5], the configuration of which is analogous to the MOSFETs, except that the semiconducting CNTs replace the conventional silicon and function as the “channel”. As already shown in Figure 2.6 (a), the insulating SiO₂ layer serves as the dielectric, which separates the channel and the source (S) and drain (D) electrodes from the third gate (G) electrode. Since the Si layer on the back is used as the gate electrode, this FET structure is called back-gated CNTFETs. In the continuous development of the device configuration, top-gated CNTFETs and wrap-around gate CNTFETs were respectively fabricated, in order to enhance the device performance by means of scaling down the thickness of gate-dielectric [22].

Significant advancement has been achieved in improving the FETs performance by incorporating densely packed and highly ordered semiconducting SWNT arrays as the conduction channel. By following this strategy, as illustrated in Figure 2.8 (a), Kang *et al.* successfully fabricated top-gated FETs, which exhibit excellent performance including carrier mobility and scaled transconductance approaching $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 3000 S m^{-1} , respectively [68]. Similarly, Ding *et al.* obtained CNTFETs with an on/off current ratio as high as 85, by selectively growing dense and parallel semiconducting SWNTs on quartz substrate [69].

Figure 2.8. (a) High-performance FETs fabricated with densely packed SWNT arrays as conduction channel. Adapted from ref. [68]. (b) A 5-stage ring oscillator assembled on one individual nanotube and its output characteristic. Adapted from ref. [70]. (c) Optical image of CNT-based ICs on flexible plastic substrates. Adapted from ref. [71]. (d) SEM image of small hysteresis CNT-based ICs by exploiting monolayer graphene as electrodes. Adapted from ref. [72].

2.1.3.2 Integrated circuits based on CNTs

The superior length and uniform structure of SWNTs allow building integrated circuit (IC) on individual nanotubes. Complementary-MOS (CMOS) devices are preferred for the integrated architecture, which involves pairs of n-type (electrons as charge carriers) and p-type (holes as charge carriers) FETs. However, the as-prepared CNTFETs normally show p-type behavior in air, due to the oxygen doping effect or the presence of Schottky barrier at the metal-nanotube contact [73]. Healing in vacuum or under inert gas could convert the p-type FETs to n-type by removing the adsorbed oxygen [3, 74]. A more stable method is to chemically dope the SWNTs with, i.e. potassium and PEI [75-77]. The dopants could alter the Fermi level of the CNTs and consequently affect their transport properties. Some CNTFETs could also exhibit ambipolar

transfer characteristics, which is n-type conducting at positive gate voltages and p-type conducting at negative gate voltages.

By adjusting the FETs behaviors, complex structures could be fabricated based on one individual SWNT, as shown in the scanning electron microscope image (Figure 2.8 (b)), a ring oscillator was integrated along one 18 μm long SWNT, by using Pd and Al as gates for p- and n-type FETs, respectively [70]. The ringing frequency was increased from 13 MHz to 52 MHz with the change of supply voltage from 0.5 V to 0.92 V.

2.1.3.3 CNT-based flexible devices

A recent innovation of CNT's application is to fabricate CNT-based flexible electronic devices and make ICs on flexible substrates. As shown in Figure 2.8 (c), Cao *et al.* fabricated medium-scale ICs on polyimide substrate, which is composed of up to 100 transistors [71]. A transfer-printing technique was employed to deposit as-grown SWNT networks onto the flexible substrate. It is noteworthy that aligned CNTs were also transfer printed onto transparent substrates, in the aim for transparent electronics. Ishikawa *et al.* obtained transparent CNTFETs with high mobility ($\sim 1300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and good transparency ($\sim 80\%$ on average) [78]. To further improve the performance of the CNT-based flexible devices, graphene sheets were exploited as the electrodes, as displayed in Figure 2.8 (d). Because of the similarity of graphene and CNTs, Ohmic contact could be formed, resulting in lower contact resistance, higher mobility, and smaller hysteresis [72]. In addition, the mechanical properties of the CNT-based flexible devices make them stretchable and bendable, showing promises as pressure and

strain sensors [79].

2.2 Introduction to CNT IMJs

2.2.1 Concept of CNT IMJs

The concept of intramolecular junctions (IMJs) stems from electronic technology. During the past decades, the great success of the electronics has relied on the continuous miniaturization of basic devices which consist of material domains and junctions between them [80]. To follow in the footsteps of downsizing, CNTs have been considered as a promising replacement of silicon to drive microelectronics into nanoelectronics. As one of the essential components of the CNT-based nanoelectronics, the junctions existing in CNTs are named as CNT IMJs, due to the fact that one individual CNT is a single large molecule [81].

2.2.2 Types, properties and applications of CNT IMJs

There are various type of IMJs based on CNTs. A typical configuration of CNT IMJs is shown in Figure 2.9 (a), which is constructed by interposing one or multiple Stone-Wales defects (pentagon-heptagon pairs) into the hexagonal bond network of one individual nanotube [82, 83]. The introduced topological defects can change the chirality of the nanotube and fundamentally alter its electronic structure, because such defects must induce zero net curvature and minimal local curvature to prevent the nanotube from flaring or closing [82]. As depicted in Figure 2.9 (a), after adding a pentagon-heptagon pair (5-7 pair) to a (8, 0) nanotube

(the symmetry axis of the 5-7 pair is non-parallel to the tube axis), its indices is transferred by one unit to (7, 1). This forms a quasi-1D semiconductor-metal junction, because the (8, 0) half nanotube is semiconducting while the (7, 1) half nanotube is metallic. Based on this creation mechanism, CNT IMJs can behave as metal-metal (M-M) junctions, metal-semiconductor (M-S) junctions, and semiconductor-semiconductor (S-S) junctions, depending on the chirality of the two CNT segments.

The exotic electrical transport properties of the M-S junctions were first experimentally reported by Yao *et al.* in 1999 [84]. They observed highly nonlinear and asymmetric $I-V$ characteristics for an M-S junction (around the kink region shown in the inset), as displayed in Figure 2.9 (b). For a positive bias, the current rose sharply above a threshold voltage, while there was only a small increase in current for large reverse bias. This rectifying behavior across the junction could be attributed to the Schottky-type barrier at the M-S interface which may arise from the difference in electronic structures and screening properties of the metallic and semiconducting segments. Fuhrer *et al.* formed an M-S junction by intersecting one metallic nanotube over another semiconducting nanotube [85]. They observed rectifying behavior from a two-terminal measurement of the M-S junction, and considered the charge transfer at the junction between the two crossing tubes should be responsible for the phenomenon. The metallic tube could locally deplete the holes in the underlying p-type semiconducting tube and align the band gap of the semiconducting tube, forming a Schottky barrier at the junction.

Figure 2.9. (a) Atomic structure of an (8, 0)/(7, 1) tube. The red balls denote the atoms forming a 5-7 defect pair on the nanotube. Adapted from ref. [82]. (b) $I - V$ characteristics across an M-S IMJ as shown in the inset, showing rectifying behavior. (c) Plot of conductances obtained from two straight metallic nanotube segments and the kink M-M junction as a function of temperature, respectively. (b) and (c) are adapted from ref. [84]. (d) $I - V$ curves of three SWNT segments, the inset show the rectifying behavior of the S-S junction. Adapted from ref. [86].

Yao *et al.* also investigated the electrical behavior of an M-M junction, where they found that the conductance was strongly suppressed [84]. As compared in Figure 2.9 (c), the resistances of the two straight metallic segments were 56 and 101 kΩ respectively, however, the resistance measured across the junction was 608 kΩ, which was much higher. In addition, the conductance of the junction was more temperature dependent than that of straight segments. They assumed that SWNTs would behave as Luttinger liquids (LLs) due to the confinement of their 1D nature [87], thus the M-M junction could be taken as the end of two

LLs. The tunneling conductance into the end of an LL should be strongly suppressed, compared with into the bulk, as a power law function of temperature, explaining the observed suppression in conductance of the M-M junction.

The S-S junctions were also found to behave like a rectifying diode [86]. As shown in Figure 2.9 (d), the measured $I-V$ curves of the two semiconducting nanotube segments (S_1 and S_2) were symmetric. On the contrary, the junction segment (S_1 - S_2) displayed an asymmetric $I-V$ characteristic. The rectification ratio ($RR = \text{current at } -1 \text{ V} / \text{current at } +1 \text{ V}$) obtained from the S-S junction was around 24, as seen in the inset. It was thought that the barrier formed at the interface of the two semiconducting nanotubes with different band gaps was the cause of the rectifying behavior.

Another type of IMJs that have been widely used in semiconductor devices is CNT-based p-n junctions. These junctions show excellent rectifying performance, and can be operated in a high frequency range [88-90]. A novel application of the p-n junctions is to build nanodevices for optoelectronics. Misewich *et al.* fabricated a light emitting device based on an ambipolar SWNT FET [91]. With the source at ground voltage, they applied appropriate biases to the gate and drain, in order to simultaneously inject electrons and holes into the nanotube, forming a p-n junction. Due to the 1D confinement, the generated electrons and holes were driven towards each other, and the infrared emission could be detected because of this radiative recombination. The efficient of electron-hole (e-h) pair generation in p-n junctions was greatly enhanced by developing a SWNT FET in split-gate geometry, as schematically illustrated in

Figure 2.10 (a) [92]. By applying voltages with opposite polarities onto the two gates, photocurrent was induced with laser illumination at temperatures of 90 K or below. A corresponding photocurrent map at $T = 50$ K is shown in Figure 2.10 (b), with a peak observed at the location of the p-n junction.

Figure 2.10. (a) Schematic of a split-gate p-n junction photodiode under focused optical illumination. (b) A spatially resolved photocurrent map with continuous wave laser excitation. Scale bar, 1 μm . (a) and (b) are adapted from ref. [92]. (c) An SEM image of the overall configuration to probe the switching behavior of a Y-junction. (d) Observation of abrupt modulation of the electrical current through terminal 2 when ~ 4.6 V DC voltage was applied onto the stem (terminal 1). (c) and (d) are adapted from ref. [93].

In order to fulfill the applications of CNTs in nanoelectronics, especially towards

constructing CNT-based ICs at the wafer level, IMJs with multiterminals were proposed as the interconnections and their properties have been intensively investigated. Intrinsic rectifying behavior has been observed from the transport measurements of Y-shaped junctions by many groups [94-97], which was attributed to the abrupt change in band gap due to the change in the nanotube diameter [94]. Another unique property of multiterminal junctions is their electrical switching functionalities, which was first experimentally demonstrated in a Y-junction by Bandaru *et al.* in 2005 [93]. Figure 2.10 (c) is an SEM image showing the overall configuration of a Y-junction-based switching device. A direct current (DC) voltage was applied on the stem (terminal 1), while the current through the other two terminals was monitored under a fixed alternating current (AC) bias ranging from 0.1 to 1.0 V. As the DC voltage was increased to a certain point (~ 4.6 V as observed in Figure 2.10 (d)), the Y-junction went from nominally conducting to a pinched-off state. They also discovered that the output voltage at the stem was negative when either of the branch voltage was negative. Only when both of the branches were applied with positive voltages, positive voltage could be obtained at the stem. Once either of the two branch voltages was negative, the output voltage became negative [93]. This result implied that the Y-junction could function as an AND logic gate.

2.3 Preparation of CNT IMJs

Although many theoretical simulations have predicted the extraordinary properties of IMJs and the fascinating perspective of utilizing IMJs in electronic circuits, however up till now, rare experimental achievements have been realized, because of the lack of synthesizing the

IMJs in a controllable way. Herein, we list some successful methods that have been reported for preparing CNT IMJs.

2.3.1 Generation of defects onto CNTs

A routine method to form CNT IMJs is to introduce topological defects into nanotubes, as stated in previous section, the 5-7 pair defects could create a small local deformation in the structure of the nanotube and may also generate a small change in the chirality, depending on their orientation in the nanotube hexagonal lattice. Admittedly, intrinsic defects can naturally occur in conventional CNT production [28, 98-100]. However, such defects are mostly induced inadvertently during the growth process. A more accessible approach is to intentionally introduce topological defects by acid treatment, sonication, and electrical field emission [101-104]. Irradiations by ion, proton, or electron and plasma treatment are also commonly used to generate defects onto the surface of CNTs [23, 24, 105-109]. Under uniform irradiation conditions, SWNTs have been observed to respond to uniform atom loss (atom removal from the irradiated CNTs occurs at a slow rate) through surface reconstruction and dimensional change [105]. Figure 2.11 (a) and (b) present an isolated SWNT before and after extensive irradiation with 100 keV electrons for 80 min, respectively. The significant changes in the TEM images indicate that the carbon atoms first on the top and bottom surfaces and then on the side were ejected, as a consequence of the knock-on damage [24]. If carbon atoms are continuously extracted at random from their honeycomb lattice, the surface of the CNTs could be either a highly defective structure with the original size or an entirely reconstructed atom

network shrunk in size [110]. This forming of non-hexagonal rings and 5-7 defect pairs in the lattice of CNTs through irradiation has been taken as a regular method to produce IMJs.

Figure 2.11. TEM images of an isolated SWNT before (a) and after (b) extensive electron irradiation at 100 keV, showing drastically dimensional change. Scale bar, 10 nm. Adapted from ref. [24].

2.3.2 Synthesis via CVD method

As the CVD method is the most widespread synthesis technique for preparing CNT samples, therefore, priorities of obtaining IMJs have been focused on the direct CVD growth process. The diameter of the as-grown CNTs has an intimate relationship with the growth conditions and can be well-tuned by the growth temperature and gas flow rate [111-114]. Based on the growth temperature effect on the nanotube diameter and chirality, Yao *et al.* reported a temperature-mediated method to controllably synthesize IMJs through diameter transition on a single nanotube [86]. It has been found that the diameter of a SWNT was smaller at higher temperature, while lower temperature led to thicker nanotubes. By oscillating the

temperature during growth (i.e. from 900 to 950 °C), diameters of different nanotube segments could be altered along the tube length, thus the junctions could be obtained in the diameter transition area, as illustrated in Figure 2.12 (a). In their subsequent work, they designed a temperature ascending (or descending) process, which involved four-step temperature increase (or decrease) during the whole growth stage (Figure 2.12 (b)) [114]. As a result, the diameter of the growing nanotube was gradually decreased (or increased) along its length, as verified by the corresponding Raman spectra shown in Figure 2.12 (c). This remarkable result suggested a possible way to simultaneously create a series of IMJs with different structures and properties along one individual ultralong SWNT.

Figure 2.12. (a) An AFM image and a schematic illustration of an S-S junction formed by changing the diameters of different segments via a temperature-mediated approach. Scale bar, 4 μm . Adapted from ref. [86]. (b) The ascending temperature-time curve and (c) corresponding Raman result of an ultralong SWNT grown under the temperature-time process, showing diameter decrease along the length. Adapted from ref. [114].

A simple two-step CVD method was developed by Jin *et al.* to directly grow SWNT/MWNT junctions [115]. In the first CVD process, MWNTs grew from the Fe-Mo catalyst particles by using C_2H_2 as the carbon source. By changing the growth temperature and using CH_4 as the feeding gas in the second CVD step, SWNTs grew continuously from the tip of MWNTs, forming the SWNT/MWNT junctions at the interface. Similarly, a two-step PECVD process was employed by AuBuchon *et al.* to synthesize Y-junctions [116]. After the initial growth of aligned CNT arrays on a silicon substrate, Ni catalyst particles were sputtered onto the surface of the as-grown CNTs, agglomerating into new smaller catalyst particles and nucleating new CNTs as branches growing aligned along a direction perpendicular to the original CNTs.

2.3.3 Doping of CNTs

Since semiconducting SWNTs in general show p-type behaviors, various chemical and nonchemical doping of SWNTs have been applied to convert p-type to n-type semiconductors. Following this type conversion mechanism, p-n junctions have been realized by chemical doping of one part of a SWNT, leaving the other part unchanged. As shown in Figure 2.13 (a), Zhou *et al.* covered the left half of a semiconducting nanotube using a layer of polymethylmethacrylate (PMMA), and heavily doped the exposed half with potassium [88]. As dopants, the potassium atoms adsorbed onto the surface of the nanotube, donating electrons to convert the segment from p- to n-type (see the diagram of band structure). In this way, a p-n junction can be obtained, exhibiting diode behaviors.

Figure 2.13. (a) Schematic structure of a p-n junction fabricated by doping half of a semiconducting SWNT with potassium. The area highlighted by dashed lines in the corresponding AFM image shows the PMMA-covered region. The bottom is the band diagram for the p-n junction. Adapted from ref. [88]. (b) $I - V$ characteristics of a p-type FET (black line), a p-n junction (red line) and an n-p junction (blue line) by applying different voltages onto the two split gates. Adapted from ref. [89].

Other than chemical doping of CNTs, p-n junctions can also be formed by electrostatic doping at room temperature. This strategy advances the functionalities of the p-n junctions by eliminating the effects of chemical dopants and enables multi-modes achieved from one junction. An example of the electrostatic doping was achieved by using a split-gate FET [89], the configuration is similar to that shown in Figure 2.10 (a). The SWNT showed unipolar p-type or n-type character if both gate biases were made positive or negative, as shown in Figure 2.13 (b) (only p-type behavior is shown for clarity). When biasing the split gates with opposite potentials, a p-n junction (red line) can be obtained with $V_{GS1} < 0$, $V_{GS2} > 0$ (herein, the gate VG1 refers to the split gate near the source electrode and the gate VG2 refers to the split gate near the drain

electrode), and an n-p junction (blue line) in the case of $V_{GS1} > 0$, $V_{GS2} < 0$. The most essential features of the junctions achieved in this way, as demonstrated, is that they could show nearly ideal diode behavior over a wide range of temperatures [89].

2.3.4 Mechanical deformation

It has been reported that the electronic band structure of CNTs can be dramatically altered by mechanical strain [117-119]. As performed by Tomblor *et al.*, an AFM tip was employed to manipulate suspended nanotubes over a trench and in-situ measure the electrical properties of the SWNT under strain. The experimental setup is illustrated in Figure 2.14 (a), where a suspended nanotube was grown over a trench and clamped at both ends by metal electrodes, the AFM tip was centered above the nanotube. Dramatic conductance decrease of the SWNT was observed when the nanotube was pushed towards the bottom of the trench by the AFM tip. The conductance as a continuous function of strain (σ) and bending angles (θ) is plotted in Figure 2.14 (b). As can be seen, the conductance decreased relatively slowly for smaller bending angles and more dramatically at higher bending angles. Simulation results attributed the conductance decrease to the local bonding deformation induced by the AFM tip. As shown in Figure 2.14 (c), for small bending angles ($\theta < 7^\circ$), the SWNT retained sp^2 bonding throughout its structure. However, with the increase of the deflection angle, the C-C bonding gradually transferred from sp^2 configuration to nearly sp^3 configuration, resulting in a delocalized electron state. Thus the local DOS at the Fermi level was decreased and a band gap was formed, causing the drastic decrease of the conductivity [117].

Figure 2.14. (a) Schematic configuration of the setup for manipulating a suspended SWNT with an AFM tip. The tip was moved in the z direction to push the nanotube towards the bottom of the trench. (b) Experimental result of conductance versus strain. Inset, conductance versus bending angle. (c) Simulated atom configurations of the nanotube pushed to 7° and 15° , respectively. (a), (b), and (c) are adapted from ref. [117]. (d) Evolution of the band gap of a strained nanotube as V_{tip} is increased. The nanotube transferred from a p-type semiconductor to a p-n-p junction. Adapted from ref. [118]. (e) Formation of junctions by AFM manipulation. A sharp buckle (upper two images) and nanotube crossing (bottom two images) can be observed from the AFM image. Adapted from ref. [120]. (f) Change of Raman spectra as a result of increasing strain to an individual CNT. Adapted from ref. [121].

By using a similar experimental setup, Minot *et al.* also discovered that the strain could open a band gap in a metallic nanotube and modify the band gap in a semiconducting nanotube [118]. In addition, after applying a voltage to the tip as the gate when straining the tube, they found that the tip voltage could change the strained tube from a p-type semiconductor

($V_{\text{tip}} = 0\text{V}$) to a p-n-p junction ($V_{\text{tip}} > 1\text{V}$), as shown in Figure 2.14 (d).

In addition to the delocalized effects, when CNTs are under strain, such as compressive strain and bending deformation, plastic deformation could take place, leading to defects forming in the deforming area [122-125]. As presented in Figure 2.14 (e), two examples of IMJs were fabricated with an AFM pushing an individual metallic nanotube on surface [120]. After dragging the nanotube in a direction perpendicular to its length, a sharp buckling with an angle of 105° was observed, resulted from the strain release by locally collapsing the cylindrical shell structure into a flattened tube structure. Furthermore, the nanotube could also be broken by the dragging force and cross each other. The corresponding electrical measurement on the nanotube confirmed its junction properties, showing tunneling conductance. The generation of defects onto strained nanotubes has also been detected using Raman spectroscopy [121]. As displayed in Figure 2.14 (f), with the increase of the applied strain, there was an increase in the intensity of the D band, which was associated with the introduction of defects in the nanotube structure under high strain.

2.3.5 Modulation of SWNTs via interaction

The interactions between the CNTs and its environment are of crucial importance in governing the structure and modulating the properties of CNTs [126]. Generally, such interactions refer to the tube-substrate interaction and tube-tube interaction.

2.3.5.1 Tube-substrate interaction

Many studies have shown that the electronic properties of SWNTs adsorbed on unpassivated silicon substrates could be dramatically tuned through the formation of covalent Si-C bonds [127-130]. This interaction between the nanotube and the substrate has been directly visualized by You *et al.* using a micro Raman imaging and further verified by the observation of extra peaks belonging to the Si-C bonds from the Raman spectra [131]. The existing strong bonding predicted a method to form an M-S junction by switching a metallic nanotube to a semiconducting one without significantly alter its structure [127].

Interactions between CNTs and crystalline SiO₂ substrates, such as quartz and sapphire, could be so strong that the absorption direction of CNTs on top of the surface could be guided by the anisotropic lattice of the substrates [132-134]. Ding *et al.* grew dense CNT arrays on ST-cut single crystal quartz substrates and observed an “up-shift” in the G band frequency when characterizing the as-grown CNTs using Raman spectroscopy [135]. They attributed the “up-shift” to the increased lattice constant, which originated from the deformation of C-C bonds caused by the strong tube-substrate interaction. They suggested that the bottom part of the lying nanotube became flat, like a monolayer of graphene, due to the strong tube-quartz interaction. Because when they transferred the nanotubes onto SiO_x wafers, the structural deformation and the corresponding “up-shift” observations of the G band disappeared simultaneously.

The hypothesis has been confirmed by Soares *et al.* in their results and explained using a

model shown in Figure 2.15 (a) [136]. For a (19, 0) nanotube sitting on the (001) surface of the quartz substrate (left image), upon relaxation, the silicon atoms in the contact region were displaced upwards and flattened the bottom part of the nanotube. The adhesion-induced deformation could elongate the C-C distance (middle image) and cause an increase in the average density of electrons per carbon atom (right image) in the tube-substrate contact region. Such effect on the nanotube could change the electronic behavior of the serpentine CNTs, depending on the tube-substrate orientation, which was responsible for the observed junctions at the curved part of the bent CNTs [133].

The tube-substrate interaction for CNTs on amorphous SiO₂ substrates was expected to be weaker, compared with the crystalline SiO₂ substrates. But still, the van der Waals tube-substrate interaction may deform the CNTs in the radial directions, thereby modifying their electronic DOS. The radial deformation was investigated by comparing the Raman spectra of the same individual nanotube between sitting-on-substrate (SOS) segments and suspended (SUS) segments [137]. As observed in Figure 2.15 (b), from SOS to SUS, both the RBM and G band exhibited a downshift in the frequency, indicating a junction was formed between the two segments of the individual nanotube.

Figure 2.15. (a) A model of the tube-quartz interaction. Left image: real space representation of the electronic states at the Fermi level for a (19, 0) SWNT sitting on the (001) surface of a quartz substrate. Middle image: average bond length along the tube axis (open circles) and along the tube circumference (filled circles). Right image: average density of electrons per carbon atom. Adapted from ref. [136]. (b) Raman spectra of one individual SWNT with the laser spot moving from the SOS segment to the SUS segment, showing downshift in frequency for both RBM and G band. Inset is RBM evolution when the laser beam was moved from SUS to SOS on the right side. Adapted from ref. [137].

Under some circumstances, the tube-substrate interaction was found to be so strong that causes suspended SWNTs to bend/buckle, especially at the edge of the support [138]. A HR-SEM image of a suspended nanotube spanning a 2- μm -diameter hole is shown in Figure 2.16 (a). Because of the tube-substrate adherence, the nanotube is bent at the edge of a silicon

pillar. A TEM example is shown in Figure 2.16 (b), by following the contour of the pillar due to the strong interaction, buckled patterns was observed on the bridging nanotube near the edge. These bending/buckling of the CNTs could drastically affect their physical and structural properties, thus can be exploited as a method to form IMJs.

Figure 2.16. (a) A HR-SEM image of a bridging nanotube adhered to the pillar edge, showing bending morphology. (b) A TEM image of a SWNT following the contour of a pillar, creating a buckled pattern at the edge of the $2\mu\text{m}$ hole. (a) and (b) are adapted from ref. [138]. (c) A top-down TEM image of a SWNT deformed in the radial direction due to tube-tube interactions. Scale bar, 5 nm . (d) A TEM image showing a CNT buckling junction. Scale bar, 5 nm . (c) and (d) are adapted from ref. [139].

2.3.5.2 Tube-tube interaction

In 1993, radial deformation was discovered in two adjacent CNTs, and was attributed to the van der Waals interactions [140]. In the following investigation of the effect of van der Waals interactions on CNTs, Abrams *et al.* also observed radial deformation and tube buckling in some SWNT Y-junctions [138, 139]. Figure 2.16 (c) and (d) exemplify two types of CNT adherence at a junction point [139]. The straight SWNT measured in Figure 2.16 (c) showed a diameter elongation due to the interactions with the top of the underlying CNT bundle, but a diameter contraction because of the interaction with the side of the bundle. In addition to the evident radial deformation, the nanotube shown in Figure 2.16 (d) also underwent buckling at the joint, as opposed to their gradual curving. A “zipper-effect” was proposed to explain the observations, as suggested, the chains of carbon atoms of each tube in the pair would zip together upon adhesion through the van der Waals interaction. Based on a quantitative analysis, they found that the extent of deformation was diameter dependent [139]. The large-tube had a higher tendency to be deformed under the same stress of “zipper-effect”, therefore they could be easily bent and buckled, in order to reduce the bending energy.

2.3.6 Welding of CNTs

Another strategy to construct IMJs is to weld different CNTs together at high temperature by electron beam irradiation, ion beam irradiation, or current annealing [26, 141-144]. Multi-terminal IMJs with various types of morphologies have been successfully fabricated using the welding technique. The formation mechanism was attributed to the coalescence and

recombination of CNTs [141]. As we introduced previously, under irradiations, topological defects can be generated as a result of knock-on damage. These defects then move, producing vacancies as the reactive sites to induce coalescence and formation of interconnections between adjacent nanotubes. Via thermal annealing, the structure could be stable and function as a multi-terminal IMJ.

Ho *et al.* reported that IMJs could be formed by fusing the tips of two adjacent MWNTs under high electric field conditions [144]. After a long time exposure to the high electric field, the C-C bonds at the tips could be broken due to the electric field and thermal effects, causing carbon atoms sublimation. The sublimated carbon atoms were then re-deposited on the cooler tube walls, eventually leading to the formation of IMJs.

2.4 Identification of CNT IMJs

2.4.1 Morphology identification

The defect pairs in CNTs are mostly creating curvatures, thus making the IMJ manifest itself as a sharp kink. Therefore, the observation of a bent geometry can be taken as an evidence for the occurrence of junctions [84]. Early in 1998, Han *et al.* frequently observed bent SWNT IMJs with bending angles ranging from 18° to 34° in their CVD productions, as shown in Figure 2.17 (a) [98]. Structural and energetic calculations suggested that the bent configurations arose from the presence of topological defects, being isolated or fused in pairs on the tube surface. The number and arrangement of the defects was determined by the tube

diameter and chirality, leading to different bending angles. Huang *et al.* specifically measured the transport properties of bent SWNT and observed a dramatic resistance increment occurring across the bent region, compared with the straight segments [133]. The change of the transport properties in the bent region could be attributed to the formation of junctions, which agreed well with the theoretical predictions.

Figure 2.17. (a) TEM and AFM (inset) images of bent SWNT IMJs produced using a CVD method. Three typical bending angles are: a) 34°, b) 26°, and c) 18°. Adapted from ref. [98]. (b) A tri-potential electrochemical setup for selectively depositing metal nanoparticles along tube length. WE, working electrode. CE, counter electrode. RE, reference electrode. (c) AFM images showing a 2 μ m nanotube segment before (left image) and after (right image) decorated with Ni nanoparticles. (d) Curved segment of the nanotube incorporate a higher density of defects. Scale bar, 15 nm. (b)-(d) are adapted from ref. [145].

With the knowledge that SWNT defect sites are more reactive than the pristine sp^2 -bonded lattice, Fan *et al.* designed a electrochemical method to selectively decorate the defects with noble metal particles, so that one could identify and even count the point defects in CNTs [145]. The experimental setup is depicted in Figure 2.17 (b), where a tri-potential electrochemical pulse was used for deposition, the SWNT served as the working electrode. As shown in the AFM images (Figure 2.17 (c)), after 60 sec deposition, the Ni nanoparticles were uniformly deposited on the 2 μm segment. To emphasize the availability this selective deposition method, they also compared the deposition results of segments with different defect density. It can be observed from Figure 2.17 (d) that the curved region of the nanotube, which was expected to have a higher density of defects, was decorated with more Ni nanoparticles. Semiconductor nanoparticles, such as titanium dioxide, could also be used as the markers for labeling the defects of CNTs [146]. This defect-induced loading method facilitates the identification of IMJs in the CNT productions.

2.4.2 Atomic structure identification

Scanning tunneling microscopy (STM) is a powerful instrument that can directly prove the existence of IMJs and characterize their atomic structure and the local electronic density of states (LDOS) [28, 147]. As reviewed in the atomically resolved STM image of a SWNT (Figure 2.18 (a)), the upper and lower portions of the nanotube have similar diameters ($1.57 \pm 0.07 \text{ nm}$) but different chiral angles [28]. This drastic change in chiral angle that occurs just across the local defect could be taken as strong evidence that this feature is an IMJ. The corresponding

scanning tunneling spectroscopy (STS) data further supported this conclusion, in which the upper and lower portions were respectively recognized as semiconducting and metallic, according to their vHSs profiles (see Figure 2.18 (b)). A more detailed characterization of electronic properties of the IMJ is shown in Figure 2.18 (c). Around the junction, the gap defined by vHSs in the semiconducting segment (black arrows) decayed into the metallic segment within < 1 nm, whereas the features of the metallic segment (red arrows) decayed more quickly across the junction interface.

Figure 2.18. (a) A STM image of an M-S junction formed between a (21, -2) upper portion and a (22, -5) lower portion. (b) Tunneling conductance recorded at the upper and lower locations indicated in (a), exhibiting a semiconducting profile for the upper portion and a metallic profile for the lower portion. (c) A detailed STS spectra evolution of the IMJ. The black arrows and red arrows respectively highlight the first vHS of the semiconducting and metallic structure. Scale bar, 1 nm. (a)-(c) are apated from ref. [28]. (d) HRTEM image of a 5-7 defect found in an SWNT. (e) An enlarged image showing the 5-7-7-5 defects. (d) and (e) are adapted from ref. [29].

It has been demonstrated that HRTEM can also provide the atomic sensitivity for imaging topological defects in SWNTs [29]. As shown in Figure 2.18 (d), 5-7 defect pairs could be directly found in the HRTEM image of a SWNT that was heated at 2273 K. From the enlarged image of the area enclosed with green line, the topological defects could be clearly recognized. As marked with bright dots, the green dots represented the carbon atoms that have six neighbors. The defects were indicated with red and blue dots, in which the two red dots had seven neighbors, while the two blue dots only had five neighbors.

2.4.3 Resonance Raman spectroscopy

The speed and resolution are always two extremes in any measurement. Although STM and HRTEM are useful instruments that can identify and characterize IMJs at the atomic level, yet, they have not been widely utilized in the SWNT IMJs research area, because they are too slow and painstaking for statistical material characterization, and they cannot be performed on insulating oxides surface. Raman spectroscopy has been proven to be a powerful technique for CNT-based research by many reports during the past decades. At single nanotube level, it can provide detailed information of the characterized CNT samples with respect to diameter and chirality, specific (n,m) species, sample quality, doping, functionalization, as well as temperature, pressure and strain effects.

2.4.3.1 Resonance Raman spectroscopy of CNTs

Resonance Raman spectroscopy (RRS) is associated with a single resonance process, in

the case of a SWNT, the signals are greatly enhanced if the excitation laser energy (E_{laser}) matches the optically allowed transition energy (E_{ii}) between vHSs in the valence and conduction bands from the SWNT [80]. Because of this resonance process, Raman spectra allow us to study the electronic and phonon structures of SWNTs at single nanotube level. If the Raman spectra are taken from a SWNT bundle, only those nanotubes with E_{ii} in resonance with E_{laser} will contribute predominantly to the spectra. To analyze the resonance Raman spectra of SWNTs, it is useful to have a plot of these resonant transition energies E_{ii} as a function of tube diameter d_t for all (n,m) SWNTs. We call such a plot a Kataura plot, as shown in Figure 2.19 (a), which was first proposed by H. Kataura in 1999 [148]. From the Kataura plot, we see that the resonant transition energies E_{ii} are approximately inversely proportional to d_t . Under resonance condition, with a given (E_{ii}, d_t) values for an individual SWNT, the (n,m) indices for that SWNT can be determined from the Kataura plot [45].

Figure 2.19. (a) Kataura plot showing transition energies for all possible (n,m) SWNTs with diameters in the range $0 < d_t < 3.0$ nm, using a tight-binding method. Schematic picture showing atom vibrations for (b) the RBM and (c) the G band. Adapted from ref. [149].

2.4.3.2 Special Raman modes

In general, there are three main Raman active features associated with probing and acquiring detailed structural information of SWNTs at single nanotube level: the low frequency radial breathing mode (RBM), defect-induced D band at $\sim 1300 \text{ cm}^{-1}$ and the tangential stretching G band observed between 1500 and 1600 cm^{-1} . We will have a detailed introduction and discussion of these three modes below.

(a) Radial breathing modes—RBM

The RBM is a totally symmetric vibrational mode corresponding to the coherent vibration of carbon atoms in the radial direction, as if the tube were “breathing” (see Figure 2.19 (b)). The RBM frequency (ω_{RBM}) of SWNTs mostly appears in the range $150\text{-}300 \text{ cm}^{-1}$. Theoretical and experimental results show that ω_{RBM} is inversely proportional to the nanotube diameter, following the equation $\omega_{\text{RBM}} = A / d_t + B$. The parameters A (cm^{-1}nm) and B (cm^{-1}) are determined experimentally, different values have been obtained for (a) nanotubes on a Si/SiO₂ substrate (A=248, B=0) [150], (b) bundled nanotubes (A=239, B=0) [151], (c) nanotubes dispersed in aqueous solution (A=218, B=16) [152], and (d) free standing nanotubes (A=204, B=27) [153]. Based on the observation of the RBM for an isolated SWNT, it is possible to acquire its diameter value, and further to get the (n, m) assignment for the specific SWNT by utilizing the Kataura plot. Moreover, because of the dependence on the nanotube diameter, the frequencies of RBM are largely used for the characterization of the

diameter distribution in a CNT sample.

(b) Tangential modes—G band

The stretching of the C-C bond gives rise to the so-called G band, in graphite it usually displays one single sharp peak at $\sim 1582 \text{ cm}^{-1}$ (see Figure 2.20 (a)). However, due to the quantum confinement of phonon wave vector along the SWNT circumferential direction and due to symmetry-breaking effects associated with SWNT curvature, the G band in SWNTs exhibits a multi-peak feature, where up to six Raman peaks can be observed [154]. Normally, a simple analysis can be carried out by only considering the two most intense peaks, the so-called G^+ and G^- components. As illustrated in Figure 2.19 (c), the G^+ peak is associated with atomic displacements along the tube axis (LO phonon mode), and the G^- peak corresponds to atomic displacements along the circumferential direction (TO phonon mode).

Figure 2.20. (a) The G band acquired for highly oriented pyrolytic graphite (HOPG), one semiconducting SWNT and one metallic SWNT. (b) RBM and G band features for three isolated SWNTs of the indicated (n, m) values. (c) Plot of G band frequencies as a function of $1/d_t$, for both semiconducting SWNTs (solid circles) and metallic SWNTs (open circles). The lines are fit to the experimental points. Adapted from [154].

The G band can be used to distinguish between semiconducting and metallic SWNTs, through the strong differences in their line shapes [149]. As compared in Figure 2.20 (a), semiconducting SWNTs show two dominant Lorentzian components, which are assigned to higher-frequency mode G^+ and lower-frequency mode G^- , respectively. Although the G^+ feature also has a Lorentzian line shape for the metallic nanotubes, the G^- feature of metallic SWNTs, in contrast, shows a broad, asymmetric Breit-Wigner-Fano (BWF) line shape.

Measurements on the G band at single nanotube level reveal that the frequency of G^+ feature is both diameter and chiral-angle independent, while the G^- feature shows a dependence on the nanotube diameter. The frequencies of the G^+ and G^- bands are plotted in Figure 2.20 (c) as a function of $1/d_t$ for 46 isolated semiconducting (solid circles) and 16 isolated metallic (open circles) SWNTs [154]. The plots can be well fitted using the equation $\omega_{G^-} = \omega_{G^+} - C/d_t^2$, where $C = 47.7 \text{ cm}^{-1}\text{nm}^2$ for semiconducting SWNTs and $C = 79.5 \text{ cm}^{-1}\text{nm}^2$ for metallic SWNTs. In this way, the splitting in the two G band features can be used for diameter characterization, which supplements the utility of Raman study of SWNTs in the case that the RBM is absent in the spectra.

(c) Disorder-induced D band

The D band comes from a double resonance process, normally it can be observed in the $1300\text{-}1400 \text{ cm}^{-1}$ range. In SWNTs, the presence of disorder could lead to rich and intriguing phenomena in D band. Therefore, the appearance of D band and the intensity ratio of D band to G band (I_D/I_G) can be taken as fingerprints for identifying defects in SWNTs and evaluating

the defect concentration and sample purity [149].

2.4.3.3 Raman spectroscopy for IMJs identification

According to the strong correlation between the Raman modes and the structure and vibrational properties of CNTs, Raman spectroscopy has become a key tool and is widely used to identify IMJs in CNTs. The effectiveness of Raman spectroscopy is all-round: first of all, the frequency of RBM allows one to directly obtain the values of the measured nanotube diameters. As a result, through the shift of RBM frequencies along one tube axis, Yao *et al.* identified the junctions formed by diameter change [86]. Since semiconducting and metallic SWNTs possess different G band features in the line shape, a transition in the G band line shape can thus be imaged by confocal Raman scattering, pointing out a junction site in the transition region [100]. As introduced in the previous section, the presence of D band and its relative intensity to G band can always be taken as an evidence of the occurrence of topological defects in CNTs [155].

2.5 Summary

IMJs based on CNTs have displayed exotic properties and shown potential to function as active components for the next generation nanoelectronics. Tremendous formation techniques and diverse characterization methods have been proposed to make the use of IMJs more realistic. However, the lack of controllable synthesis and rapid identification of IMJs hinders the process of achieving goals. In this thesis, we will devote to designing protocols to overcome the limitation of these two aspects.

Chapter 3 Experimental Details

As stated in the introduction, our study will primarily focus on the controllable synthesis and rapid identification of CNT IMJs. To achieve this goal, there are several stages involved. It is important first and foremost to grow ultralong, horizontally aligned, and defect-free SWNTs, because they serve as the carriers of IMJs. If we cannot control the morphology, orientation, and structure of the parent SWNTs, it would be meaningless to study the controllable synthesis of CNT IMJs. Another merit of preparing IMJs from defect-free SWNTs is that the influence of random defects on the properties of the nanostructures could be excluded, which allows the exploration of intrinsic properties of functional IMJs.

On the basis of this prerequisite, herein we propose three strategies to controllably preparing CNT IMJs, including IMJs induced by tube-substrate interaction, IMJs induced by tube-tube interaction, and IMJs induced by strain. The highlight of our strategies is to make use of trenched structures in the synthesis procedure, in other words, we intentionally prepare IMJs by growing SWNTs across trenches. Because nanotubes are capable of lying suspended across the trenches without getting in contact with the substrate, it is quite feasible to probe the peculiarities of IMJs induced by tube-substrate interaction, by comparing the sitting-on-substrate (SOS) segment and suspended (SUS) segment of the same individual nanotube. At the same time, IMJs induced by tube-tube interaction are more discernible owing to the suspended morphology, which facilitates the identification and characterization. Last but most important, controllable synthesis and rapid identification of SWNT IMJs could be simultaneously realized

through our third approach. For a nanotube partially lying on the trenched substrates, owing to the trench configuration, strains will be induced to the nanotube which may make it stretched and even bent at the edge of the trench, depending on the geometry. Under bending deformation and corresponding uniaxial strain, topological defects can be introduced to the nanotube, forming IMJs at the edge of the trenches. The specific formation location, the edge of the trenches, provides a feasible platform to rapidly and accurately identify the IMJs and extensively study their exotic properties.

3.1 Synthesis of Ultralong, Horizontally Aligned SWNTs

Compared with other growth methods, gas-flow-directed CVD approach is more appealing to obtain horizontally aligned ultralong CNTs on flat surfaces, which almost invariably requires the presence of transition metal nanoparticles as the catalysts. A typical schematic experimental setup for CVD growth is depicted in Figure 3.1, the growth procedure is similar to our previous work but with some appropriate improvements [56]. FeCl_3 (iron (III) chloride, Sigma-Aldrich) ethanol solution, with a concentration ranging from 0.005 M to 0.1 M, was used as catalytic precursor and was applied on one edge of Si substrates with 500 nm thermally grown oxide (substrate length: 1.5 cm, substrate width: 1 cm). The sample was then placed in the center of a horizontal quartz tube furnace (tube diameter: 1 inch, tube length: 2 feet), with the catalyst edge directed toward the gas flow. At ambient pressure, the furnace was heated to the growth temperature and was kept at that temperature for amount of time under a flow of Ar (120 sccm) and H_2 (30 sccm). This procedure, referred as catalyst pretreatment, intends to

decompose and reduce the catalyst complex into Fe nanoparticles. After the pretreatment, the flow rate was reduced to 4 sccm and 6 sccm for Ar and H₂, respectively, serving as the carrier gas during growth. In the meantime, ethanol vapor was introduced into the quartz tube by bubbling Ar stream through ethanol vessel (20 °C) at a controlled rate of 20 sccm to start the CNT growth. After a 50 min synthesis period, the ethanol supply was terminated by switching off the ethanol vapor and H₂, and the furnace was cooled to room temperature under ~120 sccm Ar atmosphere.

Figure 3.1. A schematic diagram of ethanol CVD setup for the synthesis of ultralong CNTs.

To investigate the effect of growth parameters on the synthesis of CNTs, we carried out a parametric study by varying the catalyst concentration, the pretreatment time, and the growth temperature. On the purpose of comparison, only one operating condition was changed for each growth process, with all the other growth parameters maintaining the same. A typical

variation on the growth parameters is shown in Table 3.1 in details.

Table 3.1. A typical list shows variation on the growth parameters.

No.	catalyst concentration (M)	pretreatment time (min)	growth temperature (°C)
#b1	0.005	20	975
#b2	0.01	20	975
#b3	0.05	20	975
#b4	0.1	20	975
#b5	0.005	20	950
#b6	0.1	20	950
#b7	0.005	20	925
#b8	0.1	20	925
#b9	0.005	10	975
#b10	0.005	30	975

3.2 Preparation of CNT IMJs

3.2.1 Fabrication of trenched structures on flat substrates

In the aim to investigate CNT IMJs induced by van der Waals interactions (tube-substrate and tube-tube) and controllably synthesize CNT IMJs by taking advantage of the trenches, we intentionally fabricated trenched structures on silicon wafers in two respective procedures. As shown in Figure 3.2 (a), the first approach started with directly developing stripe patterns on the surface of Si/SiO₂ substrates using a photolithographic technique, where the

500-1000 nm thick SiO_2 layer was thermally grown on the 4 inch Si wafer. In the following step, trenches were formed by using deep reactive ion etching (RIE). After removing the photoresist (PR), the trenched substrates are ready for CNT growth. Figure 3.2 (b) illustrates the second protocol, where trenched structures were produced on top of bare n-dope Si wafer using photolithography and deep RIE. Then the PR was removed and a 1000 nm SiO_2 layer was sequentially deposited onto the wafer by means of plasma enhanced CVD (PECVD). For both methods, due to the mask design, the width of the trench was varied from 5 to 100 μm , and the depth was ranged from 1 to 10 μm , depending on the deep RIE etch time.

Figure 3.2. Schematic of photolithographic fabrication of trenched structures for CNT growing on, (a) thermally grown SiO_2 layer, and (b) PECVD grown SiO_2 layer, respectively.

3.2.2 Growth of SWNTs across trenches

By applying catalyst precursors on the top surface of the as-fabricated trenched substrates, CVD process was carried out to grow SWNTs lying across trenches, for the purpose of controllably prepare IMJs. The growth recipe was similar to that mentioned in section 3.1. A

schematic description is represented Figure 3.3.

Figure 3.3. Schematic representation of the preparation of CNT IMJs. The trenched structures were pre-fabricated on Si/SiO₂ substrates, using standard photolithography technique. The CVD process was then carried out to grow SWNT arrays across the trenches.

3.3 General Characterization Methods

Several instruments were utilized to systematically characterize the as-grown CNTs and CNT-based IMJs, to acquire information about their structures, morphologies, orientations and properties.

3.3.1 Scanning electron microscopy

SEM (Jeol, JSM-7600F) was utilized to reveal the morphology of CNTs over a large area. SEM characterization was operated at an acceleration voltage of 1 kV. Images with magnifications as low as 25× could still clearly show the existence of CNTs, due to the charging contrast in the vicinity of CNTs on substrates [156]. Analyses of orientation, length and density distributions of CNTs can be carried out on the basis of SEM observations.

3.3.2 Atomic force microscopy

AFM (Asylum Research, Cypher AFM) in tapping mode was utilized to obtain 2D and 3D morphologies of CNTs. The AFM height profile can provide information of the CNT diameters and the size of catalyst particles. Furthermore, the roughness of the surface can be revealed via the AFM mapping over an area.

3.4 Resonance Raman Spectroscopy

Raman imaging and spectroscopy is a fast and effective method for characterizing the as-grown CNTs. On one hand, CNTs can be spatially resolved in Raman mapping images, with respect to morphology and consistency. Raman spectra, on the other hand, provide detailed structural information of the examined CNTs. Basic utilization of Raman spectra in SWNTs involves identification of individual nanotubes, calculation of SWNT diameters, discrimination of SWNT chirality, and evaluation of the quality of as-produced SWNTs. In addition, Raman spectroscopy is also a powerful and feasible tool to inspect tube-tube and tube-substrate interactions and investigate strains induced to SWNTs. The capabilities of Raman spectroscopy were largely exploited for rapidly identifying and specifically characterizing CNT IMJs in this study.

Particularly, a Raman spectrometer (Renishaw, via Microscope, 10 mW) combined with a confocal imaging microscope was used for Raman imaging and Raman spectra in our experiments. Lasers with three different excitation wavelengths of 488, 514, and 633 nm were

used to sufficiently characterize the as-grown SWNTs. The laser beam was focused onto the sample with a 100× objective, providing a 1 μm excitation spot size. To avoid heating effects, the Raman measurements were performed with laser power below 10 mW at room temperature. For every single Raman spectrum, it was collected with the excitation laser power of 1 mW, integrated by three times with each integration time of 10 s.

3.5 Electrical Measurements

The electrical transport properties of individual SWNTs and SWNT-based IMJs were explored using a back-gate FET configuration at room temperature. As drawn in Figure 3.4 (a), individual as-grown SWNT was assembled into a FET device, serving as the conduction channel bridging a pair of source (S) and drain (D) electrodes. The metal contacts (Ti/Au = 10/60 nm) were deposited on top of the nanotube, using photolithography technique and electron beam evaporation. The silicon wafer itself was used as the gate (G) electrode, while the SiO_2 layer acts as the gate dielectric. Depending on mask design, the channel length was varied from 20 to 300 μm . The FET setup is also applicable for probing the transport properties of the as-fabricated IMJs. Two neighboring FETs with equal channel length were fabricated on different segments of one individual SWNT, as depicted in Figure 3.4 (b). The FET based on the SOS segment delivers the electrical properties of the parent SWNT, while the electrical properties of SWNT with IMJs can be conveyed by SUS segment-based FET, because the IMJs will dictate the properties of the entire nanostructures. Furthermore, by comparing the electrical performances obtained from the SOS segment and SUS segment, the impact of IMJs on CNTs could also be elucidated.

Figure 3.4. (a) Typical FET geometry for electrical measurements on individual SWNTs. (b) FET setup to probe the electrical properties of SWNT-based IMJs and the impact of IMJs on the parent nanotube.

For every FET device, the source-drain current (I_{ds}) versus gate voltage (V_{G}) characteristic was recorded under constant source-drain bias V_{ds} of 2 V, when V_{G} was swept from -24 V to +24 V in steps of 50 mV, giving transfer output ($I_{\text{ds}} - V_{\text{G}}$). The corresponding $I_{\text{ds}} - V_{\text{ds}}$ curves of each device were obtained by sweeping the V_{ds} from -1 V to +1 V, under seven different gate voltages.

Chapter 4   Synthesis of Ultralong, Horizontally

Aligned Single-Walled Carbon Nanotubes

4.1 Introduction

For the purpose of preparing useful CNT IMJs in a controlled way, it has been taken as first priority to grow ultralong, uniform and high-quality SWNT arrays (the carriers of IMJs) with defined morphology and orientation. Catalytic chemical vapor deposition (CCVD) is an effective approach to controllably synthesize horizontally aligned CNTs with desired structure and chirality [157-159]. However, the yields and morphology of the production via this technique essentially rely on the properties of the catalysts used. Even using the same catalysts for CVD growth of CNTs, the exhibited activity and lifetime of the catalysts, the two main properties that control the length and density of the produced CNTs, can be quite different with respect to the size of the catalyst nanoparticles [160].

From the reaction point of view, the growth of a nanotube involves the carbon feedstock going through a dissociation-diffusion-precipitation process over the catalyst nanoparticles, according to the well-accepted vapor-liquid-solid (VLS) growth mechanism [62]. Studies have suggested that the catalytic dissociation & diffusion of the carbon source, and the nucleation of new nanotube structures are intrinsically related to the size of the catalyst nanoparticles [161-163], and catalyst nanoparticles with proper size are more efficient at growing nanotubes. Apparently, this correlation between the growth behavior and the catalyst

attributes the discussed influence of the catalyst properties (activity and lifetime) on the resultant CNT's morphology (density and length) to a size-related effect. Therefore, engineering the size of the catalyst nanoparticles should be taken as higher priority for CVD growth, in order to enhance the catalytic activity and lifetime. Based on this understanding, many methods have been developed to obtain nanoparticles with uniform size, i.e. by thermally decomposing the catalyst precursors to obtain monodispersed nanoparticles [160], and using nanoscaled molecular clusters as the catalyst precursors [164]. In another aspect, intensive studies have revealed that the growth conditions of a CVD process, such as the growth temperature, flow rate, and catalyst concentration, also play a significant role in determining the morphology of the nanotubes [112, 165-167]. In this regard, it is quite rational to speculate that the size-dependent properties of the catalysts could be extensively affected and modified by the growth conditions, which in turn control the subsequent nanotubes morphology. In other words, for CNTs grown by CVD method, the growth condition channels the influence of the size-dependent catalytic activity and lifetime on the density and length of the produced CNT arrays.

Unfortunately, the aforementioned "growth condition mediated" effect has not been systematically explored. Herein, we directly addressed this issue by preparing horizontally aligned CNTs with catalysts dip-coated on flat substrates. By comparing the density and length of CNT arrays obtained under different growth conditions, the effect of growth parameters, including the catalyst concentration, pretreatment time, and growth temperature, on the morphology of the nanotubes were systematically investigated. At the same time, the catalysts behaviors influenced by the parameters were elaborately discussed. In addition, we also

investigated the alignment difference with respect to the CNT array density. Finally, the electrical properties of the as-produced CNTs were measured. The performance parameters of the CNT-based FETs were also analyzed. This controllable synthesis methodology paves the way for fabricating IMJs in the following steps.

4.2 Synthesis of Ultralong and Dense SWNT Arrays

A representative CVD synthesis of CNTs was carried out using Fe nanoparticles derived from 0.005 M FeCl₃ ethanol solution as catalyst. After 20 min pretreatment in Ar and H₂, the furnace was kept at 975 °C for growing CNTs on Si/SiO₂ substrate. Figure 4.1 (a) reveals the morphology of as-grown CNTs, where ultralong, dense, and well-oriented CNT arrays can be clearly observed. Continuous SEM mapping over the surface of the sample shows that majority of the nanotubes can grow over 1 cm in length, only limited by the length of the substrate. A typical Raman spectrum collected on nanotubes outside the catalyst area is shown in Figure 4.1 (b), with 488 nm excitation wavelength. The position and profile of the radial breathing mode (RBM) and G band in this spectrum allow positive identification of SWNTs [168], the extremely weak D band indicates that the produced SWNTs are of high quality. The distinct RBM frequency enables us to calculate the diameter of the SWNTs based on the relationship between RBM frequency and nanotube diameter: $d_t = 248 / \omega_{RBM}$ [150]. Figure 4.1 (c) presents the corresponding diameter distribution obtained from ultralong nanotubes that exhibit RBM in their Raman spectra. According to the statistic based on 38 nanotubes, the diameters range from 1.3 to 2.2 nm, with the average value around 1.7 nm.

Figure 4.1. (a) SEM image of as-synthesized CNT arrays. (b) A typical Raman spectrum obtained from the sample shown in (a), the frequencies of RBM and G band are indicated, the peak at $\sim 304 \text{ cm}^{-1}$ is associated with the Si/SiO₂ substrate. (c) Diameter distribution of 38 individual CNTs that exhibited RBM in their Raman spectra. (d) The catalyst region after being pretreated for 20 min but before CNT growth, where uniform nanoparticles can be observed at the edge.

The narrow diameter distribution intrigued us to examine the catalyst area of the sample because theoretically, catalyst nanoparticles with proper size are prone to attain nanotubes with uniform diameters. The catalyst region before CVD growth is shown in Figure 4.1 (d), as is expected, uniform Fe nanoparticles are formed after being reduced for 20 min, which will serve as the catalyst during the following growth process. The correlation between

the properties of catalyst nanoparticles and the morphology of the produced CNTs were further discovered by means of a series of parametric studies, including catalyst concentration, pretreatment time, and growth temperature.

4.3 Density and Length Control

4.3.1 Influence of growth parameters on CNTs morphology

4.3.1.1 Effect of catalyst concentration

In order to investigate the effect of catalyst concentration on the nanotubes morphology, we performed CVD process using FeCl_3 ethanol solution with varying concentrations of 0.005 M, 0.01 M, 0.05 M, and 0.1 M, respectively. All the other parameters were kept the same: 975 °C growth temperature and 20 min pretreatment time for reducing catalyst nanoparticles. The results are shown in SEM images 4.2 (a)-(d). Apparently, with the increase of the solution concentration, both the density and the length of the CNT arrays decrease significantly. In the aim for quantitative comparison, we grow CNTs on substrates that have the same dimension (1.5 cm long and 1 cm wide) for all samples, and then counted the number of the as-grown CNTs within the whole surface area of each sample. Figure 4.2 (e) plots the length distribution of nanotubes prepared with different catalyst concentrations. The drop of the nanotube number at particular length is catalyst concentration dependent: the majority of the nanotubes grown with lower catalyst concentration (0.005 M and 0.01 M) can reach a length up to 7 mm, however, most of the nanotubes grown with higher catalyst concentration (0.05 M and 0.1 M) stopped growing within the range of 2 mm.

Figure 4.2. SEM images of CNT arrays grown using CVD method, with different catalyst concentrations: (a) 0.005 M, (b) 0.01M, (c) 0.05M, and (d) 0.1 M. (e) Comparison of the number distribution of CNTs along their axial direction for the four as-prepared samples.

The phenomenal difference in the density and length from the four observations can be attributed to the size difference of catalyst nanoparticles that are altered by different catalyst concentrations. The catalyst region of the four samples were further revealed by SEM images (Figure 4.3 (a)-(d)), dense CNT networks with small catalyst nanoparticles attached on them were grown with lower catalyst concentration, on the contrary, samples with higher catalyst concentration tend to produce larger nanoparticles and more amorphous carbon covering the nanotubes.

Figure 4.3. SEM images of the catalyst region from samples prepared with 0.005 M (a), 0.01 M (b), 0.05 M (c), and 0.1 M (d) FeCl_3 ethanol solution, respectively.

These results suggest that low concentration normally yield small catalyst nanoparticles, and favor more nanotubes to grow long. High concentration, on the opposite, increases the possibility of forming nanoparticles with large size or making small nanoparticles agglomerate, resulting in growing short nanotubes, or even only producing amorphous carbon instead of CNTs.

4.3.1.2 Effect of pretreatment time

Pretreatment is an essential step for CNT growth, because the transition metal nanoparticles can only catalytically decompose hydrocarbon molecules after being reduced from the catalyst precursor. The properties of the nanoparticles are closely related to the pretreatment conditions. Here we keep the flow rate of the mixed gas constant, only change the pretreatment time to investigate how the morphology of the grown CNTs is affected. In the initial step, we set the pretreatment time to be 10 min, 20 min, and 30 min, respectively, and then grew CNTs at 975 °C using 0.005 M FeCl₃ as the catalyst precursor. The results are shown in Figure 4.4 (a)-(c), respectively, and the length distribution of CNTs with different pretreatment time is obtained and presented in Figure 4.4 (g). It is found that catalysts pretreated for 20 min are more favorable to grow dense and long CNT arrays than the ones pretreated for shorter or longer time.

We also compared the corresponding catalyst region of the samples with different pretreatment time (Figure 4.4 (d)-(f)). As shown in Figure 4.4 (d) (10 min pretreatment), the nanoparticles are not uniform, and some of the nanoparticles are not separated enough,

resulting in nanotubes clustering around them. This observation implies that 10 min pretreatment may be insufficient to reduce the nanoparticles from the precursors. With the pretreatment time increased to 20 min, it can be observed that more nanoparticles were derived and attached on the nanotubes (Figure 4.4 (e)). However, by further prolonging the pretreatment time to 30 min, the catalyst nanoparticles seem to be over-pretreated, as observed in Figure 4.4 (f). Due to the long-time exposure at high temperature, nanoparticles may lose their activity by aggregation or atom diffusion into substrate, leaving only a few nanoparticles active for catalyzing CNT growth.

Figure 4.4. SEM observations of CNT arrays and their corresponding catalyst regions with the pretreatment time of 10 min (a and d), 20 min (b and e), and 30 min (c and f), respectively. (g) Density of CNTs as a function of length obtained from samples with different pretreatment time.

4.3.1.3 Effect of growth temperature

Growth temperature is another critical factor that determines the morphology of CNTs,

for this reason, we lowered the growth temperature to 950 °C and 925 °C to grow nanotubes, while leaving other parameters unchanged. In order to compare the influence of growth temperature on catalyst nanoparticles with different sizes, we carried out two sets of experiments using 0.005 M (the lowest concentration) and 0.1 M (the highest concentration) FeCl_3 ethanol solutions at each growth temperature, respectively.

Figure 4.5. SEM images showing the morphology of CNT arrays grown at 975 °C (a), 950 °C (b), and 925 °C (c), respectively. The samples were prepared with 0.005 M FeCl_3 ethanol solution. (d) Length distribution of CNTs, showing temperature dependence.

For nanotubes grown with different catalyst concentrations, as shown in Figure 4.5 and

Figure 4.6, the variations of density and length show different trends upon the decrease of growth temperature. With lower catalyst concentration, the higher the growth temperature is, the denser and longer the nanotube arrays will be. However, for nanotubes originated from higher catalyst concentration, the density and length will be promoted at a moderate growth temperature instead of high temperature.

Figure 4.6. SEM images from the sample grown with 0.1 M catalyst solution at different temperatures: (a) 975 °C, (b) 950 °C, and (c) 925 °C. The corresponding comparison of length distribution is shown in (d).

The discriminating temperature dependences of the two outcomes indicate that catalyst nanoparticles may behave differently due to their particle size. For smaller nanoparticles

(prepared with lower catalyst concentration), higher temperature will increase their activity to nucleate CNTs. Relatively, the acceleration in carbon decomposition by increasing the growth temperature seems too aggressive for nanoparticles with larger size (prepared with higher catalyst concentration), the additive formation of amorphous carbon and graphite on their surface may deactivate the catalyst nanoparticles in an early stage [169].

4.3.2 Growth condition mediated catalysts effects

On the basis of the VLS growth mechanism for CNT synthesized via CCVD method, the first role of the metal catalysts is to confine dissociated carbon adatoms, which were decomposed from the gaseous hydrocarbon feedstock, close to the surface of the nanoparticles [170, 171]. The adsorbed carbon atoms then diffuse in the bulk catalyst nanoparticles or along the catalyst surface [172], when the solubility limit of carbon in the transition metal is reached, the carbon atoms precipitate out to nucleate ordered nanotube structure. Following this nucleation, with more carbon transformed through the catalysts, the nanotube then elongates by continuously incorporating the carbon into its sidewall [173]. It is important to note that each step of the growth process can be governed by the properties of the catalyst nanoparticles, which are intrinsically related to the size of the nanoparticles.

Theoretical calculation shows that the solubility of carbon in iron increases with increasing nanoparticle size [174]. For larger catalyst nanoparticles, a great amount of carbon needs to dissolve into the nanoparticles before reaching saturation and triggering the nucleation of CNTs. This long-time phenomenon makes larger nanoparticles (prepared with

high catalyst concentration) less efficient in nucleating and growing CNTs than smaller nanoparticles (prepared with low catalyst concentration) [173]. The high growth temperature (above 900 °C) also enables smaller nanoparticles more fluid than larger ones, promoting the carbon transformation and enhancing the nucleation [161]. As a consequence of the high nucleation rate and growth rate, dense and long CNTs can be obtained, as observed in Figure 4.2 (a). At the same time, the dissociation rate is proportional to the surface area of the catalyst nanoparticles at a given growth temperature, thus larger catalyst nanoparticles could allow a rapid dissociative adsorption of the carbon precursor and diffusion through the nanoparticles (the diffusion can be bulk or surface), compared with smaller catalyst nanoparticles. However, due to the lack of effective transformation of carbon, the high concentration of carbon in larger iron nanoparticles may overcoat on the nanoparticles [175], as evidenced by the observation of dense amorphous carbon in catalyst area of the sample derived with 0.1 M FeCl₃ solution (Figure 4.3 (d)). The formation of amorphous on the surface of the larger nanoparticles will either inhibit their catalytic behavior or even terminate the nucleation and growth in the early stage, resulting in low activity and short lifetime of the larger nanoparticles. Moreover, the morphology of catalyst could be altered during the pretreatment process. Nanoparticles that were over-pretreated may lose their catalytic ability due to the Ostwald-ripening-induced particle coarsening or subsurface diffusion [162, 176]. Lowering growth temperature could weaken the particle coarsening, at the same time, the dissociation and diffuse rate is slower at lower temperature, which could prevent amorphous carbon coating on larger nanoparticles. As a result of the enhanced catalysts activity and lifetime, the nucleation and growth from larger

nanoparticles could be drastically promoted. This explanation is bolstered well with the comparison in Figure 4.6, where nanotube arrays grown at 950 °C appeared denser and longer than the ones grown at 975 °C. However, the decrease in growth temperature also leads to decrease in catalysts mobility, reducing the carbon transformation through the catalyst nanoparticles. This limitation could be more dominant for smaller nanoparticles, which is the reason why both density and length decreased significantly when the growth temperature dropped (Figure 4.5).

4.3.3 Alignment difference with respect to CNTs density

It is noteworthy that topological defects may naturally occur in the CNT productions, especially at the sites with bent morphologies. Therefore, it is important to examine the alignment of the as-produced CNT arrays and investigate the influential factors, in order to provide a better candidate for the synthesis of IMJs.

Figure 4.7 (a) is a panorama SEM image showing the CNT arrays that were already studied in the previous section (an overall view of the CNT arrays shown in Figure 4.1 (a)). The nanotube arrays were grown out of the catalyst, extending in length up to 1 cm, directed by the gas flow. With the nanotube arrays elongating, the number of ultralong nanotubes decreases moderately. Figure 4.7 (b) presents the length distribution of the as-grown ultralong CNTs along their axial direction. Notably, at the region near the catalyst edge, where dense arrays were grown (3~4 nanotubes per 100 μm), a high percentage of nanotubes appear with wavy morphology, entangled with each other (Figure 4.7 (c)). On the other hand, as shown in Figure

4.7 (d), with the density of nanotubes dropping off in the region far away from the catalyst edge, straight nanotubes become dominant in the observation.

Figure 4.7. (a) Merged SEM image shows horizontally aligned CNT arrays grown from the catalyst region on Si/SiO₂ substrates. (b) Length distribution of CNTs grown on the whole sample (1.5 cm long, 1 cm wide). (c) SEM observation of CNT arrays taken near the catalyst edge and (d) SEM observation of CNT arrays taken far away from the catalyst edge. (e) A CNT bundle is formed with the attachment of the two neighboring nanotubes, due to the strong tube-tube interaction. (f) SEM image of one representative CNT from the sample acquired at a lower temperature, showing super straight morphology.

Since the alignment of CNTs is highly dependent on the flow dynamics, we calculated the Reynolds number (R_e) under our growth condition. For a given system, $R_e = \rho v d / \mu$, where ρ is the gas density, v is the flow velocity, d is the quartz tube diameter, and μ is the gas viscosity. Detailed parameters are listed in Table 4.1. Based on our calculation, the R_e inside our CVD system is estimated to be 0.66 at 975 °C, indicating the gas flow is a laminar flow for

the CNT synthesis taking place ($R_e < 2000$). The exceedingly low R_e demonstrates that the gas flow inside the growth system is quite stable, which, in conjunction with the low gas flow rate we used (30 sccm in total) for the growth, minimizes the effect of the dynamic conditions on the alignment of the nanotubes [59, 61]. In this case, the observed difference in morphology with respect to tube density indicates that the alignment of nanotubes tends to be suppressed due to the crowding effect by high-density of nanotubes growing together [67]. This effect can be attributed to the local turbulence of the gas flow induced by neighboring nanotubes and also the strong tube-tube interaction derived from the van der Waals force between adjacent nanotubes [58]. For dense CNT arrays, the effect becomes so prominent because of the limitation of separation space, so as to force neighboring nanotubes to get attached together to form a bundle (Figure 4.7 (e)).

Table 4.1. Parameters for Reynolds number calculation (at 1248 K).

Temperature	Growth temperature (1248 K)
Gas mixture density (ρ)	0.338 kg/m ³
Flow velocity (v)	1.02×10^{-3} m/s
Gas mixture viscosity (μ)	1.3×10^{-5} Pa·s
Quartz tube diameter (d)	25×10^{-3} m
Reynolds number	0.66

To further validate the result from another aspect, we inspected another sample where sparse CNTs were grown. The sample was prepared at a lower temperature (900 °C) through

similar growth procedure, ultralong CNT arrays can also be obtained but with a lower density, around 1~2 nanotubes per millimeter, as a result of the lacked energy for catalyst nanoparticles to nucleate nanotubes at lower temperature [169]. As shown in Figure 4.7 (f), one representative individual CNT can be observed without being surrounded by any other nanotube. The isolation of the nanotube makes itself free from perturbation by other CNTs, whereupon it appears super straight throughout the length. Thus, on the basis of the strong correlation between the degree of alignment and the density of the CNT arrays as observed, it is instructive to suggest that the alignment of ultralong nanotubes could be greatly affected by the local flow condition during growth.

4.4 Electrical Measurements

4.4.1 Electrical characterization of isolated SWNTs

Since the electrical properties of a SWNT are intimately related to its diameter and chirality, we carried out electrical measurement on both metallic and semiconducting SWNTs, respectively. Figure 4.8 (a) and (c) display typical $I_{ds} - V_{ds}$ characteristics for an individual metallic SWNT and a semiconducting SWNT, respectively. For the measurements on each nanotube, seven curves were recorded by changing the gate voltage from -24 V to 24 V. The seven curves in Figure 4.8 (a) are overlapped, indicating that source-drain current of the metallic SWNT is independent of gate voltage (see Figure 4.8 (b)). For the semiconducting SWNT, in contrast, the conductance varies drastically with the change of the applied gate voltage values. The corresponding electrical behavior for the individual semiconducting SWNT

incorporated in the back-gated FET device (channel length is 300 μm) is exhibited in Figure 4.8 (d), which was recorded under constant bias voltage of 2V. The curve shows a typical p-type FET where the “on” and “off” states can be clearly resolved. The current on/off ratio ($I_{\text{on}} / I_{\text{off}}$) is around 10^3 , which is comparable to that of short channel length SWNT FETs.

Figure 4.8. Measured $I_{\text{ds}} - V_{\text{ds}}$ curves for (a) an individual metallic SWNT and (c) an individual semiconducting SWNT under seven different gate voltages. Their corresponding electrical behavior of the room-temperature current (I_{ds}) versus gate voltage (V_{g}) is exhibited in (b) and (d), respectively, under a bias voltage $V_{\text{ds}} = 2$ V.

4.4.2 Performance of SWNT FETs

According to the $I_{\text{ds}} - V_{\text{g}}$ graph, several important electrical features associated with

the FET performance can be obtained. A simple introduction is given here to explain how we measured the values of each electrical feature.

(1) The on-current (I_{on}), off-current (I_{off}) and current on/off ratio ($I_{\text{on}} / I_{\text{off}}$). In our case,

I_{on} and I_{off} correspond to the drain currents at $V_G = -24 \text{ V}$ and $V_G = 24 \text{ V}$, respectively.

(2) The threshold voltage (V_{th}) is the voltage where the nanotube begins to be conductive (switch on). It can be extracted using the steepest portion of the from the $I_{\text{ds}} - V_G$ curve intersecting the x-axis.

(3) Transconductance (g_m) measures the efficiency of the gate response. It can be obtained from the slope of the $I_{\text{ds}} - V_G$ curve at the voltage of V_{th} .

(4) Hysteresis width (ΔV_{th}) is the difference in threshold voltage between the forward and reverse gate voltage sweeps.

For FETs fabricated with individual SWNTs, the diameter of the nanotube is one critical factor that dictates band gap and injection barriers, which in turn determines the performance of a FET. Therefore, we analysed the above-mentioned performance parameters with regards to nanotube diameter. We conducted the electrical measurements on seven SWNT FETs, all of which were fabricated using one individual semiconducting SWNT as conduction channel. Prior to the measurements, the diameter of each SWNT was acquired using Raman characterization with three excitation lasers, based on the relationship between RBM frequency and nanotube

diameter: $d_t = 248 / \omega_{RBM}$ [150]. The recorded RBM frequencies and the calculated diameters are listed in Table 4.2.

Table 4.2. Lists of nanotube diameters for each SWNT FET, obtained from the corresponding RBM frequencies.

Device No.	RBM frequency (cm ⁻¹)	Diameter (nm)
#1	202.6	1.22
#2	170.8	1.45
#3	153.7	1.61
#4	155.3	1.6
#5	173.4	1.43
#6	165.3	1.5
#7	160	1.55

Figure 4.9 (a)-(f) shows the performance parameters as a function of nanotube diameter. With the increase of d_t , I_{on} and I_{off} increase from around 62.5 nA and 30 pA to around 202 nA and 900 pA respectively, as displayed in Figure 4.9 (a) and (b) in logarithmic scale. As the band gap can be seen to depend inversely on diameter ($E_g = 0.84\text{eV} / d_t$ [177]), when the tube diameter increases, the band shifts and band bending at the contacts become smaller. This allows larger carrier transport through the valence bands and conduction bands, hence both I_{on} and I_{off} increase. The I_{on} / I_{off} decreases from 2083 to 224 when the diameter increases from 1.22 nm to 1.61 nm, as plotted in Figure 4.9 (c). However, the peak transconductance increases from 32.8 nS to 81 nS with increasing nanotube diameter (see Figure 4.9 (e)). It is because reduced band gap favours carrier transport and minors the influence of Schottky barrier on carrier transport, resulting in a steeper slope of the $I_{ds} - V_G$ curve.

Figure 4.9. Variation in FET parameters with nanotube diameter. All the FETs were made of one isolated SWNT. (a) on-current (I_{on}), (b) off-current (I_{off}), (c) current on/off ratio (I_{on}/I_{off}), (d) threshold voltage (V_{th}), (e) transconductance (g_m), and (f) hysteresis (ΔV_{th} , black square) and the estimation of charge traps in the SWNT FETs (using number of charges trapped per unit length, blue circle). The error bar given in the plots are related to estimates in the measurements.

As shown in Figure 4.9 (d), the threshold voltage reduces from 12 V to 5 V with the increase of d_t , indicating a smaller gate voltage is required to turn “on” the device. However, there are large derivations of our experimental values from the theoretical values which can be obtained using the equation of $V_{th} = 0.577aV_{\pi} / d_t$, where $a \approx 2.49 \text{ \AA}$ is the carbon to carbon atomic distance, $V_{\pi} \approx 3.033 \text{ eV}$ is the carbon p-p bond energy in the tight bonding model [178, 179]. One possible reason is due to the presence of charge traps along the SWNTs, which can largely affect the voltage required to turn “on” the device. Because at the Si/SiO₂ interface of conventional silicon transistors, thermally grown silicon oxide has interface traps and oxide traps [180]. Our measurement of the hysteresis corroborates this suspect, because hysteresis is not an intrinsic property of the SWNTs, the appearance of hysteresis is due to the presence of charge traps along and around the SWNT during electrostatic gating. These traps result in a residual electric field that continues to electrostatically dope the SWNT upon removal of the applied electric field. Figure 4.9 (f) shows the hysteresis obtained from all the devices, it can be seen that the trend is dependent on the tube diameter. The estimation the approximate number of charges trapped per unit length can be derived by $N = (C / L)\Delta V_{th} / 2e$, where C / L is the capacitance per unit length and can be derived from simple capacitor model, e is electronic charge and ΔV_{th} is hysteresis width [181]. As included in Figure 4.9 (f), the calculated trap number has the same diameter dependence. The reason for such diameter dependence is that the charges are trapped at the CNT-SiO₂ interface, nanotubes with larger diameter have larger effective contact area, leading to more trapped charges and higher hysteresis.

4.5 Conclusions

We have successfully synthesized horizontally aligned CNT arrays on Si/SiO₂ substrate by employing CVD method. By simply dip-coating catalysts on substrates, CNT arrays with density up to 3~4 nanotubes per 100 μm and lengths greater than centimetre scale can be obtained under appropriate growth condition. The density and length of such CNTs could be well controlled by growth parameters, such as catalyst concentration, pretreatment time, and growth temperature. The mechanism could be explained by the activity and lifetime of the catalyst nanoparticles which could be significantly altered by growth parameters. As a direct result, the catalyst nanoparticles with different properties could impact the resultant nanotubes density and length.

We also investigated the alignment difference of the CNTs with respect to the density of the array and found that the alignment of nanotubes tend to be suppressed due to the crowding effect by high-density of nanotubes growing together. The study of the flow dynamics suggested that the local flow condition of the CNTs could be disturbed by other neighboring nanotubes, which induces turbulence to the growing nanotube, resulting in degradation in the alignment.

Finally, electrical measurements were conducted on isolated SWNTs, which revealed the intrinsic transport properties of metallic and semiconducting SWNTs respectively. FETs were fabricated by incorporating individual semiconducting SWNTs as the conduction channel. The corresponding analyses of the performance parameters showed that the electrical performance

of the FETs was highly dependent on the nanotube diameters. This result suggests a possible way to achieve high-performance SWNT FETs.

The successful synthesis of high-quality SWNT arrays provides a direct platform for the preparation of IMJs. The controllability with regards to the length, density and alignment of such IMJ carriers will allow us to create IMJs with feasible configurations and tuneable properties.

Chapter 5 Carbon Nanotube Intramolecular

Junctions Induced by Strain

5.1 Introduction

In this chapter, we developed an advanced strategy to controllably prepare CNT IMJs, by intentionally inducing strains into individual SWNTs based on a CVD process. A general description of the approach involves growing ultralong SWNTs on trenched substrates. It is well accepted that the CVD growth of ultralong and well-oriented SWNTs follows the empirical “floating growth” mode, in other words, the catalyst particles and the growing nanotubes are first lifted up by the gas flow at the initial growth stage, and then the gas flow will keep the nanotubes floating during their elongation [31]. On the basis of this growth mechanism, the ultralong SWNTs are capable of flying over the substrate and eventually lying suspended across a series of trenches. For this reason, the nanotubes that are partially suspended across trenches may be subject to mechanical deformations, which will influence the nanotubes lattice and electronic structures, resulting in the formation of SWNT IMJs.

Aside from introducing regular strains into nanotubes, the trenches can also define the as-prepared IMJs location—in the vicinity of the trench edge, owing to their geometric configuration. In this way, by taking the trenches as markers and with the help of SEM, we utilize Raman spectroscopy to rapidly and precisely identify the SWNT IMJs and comprehensively investigate their properties and their impacts on the parent SWNTs. Moreover,

it is feasible to probe the unique electrical transport properties of the IMJs by means of electrical characterization on the partially suspended SWNTs.

5.2 Preparation of SWNT IMJs

Prior to performing the CVD growth, 20/50 μm wide, 2 μm deep trench patterns were fabricated on the surface of Si/SiO₂ wafers. The space between two adjacent trenches was 200 μm . A strip of FeCl₃ catalysts was deposited on the top surface of the trench, CVD process was then carried out to grow ultralong SWNT arrays on such trenched substrates. For the sake of making sure that we are introducing strains and generating defects onto isolated nanotubes instead of thin bundles, sparse SWNT arrays with wide separation are better candidates in this study. As discussed in Chapter 4, the density of the SWNT arrays can be greatly affected by the growth conditions. Therefore, we set the growth conditions as: 0.01 M FeCl₃ ethanol solution (pretreated for 20 min) was used to catalyze SWNTs grown at 950 °C in 4 sccm Ar, 6 sccm H₂ and ethanol vapor (bubbled by 20 sccm Ar through the ethanol vessel at 20 °C) mixed gas environment.

Figure 5.1 (a) shows a typical result of the SWNTs stemming from the catalyst region and elongating downstream while crossing trenches. As seen in the SEM observation, the SWNTs are lying parallel to each other, and the separation distance between any two adjacent SWNTs is more than 100 μm , which is large enough for carrying out specific Raman spectroscopy study on spatially isolated nanotubes. From the high magnified SEM image (Figure 5.1 (b)) of a representative individual SWNT, which extends over 1 cm in length, the nanotube

can be clearly recognized as three different segments: the sitting-on-substrate segment (SOS), the transition segment (trans, in the vicinity of the trench edge), and the suspended segment (SUS). The SOS portion of the nanotube appears much brighter and wider than the SUS portion at the accelerating voltage of 1 kV.

Figure 5.1. (a) An SEM image showing oriented SWNTs grown on a trenched Si/SiO₂ substrate. (b) A zoom-in SEM observation at one edge of a 20 μm wide, 2 μm deep trench, showing that the nanotube is well suspended over the trench.

5.3 Identification and Characterization of SWNT IMJs

Using Raman Spectroscopy

To validate that IMJs have been generated onto the SWNTs using Raman characterization, it is important to make sure that we are studying isolated SWNTs instead of

thin bundles, and the studied SNWTs are relatively defect-free. Because only after we have eliminated other possibilities that may affect the tube structure and properties, can we attribute the changes of the tube structure and properties to the formation of IMJs. Therefore, the structure and properties of the as-grown SWNTs were characterized using Raman spectroscopy in the first place.

5.3.1 Raman Characterization of individual SWNTs

At single nanotube level, resonance Raman measurements were performed on the SOS segments of one representative ultralong SWNT (longer than 1 cm). From a Raman G band mapping image (inset of Figure 5.2), the SWNT can be spatially resolved. To study its characteristics, Raman spectrum was collected on a single point (more than 1 mm away from the catalyst region) of the nanotube with 514 nm laser excitation, as shown in Figure 5.2. As expected for an individual SWNT, the Raman spectrum displays one single RBM peak centered at 126 cm^{-1} , with a line width (full width at half maximum, FWHM) of 8 cm^{-1} , we thus obtain $d_t = 1.97 \text{ nm}$ by using the relation $d_t = 248 / \omega_{\text{RBM}}$ for nanotubes grown on Si/SiO₂ substrates [150]. By comparing with the theoretical Kataura plot, this nanotube is tentatively assigned to the (22, 5) semiconducting tube [182], whose optical transition energy E_{44}^S is in resonance with the 2.41 eV laser excitation energy. The intense G band of the nanotube is also displayed in Figure 5.2, which can be fitted by two principal Lorentzians, with the peak at 1596 cm^{-1} (FWHM = 7 cm^{-1}) for the G^+ component and the peak at 1586 cm^{-1} (FWHM = 9 cm^{-1}) for the G^- component, respectively. This G band feature further corroborates the semiconducting nature of the

nanotube [154], which is consistent with the RBM assigning. Moreover, the narrow line widths of the two G band components indicate that the Raman spectrum is taken from one isolated SWNT instead of a thin bundle [183]. No obvious D band is observed in the Raman spectrum, indicating the nanotube is of high quality and the density of defects in this nanotube is exceedingly low [149]. Finally, a single sharp and symmetric Lorentzian peak is observed at 2694 cm^{-1} , with $\text{FWHM} = 34\text{ cm}^{-1}$. This peak is assigned to the G' band, which comes from a double resonance process [168]. The symmetric line shape, narrow line width and high intensity of the G' band suggests the examined nanotube is an isolated SWNT, rather than a DWNT or a small bundle of SWNTs [168].

Figure 5.2. A typical G band mapping image (inset) of the SOS segment of one isolated as-grown SWNT, with 514 nm excitation wavelength. A representative Raman spectrum acquired from one single point of the SOS segment, exhibiting strong Raman features of RBM, D band, G band, and G' band.

To provide additional confidence that the examined ultralong nanotube is an isolated SWNT, we mapped the nanotube using SEM and AFM over a large area. There is only one nanotube observed in both SEM and AFM images. Tapping mode AFM imaging was also carried out on an SOS segment for a total length of 200 μm . The 2D mapping image in Figure 5.3 (a) shows a 30 μm portion of the probed SOS segment, a more detailed image of the nanotube is shown in the enlarged AFM image of Figure 5.3 (b). The corresponding height profile indicates the diameter of the nanotube is around 1.9 nm, which is consistent with our Raman calculation. Furthermore, the AFM height profiles acquired along the tube length over the entire image show a consistency of 1.85-1.95 nm for the range of the nanotube diameters, which is indicative of a uniform individual SWNT [100].

Figure 5.3. (a) Tapping mode AFM mapping of an SOS segment in a $30 \times 30 \mu\text{m}^2$ area. (b) An enlarged AFM image of the area enclosed by the blue dashed square in (a), showing the isolated nanotube. (c) A typical height profile of the nanotube indicated in (b), showing the diameter is around 1.9 nm.

5.3.2 Chiral and dimensional uniformity

As mentioned previously, the 1 cm long isolated nanotube lies partially on the Si/SiO₂ substrate with spanning across plenty of 20/50 μm trenches along its length, as sketched in Figure 5.4 (a). To evaluate its structural and chiral uniformity, a series of Raman spectra were acquired at different on-substrate locations (denoted as i.e. A, B, etc. in Figure 5.4 (a)), as the laser beam was moved along this nanotube.

Figure 5.4. (a) A sketch of the 1 cm-long isolated nanotube lying on Si/SiO₂ substrate, spanning over 20/50 μm trenches. (b) Evolution of Raman features along the nanotube length. The series of Raman spectra were acquired as the 514 nm laser beam moving along the nanotube. The labels (#A-#D) indicate different locations on the Si/SiO₂ substrate, referring to (a).

The corresponding evolutions of the Raman features are presented in Figure 5.4 (b). It is seen that both the RBM and the G band almost sustain their frequencies unshifted and their line shapes unchanged at every single spot along the nanotube, indicating a high degree of structural and chiral consistency in this SWNT. The good uniformity of the dimension and chirality of the nanotube along its length promises the possibility to controllably create SWNT IMJs in desired locations.

5.3.3 Identification and characterization of SWNT IMJs

As we proposed, patterns of trenches were pre-fabricated onto the Si/SiO₂ substrates, after performing CVD growth of SWNTs, the IMJs are expected to be synthesized at the edge of the trenches. The pre-defined location not only enables fast identifying the as-prepared nanotube junctions, but also facilitates clarifying their properties via multiple characterization tools. Because Raman modes in SWNTs are quite sensitive to the nanotube structure and chirality, accordingly, we utilized Raman scattering to continuously track different segments along one specific nanotube axis. By thoroughly examining changes in the tube structure and chirality, we explored the IMJs formation on such a partially suspended nanotube.

We continuously mapped the (22, 5) nanotube with it extending across a 20 µm wide trench, using the laser excitation $E_{\text{laser}} = 2.41$ eV. Figure 5.5 shows a 2D Raman mapping image of the partially suspended SWNT superimposed on a confocal optical image where the trenched structure is visible. The corresponding SEM image additionally provides spatial information about the nanotube lying across the 20 µm wide, 2 µm deep trench. From the substrate to the

trench along the tube length, the “SOS”, “trans”, and “SUS” segments, as we named previously, are respectively discernible. Apparently, the SUS segment looked taut and straight both in the mapping image and its corresponding SEM image.

Figure 5.5. A 2D G band map of the (22, 5) nanotube partially suspended on a 20 μm wide trench, its confocal optical image shows the geometric configuration of the trench. The three regions can be clearly differentiated from the mapping image, as indicated as “SOS”, “trans”, and “SUS”. Its corresponding SEM image provides spatial information about the nanotube lying suspended over the trench.

To investigate the formation of the IMJ and elucidate the formation mechanism, we acquired Raman spectra from each region and displayed them in sequence for comparison, as shown in Figure 5.6. First of all, the RBM mode shows a downshift in the frequency by 2.5 cm^{-1} from SOS segment to SUS segment, while no obvious RBM signal is detected for the trans segment. The observed downshift in RBM frequency is in agreement with the results reported

previously [137, 184], which attributed this shift to the radial deformation of the nanotube induced by tube-substrate interactions, which distort the nanotube cross section from a circle to an ellipse. In addition, the FWHM of the RBM is reduced significantly in the SUS segment (5 cm^{-1}) compared with the SOS segment (8 cm^{-1}), which is thought to be a result of a relatively undisturbed environment for the SUS segment [185]. Moreover, since the RBM is highly sensitive to the resonance condition, the absence of RBM in the trans segment suggests a change occurred to the nanotube structure within this area, which turns it “off resonance” with the laser excitation. Based on the drastic evolution of the RBM modes through the three regions, we speculate that an IMJ may have been formed in the trans segment.

Figure 5.6. Comparison of Raman features obtained from SOS, trans, and SUS segments respectively, showing evolutions through the three regions. ($E_{\text{laser}} = 2.41 \text{ eV}$).

Accordingly, the higher-frequency Raman features (G band and D band) also undergo a drastic evolution pattern through the three segments. As described above, the G band of the SOS segment displays a semiconducting line shape, with G^+ peak at 1596 cm^{-1} and G^- peak at 1586 cm^{-1} , respectively. The weakness of the D band implies this nanotube is defect-free. As the laser beam goes towards the trench, although the nanotube sustains its semiconducting characteristic, the G^+ band downshifts in the frequency to 1589 cm^{-1} for the trans segment and further to 1585 cm^{-1} for the SUS segment (see Figure 5.6, right comparison). Several possible reasons may account for this continuous downshift in the G band frequency, such as temperature effect, doping, and strain [186-188]. Since all the Raman measurements were carried out at room temperature, we can thus eliminate the temperature effect. Besides, due to the fact that all SWNTs lie on the SiO_2 layer, which is an insulating material, the electron donation from the substrate to the nanotubes is unlikely [137]. Another possibility of the downshift is due to the “self-built” tensile strain, existing in the SWNTs decorated with graphite dots [189]. However, there is no graphite dots decorated on our SWNT, as observed in the enlarged AFM image, which demonstrates the so-called “self-built” tensile strain does not exist in our SWNT sample. Therefore, it is reasonable to attribute the downshift in G band frequency to the uniaxial strain induced by the trenched structure, which could low the G^+ peak frequency by 40 cm^{-1} under a strain of 1.65% [190]. Finally, a strong D band at 1349 cm^{-1} becomes clearly visible for Raman spectrum taken from the trans segment. With the knowledge that the D band is associated with the presence of defects, it is quite reasonable to suggest that defects have been generated in the trans segment of this nanotube, which is consistent with that concluded

based on the RBM observations.

We further specifically investigated the G band feature obtained from the trans segment. Unlike the G band profiles of the SOS and SUS segments, which only consist of two components, the G band curve of the trans segment can be well fitted by five Lorentzian peaks, as shown in Figure 5.7. For each component, its peak position and FWHM is indicated in the figure. Previous studies have reported that due to the nanotube curvature effects, up to six G modes are Raman allowed in SWNTs [154]. In particular, polarized Raman studies of SWNTs revealed that for semiconducting tubes, the G band profile can be deconvolved into four intrinsic components with the following symmetries: $\omega_{E_2}^- [E_2(E_{2g})]$, $\omega_G^- [A(A_{1g}) + E_1(E_{1g})]$, $\omega_G^+ [A(A_{1g}) + E_1(E_{1g})]$, and $\omega_{E_2}^+ [E_2(E_{2g})]$ [191]. Thus, we can assign the two peaks located at 1589 cm^{-1} (6 cm^{-1}) and 1577 cm^{-1} (4 cm^{-1}) to the G^+ and G^- modes, respectively. The two wide shoulders appear on the low-frequency side (1568 cm^{-1} (16 cm^{-1})) and high-frequency side (1594 cm^{-1} (14 cm^{-1})) are assigned to E_{2g}^- and E_{2g}^+ phonon modes, respectively. The appearance of new G peaks suggest that in addition to uniaxial strain, bending deformation may also be induced to the SWNT at the edge of the trench (trans segment region). Because, the uniaxial strain does not change the numbers of Raman modes [188], however, the predominant effect of bending deformation on Raman spectra of SWNTs is to give rise to number of active Raman modes [192]. Intriguingly, a new component at $\sim 1619 \text{ cm}^{-1}$ (26 cm^{-1}) emerges as a shoulder of the G profile in this region, which is normally assigned to the D' band in graphitic materials [193]. It is well established that the D' band is a defect-induced double resonance feature in CNTs [194]. As a consequence, its

appearance in the Raman spectrum of trans segment, in conjunction with the rather active D band in this region, can be taken as a fingerprint of the generation of defects onto the investigated SWNT. Based on the above analyses, we may conclude that topological defects have been generated onto the partially suspended SWNT, leading to the formation of IMJs upon certain conditions. In another aspect, the reviewed transition in the line shape of the G band along the nanotube identifies the IMJ as a semiconducting-semiconducting (S-S) junction.

Figure 5.7. A specific analysis of the G band taken from the trans segment, using Lorentzian function fitting. The experimental profile (blue line), each fitting Lorentzian profile (green line), and calculated total profile (red line) are displayed respectively.

Giving that the I_D/I_G and the G band frequency provide great information in

identifying the as-fabricated IMJs, the evolutions of the I_D/I_G and the G band frequency are thereby plotted as a function of the positions along the tube length. As shown in Figure 5.8 (a), the I_D/I_G reaches its maximum value in the transition area, while the G band starts significantly downshifting in frequency at the edge of the trench. It is worth noting that this is a common phenomenon when we studied other trenches with SWNTs lying across them, i.e. three other trenches revealed similar trend of I_D/I_G and G band frequency, as displayed in Figure 5.8 (b) and 5.8 (c), respectively. This incredible result suggests that the formation of IMJs is universal in our experiment, regardless of the structure and chirality of SWNTs and the dimension of the trenches.

Figure 5.8. I_D/I_G and ω_G versus position along the axis of the nanotube. The Raman mapping image of the nanotube across the trench is used as a reference indicating the relative positions, where the middle of the trench is set as "0". Similar trend of the I_D/I_G variation (b) and G band frequency shift (c) can be also observed in other trenches.

5.4 Formation Mechanism

As discussed in the previous section, it has been validated that uniaxial strain and bending deformation have been induced to the SWNTs that lie across trenched structures. This trench-induced strain could alter the structure and properties of the nanotubes, resulting in IMJs formed at specific locations. The next questions may be: how the strains were induced, and how IMJs were formed because of the strains.

We try to explore the formation mechanism from the perspective of structural manipulation of the growing SWNT by trenched structures. According to the tip growth mechanism, ultralong SWNTs are believed to float above the substrate and then settle down. The trenches on the substrates produce a height difference between the top flat surface and the trench bottom, which will deflect the suspended segments downwards due to the gravity of the SWNTs. The deflection varies with respect to the trench dimensions. For narrow and deep trenches, the SWNTs could lie fully suspended across the trenches. On the contrary, the suspended SWNTs are quite possible to touch the trench bottom when they are lying across wide and shallow trenches, as shown in Figure 5.9 (a) (100 μm wide, 5 μm deep trench). Additionally, the trenched structures may cause local turbulence to the gas flow, as reviewed in Figure 5.9 (b), which may bring the nanotube stuck to the lower substrate. Furthermore, previous studies reported that thermal oscillations could also be responsible for the unsuccessful nanotube suspensions [195]. In particular, for our investigated SWNT, which lies across a 20 μm wide, 2 μm deep trench, the speculation was confirmed by the fact that we did

not acquire Raman spectra from the middle portion (6 μm long) of the SUS segment. Admittedly, this “missing” phenomenon may also arise from other possibilities, for example, the laser beam was not focused on the nanotube or the nanotube was broken after performing Raman characterization. However, when we adjusted the focus to make the laser beam focused on the bottom of the trench and then run the Raman mapping procedure. Still, the middle part of the nanotube is “missing” in the Raman mapping image. In another aspect, the suspended nanotube still can be seen from the SEM observations after it was characterized using Raman spectroscopy. Thus we may conclude that SWNTs are not fully suspended across wide and shallow trenches, leaving the middle part in contact with the lower substrates. The strong interactions between the substrate and the stuck SWNT may change the resonance window, resulting in the stuck portion out of resonance.

Figure 5.9. (a) SEM image of an individual SWNT growing across a 100 μm wide, 5 μm deep trench. A portion of the SUS segment is stuck to the lower substrate. (b) SEM image showing the nanotube with curve morphology, which is induced by local turbulence because of the trenched structure.

According to previous calculation, the interaction between CNTs and Si/SiO₂ surface

could be as large as 5 pN/nm and propagate along the tube length [196]. In this way, the stuck portion would drag the suspended portion downwards, which introduces elongation to the nanotube and promotes bending deformation at the edge of the trench. When the SWNT is subjected to such bending deformation and uniaxial strain, its outer side will be stretched while its inner side will be compressed. As a result, the C-C bonds are lengthened and shortened on the outer and inner side, respectively. The vibration of carbon atoms in the tangential direction of the nanotube gives rise to the G band shifting in frequency accordingly. To some extent the carbon atoms vibrate, the C-C bonds will be broken and rebounded due to the mechanical instability, leading to the formation of topological defects in nanotubes in order to release the strain energy.

5.5 Electrical Measurements on SWNT IMJs

A typical FET setup was designed for electrical transport measurements on the as-fabricated SWNT IMJs. As depicted in Figure 3.4 (b), source and drain electrodes were deposited on top of the Si/SiO₂ surface, connected by one individual suspended SWNT. This design could deliver the electrical transport properties of the IMJ, because the IMJ will dictate the performance of the entire nanostructure. For comparison, another pair of electrodes was fabricated next to the IMJ device, on the same individual SWNT, exhibiting the intrinsic transport properties of this semiconducting SWNT.

Typical $I-V$ characteristics of the SWNT (SOS) and the IMJ (SUS) obtained at zero gate voltage are presented in Figure 5.10. The SOS segment shows a symmetric $I-V$ curve, with a

conductance of 26.4 nS at zero gate voltage. In striking contrast, the SUS segment exhibits an asymmetric nonlinear feature, which is similar to that of a rectifying diode. Basically, this rectifying behavior can be taken as a possible signature for an M-S junction [84] or an S-S junction [86]. In our case, with a combination of the Raman results, we consider it as an S-S junction rather than an M-S junction, and can be explained on the basis of the following speculations: the band gap of the ultralong SWNT was tuned by the induced strain [118], switching the parent nanotube into a small-gap semiconducting SWNT, enabling an S-S junction at the interface of these two segments.

Figure 5.10. $I - V$ characteristics of the SWNT (SOS segment) and the IMJ (SUS segment), respectively.

5.6 Conclusions

In this chapter, we demonstrated a simple and reliable method to controllably prepare SWNT IMJs, by growing ultralong SWNTs on trenched Si/SiO₂ substrates. With a combination of SEM and Raman spectroscopy, the presence of IMJs has been verified. Rectifying behavior was observed from the electrical measurements on the as-prepared IMJs. Elaborate Raman characterizations of the IMJs identified the junction as an S-S type, and attributed the formation to the strains induced onto the suspended SWNTs by the trenched structures. Because of the introduced uniaxial strain and bending deformation, C-C bonds were significantly changed and topological defects were generated onto the parent SWNT, resulting in the formation of IMJs. From the electronic structural point of view, the strains could drastically tune the band gap of the parent SWNT, forming a conduction barrier at the interface of the two semiconducting nanotube segments, which should be responsible for the exhibiting rectifying behavior of the S-S junction.

The trenches employed here show tremendous advantages: firstly, they provide a feasible, controllable, and straightforward way to synthesize SWNT IMJs. Secondly, the geometry of the trench defines specific IMJs formation location, facilitating the identification and characterization of the IMJs. Finally, the structures and properties of the IMJs can be modulated by adjusting the dimensions of the trenches, promising an approach to fabricate different types of IMJs at the same time. Our research into the IMJs is directed toward improving the fabrication and integration of CNT-based nanoelectronics.

Chapter 6 Carbon Nanotube Intramolecular

Junctions Induced by Interactions

6.1 Introduction

For the CVD production of CNTs, inevitably, the structures and properties of the CNTs are affected by the surrounding environment. A direct consequence of the tube-environment interactions is the deformation of nanotubes. CNTs placed on flat dielectric substrates, such as Si/SiO₂ substrates, could be compressed in the radial and axial direction, due to the surface van der Waals forces [32]. Nanotube/lattice or nanotube/atomic steps interactions could be introduced to CNTs grown on single crystal substrates, i.e. quartz, or polycrystalline silicon substrates [135, 185, 197]. Intertube coupling, which is dominated by van der Waals interaction, but also contains a covalent component, could deform SWNT in pairs or in bundles, causing the contact region flattening [140]. Upon these interactions, the structural and physical properties of CNTs will be significantly modified. In this way, an IMJ have been formed between the suspended and supported parts of one individual SWNT [198]. Y-junctions have also been observed as a portion of SWNT pairs or bundles [58, 138].

Resonance Raman spectroscopy is a powerful and nondestructive tool for characterizing the lattice structure and electronic structure of SWNTs at single nanotube level. In particular, it has been largely employed to reveal changes in SWNTs caused by environmental effects, because Raman modes could respond differently to these effects [199]. In this chapter, we

intentionally fabricated IMJs by use of tube-substrate and tube-tube interactions, and comprehensively characterized the as-obtained IMJs by means of resonance Raman spectroscopy.

In addition to experimental observations, we also performed first principle calculations to describe the role of tube-tube interaction in the formation of Y-junctions. To optimize the geometry of individual SWNTs in the thin bundle, we used density functional theory (DFT) within the generalized gradient approximation (GGA). Here we brief the fundamental information of first principle theory for our simulation.

In first principle theory, the basic equation that is used to describe the electronic properties of molecular system (N_e electrons and N_n nuclei) is the many-body Schrödinger equation:

$$\hat{T}\Psi_{\text{MB}} + \hat{V}\Psi_{\text{MB}} = -i\frac{d\Psi_{\text{MB}}}{dt} \quad (6.1)$$

where $\Psi_{\text{MB}}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{N_e}; \vec{R}_1, \vec{R}_2, \dots, \vec{R}_{N_n})$ is the many-body wavefunction, $\hat{T}$ and $\hat{V}$ are the kinetic and potential energy operators respectively, and the coordinates of electrons and nuclei are $\vec{r}_i$ and $\vec{R}_i$. Based on the Born-Oppenheimer approximation [200], the nuclei can be treated as classical particles and considered to be fixed in space, the many-body problem is therefore reduced to concern a system of electrons moving in some external potential $V_{\text{ext}}(\vec{r}_i)$, i.e. the potential created by the interaction between the electrons and nuclei. For most purposes, only

the ground state of the electronic system is considered, then it becomes the time-independent many-electron Schrödinger equation:

$$\hat{H} \Psi = [\hat{T} + \hat{V}] \Psi = E \Psi \quad (6.2)$$

where $\hat{H}$ is the Hamiltonian, E is the ground state energy of the system of electrons.

There are many methods for solving time-independent many-electron Schrödinger equation. Here DFT provides one computationally appealing approach by assuming that the ground state in an external potential is only determined by the electron density $n(\vec{r})$. In history, two important theorems were proved by Hohenberg and Kohn to introduce the fundamental references for the DFT. Theorem one: If two systems of electrons, one trapped in a potential $V_{ext,1}(\vec{r})$ and the other in $V_{ext,2}(\vec{r})$, have the same ground-state density $n(\vec{r})$ then necessarily $V_{ext,1}(\vec{r}) - V_{ext,2}(\vec{r}) = const$. Theorem two: For any positive integer N and potential $V_{ext}(\vec{r})$, the ground state energy E_0 can be obtained by minimizing the density functional:

$$E[n(\vec{r})] = F[n(\vec{r})] + \int V_{ext}(\vec{r}) n(\vec{r}) d^3r \quad (6.3)$$

The function $F[n(\vec{r})]$ can be expressed by Kohn-Sham equation as:

$$F[n] = T_0[n] + \frac{1}{2} \int n(\vec{r}) V_H(\vec{r}) d^3r + E_{xc}[n] \quad (6.4)$$

where $T_0[n]$ is the kinetic energy, $V_H(\vec{r})$ is Hartree potential, and $E_{xc}[n]$ is related to the

exchange and correlation potential. The major problem with DFT is that the exact functions for exchange and correlation are unknown. One of the widely used approximation is the GGA, which is derived from homogeneous electron gas model and taken into account the gradient of the density at the same coordinate:

$$E_{XC}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int \varepsilon_{XC}(n_{\uparrow}, n_{\downarrow}, \vec{\nabla} n_{\uparrow}, \vec{\nabla} n_{\downarrow}) n(\vec{r}) d^3r \quad (6.5)$$

where ε_{XC} is exchange and correlation energy density. Good results for molecular geometries and ground-state energies have been achieved by using GGA.

6.2 IMJs Induced by Tube-Substrate Interaction

To realize the fabrication of the substrate-induced IMJs, we intentionally grew SWNTs on trenched substrates. As discussed in Chapter 5, nanotubes could be deflected by the trenches, depending on the trench dimension. For this reason, we chose narrow and deep trenches for SWNT growth, in order to decrease the deflection and minimize the corresponding uniaxial strain due to the elongation. Because, when SWNTs lie across narrow and deep trenches, the length of the suspended portion is so small that the rigidity of the nanotubes is sufficient to oppose the gravity. In this case, only a small amount of uniaxial strain or even no strain at all is induced onto the nanotube. Figure 6.1 (a) is an SEM image of an isolated SWNT lying across a 10 μm wide, 10 μm deep trench. As seen from the figure, the SUS segment looks perfectly straight and taut, indicating the nanotube is fully suspended without touching the bottom surface. To confirm its suspension, resonance Raman mapping was carried out on the

SUS segment, the constant G^+ peak frequency at $\sim 1591\text{ cm}^{-1}$ and unchanged line shape along its axis enables us to conclude that the tube is fully suspended, not under a uniaxial strain [201]. Hence, this SUS segment can be considered as a “free-standing” nanotube, which is free from any disturbance from the surrounding environment, reviewing the intrinsic structure and properties of the SWNT.

Figure 6.1. (a) SEM image of an isolated SWNT lying across a $10\text{ }\mu\text{m}$ wide, $10\text{ }\mu\text{m}$ deep trench. The SOS segment is wider and brighter than the SUS segment. The SiO₂ layer of the substrate was grown using PECVD. (b) Comparison of Raman spectra obtained from SUS and SOS segments, respectively. The nanotube was on PECVD grown SiO₂ layer. (c) Lorentzian fitting of the G band from the SOS segment, referring to (b). (d) Another set of SOS vs SUS Raman spectra, which were acquired from SWNT lying on amorphous SiO₂ layer.

It is worth noting that the SiO₂ layer on top of this substrate was grown using PECVD after trenches were fabricated, as illustrated in Figure 3.2 (b). Figure 6.1 (b) shows the Raman spectra acquired from the SUS and SOS segments of this SWNT, respectively ($E_{\text{laser}} = 1.96$ eV). Being a free-standing nanotube, the Raman spectrum taken from the SUS segment represents its intrinsic characteristics. The single narrow, sharp and symmetric RBM positioned at 134 cm⁻¹ assigns this nanotube to a (18, 8) semiconducting nanotube [182], which is in resonance with the E_{33}^S transition. The applicable ω_{RBM} vs d_t relationship for this free-standing should be $\omega_{\text{RBM}} = 204/d_t + 27$ [153], thus the diameter of this SWNT is calculated to be 1.9 nm. The signal from Si (peak at 302 cm⁻¹) is quite weak, because we focused the laser beam on the suspended nanotube, thus the bottom of the trench could hardly be detected due to the large depth of the trench. The G profile, which can be fitted by two Lorentzians, corroborates its semiconducting nature. The absence of D band indicates that SUS segment is defect-free.

Intriguingly, abnormal Raman profile was observed when we inspected the SOS segment of the SWNT, which was grown on top of the PECVD deposited SiO₂ layer. Compared to that of the SUS segment, ω_{RBM} of the SOS segment was downshifted by 1.5 cm⁻¹ to 131.5 cm⁻¹. The D band can be observed at 1357 cm⁻¹. The G band feature, strikingly, split into seven peaks (see Figure 6.1 (c)), which were obtained by fitting the profile using Lorentzian functions. The peak with highest frequency at ~1612 cm⁻¹ is assigned to a disorder-induced D' peak [193], the other six components are active phonon modes of G band. Since the G⁺ and G⁻ peaks in Raman spectrum of SWNTs originate from the longitudinal (LO) and transverse (TO) optical phonons,

respectively. Due to phonon wave vector confinement and the curvature effect, the LO and TO modes each splits into three symmetries. Accordingly, there are six Raman allowed modes for SWNTs, which are A_{1g}^+ , E_{1g}^+ , E_{2g}^+ , A_{1g}^- , E_{1g}^- , and E_{2g}^- [202]. We can thus propose the following assignment: the peaks at 1605 cm^{-1} and 1557 cm^{-1} are attributed to E_{2g}^+ and E_{2g}^- modes, respectively; the components around $\sim 1597\text{ cm}^{-1}$ and 1583 cm^{-1} correspond to E_{1g}^+ and A_{1g}^+ modes, respectively; the modes at 1577 cm^{-1} and 1567 cm^{-1} are the resolved A_{1g}^- and E_{1g}^- modes, respectively. It is also worth mentioning that compared with the two G band components of the SUS segments, the E_{1g}^+ mode of the SOS segment was upshifted (from 1591 cm^{-1} to 1597 cm^{-1}), while the E_{1g}^- mode of the SOS segment was downshifted (from 1575 cm^{-1} to 1567 cm^{-1}).

The phenomenal splitting in G band profile, the frequency shift of the two dominant G components, the upshift in RBM frequency, and the appearance of the disorder-induced D and D' peaks, together, strongly indicate that the SOS segment was severely deformed by the tube-substrate interaction. In order to study this strong tube-substrate interaction, we utilized tapping mode AFM to inspect the morphology of SWNTs on the PECVD grown SiO_2 surface. Figure 6.2 (a) is a typical AFM image showing a CNT on the surface of PECVD grown SiO_2 layer, for comparison, a CNT on the amorphous Si/ SiO_2 layer (thermally grown) is mapped and shown in Figure 6.2 (b). It can be seen that PECVD grown SiO_2 surface is rather rough, in contrast to smooth surface of the amorphous Si/ SiO_2 layer. The color scale bar in the right panel indicates the heights of the features. From the image contrast, it is suggested that the CNT is embedded

into the PECVD grown SiO_2 surface, unlike the one freely sitting on the surface of amorphous SiO_2 layer. This strong adhesion promoted by the surface roughness may induce frictions to the SWNT, resulting in radial deformation, uniaxial strain, and torsion strain onto the nanotube. The set of Raman spectra displayed in Figure 6.1 (d) were taken from the SUS and SOS segments of one isolated SWNT that lie on top of amorphous SiO_2 layer ($E_{\text{laser}} = 2.41 \text{ eV}$). There is no variation of G band line shape, further corroborating that the tube-substrate interaction is much stronger for the adsorbed CNTs on rough surfaces.

Figure 6.2. AFM images of one SWNT on the surface of (a) PECVD grown SiO_2 layer, and (b) thermally grown SiO_2 layer. The color scale bar indicates the height of the features.

Based on the prominent effects of these strains on the Raman modes, the possible strains arose from the tube-substrate interaction could be deduced. First of all, the shift in RMB frequency is indicative of radial deformation, because RBM is related to radial displacement of carbon atoms, and it is sensitive to the variation of the SWNT cross section. Noting that G^+ peak is associated with atomic displacements along the tube axis, and the G^- peak corresponds to atomic displacements along the circumferential direction [202]. Therefore, the observed

frequency shift of G band and the splitting behavior in our Raman results provide evidence of the existence of uniaxial strain and torsional strain induced by the rough surface. The uniaxial strain could stretch or compress the C-C bond in axial direction, leading to the frequency shift of the G^+ peak. At the same time, the displacement of the C-C bond in circumferential direction, which is caused by torsional strain, could result in variation of G^- peak and also is responsible for the increased number of G modes [121, 203-206]. From the structural perspective, the vibrations of carbon atoms may lead to change of lattice structure and electronic structure, inducing disorders to the nanotube, as presented by the D and D' peaks.

All in all, we have confirmed the severe deformation on the adsorbed SOS segment induced by the tube-substrate interaction. The free standing SUS segment of the same individual SWNT, on the other hand, maintains its intrinsic characteristics. Therefore, an IMJ could be formed at the interface of these two SWNT segments.

6.3 IMJs Induced by Tube-Tube Interaction

Figure 6.3 (a) shows a pair of suspended CNTs lying across a 60 μm wide, 8 μm deep trench, intriguingly, the two adjacent nanotubes adhere to each other and end in Y-junctions at the edge of the trench. The adhesion was attributed to the zipper-effect between a pair of co-extending CNTs, as described, once two CNTs come into contact, the carbon atom chain of each tube would zip together through the van der Waals interaction [138]. Figure 6.3 (b) is a closer SEM observation of the Y-junction formed due to the tube-tube interaction between the two suspended CNTs. In the aim to examine the Y-junction and investigate the formation

mechanism, we carried out Raman characterization on the two separated CNTs and the adhering pair, respectively. Figure 6.4 (a) is a Raman mapping image corresponding to the Y-junction shown in Figure 6.3 (b). For simplicity, we denote the upper and lower separated CNTs as “CNT A” and “CNT B”, respectively, and the adhering pair as “joint”, as indicated in the figure.

Figure 6.3. (a) SEM image of a pair of suspended CNTs adhering to each other and ending in Y-junctions. (b) A zoom-in SEM image of the Y-junction at the edge of the trench.

Because of the narrow resonance window of RBM, in our Raman spectra we did not obtain a signal associated with this mode, with our limited excitation energies. Nevertheless, the diameters of the two SWNTs could be calculated based on the relationship between the nanotube diameters and the frequencies of G^+ and G^- peaks: $\omega_{G^-} = \omega_{G^+} - C/d_t^2$, where $C = 47.7 \text{ cm}^{-1}\text{nm}^2$ for the semiconducting SWNTs on Si/SiO₂ substrates [154]. According to the Raman spectra obtained from SOS segments of the two SWNTs, G^+ and G^- are located at 1592 cm^{-1} and 1580 cm^{-1} respectively for CNT A, while CNT B has G^+ and G^- peaks at 1601 cm^{-1} and 1580 cm^{-1} , respectively. Thus we acquired $d_t = 1.99 \text{ nm}$ for CNT A and $d_t = 1.51 \text{ nm}$ for CNT B.

Figure 6.4 (b) shows the G band obtained from the SUS segments of the two SWNTs, with the Lorentzian peak at 1585 cm^{-1} for CNT A and at 1567 cm^{-1} for CNT B. We also acquired the G band from the joint region, which is associated with the Y-junction. As displayed in Figure 6.4 (c), the G band exhibits typical bundle features, with components respectively at 1585 cm^{-1} , 1570 cm^{-1} , and 1540 cm^{-1} . To investigate the tube-tube interaction existing in this region, a G band feature, that obtained by simply summing up the G peaks of CNT A and CNT B, is drawn in Figure 6.4 (d). Apparently, compared to this sum result, the experimental data shows a upshift in G modes frequencies, which can be attributed to the interaction between nanotubes [207].

Figure 6.4. (a) A Raman mapping image of the Y-junction, where CNT A, CNT B, and the junction are indicated. (b) G band spectra for CNT A and CNT B, respectively. (c) Raman spectrum acquired from the joint region. (d) The spectrum obtained by simply summing up the G peaks of CNT A and CNT B.

To explain our experimental results, we used first principles to calculate the equilibrium structure of thin bundle consisting of two single-walled carbon nanotubes. DFT formalism was implemented in the CASTEP program, implementing the ultra-soft pseudopotentials. The GGA within the Perdew-Burke-Erzerhof (PBE) parametrization was employed for the exchange-correlation functional [208].

In our geometric models, we consider a SWNT with chiral index (13, 0). The whole system was periodic in both [100] and [010] directions. The period in [100] and [010] directions are 1.5 nm, which are enough to avoid the interactions between SWNTs in the cell and their repetitions. The electron wave function was expanded in a plane wave cutoff energy of 280 eV. We carried out DFT calculations with a Monkhorst-Pack 1x1x3 K point mesh to sample Brillouin zone for geometry optimization.

Figure 6.5. (a) Geometry optimization without hydrostatic stress. (b) Geometry optimization with hydrostatic stress.

Since in SWNT bundles across over a trench, there exists a pressure between the connected individual SWNTs due to the “zipper-effect”. To simulate the effect of pressure on

the structure of SWNT, we conduct geometry optimization on SWNT by applying an equivalent hydrostatic pressure on SWNT. The final structure of the (13, 0) SWNT with hydrostatic pressure is shown in Figure 6.5 (a). The C-C bond lengths in both axial and circumferential directions are 1.427 Å. Once applied 1 GPa hydrostatic pressure, as shown in Figure 6.5 (b), the final C-C bond length in axial and circumferential directions are 1.425 and 1.418 Å, respectively. Thus we can conclude that C-C bond length will decrease if there is a pressure applied on SWNT in bundle, resulting in an upshift of G band frequencies in the Raman spectrum.

6.4 Conclusions

In this chapter, we investigated the formation of SWNT IMJs induced by tube-substrate interaction and tube-tube interaction, respectively. To generate strong tube-substrate interaction, we deposited a layer of SiO₂ using PECVD on top of trenched substrates, and then synthesized ultralong SWNTs on the as-fabricated substrates. The trenched structures were designed to be narrow and deep, in order to minimize the deflection of SUS segment. Raman inspection of the SUS segment indicated that the SUS segment was free from disturbance of surrounding environment and could be taken as free standing nanotube. However, the SOS segment of the same individual SWNT was severely deformed by the substrate. Tapping AFM mode image revealed that the nanotube was embedded in the rough surface, as a result, radial deformation, uniaxial strain and torsional strain were induced onto the nanotube. This was further corroborated by the corresponding Raman characterization, where shift in the frequency of RBM and G band, splitting of G band profile, and appearance of D and D' band

were observed. Based on the fact that the lattice structure and electronic structure of the SOS segment were significantly altered by the strong tube-substrate interaction, while the SUS segment was a free standing nanotube maintaining the intrinsic characteristic of the SWNT, an IMJ could be formed at the interface of these two segments.

In addition, we utilized Raman spectroscopy to characterize a Y-junction that was formed between two adhered suspended SWNTs. The upshift of the G band modes with respect to their positions in individual SWNTs reviews the strong tube-tube interaction derived from the zipper effect. First principle calculations of CNTs in bundles were performed. The structural evolution of a CNT under pressure suggests that C-C bond could be shortened, which explains observed upshift in G band frequencies.

Chapter 7 Conclusions

CNT IMJs, due to their molecular size and exotic electronic properties, can serve as active components in next generation electronic circuits, enable new potential nanodevices, and foster innovative applications. However, the key obstacle existing in the implementation of CNT IMJs is the lack of techniques that can controllably synthesize, rapidly identify and comprehensively characterize the CNT IMJs. Herein, our study primarily focuses on these issues.

In the aim to offer structural perfect carriers, ultralong, horizontally aligned, and defect-free SWNT arrays were successfully synthesized using a CVD method. The as-grown SWNTs were of high quality, with narrow diameter distribution. The density and length of the SWNT arrays could be well controlled by growth parameters, such as catalyst concentration, pretreatment time, and growth temperature. The control mechanism was attributed to the activity and lifetime of the catalyst nanoparticles which could be significantly altered by growth conditions. As a direct result, the catalyst nanoparticles with different properties could impact the resultant nanotubes density and length. The alignment of the SWNTs with respect to the density of the array was investigated. It was found that the alignment could be suppressed due to the crowding effect arose from dense SWNTs growing together. The study of the flow dynamics in the system suggests that the local flow condition of the SWNTs could be disturbed by other neighboring nanotubes, which induces turbulence to the growing SWNTs, resulting in degradation in the alignment. Electrical transport measurements on isolated SWNTs revealed their intrinsic transport properties. The electrical performance of SWNT FETs showed

dependence on the nanotube diameters.

Raman characterization of specific isolated SWNTs indicated that the SWNTs were structural and chiral uniform along their length, thus the influence of random defects on our characterization could be eliminated. Based on these high-quality SWNTs, trenched structures were employed into the synthesis processes to intentionally induce the formation of IMJs. The trenched structures were used to strain onto SWNTs that lie suspended across them. As a result, the nanotube lattice and electronic structures could be altered and topological defects could be introduced, leading to the formation of IMJs. Drastic evolutions were observed when we compared Raman spectra obtained from the “SOS”, “trans”, and “SUS” segments. The shift in the frequencies of RBM and G band suggested that the C-C bonds were changed by uniaxial strain. The change of G band profile was indicative that the SWNT was subjected to bending deformation. The appearance of the D and D’ band at the “trans” region confirmed that topological defects were generated at the edge of the trench. Rectifying behavior was observed when we performed electrical transport measurements on the IMJ. From an electronic structural perspective, this behavior could be attributed to the formation of conduction barrier at the junction region, because of the change of nanotube band gap induced by strain.

Another type of SWNT IMJ was formed by use of tube-substrate interaction. To generate strong tube-substrate interaction, we deposited a layer of SiO₂ using PECVD on top of trenched substrates. Tapping mode AFM image revealed the surface was rather rough, compared to the smooth amorphous SiO₂ layer. Narrow and deep trenched structures were

employed in the synthesis of ultralong SWNTs, in order to minimize the deflection of SUS segments. Raman characterization on the SUS segment indicated it as a free standing nanotube, maintaining the intrinsic characteristic of the SWNT. However, the SOS segment was severely deformed due to its strong adhesion to the rough substrate. In Raman spectrum of the SOS segment, shift in the frequency of RBM and G band, splitting of G band profile, and appearance of D and D' band were observed. These phenomena suggested that radial deformation, uniaxial strain and torsional strain were introduced onto the SOS segment, drastically affecting its structure and properties. Therefore, an IMJ could be prepared at the interface of the SUS and SOS segments. We also observed Y-junctions formed at the end of two adhered suspended SWNTs. Our Raman results provided convincing evidence of the existence of tube-tube interaction at the joint point. First principle calculations of CNTs in bundles showed that C-C bonds could be shortened for a CNT under pressure, which could explain the observed upshift of G band frequencies in the Raman spectrum.

Chapter 8 Recommendation for future Work

The recommendation for future work could be directed towards several aspects, in the aim for the exploration of charge traps in the SWNT devices and the possible influence of the trapped charges on the formation of SWNT IMJs, the calculation of the strain induced by the trenched structures, and the investigation of the formation of SWNT IMJs by means of enhancing strains. Furthermore, calculation of the effect of tube-tube interaction on the SWNTs properties could also be carried out based on DFT in a more systematic way. The detailed aims are listed as below:

1) To design an experimental setup to intentionally induce variable external electrostatic potentials to the SWNT IMJs, while at the same time in-situ Raman characterize the SWNT IMJs. Monitor the change of Raman spectra as a function of the gate voltage. This is to explore the effect of trapped charge on the SWNT IMJs.

2) To alter the degree of the induced strains by varying the dimensions of trenched structures on Si/SiO₂ substrates. This could allow some of the SWNTs to be fully suspended across the trench, while the others to be adhered to the bottom substrate. By comparing the different shift from the corresponding Raman spectra, we are able to calculate the amount of strains have been induced to the SWNTs.

3) To build a model to systematically simulate the change of band structures, phonon dispersion, and even the corresponding variation of Raman features based on first principle and DFT.

Publications

Jianing An, Zhaoyao Zhan, S.V. Hari Krishna, and Lianxi Zheng. "Growth condition mediated catalyst effects on the density and length of horizontally aligned single-walled carbon nanotube arrays". Chemical Engineering Journal, 237, (2014), 16-22.

Jianing An and Lianxi Zheng. "Ultralong, aligned, and uniform single-walled carbon nanotubes-based nanodevices for advanced applications". Proceeding of SPIE, Fourth International Conference on Smart Materials and Nanotechnology in Engineering, 8793, (2013), 87930W.

Jianing An, Zhaoyao Zhan, S.V. Hari Krishna, and Lianxi Zheng. "Improvement of alignment and orientation of ultralong single-walled carbon nanotube arrays utilizing trench structures on substrate". To be submitted.

Jianing An, Zhaoyao Zhan, S.V. Hari Krishna, Jinyuan Zhou, Gengzhi Sun, and Lianxi Zheng. "Trench-induced carbon nanotube intramolecular junctions". To be submitted.

Zhaoyao Zhan, **Jianing An**, Huanchao Zhang, Reinack Varghese Hanse, and Lianxi Zheng. "Three-dimensional plasmonic photoanodes based on Au-embedded TiO₂ structures for enhanced visible-light water splitting". Applied Materials & Interfaces, 6, (2014), 1139-1144.

S.V. Hari Krishna, **Jianing An**, and Lianxi Zheng. "Identification of mobility changes induced by deoxyribo nucleic acid in the inversion regions of ultralong single walled carbon nanotube field-effect transistor using support vector machine and multi-layer perceptron". International

Journal of Nanotechnology, 11, (2014), 207-221.

S.V. Hari Krishna, **Jianing An**, and Lianxi Zheng. “Electrical field dependent mobility analysis of ultralong individual single walled carbon nanotube field-effect transistor”. Journal of Nanoelectronics and Optoelectronics, 8, (2013), 208-220.

Jinyuan Zhou, Gengzhi Sun, Zhaoyao Zhan, **Jianing An**, Lianxi Zheng, and Erqing Xie. “Probing structure and strain transfer in dry-spun carbon nanotube fibers by depth-profiled Raman spectroscopy”. Applied Physics Letters, 103, (2013), 031912.

Jinyuan Zhou, Gengzhi Sun, Zhaoyao Zhan, **Jianing An**, Yongzhe Zhang, Yani Zhang, and Lianxi Zheng. “Polarization behaviors of twisted carbon nanotube fibers”. Journal of Raman Spectroscopy, 43, (2012), 1221-1226.

References

- [1] R.H. Baughman, A.A. Zakhidov, W.A. de Heer, Carbon nanotubes-the route toward applications, *Science*, 297 (2002) 787-792.
- [2] T. Dürkop, S.A. Getty, E. Cobas, M.S. Fuhrer, Extraordinary mobility in semiconducting carbon nanotubes, *Nano Letters*, 4 (2003) 35-39.
- [3] A. Javey, H. Kim, M. Brink, Q. Wang, A. Ural, J. Guo, P. McIntyre, P. McEuen, M. Lundstrom, H.J. Dai, High-kappa dielectrics for advanced carbon-nanotube transistors and logic gates, *Nature Materials*, 1 (2002) 241-246.
- [4] Z. Yao, C.L. Kane, C. Dekker, High-field electrical transport in single-wall carbon nanotubes, *Physical Review Letters*, 84 (2000) 2941-2944.
- [5] S.J. Tans, A.R.M. Verschueren, C. Dekker, Room-temperature transistor based on a single carbon nanotube, *Nature*, 393 (1998) 49-52.
- [6] R. Martel, T. Schmidt, H.R. Shea, T. Hertel, P. Avouris, Single- and multi-wall carbon nanotube field-effect transistors, *Applied Physics Letters*, 73 (1998) 2447-2449.
- [7] H.W.C. Postma, T. Teepen, Z. Yao, M. Grifoni, C. Dekker, Carbon nanotube single-electron transistors at room temperature, *Science*, 293 (2001) 76-79.
- [8] J. Li, Q. Ye, A. Cassell, H.T. Ng, R. Stevens, J. Han, M. Meyyappan, Bottom-up approach for carbon nanotube interconnects, *Applied Physics Letters*, 82 (2003) 2491-2493.
- [9] Z.X. Chen, G.C. Cao, Z.L. Lin, I. Koehler, P.K. Bachmann, A self-assembled synthesis of carbon nanotubes for interconnects, *Nanotechnology*, 17 (2006) 1062-1066.
- [10] T. Xu, Z. Wang, J. Miao, X. Chen, C.M. Tan, Aligned carbon nanotubes for through-wafer interconnects, *Applied Physics Letters*, 91 (2007) 042108.
- [11] W.A. de Heer, A. Chatelain, D. Ugarte, A carbon nanotube field-emission electron source, *Science*, 270 (1995) 1179-1180.
- [12] W.A. de Heer, J.-M. Bonard, K. Fauth, A. Châtelain, D. Ugarte, L. Forró, Electron field emitters based on carbon nanotube films, *Advanced Materials*, 9 (1997) 87-89.
- [13] W.B. Choi, D.S. Chung, J.H. Kang, H.Y. Kim, Y.W. Jin, I.T. Han, Y.H. Lee, J.E. Jung, N.S. Lee, G.S. Park, J.M. Kim, Fully sealed, high-brightness carbon-nanotube field-emission display,

Applied Physics Letters, 75 (1999) 3129-3131.

[14] J. Kong, N.R. Franklin, C.W. Zhou, M.G. Chapline, S. Peng, K.J. Cho, H.J. Dai, Nanotube molecular wires as chemical sensors, *Science*, 287 (2000) 622-625.

[15] T. Someya, J. Small, P. Kim, C. Nuckolls, J.T. Yardley, Alcohol vapor sensors based on single-walled carbon nanotube field effect transistors, *Nano Letters*, 3 (2003) 877-881.

[16] L. Valentini, I. Armentano, J.M. Kenny, C. Cantalini, L. Lozzi, S. Santucci, Sensors for sub-ppm NO₂ gas detection based on carbon nanotube thin films, *Applied Physics Letters*, 82 (2003) 961-963.

[17] J. Wang, Carbon-nanotube based electrochemical biosensors: A review, *Electroanalysis*, 17 (2005) 7-14.

[18] Z.C. Wu, Z.H. Chen, X. Du, J.M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J.R. Reynolds, D.B. Tanner, A.F. Hebard, A.G. Rinzler, Transparent, conductive carbon nanotube films, *Science*, 305 (2004) 1273-1276.

[19] D. Zhang, K. Ryu, X. Liu, E. Polikarpov, J. Ly, M.E. Thompson, C. Zhou, Transparent, conductive, and flexible carbon nanotube films and their application in organic light-emitting diodes, *Nano Letters*, 6 (2006) 1880-1886.

[20] P. Avouris, Molecular electronics with carbon nanotubes, *Accounts of Chemical Research*, 35 (2002) 1026-1034.

[21] H.J. Dai, A. Javey, E. Pop, D. Mann, W. Kim, Y.R. Lu, Electrical transport properties and field effect transistors of carbon nanotubes, *Nano*, 1 (2006) 1-13.

[22] P. Avouris, Z.H. Chen, V. Perebeinos, Carbon-based electronics, *Nature Nanotechnology*, 2 (2007) 605-615.

[23] A.V. Krasheninnikov, K. Nordlund, M. Sirvio, E. Salonen, J. Keinonen, Formation of ion-irradiation-induced atomic-scale defects on walls of carbon nanotubes, *Physical Review B*, 63 (2001) 245405.

[24] B.W. Smith, D.E. Luzzi, Electron irradiation effects in single wall carbon nanotubes, *Journal of Applied Physics*, 90 (2001) 3509-3515.

[25] F. Banhart, J.X. Li, M. Terrones, Cutting single-walled carbon nanotubes with an electron beam: Evidence for atom migration inside nanotubes, *Small*, 1 (2005) 953-956.

[26] M. Terrones, F. Banhart, N. Grobert, J.C. Charlier, H. Terrones, P.M. Ajayan, *Molecular*

junctions by joining single-walled carbon nanotubes, *Physical Review Letters*, 89 (2002) 075505.

[27] C.H. Jin, K. Suenaga, S. Iijima, Plumbing carbon nanotubes, *Nature Nanotechnology*, 3 (2008) 17-21.

[28] M. Ouyang, J.L. Huang, C.L. Cheung, C.M. Lieber, Atomically resolved single-walled carbon nanotube intramolecular junctions, *Science*, 291 (2001) 97-100.

[29] K. Suenaga, H. Wakabayashi, M. Koshino, Y. Sato, K. Urita, S. Iijima, Imaging active topological defects in carbon nanotubes, *Nature Nanotechnology*, 2 (2007) 358-360.

[30] A.M. Rao, E. Richter, S. Bandow, B. Chase, P.C. Eklund, K.A. Williams, S. Fang, K.R. Subbaswamy, M. Menon, A. Thess, R.E. Smalley, G. Dresselhaus, M.S. Dresselhaus, Diameter-selective Raman scattering from vibrational modes in carbon nanotubes, *Science*, 275 (1997) 187-191.

[31] S.M. Huang, M. Woodson, R. Smalley, J. Liu, Growth mechanism of oriented long single walled carbon nanotubes using "fast-heating" chemical vapor deposition process, *Nano Letters*, 4 (2004) 1025-1028.

[32] T. Hertel, R.E. Walkup, P. Avouris, Deformation of carbon nanotubes by surface van der Waals forces, *Physical Review B*, 58 (1998) 13870-13873.

[33] S. Iijima, Helical microtubules of graphitic carbon, *Nature*, 354 (1991) 56-58.

[34] S. Iijima, T. Ichihashi, Single-shell carbon nanotubes of 1-nm diameter, *Nature*, 363 (1993) 603-605.

[35] D.S. Bethune, C.H. Kiang, M.S. Devries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Cobalt-catalyzed growth of carbon nanotubes with single-atomic-layerwalls, *Nature*, 363 (1993) 605-607.

[36] J.W.G. Wildoer, L.C. Venema, A.G. Rinzler, R.E. Smalley, C. Dekker, Electronic structure of atomically resolved carbon nanotubes, *Nature*, 391 (1998) 59-62.

[37] J.-C. Charlier, X. Blase, S. Roche, Electronic and transport properties of nanotubes, *Reviews of Modern Physics*, 79 (2007) 677-732.

[38] M. Scarselli, P. Castrucci, M. De Crescenzi, Electronic and optoelectronic nano-devices based on carbon nanotubes, *Journal of Physics-Condensed Matter*, 24 (2012) 313202.

[39] P.R. Wallace, The band theory of graphite, *Physical Review*, 71 (1947) 622-634.

- [40] J.-Y. Park, Band structure and electron transport physics of one-dimensional SWNTs, in: Carbon Nanotube Electronics, Springer US, 2009, pp. 1-42.
- [41] Y.A. Eva, L. Guohong, D. Xu, Electronic properties of graphene: A perspective from scanning tunneling microscopy and magnetotransport, Reports on Progress in Physics, 75 (2012) 056501.
- [42] L. Balents, M.P.A. Fisher, Correlation effects in carbon nanotubes, Physical Review B, 55 (1997) R11973-R11976.
- [43] J.W. Mintmire, C.T. White, Universal density of states for carbon nanotubes, Physical Review Letters, 81 (1998) 2506-2509.
- [44] J. Maultzsch, S. Reich, C. Thomsen, H. Requardt, P. Ordejon, Phonon dispersion in graphite, Physical Review Letters, 92 (2004) 075501.
- [45] M.S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Raman spectroscopy of carbon nanotubes, Physics Reports, 409 (2005) 47-99.
- [46] Y. Imry, R. Landauer, Conductance viewed as transmission, Reviews of Modern Physics, 71 (1999) S306-S312.
- [47] F. Leonard, J. Tersoff, Novel length scales in nanotube devices, Physical Review Letters, 83 (1999) 5174-5177.
- [48] A. Javey, J. Guo, Q. Wang, M. Lundstrom, H.J. Dai, Ballistic carbon nanotube field-effect transistors, Nature, 424 (2003) 654-657.
- [49] T. Durkop, S.A. Getty, E. Cobas, M.S. Fuhrer, Extraordinary mobility in semiconducting carbon nanotubes, Nano Letters, 4 (2004) 35-39.
- [50] S.J. Tans, M.H. Devoret, H.J. Dai, A. Thess, R.E. Smalley, L.J. Geerligs, C. Dekker, Individual single-wall carbon nanotubes as quantum wires, Nature, 386 (1997) 474-477.
- [51] J. Nygard, D.H. Cobden, M. Bockrath, P.L. McEuen, P.E. Lindelof, Electrical transport measurements on single-walled carbon nanotubes, Applied Physics a-Materials Science & Processing, 69 (1999) 297-304.
- [52] Y.-H. Dai, J.-n. Chen, D.-m. Ke, J. Sun, E. , Effective mobility in nano-scaled n-MOSFETs, in: Power Electronics and Motion Control Conference, 2006. IPEMC 2006. CES/IEEE 5th International, 2006, pp. 1-5.
- [53] S.M. Huang, X.Y. Cai, J. Liu, Growth of millimeter-long and horizontally aligned single-walled carbon nanotubes on flat substrates, Journal of the American Chemical Society, 125

(2003) 5636-5637.

[54] S.M. Huang, B. Maynor, X.Y. Cai, J. Liu, Ultralong, well-aligned single-walled carbon nanotube architectures on surfaces, *Advanced Materials*, 15 (2003) 1651-1655.

[55] Z. Yu, S. Li, P.J. Burke, Synthesis of aligned arrays of millimeter long, straight single-walled carbon nanotubes, *Chemistry of Materials*, 16 (2004) 3414-3416.

[56] L.X. Zheng, M.J. O'Connell, S.K. Doorn, X.Z. Liao, Y.H. Zhao, E.A. Akhadow, M.A. Hoffbauer, B.J. Roop, Q.X. Jia, R.C. Dye, D.E. Peterson, S.M. Huang, J. Liu, Y.T. Zhu, Ultralong single-wall carbon nanotubes, *Nature Materials*, 3 (2004) 673-676.

[57] X.S. Wang, Q.Q. Li, J. Xie, Z. Jin, J.Y. Wang, Y. Li, K.L. Jiang, S.S. Fan, Fabrication of ultralong and electrically uniform single-walled carbon nanotubes on clean substrates, *Nano Letters*, 9 (2009) 3137-3141.

[58] H. Liu, D. Takagi, S. Chiashi, Y. Homma, The controlled growth of horizontally aligned single-walled carbon nanotube arrays by a gas flow process, *Nanotechnology*, 20 (2009) 345604.

[59] Z. Jin, H. Chu, J. Wang, J. Hong, W. Tan, Y. Li, Ultralow feeding gas flow guiding growth of large-scale horizontally aligned single-walled carbon nanotube arrays, *Nano Letters*, 7 (2007) 2073-2079.

[60] W. Zhou, Z. Han, J. Wang, Y. Zhang, Z. Jin, X. Sun, Y. Zhang, C. Yan, Y. Li, Copper catalyzing growth of single-walled carbon nanotubes on substrates, *Nano Letters*, 6 (2006) 2987-2990.

[61] B.H. Hong, J.Y. Lee, T. Beetz, Y. Zhu, P. Kim, K.S. Kim, Quasi-continuous growth of ultralong carbon nanotube arrays, *Journal of the American Chemical Society*, 127 (2005) 15336-15337.

[62] R.T.K. Baker, M.A. Barber, P.S. Harris, F.S. Feates, R.J. Waite, Nucleation and growth of carbon deposits from the nickel catalyzed decomposition of acetylene, *Journal of Catalysis*, 26 (1972) 51-62.

[63] A. Reina, M. Hofmann, D. Zhu, J. Kong, Growth mechanism of long and horizontally aligned carbon nanotubes by chemical vapor deposition, *The Journal of Physical Chemistry C*, 111 (2007) 7292-7297.

[64] L. Huang, Z. Jia, S. O'Brien, Orientated assembly of single-walled carbon nanotubes and applications, *Journal of Materials Chemistry*, 17 (2007) 3863-3874.

[65] M. Hofmann, D. Nezich, A. Reina, J. Kong, In-situ sample rotation as a tool to understand chemical vapor deposition growth of long aligned carbon nanotubes, *Nano Letters*, 8 (2008) 4122-4127.

- [66] L. Huang, B. White, M.Y. Sfeir, M. Huang, H.X. Huang, S. Wind, J. Hone, S. O'Brien, Cobalt ultrathin film catalyzed ethanol chemical vapor deposition of single-walled carbon nanotubes, *The Journal of Physical Chemistry B*, 110 (2006) 11103-11109.
- [67] S. Pisana, A. Jungen, C. Zhang, A.M. Blackburn, R. Sharma, F. Cervantes-Sodi, C. Stampfer, C. Ducati, A.C. Ferrari, C. Hierold, J. Robertson, S. Hofmann, Flying and crawling modes during surface-bound single wall carbon nanotube growth, *The Journal of Physical Chemistry C*, 111 (2007) 17249-17253.
- [68] S.J. Kang, C. Kocabas, T. Ozel, M. Shim, N. Pimparkar, M.A. Alam, S.V. Rotkin, J.A. Rogers, High-performance electronics using dense, perfectly aligned arrays of single-walled carbon nanotubes, *Nature Nanotechnology*, 2 (2007) 230-236.
- [69] L. Ding, A. Tselev, J.Y. Wang, D.N. Yuan, H.B. Chu, T.P. McNicholas, Y. Li, J. Liu, Selective growth of well-aligned semiconducting single-walled carbon nanotubes, *Nano Letters*, 9 (2009) 800-805.
- [70] Z.H. Chen, J. Appenzeller, Y.M. Lin, J. Sippel-Oakley, A.G. Rinzler, J.Y. Tang, S.J. Wind, P.M. Solomon, P. Avouris, An integrated logic circuit assembled on a single carbon nanotube, *Science*, 311 (2006) 1735-1735.
- [71] Q. Cao, H.S. Kim, N. Pimparkar, J.P. Kulkarni, C.J. Wang, M. Shim, K. Roy, M.A. Alam, J.A. Rogers, Medium-scale carbon nanotube thin-film integrated circuits on flexible plastic substrates, *Nature*, 454 (2008) 495-500.
- [72] W.J. Yu, S.Y. Lee, S.H. Chae, D. Perello, G.H. Han, M. Yun, Y.H. Lee, Small hysteresis nanocarbon-based integrated circuits on flexible and transparent plastic substrate, *Nano Letters*, 11 (2011) 1344-1350.
- [73] V. Derycke, R. Martel, J. Appenzeller, P. Avouris, Controlling doping and carrier injection in carbon nanotube transistors, *Applied Physics Letters*, 80 (2002) 2773-2775.
- [74] V. Derycke, R. Martel, J. Appenzeller, P. Avouris, Carbon nanotube inter- and intramolecular logic gates, *Nano Letters*, 1 (2001) 453-456.
- [75] M. Radosavljevic, J. Appenzeller, P. Avouris, J. Knoch, High performance of potassium n-doped carbon nanotube field-effect transistors, *Applied Physics Letters*, 84 (2004) 3693-3695.
- [76] X.L. Liu, C. Lee, C.W. Zhou, J. Han, Carbon nanotube field-effect inverters, *Applied Physics Letters*, 79 (2001) 3329-3331.
- [77] M. Shim, A. Javey, N.W.S. Kam, H.J. Dai, Polymer functionalization for air-stable n-type carbon nanotube field-effect transistors, *Journal of the American Chemical Society*, 123 (2001)

11512-11513.

[78] F.N. Ishikawa, H.K. Chang, K. Ryu, P.C. Chen, A. Badmaev, L.G. De Arco, G.Z. Shen, C.W. Zhou, Transparent electronics based on transfer printed aligned carbon nanotubes on rigid and flexible substrates, *Acs Nano*, 3 (2009) 73-79.

[79] D.J. Lipomi, M. Vosgueritchian, B.C.K. Tee, S.L. Hellstrom, J.A. Lee, C.H. Fox, Z.N. Bao, Skin-like pressure and strain sensors based on transparent elastic films of carbon nanotubes, *Nature Nanotechnology*, 6 (2011) 788-792.

[80] S. Saito, Carbon nanotubes for next-generation electronics devices, *Science*, 278 (1997) 77-78.

[81] P.L. McEuen, Nanotechnology: Carbon-based electronics, *Nature*, 393 (1998) 15-17.

[82] L. Chico, V.H. Crespi, L.X. Benedict, S.G. Louie, M.L. Cohen, Pure carbon nanoscale devices: Nanotube heterojunctions, *Physical Review Letters*, 76 (1996) 971-974.

[83] J.C. Charlier, T.W. Ebbesen, P. Lambin, Structural and electronic properties of pentagon-heptagon pair defects in carbon nanotubes, *Physical Review B*, 53 (1996) 11108-11113.

[84] Z. Yao, H.W.C. Postma, L. Balents, C. Dekker, Carbon nanotube intramolecular junctions, *Nature*, 402 (1999) 273-276.

[85] M.S. Fuhrer, J. Nygard, L. Shih, M. Forero, Y.G. Yoon, M.S.C. Mazzoni, H.J. Choi, J. Ihm, S.G. Louie, A. Zettl, P.L. McEuen, Crossed nanotube junctions, *Science*, 288 (2000) 494-497.

[86] Y.G. Yao, Q.W. Li, J. Zhang, R. Liu, L.Y. Jiao, Y.T. Zhu, Z.F. Liu, Temperature-mediated growth of single-walled carbon-nanotube intramolecular junctions, *Nature Materials*, 6 (2007) 283-286.

[87] M. Bockrath, D.H. Cobden, J. Lu, A.G. Rinzler, R.E. Smalley, L. Balents, P.L. McEuen, Luttinger-liquid behaviour in carbon nanotubes, *Nature*, 397 (1999) 598-601.

[88] C. Zhou, J. Kong, E. Yenilmez, H. Dai, Modulated chemical doping of individual carbon nanotubes, *Science*, 290 (2000) 1552-1555.

[89] J.U. Lee, P.P. Gipp, C.M. Heller, Carbon nanotube p-n junction diodes, *Applied Physics Letters*, 85 (2004) 145-147.

[90] C. Biswas, S.Y. Lee, T.H. Ly, A. Ghosh, Q.N. Dang, Y.H. Lee, Chemically doped random network carbon nanotube p-n junction diode for rectifier, *Acs Nano*, 5 (2011) 9817-9823.

[91] J.A. Misewich, R. Martel, P. Avouris, J.C. Tsang, S. Heinze, J. Tersoff, Electrically induced

optical emission from a carbon nanotube FET, *Science*, 300 (2003) 783-786.

[92] N.M. Gabor, Z.H. Zhong, K. Bosnick, J. Park, P.L. McEuen, Extremely efficient multiple electron-hole pair generation in carbon nanotube photodiodes, *Science*, 325 (2009) 1367-1371.

[93] P.R. Bandaru, C. Daraio, S. Jin, A.M. Rao, Novel electrical switching behaviour and logic in carbon nanotube Y-junctions, *Nature Materials*, 4 (2005) 663-666.

[94] C. Papadopoulos, A. Rakitin, J. Li, A.S. Vedeneev, J.M. Xu, Electronic transport in Y-junction carbon nanotubes, *Physical Review Letters*, 85 (2000) 3476-3479.

[95] C. Papadopoulos, A.J. Yin, J.M. Xu, Temperature-dependent studies of Y-junction carbon nanotube electronic transport, *Applied Physics Letters*, 85 (2004) 1769-1771.

[96] D.C. Wei, Y.Q. Liu, L.C. Cao, L. Fu, X.L. Li, Y. Wang, G. Yu, D.B. Zhu, A new method to synthesize complicated multibranched carbon nanotubes with controlled architecture and composition, *Nano Letters*, 6 (2006) 186-192.

[97] P.R. Bandaru, Electrical characterization of carbon nanotube Y-junctions: A foundation for new nanoelectronics, *Journal of Materials Science*, 42 (2007) 1809-1818.

[98] J. Han, M.P. Anantram, R.L. Jaffe, J. Kong, H. Dai, Observation and modeling of single-wall carbon nanotube bend junctions, *Physical Review B*, 57 (1998) 14983-14989.

[99] M. Freitag, A.T. Johnson, S.V. Kalinin, D.A. Bonnell, Role of single defects in electronic transport through carbon nanotube field-effect transistors, *Physical Review Letters*, 89 (2002) 216801.

[100] S.K. Doorn, M.J. O'Connell, L.X. Zheng, Y.T. Zhu, S.M. Huang, J. Liu, Raman spectral imaging of a carbon nanotube intramolecular junction, *Physical Review Letters*, 94 (2005) 016802.

[101] J. Zhang, H.L. Zou, Q. Qing, Y.L. Yang, Q.W. Li, Z.F. Liu, X.Y. Guo, Z.L. Du, Effect of chemical oxidation on the structure of single-walled carbon nanotubes, *Journal of Physical Chemistry B*, 107 (2003) 3712-3718.

[102] K.L. Lu, R.M. Lago, Y.K. Chen, M.L.H. Green, P.J.F. Harris, S.C. Tsang, Mechanical damage of carbon nanotubes by ultrasound, *Carbon*, 34 (1996) 814-816.

[103] F. Hennrich, R. Krupke, K. Arnold, J.A.R. Stutz, S. Lebedkin, T. Koch, T. Schimmel, M.M. Kappes, The mechanism of cavitation-induced scission of single-walled carbon nanotubes, *Journal of Physical Chemistry B*, 111 (2007) 1932-1937.

- [104] Z.L. Wang, R.P. Gao, W.A. de Heer, P. Poncharal, In situ imaging of field emission from individual carbon nanotubes and their structural damage, *Applied Physics Letters*, 80 (2002) 856-858.
- [105] P.M. Ajayan, V. Ravikumar, J.C. Charlier, Surface reconstructions and dimensional changes in single-walled carbon nanotubes, *Physical Review Letters*, 81 (1998) 1437-1440.
- [106] B. Khare, M. Meyyappan, M.H. Moore, P. Wilhite, H. Imanaka, B. Chen, Proton irradiation of carbon nanotubes, *Nano Letters*, 3 (2003) 643-646.
- [107] Z. Osvath, G. Vertesy, L. Tapasztó, F. Weber, Z.E. Horváth, J. Gyulai, L.P. Biro, Atomically resolved STM images of carbon nanotube defects produced by Ar⁺ irradiation, *Physical Review B*, 72 (2005) 045429.
- [108] J.A. Rodriguez-Manzo, F. Banhart, Creation of individual vacancies in carbon nanotubes by using an electron beam of 1 angstrom diameter, *Nano Letters*, 9 (2009) 2285-2289.
- [109] D.Q. Yang, E. Sacher, Strongly enhanced interaction between evaporated Pt nanoparticles and functionalized multiwalled carbon nanotubes via plasma surface modifications: Effects of physical and chemical defects, *Journal of Physical Chemistry C*, 112 (2008) 4075-4082.
- [110] J.C. Charlier, Defects in carbon nanotubes, *Accounts of Chemical Research*, 35 (2002) 1063-1069.
- [111] T. Hiraoka, S. Bandow, H. Shinohara, S. Iijima, Control on the diameter of single-walled carbon nanotubes by changing the pressure in floating catalyst CVD, *Carbon*, 44 (2006) 1853-1859.
- [112] C.G. Lu, J. Liu, Controlling the diameter of carbon nanotubes in chemical vapor deposition method by carbon feeding, *Journal of Physical Chemistry B*, 110 (2006) 20254-20257.
- [113] Q.F. Liu, W.C. Ren, Z.G. Chen, D.W. Wang, B.L. Liu, B. Yu, F. Li, H.T. Cong, H.M. Cheng, Diameter-selective growth of single-walled carbon nanotubes with high quality by floating catalyst method, *Acs Nano*, 2 (2008) 1722-1728.
- [114] Y.G. Yao, X.C. Dai, R. Liu, J. Zhang, Z.F. Liu, Tuning the diameter of single-walled carbon nanotubes by temperature-mediated chemical vapor deposition, *Journal of Physical Chemistry C*, 113 (2009) 13051-13059.
- [115] Z. Jin, X. Li, W. Zhou, Z. Han, Y. Zhang, Y. Li, Direct growth of carbon nanotube junctions by a two-step chemical vapor deposition, *Chemical Physics Letters*, 432 (2006) 177-183.
- [116] J.F. AuBuchon, L.-H. Chen, C. Daraio, S. Jin, Multibranching carbon nanotubes via self-

seeded catalysts, *Nano Letters*, 6 (2006) 324-328.

[117] T.W. Tomblor, C.W. Zhou, L. Alexseyev, J. Kong, H.J. Dai, L. Lei, C.S. Jayanthi, M.J. Tang, S.Y. Wu, Reversible electromechanical characteristics of carbon nanotubes under local-probe manipulation, *Nature*, 405 (2000) 769-772.

[118] E.D. Minot, Y. Yaish, V. Sazonova, J.-Y. Park, M. Brink, P.L. McEuen, Tuning carbon nanotube band gaps with strain, *Physical Review Letters*, 90 (2003) 156401.

[119] L. Vitali, M. Burghard, P. Wahl, M.A. Schneider, K. Kern, Local pressure-induced metallization of a semiconducting carbon nanotube in a crossed junction, *Physical Review Letters*, 96 (2006) 086804.

[120] H.W.C. Postma, M. de Jonge, Z. Yao, C. Dekker, Electrical transport through carbon nanotube junctions created by mechanical manipulation, *Physical Review B*, 62 (2000) R10653-R10656.

[121] S.W. Lee, G.-H. Jeong, E.E.B. Campbell, In situ Raman measurements of suspended individual single-walled carbon nanotubes under strain, *Nano Letters*, 7 (2007) 2590-2595.

[122] B.I. Yakobson, C.J. Brabec, J. Bernholc, Nanomechanics of carbon tubes: Instabilities beyond linear response, *Physical Review Letters*, 76 (1996) 2511-2514.

[123] O. Lourie, D.M. Cox, H.D. Wagner, Buckling and collapse of embedded carbon nanotubes, *Physical Review Letters*, 81 (1998) 1638-1641.

[124] P. Zhang, P.E. Lammert, V.H. Crespi, Plastic deformations of carbon nanotubes, *Physical Review Letters*, 81 (1998) 5346-5349.

[125] D. Srivastava, M. Menon, K. Cho, Nanoplasticity of single-wall carbon nanotubes under uniaxial compression, *Physical Review Letters*, 83 (1999) 2973-2976.

[126] A. Jodo, M.S. Dresselhaus, Nanometrology links state-of-the-art academic research and ultimate industry needs for technological innovation, *Mrs Bulletin*, 32 (2007) 988-993.

[127] R.H. Miwa, W. Orellana, A. Fazzio, Substrate-dependent electronic properties of an armchair carbon nanotube adsorbed on H/Si(001), *Applied Physics Letters*, 86 (2005) 213111.

[128] S. Berber, A. Oshiyama, Atomic and electronic structures of carbon nanotubes on Si(001) stepped surfaces, *Physical Review Letters*, 96 (2006) 105505.

[129] G.W. Peng, A.C.H. Huan, L. Liu, Y.P. Feng, Structural and electronic properties of 4Å carbon nanotubes on Si(001) surfaces, *Physical Review B*, 74 (2006) 235416.

- [130] M.A. Peter, W.L. Joseph, Local stabilization of single-walled carbon nanotubes on Si(100)- 2×1 :H via nanoscale hydrogen desorption with an ultrahigh vacuum scanning tunnelling microscope, *Nanotechnology*, 18 (2007) 125302.
- [131] Y.M. You, T. Yu, J. Kasim, H. Song, X.F. Fan, Z.H. Ni, L.Z. Cao, H. Jiang, D.Z. Shen, J. Kuo, Z.X. Shen, Visualization and investigation of Si-C covalent bonding of single carbon nanotube grown on silicon substrate, *Applied Physics Letters*, 93 (2008) 103111.
- [132] N. Geblinger, A. Ismach, E. Joselevich, Self-organized nanotube serpentines, *Nature Nanotechnology*, 3 (2008) 195-200.
- [133] J. Huang, W. Choi, Controlled growth and electrical characterization of bent single-walled carbon nanotubes, *Nanotechnology*, 19 (2008) 505601.
- [134] Y.G. Yao, X.C. Dai, C.Q. Feng, J. Zhang, X.L. Liang, L. Ding, W. Choi, J.Y. Choi, J.M. Kim, Z.F. Liu, Crinkling ultralong carbon nanotubes into serpentines by a controlled landing process, *Advanced Materials*, 21 (2009) 4158-4162.
- [135] L. Ding, W. Zhou, T. McNicholas, J. Wang, H. Chu, Y. Li, J. Liu, Direct observation of the strong interaction between carbon nanotubes and quartz substrate, *Nano Res.*, 2 (2009) 903-910.
- [136] J.S. Soares, A.P.M. Barboza, P.T. Araujo, N.M. Barbosa Neto, D. Nakabayashi, N. Shadmi, T.S. Yarden, A. Ismach, N. Geblinger, E. Joselevich, C. Vilani, L.G. Cançado, L. Novotny, G. Dresselhaus, M.S. Dresselhaus, B.R.A. Neves, M.S.C. Mazzoni, A. Jorio, Modulating the Electronic Properties along Carbon Nanotubes via Tube-Substrate Interaction, *Nano Letters*, 10 (2010) 5043-5048.
- [137] Y. Zhang, J. Zhang, H. Son, J. Kong, Z. Liu, Substrate-induced Raman frequency variation for single-walled carbon nanotubes, *Journal of the American Chemical Society*, 127 (2005) 17156-17157.
- [138] Z.R. Abrams, Y. Hanein, Tube-tube and tube-surface interactions in straight suspended carbon nanotube structures, *Journal of Physical Chemistry B*, 110 (2006) 21419-21423.
- [139] Z.R. Abrams, Y. Hanein, Radial deformation measurements of isolated pairs of single-walled carbon nanotubes, *Carbon*, 45 (2007) 738-743.
- [140] R.S. Ruoff, J. Tersoff, D.C. Lorents, S. Subramoney, B. Chan, Radial deformation of carbon nanotubes by van der Waals forces, *Nature*, 364 (1993) 514-516.
- [141] M. Terrones, H. Terrones, F. Banhart, J.C. Charlier, P.M. Ajayan, Coalescence of single-walled carbon nanotubes, *Science*, 288 (2000) 1226-1229.

- [142] A.V. Krashenninnikov, K. Nordlund, J. Keinonen, F. Banhart, Ion-irradiation-induced welding of carbon nanotubes, *Physical Review B*, 66 (2002) 245403.
- [143] K. Metenier, S. Bonnamy, F. Beguin, C. Journet, P. Bernier, M.L. de La Chapelle, O. Chauvet, S. Lefrant, Coalescence of single-walled carbon nanotubes and formation of multi-walled carbon nanotubes under high-temperature treatments, *Carbon*, 40 (2002) 1765-1773.
- [144] G.W. Ho, A.T.S. Wee, J. Lin, Electric field-induced carbon nanotube junction formation, *Applied Physics Letters*, 79 (2001) 260-262.
- [145] Y.W. Fan, B.R. Goldsmith, P.G. Collins, Identifying and counting point defects in carbon nanotubes, *Nature Materials*, 4 (2005) 906-911.
- [146] X.H. Li, J.L. Niu, J. Zhang, H.L. Li, Z.F. Liu, Labeling the defects of single-walled carbon nanotubes using titanium dioxide nanoparticles, *Journal of Physical Chemistry B*, 107 (2003) 2453-2458.
- [147] H. Kim, J. Lee, S.J. Kahng, Y.W. Son, S.B. Lee, C.K. Lee, J. Ihm, Y. Kuk, Direct observation of localized defect states in semiconductor nanotube junctions, *Physical Review Letters*, 90 (2003) 216107.
- [148] H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, Y. Achiba, Optical properties of single-wall carbon nanotubes, *Synthetic Metals*, 103 (1999) 2555-2558.
- [149] A. Jorio, M.A. Pimenta, A.G. Souza, R. Saito, G. Dresselhaus, M.S. Dresselhaus, Characterizing carbon nanotube samples with resonance Raman scattering, *New Journal of Physics*, 5 (2003) 1-17.
- [150] A. Jorio, R. Saito, J.H. Hafner, C.M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, M.S. Dresselhaus, Structural (n, m) determination of isolated single-wall carbon nanotubes by resonant Raman scattering, *Physical Review Letters*, 86 (2001) 1118-1121.
- [151] M. Milnera, J. Kurti, M. Hulman, H. Kuzmany, Periodic resonance excitation and intertube interaction from quasicontinuous distributed helicities in single-wall carbon nanotubes, *Physical Review Letters*, 84 (2000) 1324-1327.
- [152] C. Fantini, A. Jorio, M. Souza, M.S. Strano, M.S. Dresselhaus, M.A. Pimenta, Optical transition energies for carbon nanotubes from resonant Raman spectroscopy: Environment and temperature effects, *Physical Review Letters*, 93 (2004) 147406.
- [153] J.C. Meyer, M. Paillet, T. Michel, A. Moreac, A. Neumann, G.S. Duesberg, S. Roth, J.L. Sauvajol, Raman modes of index-identified freestanding single-walled carbon nanotubes, *Physical Review Letters*, 95 (2005) 217401.

- [154] A. Jorio, A.G. Souza, G. Dresselhaus, M.S. Dresselhaus, A.K. Swan, M.S. Unlu, B.B. Goldberg, M.A. Pimenta, J.H. Hafner, C.M. Lieber, R. Saito, G-band resonant Raman study of 62 isolated single-wall carbon nanotubes, *Physical Review B*, 65 (2002) 155412.
- [155] M. Kalbac, Y.P. Hsieh, H. Farhat, L. Kavan, M. Hofmann, J. Kong, M.S. Dresselhaus, Defects in individual semiconducting single wall carbon nanotubes: Raman spectroscopic and in situ Raman spectroelectrochemical study, *Nano Letters*, 10 (2010) 4619-4626.
- [156] Y. Homma, S. Suzuki, Y. Kobayashi, M. Nagase, D. Takagi, Mechanism of bright selective imaging of single-walled carbon nanotubes on insulators by scanning electron microscopy, *Applied Physics Letters*, 84 (2004) 1750-1752.
- [157] Y.N. Zhang, L.X. Zheng, Towards chirality-pure carbon nanotubes, *Nanoscale*, 2 (2010) 1919-1929.
- [158] C.Z. Loebick, R. Podila, J. Reppert, J. Chudow, F. Ren, G.L. Haller, A.M. Rao, L.D. Pfefferle, Selective synthesis of subnanometer diameter semiconducting single-walled carbon nanotubes, *Journal of the American Chemical Society*, 132 (2010) 11125-11131.
- [159] B. Yu, C. Liu, P.X. Hou, Y. Tian, S.S. Li, B.L. Liu, F. Li, E.I. Kauppinen, H.M. Cheng, Bulk synthesis of large diameter semiconducting single-walled carbon nanotubes by oxygen-assisted floating catalyst chemical vapor deposition, *Journal of the American Chemical Society*, 133 (2011) 5232-5235.
- [160] Y. Li, J. Liu, Y.Q. Wang, Z.L. Wang, Preparation of monodispersed Fe-Mo nanoparticles as the catalyst for CVD synthesis of carbon nanotubes, *Chemistry of Materials*, 13 (2001) 1008-1014.
- [161] F. Cervantes-Sodi, T.P. McNicholas, J.G. Simmons, J. Liu, G. Csanyi, A.C. Ferrari, S. Curtarolo, Viscous state effect on the activity of Fe nanocatalysts, *Acs Nano*, 4 (2010) 6950-6956.
- [162] S.M. Kim, C.L. Pint, P.B. Amama, D.N. Zakharov, R.H. Hauge, B. Maruyama, E.A. Stach, Evolution in catalyst morphology leads to carbon nanotube growth termination, *Journal of Physical Chemistry Letters*, 1 (2010) 918-922.
- [163] R. Rao, N. Pierce, D. Liptak, D. Hooper, G. Sargent, S.L. Semiatin, S. Curtarolo, A.R. Harutyunyan, B. Maruyama, Revealing the impact of catalyst phase transition on carbon nanotube growth by in situ Raman spectroscopy, *Acs Nano*, 7 (2013) 1100-1107.
- [164] L. An, J.M. Owens, L.E. McNeil, J. Liu, Synthesis of nearly uniform single-walled carbon nanotubes using identical metal-containing molecular nanoclusters as catalysts, *Journal of the American Chemical Society*, 124 (2002) 13688-13689.

- [165] L. Zheng, X. Liao, Y.T. Zhu, Parametric study of carbon nanotube growth via cobalt-catalyzed ethanol decomposition, *Materials Letters*, 60 (2006) 1968-1972.
- [166] H.E. Unalan, M. Chhowalla, Investigation of single-walled carbon nanotube growth parameters using alcohol catalytic chemical vapour deposition, *Nanotechnology*, 16 (2005) 2153-2163.
- [167] E. Mora, J.M. Pigos, F. Ding, B.I. Yakobson, A.R. Harutyunyan, Low-temperature single-wall carbon nanotubes synthesis: Feedstock decomposition limited growth, *Journal of the American Chemical Society*, 130 (2008) 11840-11841.
- [168] M.S. Dresselhaus, G. Dresselhaus, A. Jorio, A.G. Souza Filho, R. Saito, Raman spectroscopy on isolated single wall carbon nanotubes, *Carbon*, 40 (2002) 2043-2061.
- [169] L.X. Zheng, B.C. Satishkumar, P.Q. Gao, Q. Zhang, Kinetics studies of ultralong single-walled carbon nanotubes, *Journal of Physical Chemistry C*, 113 (2009) 10896-10900.
- [170] H. Amara, C. Bichara, F. Ducastelle, Understanding the nucleation mechanisms of carbon nanotubes in catalytic chemical vapor deposition, *Physical Review Letters*, 100 (2008) 056105.
- [171] M. Picher, E. Anglaret, R. Arenal, V. Jourdain, Self-deactivation of single-walled carbon nanotube growth studied by in situ Raman measurements, *Nano Letters*, 9 (2009) 542-547.
- [172] S. Hofmann, G. Csanyi, A.C. Ferrari, M.C. Payne, J. Robertson, Surface diffusion: The low activation energy path for nanotube growth, *Physical Review Letters*, 95 (2005) 036101.
- [173] A.J. Page, Y. Ohta, S. Irle, K. Morokuma, Mechanisms of single-walled carbon nanotube nucleation, growth, and healing determined using QM/MD methods, *Accounts of Chemical Research*, 43 (2010) 1375-1385.
- [174] A.R. Harutyunyan, N. Awasthi, A. Jiang, W. Setyawan, E. Mora, T. Tokune, K. Bolton, S. Curtarolo, Reduced carbon solubility in Fe nanoclusters and implications for the growth of single-walled carbon nanotubes, *Physical Review Letters*, 100 (2008) 195502.
- [175] T. Yamada, A. Maigne, M. Yudasaka, K. Mizuno, D.N. Futaba, M. Yumura, S. Iijima, K. Hata, Revealing the secret of water-assisted carbon nanotube synthesis by microscopic observation of the interaction of water on the catalysts, *Nano Letters*, 8 (2008) 4288-4292.
- [176] Z.Y. Zhan, Y.N. Zhang, G.Z. Sun, L.X. Zheng, K. Liao, The effects of catalyst treatment on fast growth of millimeter-long multi-walled carbon nanotube arrays, *Applied Surface Science*, 257 (2011) 7704-7708.
- [177] Z. Yang, A. Liao, E. Pop, Multiband mobility in semiconducting carbon nanotubes, *Electron*

Device Letters, IEEE, 30 (2009) 1078-1080.

[178] D. Jie, H.S.P. Wong, A compact SPICE model for carbon-nanotube field-effect transistors including nonidealities and its application-part I: model of the intrinsic channel region, *Electron Devices, IEEE Transactions on*, 54 (2007) 3186-3194.

[179] D. Jie, H.S.P. Wong, A compact SPICE model for carbon-nanotube field-effect transistors including nonidealities and its application-part II: full device model and circuit performance benchmarking, *Electron Devices, IEEE Transactions on*, 54 (2007) 3195-3205.

[180] T. Ando, A.B. Fowler, F. Stern, Electronic properties of two-dimensional systems, *Reviews of Modern Physics*, 54 (1982) 437-672.

[181] H. Wang, Y. Wu, C. Cong, J. Shang, T. Yu, Hysteresis of electronic transport in graphene transistors, *ACS Nano*, 4 (2010) 7221-7228.

[182] M.S. Strano, Probing chiral selective reactions using a revised Kataura plot for the interpretation of single-walled carbon nanotube spectroscopy, *Journal of the American Chemical Society*, 125 (2003) 16148-16153.

[183] A. Jorio, C. Fantini, M.S.S. Dantas, M.A. Pimenta, A.G. Souza Filho, G.G. Samsonidze, V.W. Brar, G. Dresselhaus, M.S. Dresselhaus, A.K. Swan, M.S. Ünlü, B.B. Goldberg, R. Saito, Linewidth of the Raman features of individual single-wall carbon nanotubes, *Physical Review B*, 66 (2002) 115411.

[184] Y. Zhang, H. Son, J. Zhang, M.S. Dresselhaus, J. Kong, Z. Liu, Raman spectra variation of partially suspended individual single-walled carbon nanotubes, *The Journal of Physical Chemistry C*, 111 (2007) 1983-1987.

[185] H.B. Son, Y. Hori, S.G. Chou, D. Nezich, G.G. Samsonidze, G. Dresselhaus, M.S. Dresselhaus, E.B. Barros, Environment effects on the Raman spectra of individual single-wall carbon nanotubes: Suspended and grown on polycrystalline silicon, *Applied Physics Letters*, 85 (2004) 4744-4746.

[186] N.R. Raravikar, P. Keblinski, A.M. Rao, M.S. Dresselhaus, L.S. Schadler, P.M. Ajayan, Temperature dependence of radial breathing mode Raman frequency of single-walled carbon nanotubes, *Physical Review B*, 66 (2002) 235424.

[187] L. Kavan, P. Rapt, L. Dunsch, M.J. Bronikowski, P. Willis, R.E. Smalley, Electrochemical tuning of electronic structure of single-walled carbon nanotubes: In-situ Raman and vis-NIR study, *Journal of Physical Chemistry B*, 105 (2001) 10764-10771.

[188] G. Wu, J. Zhou, J. Dong, Raman modes of the deformed single-wall carbon nanotubes,

Physical Review B, 72 (2005) 115411.

[189] P. Gao, L. Zheng, Q. Zhang, S. Yuan, Y. You, Z. Shen, D. He, Self-built tensile strain in large single-walled carbon nanotubes, *ACS Nano*, 4 (2010) 992-998.

[190] S.B. Cronin, A.K. Swan, M.S. Ünlü, B.B. Goldberg, M.S. Dresselhaus, M. Tinkham, Measuring the uniaxial strain of individual single-wall carbon nanotubes: resonance raman spectra of atomic-force-microscope modified single-wall nanotubes, *Physical Review Letters*, 93 (2004) 167401.

[191] A. Jorio, G. Dresselhaus, M.S. Dresselhaus, M. Souza, M.S.S. Dantas, M.A. Pimenta, A.M. Rao, R. Saito, C. Liu, H.M. Cheng, Polarized Raman study of single-wall semiconducting carbon nanotubes, *Physical Review Letters*, 85 (2000) 2617-2620.

[192] S. Malola, H. Häkkinen, P. Koskinen, Effect of bending on Raman-active vibration modes of carbon nanotubes, *Physical Review B*, 78 (2008) 153409.

[193] M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, L.G. Cancado, A. Jorio, R. Saito, Studying disorder in graphite-based systems by Raman spectroscopy, *Physical Chemistry Chemical Physics*, 9 (2007) 1276-1290.

[194] P. Tan, L. An, L. Liu, Z. Guo, R. Czerw, D.L. Carroll, P.M. Ajayan, N. Zhang, H. Guo, Probing the phonon dispersion relations of graphite from the double-resonance process of Stokes and anti-Stokes Raman scatterings in multiwalled carbon nanotubes, *Physical Review B*, 66 (2002) 245410.

[195] M.S. Marcus, J.M. Simmons, S.E. Baker, R.J. Hamers, M.A. Eriksson, Predicting the results of chemical vapor deposition growth of suspended carbon nanotubes, *Nano Letters*, 9 (2009) 1806-1811.

[196] H. Son, G.G. Samsonidze, J. Kong, Y.Y. Zhang, X.J. Duan, J. Zhang, Z.F. Liu, M.S. Dresselhaus, Strain and friction induced by van der Waals interaction in individual single walled carbon nanotubes, *Applied Physics Letters*, 90 (2007) 253113.

[197] J.S. Soares, A.P.M. Barboza, P.T. Araujo, N.M.B. Neto, D. Nakabayashi, N. Shadmi, T.S. Yarden, A. Ismach, N. Geblinger, E. Joselevich, C. Vilani, L.G. Cancado, L. Novotny, G. Dresselhaus, M.S. Dresselhaus, B.R.A. Neves, M.S.C. Mazzoni, A. Jorio, Modulating the electronic properties along carbon nanotubes via tube-substrate interaction, *Nano Letters*, 10 (2010) 5043-5048.

[198] D. Wei, Y. Liu, The intramolecular junctions of carbon nanotubes, *Advanced Materials*, 20 (2008) 2815-2841.

- [199] A.M. Rao, J. Chen, E. Richter, U. Schlecht, P.C. Eklund, R.C. Haddon, U.D. Venkateswaran, Y.K. Kwon, D. Tománek, Effect of van der Waals interactions on the Raman modes in single walled carbon nanotubes, *Physical Review Letters*, 86 (2001) 3895-3898.
- [200] M. Born, R. Oppenheimer, Zur Quantentheorie der Molekeln, *Annalen der Physik*, 389 (1927) 457-484.
- [201] M. Paillet, T. Michel, J.C. Meyer, V.N. Popov, L. Henrard, S. Roth, J.L. Sauvajol, Raman active phonons of identified semiconducting single-walled carbon nanotubes, *Physical Review Letters*, 96 (2006) 257401.
- [202] R. Saito, A. Jorio, J.H. Hafner, C.M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, M.S. Dresselhaus, Chirality-dependent G-band Raman intensity of carbon nanotubes, *Physical Review B*, 64 (2001) 085312.
- [203] X. Duan, H. Son, B. Gao, J. Zhang, T. Wu, G.G. Samsonidze, M.S. Dresselhaus, Z. Liu, J. Kong, Resonant Raman spectroscopy of individual strained single-wall carbon nanotubes, *Nano Letters*, 7 (2007) 2116-2121.
- [204] B. Gao, X. Duan, J. Zhang, T. Wu, H. Son, J. Kong, Z. Liu, Raman spectral probing of electronic transition energy E_{ii} variation of individual SWNTs under torsional strain, *Nano Letters*, 7 (2007) 750-753.
- [205] X. Li, Y. Jia, J. Dong, Y. Kawazoe, Resonant Raman spectroscopy of deformed single-walled carbon nanotubes under both torsional and tensile strain, *Physical Review B*, 81 (2010) 195439.
- [206] Z. Liu, J. Zhang, B. Gao, Raman spectroscopy of strained single-walled carbon nanotubes, *Chemical Communications*, (2009) 6902-6918.
- [207] M. Paillet, S. Langlois, J.L. Sauvajol, L. Marty, A. Iaia, C. Naud, V. Bouchiat, A.M. Bonnot, Raman spectroscopy of free-standing individual semiconducting single-wall carbon nanotubes, *The Journal of Physical Chemistry B*, 110 (2006) 164-169.
- [208] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Physical Review Letters*, 77 (1996) 3865-3868.