Field-effect transistors based on carbon nanotube networks

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FIELD-EFFECT TRANSISTORS BASED ON CARBON NANOTUBE NETWORKS

LEE CHUN WEI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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

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SUMMARY

Single-walled carbon nanotubes (SWNTs) can be described as a roll-up of graphene sheet into a hollow cylinder with diameters in a nanometer range and lengths varying from tens of nanometers to centimeters. Owing to its roll-up chirality, SWNTs exhibit either metallic or semiconducting behaviour. The ballistic electron transport in semiconducting SWNTs manifests superior field-effect behavior and its intrinsic carrier mobility of about $100,000 \text{ cm}^2/\text{V-s}$ due to its nearly one-dimensional and defect-free electronic structure makes it one of most promising candidates for electronic applications. However, precise positioning and alignment of SWNTs, inconsistency of its electrical properties due to variations of its chirality and diameter in SWNTs assembly, and the integration of single-tube devices into a circuit as well as scalability of its fabrication process are remaining major technical hurdles for realizing its electronic applications. Therefore the development of field-effect transistor (FET) based on SWNTs network has been intensified and desirable. In this thesis, the author focuses on the purification and preparation of carbon nanotubes and its solution for solution processable semiconducting FETs devices based on SWNT networks or thin films. Density gradient ultracentrifugation (DGU) technique is adopted to separate various tubes, including arc-discharged (its diameter distribution 1.0 ~1.4 nm) and CoMCM41 (its diameter distribution 0.7 ~0.9 nm) tubes. The results reveal that DGU can effectively improve the on-off ratio characteristics of the FETs devices. Removal of bundled tubes via interfacial purification can further enhance the field-effect mobility. The (7,5) and (6,5) enriched SWNTs are produced by SC and co-surfactant encapsulation (sodium dodecyl sulfate (SDS) – sodium cholate (SC) at 1:4 ratio) respectively from small diameter tubes (its

diameter distribution 0.7 ~ 0.9 nm) and further refine via DGU. Combination of functionalizing SWNTs with diazonium salts and purifying from DGU separation technique can accomplish high performance solution-processable FETs based on carbon nanotube thin-films with a full semiconductor device yield and decent effective mobility ($\sim 10 \text{ cm}^2/\text{V}\cdot\text{s}$). The gating hysteresis of the FETs devices with thin SiO_2 dielectrics (80 nm) is attributed to the generation of hole traps at SiO_2 surfaces proximate to SWNTs.

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbols and abbreviations used consistently throughout the text are listed below. Further symbols are defined in the text as necessary in cases where the scope of the definition is limited to the specific context.

a	lattice constant
$\vec{a}_1, \vec{a}_2$	unit vectors
a_{cc}	C-C bond length
AFM	atomic force microscopy
$\vec{b}_1, \vec{b}_2$	reciprocal-lattice basis vectors
BBDT	4-bromobenzene diazonium tetrafluoroborate
$\vec{C}_h$	chiral vector
CN-FET	single-walled carbon nanotube networks or thin films field-effect transistor
CVD	chemical vapour deposition
C_1, C_2	conduction band
DGU	density gradient ultracentrifugation
$D(E)$, DOS	density of states
d_t	diameter of tubes
EEL	electron energy loss
E_g	bandgap energy
E_F	Fermi energy
FET	field-effect transistor
FIB	focus ion beam
H	Hamiltonian of the solid
IEX	ion-exchange chromatography
ITP	interfacial trapping purification
M	metallic
MOSFET	metal-oxide-semiconductor field-effect transistor

List of Symbols and Abbreviations

MWNT	multi-walled carbon nanotube
M11	lowest electronic transition of metallic species
NP	nanoparticle
PLE	photoluminescence excitation
PMDE	perfluoro (5-methyl-3,6-dioxanon-1-ene)
p, q	quantum numbers in graphite rolling condition $n-m = 3p+q$
PSEPVE	perfluoro-2(2-fluorosulfonylethoxy) propyl vinyl ether
RBM	radial breathing mode
S	semiconducting
SAM	self-assembled monolayer
SC	sodium cholate
SDS	sodium dodecyl sulfate
SEC	size exclusion chromatography
SWNT	single-walled carbon nanotube
SWNT-FET	individual single-walled carbon nanotube-based field-effect transistor
S11	lowest electronic transition of semiconducting species
S22	second electronic transition of semiconducting species
S33	third electronic transition of semiconducting species
VHS	van Hove singularities
V_1, V_2	valence band
θ	chiral angle
σ	bonding orbital
σ^*	antibonding orbital
$\phi_{sk}(r)$	tight binding Bloch wavefunction in a solid
$\psi_k(r)$	total wavefunction in a solid

1. Research Rational

1.1 Background & Motivation

Single-walled carbon nanotubes (SWNTs), which can be described as rolled-up cylinders of graphite monolayer with ~ 1 nm diameter and tens of nanometers to several centimeters length, are widely regarded to be an excellent candidate for field-effect transistors (FETs) owing to their unique properties. The electronic property of SWNTs is either metallic (M) or semiconducting (S) depending on their roll-up chirality (1-2). Owing to the nearly one-dimensional and defect-free electronic structure, electronic transport in SWNTs is ballistic, resulting that the electron transport in semiconducting SWNTs manifests superior field-effect behavior and its intrinsic carrier mobility can achieve about $100,000 \text{ cm}^2/\text{V}\cdot\text{s}$. Owing to its outstanding electrical properties, SWNTs have been widely anticipated as one of most promising candidate for electronic applications. However, the variations of chirality and diameter in SWNT assembly lead to inconsistency of electrical properties from single-tube devices. In addition, the integration of single-tube devices into a circuit is another technological hurdle for realizing its electronic applications. Therefore the development of FETs based on SWNT networks or thin films (CN-FETs) is intensified with tremendous efforts from carbon nanotubes researchers. There are several remarkable advantages from SWNTs devices based on random network structure such as ease of production, high reproducibility with consistent electrical properties and high scalability as well as high compatibility with conventional Si technology processing methods. Hence, Random SWNTs networks or thin films are anticipated as one of ideal semiconducting materials for low-cost carbon-based electronics. Despite the great

Chapter 1 Research Rational

promise, low-cost carbon-based electronics are still far from practical reality owing to unsolved technical and technological challenges in device fabrication. The major challenges on using SWNT random networks or thin films for low-cost high-performance electronic applications include as follow:

- (1) Coexistence of M- and S-SWNTs leads to low on-off ratio in FET configuration.
- (2) Low effective field-effect mobility from CN-FETs is widely attributed from the contact resistance of inter-nanotubes junction existing within SWNTs network or thin film.
- (3) Low yield and ease of CN-FETs production as well as compatibility issue with conventional processing method have to be carefully addressed for making commercial applications.
- (4) Existence of Hysteresis in CN-FETs causes reliability and reproducibility issues.

Despite widespread regarding as most promising candidate for realizing low-cost high performance carbon-based electronics, CN-FETs possess the above issues which require tremendous research efforts and innovatively strategic approaches for effectively resolving them. Thus, the intensive studies on understanding above issues arising from CN-FETs are essential from various aspects such as fundamental researches and technological challenges in order to achieve high performance solution-processable printable electronics based on carbon nanotubes network or thin film.

1.2 Scope of the Thesis

Exploitations of superior electronic properties of SWNTs have offered exciting opportunities in high performance, low-cost carbon-based printed electronics particularly

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from random carbon nanotube networks or thin films which are more practical and economical for large-scale integration compare to single-tube. This thesis is concerned with electrical characteristic of FETs based on random carbon nanotube networks or thin films (CN-FETs). The author focuses on the purification and preparation of carbon nanotubes and its solution for high performance solution-processable CN-FET devices. Chapter 2 describes the geometrical and electronic structure of SWNTs and reviews the development of CN-FETs in term of electrical performance. Chapter 3 introduces all the essential instruments and experiments setup in this research work.

In chapter 4, the author focuses on the purification and preparation of carbon nanotubes and its solution for solution-processable CN-FET devices. Density gradient ultracentrifugation (DGU) is adopted to enrich S species content for arc-discharge SWNTs (its diameters 1.0-1.4 nm) with aid of co-surfactants encapsulation (SDS-SC at 1:4 ratio) leading to improvement of device's on-off ratio.

In chapter 5, the author reports that removing the SWNT bundles using organic-aqueous interfacial purification can further enhance the electrical performance of CN-FETs. Its on-off ratio is improved by ~ 1 order of magnitude and other characteristics such as subthreshold swing and off current are also improved. By combining DGU and interfacial purification, it is possible to obtain high on-off ratio and high mobility of solution-processed CN-FETs at a promising yield.

In chapter 6, the (7,5) and (6,5) enriched SWNTs are produced by alone SC and (SDS-SC at 1:4 ratio) co-surfactant extraction respectively from small-diameter CoMCM41 tubes (its diameter 0.7-0.9 nm). DGU is adopted for further refining the separation as well as enhancing on-off ratio characteristic of device in both SC alone and

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co-surfactant encapsulation (SDS-SC at 1:4 ratio). Despite great promise on improving device's on-off ratio via DGU, the S enrichment efficiency of DGU heavily depends on the diameter distribution of starting SWNT materials.

In chapter 7, the author demonstrates that high performance solution-processable FETs based on carbon nanotube thin-films with a full semiconductor device yield can be accomplished by functionalizing with diazonium salts and purifying from DGU separation technique. This strategy is suitable for small diameter SWNTs where the differences between chiralities are significantly large in terms of the reactivity with diazonium salts.

In chapter 8, the issue of hysteresis in CN-FETs comprising Si-backgate is widely addressed and discussed. The experimental result suggest that the gating hysteresis is attributed to the generation of hole traps at SiO₂ surfaces proximate to SWNTs.

In chapter 9, the concluding remarks on significance of the works in this thesis and the insight of further improvement on mobility have been concisely mentioned in order to accomplish superior electrical performance of CN-FETs for realizing high performance solution-processable printed electronics.

2. Literature Review

2.1 History of Carbon Nanotubes

Fullerenes are widely known as a closed-cage carbon cluster comprising pentagonal and hexagonal faces with sp^2 hybridization bonding between carbon atoms. C_{60} was discovered by Harold Kroto and Richard Smalley in 1985.(3) After discovering fullerene C_{60} , an intensive research on carbon system is simulated owing to its intrinsic unique properties. In 1991, Iijima and coworkers imaged carbon nanotubes using transmission electron microscopy as an experimental evidence for verifying the existence of the carbon nanotubes.(4) Two year later, Iijima's group (5) and Bethune together with his coworkers(6) report simultaneously an experimental observation of single-walled carbon nanotube (SWNT). In particular, SWNTs can be described as rolling up graphene to form a seamless cylinder which possesses ~nm in diameter and few tens nm to several centimeters in length, resulting in a large aspect ratio. Thus, the SWNT is generally treated as the classical carbon-based with high aspect ratio system. Its high aspect ratio and sp_2 hybridization of bonding between carbon atoms provide the unique electronic, molecular and structural properties of SWNT, which is anticipated as a promising candidate for future applications.

2.1.1 Synthesis Method

SWNT synthesis has been intensively studied for producing high purity and outstanding quality of nanotubes. The several common SWNT synthesis methods, such as arc

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discharge (7), laser ablation (8), chemical vapour deposition (9), and etc, are developed for the formation of SWNTs. Despite different SWNT synthesis methods, the basic prerequisites for the production of SWNT are an active catalyst, a source of carbon and adequate energy. The main challenge in SWNT synthesis is to find out a more economic and selective way for producing specific type of nanotubes to particular applications.

2.1.2 Geometrical Structure of Single-Walled Carbon Nanotubes (SWNT)

SWNT is widely depicted as a rolled-up tubular shell of graphene sheet, which is assembled with benzene-type hexagonal rings of carbon atoms. SWNTs can be identified by graphene lattice vectors owing to highly similar microscopic structure between graphene and SWNT. Its circumferential vector ($\vec{C}_h$) is used to index its structure as illustrated in Figure 2-1 (10). The chiral vector is defined as a vector for bonding two specific atoms on the graphene sheet. Bonding carbon atoms via sp_2 hybridization forms a tube called as SWNT. In General, a (n,m) SWNT is denoted from its chiral vector $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$, where $\vec{a}_1$ and $\vec{a}_2$ are unit vectors of the graphite primitive lattice. Its chiral angle θ is defined as the angle between $\vec{C}_h$ and $\vec{a}_1$, as illustrated in Fig. 2-1.

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Figure 2-1: Graphene sheet with lattice vectors $\vec{a}_1$ and $\vec{a}_2$. The chiral vector $\vec{C}_h = 5\vec{a}_1 + 3\vec{a}_2$ represents a possible direction for rolling of the two-dimensional graphene sheet into a seamless tubular cylinder. The tube axis is perpendicular with $\vec{C}_h$. The chiral angle θ is defined as the angle between $\vec{C}_h$ and $\vec{a}_1$. The physical structure of (5,3) SWNT is illustrated on the right. Reproduced from ref. 10.

The nanotube diameter (d_t) can be estimated from the following equation

$$d_t = |\vec{C}_h| / \pi = \frac{a}{\pi} \sqrt{n^2 + nm + m^2} \quad (1)$$

Where a is the lattice constant of graphite and its value is equivalent to $a = \sqrt{3} \times a_{cc}$, where $a_{cc} = 1.42 \text{ \AA}$, the C-C bond length. The chiral angle θ is defined as the angle between $\vec{C}_h$ and $\vec{a}_1$ with value ranging from 0° to 30° owing to the hexagonal symmetry of the graphene lattice. Based on its indices as well as its chiral angle, nanotubes can be classified zigzag, armchair and chiral tubes as shown in Figure 2-2. The zigzag tube possesses $(n, 0)$ index and $(\theta = 0^\circ)$, where its circumferential vector lies along one of the two vectors showing zigzag pattern along its circumference. While the armchair tube

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possesses $m=n$ and $(\theta = 30^\circ)$ expressing armchair pattern along its circumference. Others are called chiral tubes with $(n, m \neq n \neq 0)$ and $(0^\circ < \theta > 30^\circ)$.

Figure 2-2: Atomic structure of (12,0) zigzag, (6,6) armchair, and (6,4) chiral nanotubes. Reproduced from ref. 10.

2.2 Electronic Properties of Single-Walled Carbon Nanotubes (SWNT)

The bonding structure of SWNT, similar with graphene sheet, is planar sp^2 hybridization. An individual carbon atom in graphene sheet possesses 4 valence orbitals ($2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals). The in-plane σ (bonding or occupied) and σ^* (antibonding or unoccupied) orbitals are formed by combining s , p_x and p_y orbitals. The interaction of P_z orbital, as perpendicular to the sheet, with the neighboring P_z orbitals forms delocalized π (bonding) and π^* (antibonding) orbitals. Similarity, the carbon atoms in SWNT are bonded by in-plane σ bonds which are responsible for binding energy between them. A delocalized π networks across SWNT are responsible for its electronic properties as well as bundled tubes formation through van der Waals forces. It is necessary to study the

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electronic structure of graphene in order to understand the electronic properties of SWNT.

2.2.1 Tight Binding Calculation from 2-D Graphite to Nanotube

The tight binding model has been adopted and widely discussed on SWNT by Saito and Dresselhaus(11) in 1991 due to applying it on 2-dimensional graphite system, which provide a fundamental study on understanding electronic properties of SWNT. A unit cell of hexagonal graphene lattice consists of two atoms (A and B). The lattice basis vectors ($\vec{a}_1$ and $\vec{a}_2$) in the graphene sheet and the corresponding reciprocal-lattice basis vectors ($\vec{b}_1$ and $\vec{b}_2$) in the Brillouin zone are shown in Figure 2-3(a) and 2-3(b) respectively.

Figure 2-3 Brillouin zone and reciprocal space. (a) Basis vectors in the hexagonal lattice of graphene. (b) Brillouin zone. The corresponding reciprocal basis vectors read $b_1 = b(1/2, \sqrt{3}/2)$ and $b_2 = b(1/2, -\sqrt{3}/2)$, with $b = 4\pi/a\sqrt{3}$. Reproduced from ref. 10.

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A carbon atom at position $\mathbf{r}_s$ has an unsaturated π orbital described by the wave function $\chi_{rs}(\mathbf{r})$ (12). According to the tight binding model, the interaction between P_z orbitals only takes places with the nearest-neighbor atoms. By solving the corresponding Schrödinger equation and applying the Bloch theorem, the wave function of the carbon atoms interaction can be written as

$$\langle \chi_{rA} | H | \chi_{rA} \rangle = \langle \chi_{rB} | H | \chi_{rB} \rangle = 0 \quad (2)$$

$$\langle \chi_{rA} | H | \chi_{rB} \rangle = \langle \chi_{rB} | H | \chi_{rA} \rangle = \gamma \delta_{\mathbf{rA}-\mathbf{rB}=\mathbf{a}}, \quad (3)$$

Where $\mathbf{a}$ is a vector connecting nearest-neighbors between the A and B sublattices and the on-site interaction energy is zero.

In order to calculate the electronic structure, the Bloch wavefunction of each sublattices is expressed as

$$\phi_{sk}(\mathbf{r}) = \sum_{\mathbf{r}_s} e^{i\mathbf{k} \cdot \mathbf{r}_s} \chi_{\mathbf{r}_s}(\mathbf{r}), \quad (4)$$

Where s refers to sublattices (A or B) and $\mathbf{r}_s$ is a set of data related to sublattice s . the linear combination of these two functions is applied to derive the total wavefunction as

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{2}} [\phi_{Ak}(\mathbf{r}) + \lambda_k \phi_{Bk}(\mathbf{r})], \quad (5)$$

The Hamiltonian matrix elements are

$$\langle \phi_{Ak} | H | \phi_{Ak} \rangle = \langle \phi_{Bk} | H | \phi_{Bk} \rangle = 0, \quad (6)$$

$$\langle \phi_{Ak} | H | \phi_{Bk} \rangle = \langle \phi_{Bk} | H | \phi_{Ak} \rangle^* = H_{AB} = \gamma \sum_{\mathbf{a}} e^{i\mathbf{k} \cdot \mathbf{a}}, \quad (7)$$

To obtain the Schrodinger equation in matrix form:

$$\begin{pmatrix} E & -H_{AB} \\ -H_{AB}^* & E \end{pmatrix} \begin{pmatrix} 1 \\ \lambda_k \end{pmatrix} \quad (8)$$

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After solving this matrix, the solution is as:

$$E = \pm |H_{AB}| = \pm \lambda \sqrt{1 + 4 \cos\left(\frac{3}{2} k_y a\right) \cos\left(\frac{\sqrt{3}}{2} k_x a\right) + 4 \cos^2\left(\frac{\sqrt{3}}{2} k_x a\right)} \quad (9)$$

This is the band structure of graphene as function of K_x and K_y as illustrated in Fig.2-4.

The valence and conduction bands connect at six corners of the Brillouin zone, resulting that graphene is a semi-metal with zero-gap.

Figure 2-4: Electronic structure of graphene only consisting of π electrons calculating from tight-binding model. Reproduced from ref. 12.

To find out the electronic structure of SWNTs, the quantization of the electron wavevector along the circumferential direction from graphene structure is expressed as:

$$k \cdot C = k_x C_x + k_y C_y = 2\pi p \quad (10)$$

where C and p are wrapping vector of the tube and an integer respectively. A relation between K_x and K_y defining lines in the (k_x, k_y) plane is indicated at equation 10.

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The intersection point in graphene band structure is determined by value of C_x , C_y and p . Therefore, different type of SWNTs exhibit different electronic structure owing to its own set of C_x , C_y and p value. From the band structure perspective, SWNT exhibits semiconducting electronic structure as there is no intersection between quantized wavevector lines and Fermi points. Whereas metallic SWNT is obtained as there is intersection between quantized wavevector lines and Fermi points as shown in Fig. 2-5. The band structure of semiconducting and metallic zigzag CNTs are illustrated in Figure 2-5.

In general, the determination of (n,m) metallic SWNTs is governed by $n-m = 3p$, where p is an integer. The (n,m) SWNTs with $n-m \neq 3p$ and $n-m = 3p$ exhibit semiconducting and metallic characteristic respectively. The electronic and transport properties of SWNTs are closely related to the states near the K point where is referred to the states near the Fermi energy. For instance, the states along line closest to the K point represent the conduction band and valence band in a semiconducting tube. In addition, the relations between the bandgap and diameter(13-14), which is depicted as $E_g \approx \hbar v/R$, can be found out by looking at the two lines which are closest to graphene Fermi point.

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Figure 2-5: Illustration of allowed wavevector lines leading to semiconducting and metallic CNTs. The band structures of semiconducting and metallic zigzag CNTs. Reproduced from ref. 12.

2.2.2 Density of States (DOS) of SWNT

The electronic properties of SWNTs can be predicted from DOS of SWNTs which can be expressed as:

$$D(E) = \frac{\sqrt{3}a^2}{2\pi R} \sum_i \int dk \delta(k - k_i) \left| \frac{\partial \epsilon}{\partial k} \right|^{-1}, \quad (11)$$

Where $\epsilon(k_i) = E$. The calculated DOS of SWNTs exhibits one-dimensional Van Hove singularities as the band edges as illustrated in Figure 2-6. Experimentally, scanning-tunneling microscopy is adopted for verifying the existence of these singularities in DOS of SWNT. In general, SWNT exhibits metallic characteristic as there is presence of DOS

at Fermi energy level. Whereas there is absence of DOS at Fermi energy level for semiconducting tubes.

Figure 2-6: Density of states for (11,0) semiconducting and (12,0) metallic CNTs showing van Hove singularities from tight-binding model. Reproduced from ref. 12.

2.3 Individual Single-Walled Carbon Nanotube-Based Transistor (SWNT-FET)

Surprisingly, the prototype SWNT-FET has been demonstrated to outperform the best silicon-based metal-oxide-semiconductor FET (MOSFET)(15-16). Indeed, it is reasonable from material science perspective. First, due to high aspect ratio structure of SWNT results weak scattering probability of carriers within SWNT leading to outstanding electronic transport properties. Thus, short channel SWNT-FET operates in the ballistic transport regime which unlikely occurs at MOSFET. In addition, requirement of passivation, which is technologically adopted at MOSFET, is not necessary at

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nanotube and gate dielectric interface due to absence of dangling bond at its surface. Based on the above merits, it attracts tremendous efforts from nanotube researchers on development of SWNT-FET to fully utilize its unique and astonishing properties.

2.3.1 Top-gated SWNT-FET

Initially, the Si backgate configuration with noble metal as electrodes is used for demonstrating SWNT-FET. Despite showing fascinating electrical properties, such kind of device configuration exhibits large contact resistances and poor electrical characteristic of SWNT-FET resulting in underperforming its intrinsic electrical properties (17-18). With enormous efforts on improvement of device performance from nanotube researchers, there is a remarkable achievement in term of device performance (19). The top-gate configuration has been established in conventional MOSFET and proved superior to Si backgate configuration. Dai's group has demonstrated top-gate SWNT-FET with Pd electrodes and Al top-gate separated with HfO₂ high-k dielectric (20). The high performance enhancement-mode semiconducting SWNT-FETs exhibited high on-off ratio up to 5 orders, no ambipolar conduction as well as 80 mV/decade subthreshold swings as shown in Figure 2-7.

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Figure 2-7: A SEM image of top-gated SWNT-FET and its transfer characteristic. Reproduced from ref. 20.

2.3.2 Ambipolar SWNT-FET

Figure 2-8: (a) A plot for transfer characteristic of an ambipolar SWNT-FET with indicating the hole accumulation, depletion and electron accumulation region. (b) A plot for output characteristic of an ambipolar SWNT-FET with various temperatures. Ohmic behaviour is observed at room temperature suggesting small energy barrier. (inset) An Arrhenius plot for this device indicates occurrence of thermal assisted tunneling. Reproduced from ref. 21.

Theoretically, it is possible to observe an ambipolar characteristic from SWNT-FETs with appropriate energy-level alignment between metal electrode and nanotube. In Figure

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2-8, an ambipolar SWNT-FET is observed likely due to the Fermi level of metal electrode aligns with the midgap of nanotube, leading to highest schottky barrier for both electron and hole injection. Surprisingly, output curve (I_{ds} - V_{ds}) exhibits ohmic at room temperature as shown in Figure 2-8, indicating that no barrier exists at nanotube/metal interface (21). Based on the temperature dependence data, the observation of electron and hole accumulation region indicated from transfer curve suggest that barrier height for both electron and hole injection are shallow. Thus, carriers easily tunnel through thin quasi-transparent junction at the nanotube/metal interface with thermal assisted and it is known as tunneling mechanism. In addition, SWNT is highly sensitive to surrounding environment which could alter its intrinsic characteristic. For instance, a SWNT-FET fabricated with Co metal as electrodes and annealing under hydrogen gas condition exhibited air-stable and ambipolar characteristic (22), suggesting that the electrical characteristic of SWNT-FET is significantly influenced from both of metal electrodes used and surrounding environment condition.

2.4 Single-Walled Carbon Nanotubes Network or Thin Film Field-Effect Transistor (CN-FET)

In the previous section 2.3, high performance individual SWNT-FET has been discussed from device configuration perspective. Despite demonstrating an incredible electrical performance in FET configuration, a precise positioning and well alignment of SWNT for SWNT-FET fabrication still remains as a main technological challenge for its

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application. In contrast, the formation of SWNT networks is relatively easy and possibly adopting established conventional techniques either by direct growth on a catalyzed substrate or by deposition on substrate from SWNT solution. The aligned arrays of SWNTs by direct growth on the substrate with catalyst deposited and their characterizations have been demonstrated (23-25). The electrical performance of aligned SWNTs arrays FETs will be discussed later. Similarly, SWNT network or thin film field-effect transistor (CN-FET) has also been intensively studied for realization of future electronic applications. Fundamentally, there are several major issues arise from CN-FET such as poor electrical performance owing to coexistence of metallic and semiconducting tubes in pristine SWNTs, tendency of forming bundled SWNTs caused by van der Waal interaction between SWNTs as well as gate hysteresis arising from field-effect transistor configuration. The above issues require intensive fundamental researches and subsequently seeking effective approaches to tackle them in order to obtain high electrical performance CN-FETs. Recently, there is an incredible breakthrough in improving CN-FET performance owing to enormous efforts from numerous research groups. In the subsequent few sections, the issues and current available solutions for improving electrical performance of CN-FET will be addressed.

2.4.1 Techniques for Sorting Single-Walled Carbon Nanotubes

The selection of SWNTs with desired properties is the bottleneck of electronic applications from CN-FET. For instance, enrichment of semiconducting SWNTs from the pristine nanotubes by all means is the major challenge for realizing the electronic

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applications based on CN-FET owing to coexistence of M and S-SWNTs. Despite tremendous efforts on development of the SWNTs growth method, the selective SWNTs growth technique for effective producing identical population of SWNTs with desired properties is still in progress. Ever since the discovery of SWNTs in 1991, it has been widely regarded as most potential candidate for carbon-based electronics. However, the lack of uniformity in the electronic properties of SWNTs obstructs realization of electronics based on CN-FET. Thus, development of effective and innovative solutions is essential for overcoming this drawback. Recently, the development of post-synthetic sorting schemes and selective growth methods for assembly of bulk SWNTs with desired properties have been intensively investigated with the substantial effort from researches (26-28).

To accomplish optimal performance of CN-FET in electronic applications, populations of SWNTs should be monodisperse with respect to electronic type (semiconducting tubes). Besides, obtaining semiconductor-enriched tubes, the evaluation of an effective SWNT sorting technique should consider the subsequent several factors: (1) high scalability technique for fulfilling the demand of increase in SWNTs production, (2) high compatibility with bulk SWNTs with respect to lengths and diameters for avoiding the secondarily issues arising from as-synthesized bulk SWNTs, (3) non-degradation of SWNTs for retaining its outstanding electronic transport properties by preferably introducing nondestructive sorting technique, (4) high reproducibility of sorting technique for further improving in purity level, (5) high affordability for realizing incorporation into target applications. Ultimately, the above requirements for a SWNTs

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sorting technique should be met in order to implement it for realizing SWNTs in commercial applications.

2.4.1.1 Electrophoretic Separation

Owing to the similar dimension and size between SWNTs and many biomolecules, researchers have borrowed the established separation technique from life science research field such as electrophoretic separation for sorting out SWNTs in term of their physical and electronic properties. The high aspect ratio SWNTs in nano scale which is relatively mobile in gel, capillary with aid of a direct current (d.c.) and such merit is widely used for electrophoretic separation of SWNTs. The gel and capillary electrophoresis techniques have been demonstrated as effective separation technique on SWNTs in term of diameter and length (29-32). Despite great diameter and length selectivity of SWNTs, selectivity on electronic type of SWNTs is still impossible. In 2003, R. Krupke and coworkers have demonstrated that alternating current (a.c.) dielectrophoresis technique can successfully sorts SWNTs with electronic type owing to differences in dielectric constant between metallic and semiconducting SWNTs (33). Figure 2-12 illustrates the experimental setup for dielectrophoresis of introducing a drop of SWNTs dispersion on a microelectrode array and metallic SWNTs have greater tendency towards high electric field resulting in selective depositing on the substrate between microelectrodes via applying a.c.. It has been reported that the efficiency of sorting SWNTs based on electronic type can be significantly enhanced by optimizing the electric field intensity as well as its frequency (34-35). In addition, neutralization of the surface charges on semiconducting SWNTs via the aid of surfactant encapsulation can further improve the

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electronic type selectivity of SWNTs (36). Despite exhibiting an effective SWNT sorting technique, the relatively low throughput hinders its potential to be established as most promising sorting technique.

Figure 2-9: (a) A schematic illustration of the typical experimental setup for dielectrophoresis of a drop of SWNTs solution using a microelectrode array. (b) From dark-field microscope image during dielectrophoresis, the Rayleigh scattered light indicates SWNTs alignment between microelectrodes with the electric field. Reproduced from ref. 33.

2.4.1.2 Ultracentrifugation

Ultracentrifugation is another fascinating post-synthetic sorting approach which is scalable and compatible with Si conventional processing technology. In conventional ultracentrifugation, SWNTs are sorted in a constant density medium based on their sedimentation coefficient. It is crucial to consider buoyant density and molecular weight for further enhancing SWNTs sorting efficiency by conventional ultracentrifugation due to greatly depend on the sedimentation coefficient. Thus, the achievement of sorting SWNTs electronic type either metallic or semiconducting tubes via conventional ultracentrifugation has been reported through strategic utilizing the specific chemical

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interaction between adding molecules and specific electronic type of SWNTs for differentiating their sedimentation coefficient (37-38).

Amazingly, M. C. Hersam's group has discovered a powerful sorting technique known as density gradient ultracentrifugation (DGU) which basically exploits a gradient density medium for creating density gradient within the centrifuge tube and is exclusive SWNTs separation by their buoyant density after ultracentrifugation (39). Theoretically, SWNTs diffuse to their respective isopycnic points (point that SWNT density matches the density of the gradient) within the gradient via ultracentrifugation resulting in accomplishment of SWNTs separation. According to their buoyant density, SWNTs are differentiated in several layers in centrifuge tube. Assuming formation of uniform encapsulating surfactant layer surrounding SWNTs, the only difference in SWNTs physical property to affect its buoyant density is diameter resulting in high selectivity on diameter. A hydrodynamic model is adopted to describe the motion of SWNTs and surfactant encapsulation surrounding SWNTs during DGU (40).

Sorting SWNTs by diameter via DGU separation technique was primarily demonstrated in DNA-SWNT hybrids system(39). Despite high selectivity on SWNT diameter, this system fundamentally exists several sticking issues such as irreversible wrapping DNA surrounding SWNTs obstructing recovery of its intrinsic properties, high cost of DNA limiting the potential to be promising separation technique in future applications and limitation on inability to disperse large-diameter (>1.2nm) SWNTs resulting in low flexibility on pristine SWNTs starting material used. Therefore, it is crucial to search a replacement of DNA for dispersing SWNTs and the most widely used candidate is surfactant such as sodium dodecyl sulfate (SDS), sodium

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dodecylbenzenesulphonate (SDBS) and sodium cholate (SC). The pioneer research group on discovery of DGU separation technique has reported that the achievement of SWNTs diameter and electronic sorting via DGU can be realized with the aid of SC surfactant encapsulation and co-surfactant system mixtures of SC and SDS (4:1 wt % ratio) respectively as shown in Figure 2-10 (41). It is speculation that the inequivalent binding of the two surfactants as a function of the SWNT polarizability causes differences in the density of the SWNT-surfactant hybrid resulting in electronic type sorting of SWNTs in cosurfactant encapsulation assisted DGU.

Figure 2-10: (a) A image of SWNT sorting with diameter by density gradient ultracentrifugation. The optical absorbance spectra of different fractions indicate the selectivity of SWNTs diameter. (b) Sorting SWNT with electronic type can be achieved by density gradient ultracentrifugation with co-surfactant system. The optical absorbance spectra confirm sorting by electronic type from analyzing the unique optical transitions of semiconducting SWNTs (S22 and S33) and metallic SWNTs (M11). Reproduced from ref. 41.

2.4.1.3 Chromatography

Adopting the established method from biochemistry on sorting molecules or compounds, it is possible for sorting SWNTs owing to similar chemistry properties. The most popular sorting approach in biochemistry field is chromatographic method. Indeed, ion-exchange

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chromatography (IEX) of DNA-encapsulated SWNTs hybrids system has recently shown a decent promise for sorting SWNTs by diameter or electronic type (42). Despite the encouraging results from adopting IEX sorting process, variation in SWNT length complicates the IEX diameter and electronic type sorting process (43). Therefore, it is necessary to sort the SWNTs length as well for ensuring the effectiveness of IEX diameter and electronic type sorting process. Hence, size exclusion chromatography (SEC) is widely used for sorting SWNTs length first and then carrying out IEX sorting process for improving the SWNT sorting quality on diameter and electronic type (44-46). The success of desired SWNT length and chiral angle separation has been achieved by combining SEC and IEX sorting process on narrow diameter SWNTs (42). However, such approach on DNA-SWNT hybrid system is highly sensitive to SWN diameter distribution and only effective for SWNT with small diameter ($<1.2\text{nm}$). It is essential to understand the role of the DNA sequence used for SWNTs sorting and the dynamic mechanism of DNA-SWNT hybrid system formation in order to figure out the selectivity of SWNT in diameter and length as well as electronic type. The sequence and length of DNA determine the effectiveness of SWNT sorting. DNA length must be comparable with the sorted SWNT length. Experimentally, the SWNTs sorting results from DNA-SWNT hybrid system can generally be obtained with a sequence of $(\text{GT})_n$ where n is 10 to 45 (47). Amazingly, Zheng Ming's research group has recently observed the DNA sequence specificity in SWNT separation and reported that by IEX with specific DNA sequence wrapping SWNTs which allows purifying each and every single-chirality semiconducting species from a synthetic mixture of SWNTs (48). Table 2-1 summarizes a list of DNA sequences enabling chromatographic purification of single chirality

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semiconducting SWNTs. Figure 2-11 reveals that optical absorption spectra of all purified semiconducting (n,m) species after undergoing chromatographic purification and the starting material HiPCO SWNTs for comparison. Owing to the extremely high purity of specific purified semiconducting (n,m) species obtained, the third lowest electronic transition of semiconducting species (S33) can be clearly observed in the respective optical absorption spectra. Despite demonstrating an astonishing finding on single-chirality purification, the structural basis for the observed DNA sequence specificity in SWNT purification is still under investigation. It is exceptionally important to find out the DNA sequence specificity for further purifying wider range of semiconducting species as well as metallic species.

Table 2-1: DNA sequence versus SWNT chirality. Reproduced from ref. 48.

Chirality (n,m)	Sequences
(9,1)	(TCC) ₁₀ , (TGA) ₁₀ , (CCA) ₁₀
(8,3)	(TTA) ₄ TT, (TTA) ₃ TTGTT, (TTA) ₅ TT
(6,5)	(TAT) ₄ , (CGT) ₃ C
(7,5)	(ATT) ₄ , (ATT) ₄ AT
(10,2)	(TATT) ₂ TAT
(8,4)	(ATTT) ₃
(9,4)	(GTC) ₂ GT, (CCG) ₄
(7,6)	(GTT) ₃ G, (TGT) ₄ T
(8,6)	(GT) ₆ , (TATT) ₃ T, (TCG) ₁₀ , (GTC) ₃ , (TCG) ₂ TC, (TCG) ₄ TC, (GTC) ₂
(9,5)	(TGTT) ₂ TGT
(10,5)	(TTTA) ₃ T
(8,7)	(CCG) ₂ CC

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Figure 2-11: Optical absorption spectra and atomic structures of purified semiconducting SWNTs and the starting HiPco mixture. The structure of each purified SWNT species (viewed along the tube axis) and its (n,m) notation are given at the right side of the corresponding spectrum. Reproduced from ref. 48.

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2.4.1.4 Selective Chemistry

Owing to the perfect hexagonal geometrical structure of SWNT surface, it is widely anticipated that the high specificity reaction with reactive chemical molecules such as diazonium reagent and etc with hexagonal benzene structure. The exploration of chemical selectivity with respect to SWNT electronic type, diameter and/or chiral handedness always remains as a promising approach for searching a way to obtain SWNTs with uniform desired properties to target applications. Based on different strategies for chemistry on SWNTs, selective chemistry on SWNTs basically can be classified into five different major categories in term of chemistry nature as follow: (1) covalent sidewall chemistry; (2) covalent chemistry at defect sites or open ends; (3) non-covalent surfactant encapsulation; (4) non-covalent polymer wrapping; (5) presence of molecules into the SWNT interior (49) as schematically illustrated in Figure 2-12. Owing to high reactivity and ease of accessibility, chemistry on SWNT exterior sidewalls is widely regarded a most effective approach for sorting SWNTs. For instance, functionalization of SWNTs with diazonium reagents reveals high selectivity on metallic SWNTs by covalent sidewall chemistry (50-51). The proposed mechanism on selectivity of metallic SWNTs is the availability of electrons near the Fermi level in metallic SWNTs facilitates the reaction, resulting in preferably forming covalent bond between metallic SWNTs and diazonium reagents rather than semiconducting SWNTs. Covalent functionalization of metallic SWNT with diazonium reagents under highly favourable condition lead to suppression of metallic SWNTs conductance in thin-film electronic device owing to change in the electronic properties of metallic SWNTs (52-53).

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In addition, dichlorocarbene covalent chemistry has been reported as an effective method for converting metallic SWNTs to semiconductors. The attachment of dichlorocarbene on preferential metallic SWNTs via covalent bonding causes splitting of band structure at its Fermi level resulting in band gap formation behaving like semiconductors (54). Furthermore, achievement on diameter selectivity of SWNTs has been demonstrated via direct protonation using binary sulphonic acid mixtures due to great sensitivity of geometric strain from protonation (55). Normally, there is no significant difference between metallic and semiconducting SWNTs in term of physical properties resulting in difficulties in identification and separation via conventional separation technique. By utilizing the discrete functionalization of specific electronic type SWNTs, it is possible to sort SWNTs according to electronic type with aid of conventional separation technique. One approach is the cycloaddition of azomethine ylides derived from trialkylamine-N-oxides labeled with polycyclic aromatics for functionalizing semiconducting SWNTs (56) and subsequently sorting functionalized semiconducting SWNTs from pristine SWNTs. Despite accomplishing electronic type SWNTs sorting, Addition of conventional separation technique is required for complicating the approach. Recently, the cycloaddition of fluorinated olefins has been explored and proved that great effectiveness for suppressing metallic conductivity without degrading semiconducting lead to ease of production in semiconducting-like SWNTs suspension (57).

Figure 2-12: A schematic illustration of several selective chemical functionalization of SWNTs approaches for sorting out SWNTs. (a) Covalent sidewall chemistry. (b) Covalent chemistry at defects or open ends. (c) Non-covalent surfactant encapsulation. (d) Non-covalent polymer wrapping. (e) Molecular insertion into the SWNT interior. Reproduced from ref. 49.

As knowing that SWNTs possess outstanding unique properties, it is crucial to retain these unique properties for future applications. Hence, selective non-covalent chemistries are preferable compare to selective covalent chemistry owing to small alteration on the unique properties of SWNTs upon functionalization. The selective non-covalent chemistries from amines derivatives such as propylamine and isopropylamine has been confirmed the ability of selectivity on SWNTs electronic type by preferential functionalization of metallic SWNTs (58-59). By contrast, semiconducting SWNTs exhibiting relatively greater extent of interaction with octadecylamine compare to metallic SWNTs species (60-61). In addition, the ease of charge-transfer complex

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formation between bromine(37) and charge-transfer aromatics(62) with metallic SWNTs owing to carrier abundance paves a way for possibility of electronic type selectivity. Common surfactants (sodium dodecyl sulphate, sodium dodecylbenzene sulphonate and sodium cholate) have not only exhibited the marvelous ability of dispersing SWNTs in aqueous phase, but also experimentally confirmed with certain degree of diameter selectivity due to distinct interaction with SWNTs (63).

Owing to the remarkable merit of selective non-covalent chemistry, it has motivated researchers for exploring the possibility of sorting electronic type SWNTs while retaining its incredible unique properties. With enormous efforts, another effective approach on functionalization of semiconducting SWNTs has been demonstrated based on porphyrin chemistry via utilizing discrete interaction between porphyrin and semiconducting SWNTs (64). Besides revealing the effectiveness of sorting electronic type SWNTs, the SWNTs chiral handedness selectivity has recently demonstrated by using chiral diporphyrin molecules (65). By utilizing the non-covalent interaction between polymers such as fluorine-based polymers and SWNTs, the fluorine-based polymers not only easily wrap SWNTs but also exhibit high selectivity on SWNT diameter and electronic type particular in small-diameter SWNTs (66-67). Moreover, it has been demonstrated that high affinity to metallic SWNTs from the solvents which comprise of aromatic backbones and electron-withdrawing groups owing to existence of electrons near its Fermi level (68).

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2.4.1.5 Selective Destruction

Elimination of undesired SWNTs species is critical to obtain the SWNTs with desired properties. The feasibility of adopting selective destruction approaches have also been explored owing to the high reactivity of SWNTs. However, the selective destruction typically is an irreversible process as well as lack in controllability and reproducibility, resulting in non-favourable sorting technique approach. Nevertheless, the effectiveness of selective destruction approaches is promising and the research findings are interesting in term of understanding nature of SWNTs. For instance, gas-phase selective etching of targeted SWNTs species can be achieved under favourable conditions due to various extent of oxidation from different SWNTs species. Dai's group has demonstrated that SWNTs with small diameters and high chiral angles are preferentially oxidized under an oxygen-rich atmosphere with thermal annealing condition (69). Thus, gas-phase selective reaction deliberately achieves reduction in SWNT diameter distribution leading to small diameter variation. Another popular selective destruction approach is known as selective electrical breakdown of metallic SWNTs. The precondition for ensuring the success of this approach is that FET device deliberately operates at the depletion region of semiconducting SWNTs by applying sufficient gate bias and only permits vast currents passing through highly conductive M SWNTs pathway resulting in electrical breakdown of M SWNTs for accomplishing S FET characteristic.

2.4.1.6 Selective Growth

The above strategies are basically post-growth approach which adopts a wide variety of effective treatments on as-grown pristine SWNTs for achieving treated SWNTs with

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desired properties. Another category of SWNT sorting technique approach is known as selective growth approach which paves the way for obtaining narrow distribution of SWNTs' structure and/or electronic type with retaining its outstanding intrinsic properties. The SWNT synthesis method is briefly discussed at section 2.1.1. Regardless with the type of synthesis method, factors such as precursor and catalyst as well as growth conditions are extremely crucial in order to grow SWNTs. The requirement on these factors is even more stringent for accomplishing selective SWNT growth with targeted desire properties. With enormous efforts on exploring these factors, the research findings suggest that the SWNT growth conditions such as temperature(70), pressure(71-72), carbon feedstock(73-74), catalyst particle size(75) and catalyst material(76-77) play determining role for optimizing the selective growth with respect to either physical and/or electronic properties. For instance, exploitation of bimetallic catalysts such as CoMo(74, 76) and FeRu(77) offer precise controlling catalyst size resulting in high selectivity of SWNT diameter. The additional merit by wise selecting appropriate catalyst is able to obtain narrow (n,m) SWNT distribution with more uniform properties. In addition, Plasma enhanced chemical vapour deposition is preferable for growing enriched semiconductor SWNTs under highly controlled conditions (78).

2.4.2 Removal of SWNT bundles

SWNTs have high tendency on forming SWNT bundles via substantial van der Waals forces (950 meV/nm)(79) resulting in difficulty of obtaining individual SWNT in solution. Ever since discovery on SWNT in 1991, dispersibility of SWNT commonly remains as major issue. With tremendous efforts on finding the suitable candidates for

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dispersing SWNT in solution form, it can be achieved using surfactants or polymers to stabilize SWNTs dispersion via reducing its surface energy (80-81). In the conventional method, SWNT is dispersed in aqueous solution with aid of surfactant encapsulation via ultrasonication and then follow by ultracentrifugation for obtaining individual dispersed SWNTs. Despite encapsulating with surfactant, the stability of individual dispersed SWNTs is relatively low resulting in gradual aggregation forming bundled tubes after without ultrasonication. Besides low stability, the quantity of individual dispersed SWNTs in aqueous solution is rather low after ultracentrifugation.

Figure 2-13: (a) A separatory funnel showing the interface between the oil and water phases. (b) Optical micrograph of toluene/water emulsions stabilized by SWNTs. (c) Illustration of the SWNTs adsorption at the interface resulting in change in the interfacial area and the wetting properties of the nanotube. Reproduced from ref. 85.

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Searching promisingly alternative approach on debundling of SWNTs has been persistently intensified in order to achieve individual well-dispersed SWNTs. Recently, Coleman's group has demonstrated that the achievement of SWNTs debundling by dispersing SWNTs in amide solvent (82) as well as in DNA-based dispersion (83) via isolation preventing individual SWNT contacts with each other and bundles through van der Waals interaction. Despite effective debundling of SWNT in DNA-based dispersion, inclusive removal of strongly attached DNA on its surface still remains as scientific challenge to recover its outstanding intrinsic properties. In addition, another strategical approach on SWNTs debundling demonstrated from Noda's group is known as nanoball-penetrating method which experimentally claims to be remarkably effective method for achieving nearly bundle-free SWNTs dispersion (84). The functionalized SWNTs via acid treatment possessing negatively charges on its surface can be easily dispersed in Tetramethylammonium hydroxide (TMAOH) solution with aid of water-based FePt nanoparticles (NPs) under appropriate conditions. Despite functionalization of SWNTs, their intrinsic properties and length remain unchanged owing to mild experimental conditions. Recently, Ziegler's group has reported that the viability of bundled SWNTs removal from aqueous solution has been demonstrated via organic-aqueous interfacial trapping at toluene-water interfaces without ultracentrifugation (85). The significantly valuable merit of this technique on accomplishing bundle-free SWNTs dispersion is without expense of its concentration which is habitually observed undergoing ultracentrifugation. The proposed mechanism on bundled SWNTs removal via interfacial trapping is likely due to reduction in free energy induced by change in wetting properties as well as interfacial area at toluene-water interface resulting in great tendency of

diffusion of bundled SWNTs towards the interface as schematically illustrated in Figure 2-13. The effectiveness of interfacial trapping method for bundled SWNTs removal has experimentally confirmed based on the increase in its fluorescence intensity after adopting this method. Obtaining high magnitude of fluorescence intensity after undergoing interfacial trapping method suggests that high concentration of individually dispersed SWNTs aqueous solution.

2.5 High Electrical Performance of CN-FET

Networks or thin films of SWNTs are widely regarded as most potential candidates of electronic material that can behave as high performance either semiconducting or conducting layers according to its electronic properties in field-effect transistors (FET) configuration. Such networks or films could pave the way for realizing sensible tube-based electronics systems by technical avoiding the fundamental challenge on rigorous control over the properties as well as accurate positions of individual SWNTs. They comprise any array of tubes ranging from random networks to nicely aligned arrays. The most remarkable difference between these two extreme circumstances is tube-tube contacts which widely anticipate as a major factor for causing high electrical resistance directly resulting in electrical performance of FET devices. Therefore, the electrical performance of the aligned arrays of SWNTs FETs in term of mobility generally is superior compared to random networks of SWNTs FETs as extensively revealed in details in subsequent sections. Nonetheless, high electrical performance of CN-FETs is

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determined by several electrical characteristics such as on-off ratio, mobility, threshold voltage and etc. In order to evaluate the electrical performance of semiconducting CN-FET, on-off ratio and mobility features are particularly crucial for determining the viability of realizing carbon-based electronics based on SWNT networks or thin films. On-off ratio is defined as division “ON” current versus “OFF” current; the ON and OFF current correspond to maximum and minimum current observed from the fixed range of gate bias at fixed source-drain bias, respectively. OFF current represents the proportion of metallic tube existing in its network or thin film. On the other hand, on-off ratio is also widely used for assessing the effectiveness of tube separation techniques which have been extensively discussed in section 2.4.1. Another feature is linear-regime effective field-effect mobility which is conventionally governed by this

equation: $\mu_{eff} = \frac{\left(\frac{\partial I_{sd}}{\partial V_g} \right)}{\left(\frac{\epsilon V_{sd} W}{L_{ox} L} \right)}$ where V_{sd} is source-drain bias, L_{ox} and ϵ are

thickness and dielectric constant of the SiO_2 gate oxide, W and L are channel width and length. The subsequent sections will systematically review the current significant achievement on demonstrating high electrical performance of CN-FETs for both perfectly aligned arrays of SWNTs and random networks of SWNTs.

2.5.1 Aligned Arrays of As-Grown SWNTs FETs

Despite outstanding electrical performance of single-tube transistor, integration of single-tube transistor remains a major challenge for realistic SWNT-based integrated circuits. Therefore, it is necessarily crucial to grow a well-aligned arrays of SWNTs which can be

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visualized as multiplying of numerous individual tube for retaining its incredible electrical performance and avoiding the technological challenge arise from single-tube FETs. There is a remarkable breakthrough on well-aligned arrays of SWNT growth field by J. Roger's group whose has demonstrated high-performance electronics using dense, perfectly aligned arrays of SWNTs from CVD growth with optimized parameters can be accomplished without compromising the outstanding properties of the individual SWNTs (25). The exceptional merits of using these arrays are large current outputs, relatively large active areas and small variation in device-to-device properties. The dense, perfectly aligned SWNT arrays not only preserve the intrinsic properties of SWNTs but also eliminate the effect of percolating transport pathways, inter-nanotubes overlap junctions, electrostatic screening as well as non-ideal electrical properties (86-88). In addition, the well-aligned SWNT arrays FETs exhibiting p-channel characteristic at ambient condition could be effectively converted to n-channel characteristic by coating with PEI on top of present FET device and its electrical characteristic is shown in Figure 2-14(b). Interestingly, thousands of fabricated devices possess average $1,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $3,000 \text{ S m}^{-1}$ in their's mobility and transconductance respectively, together with exceptionally high output current up to 1 A. Despite highly impressive electrical performance, development on precise control growth and large-scale production of these dense, perfectly aligned arrays of SWNTs still require massive efforts and researchs in order to implement in commercial applications. The major fundamental issue on this field is coexistence of metallic and semiconducting tubes in the dense, perfectly well-aligned SWNT arrays resulting in low on-off ratio and low yield of semiconducting device's production.

Figure 2-14: (a) optical (inset) and SEM images of dense, perfectly aligned arrays of SWNTs. (b) A plot for transfer characteristic of p- and n-channel transistors from aligned arrays of SWNTs and PEI-coated arrays of SWNTs, respectively. (c) Optical micrograph of high performance top-gated transistor with $L=32\text{ }\mu\text{m}$ and $W=200\text{ }\mu\text{m}$. (d) A plot for expressing mobilities as function of channel length by using parallel plate (μ_{dev} , blue triangle), rigorous (μ_r , black square) model, together with average mobilities per tube (μ_t , red circles). (e) A plot for scaled transconductances (g_m/W_{eff}) as function of channel length. Reproduced from ref. 25.

2.5.2 Random As-Grown SWNTs network FETs

Owing to intrinsic electronic properties of SWNTs, coexistence of metallic and semiconducting tube in as-grown SWNT network or thin film is most sticky hurdle. Recently, J. Joger's group has strategically exploited post-grown treatment on the SWNTs grown by CVD to improve on-off ratio through trivial compromising its mobility. Basically, a sub-monolayer, random SWNTs networks grown by CVD on the substrate was cut into desire strips geometries by combining phase-shift lithography and

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reactive-ion etching for preventing formation of metallic conductive path, resulting in electrical characteristic is favorably dominated by semiconducting path. Such networks serve as semiconducting material, were fabricated into integrated circuits with exceptionally decent electrical performance. The electronic properties of the medium-scale integrated circuits comprised of nearly 100 carbon-based transistors are high mobilities ($80 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), low subthreshold slopes (140 V dec^{-1}), low operating voltage ($<5 \text{ V}$), high on-off ratio up to 5 orders, relatively good switching speed in KHz range with $\sim 100 \text{ }\mu\text{m}$ channel length device geometries as shown in Figure 2-15 (89). Besides having outstanding electrical performance, the fabricated integrated circuits on plastic substrate possess good mechanical flexibility with high uniformity and reproducibility. The exceptional performance characteristic from sub-monolayer, random single-walled carbon nanotubes networks suggests that it is possibly for using random single-walled carbon nanotubes networks in commercial electronic applications such as flexible integrated circuits. However, scalability and productivity are the remaining challenges in order to realistically implement carbon-based electronics base on this approach in commercial applications.

Figure 2-15: (a) A SEM image of part of SWNTs circuit with presence of SWNTs strips in channel region. The inset is magnified view of the network strips corresponding to the highlighted channel region. (b) A photograph of a collection of SWNT transistors and circuits on a flexible plastic substrate (PI). (c) A plot of the measured (filled) and stimulated (open) data on the on-off ratio and normalized transconductance (g_m/g_{m0} , where g_{m0} represents the response without strips, blue) of devices with $100\mu m$ channel length as function of strips width. (d) Measured (solid) and stimulated (dashed) transfer curve of depletion-mode (blue) and enhancement-mode (black) transistors with $L=100\mu m$ and $W=200\mu m$. inset shows its transfer curve with various $V_{DS}=-0.5V$ (navy), $-2V$ (green) and $-5V$ (magenta). Reproduced from ref. 89.

2.5.3 Solution Processable Field-Effect Transistor Based on Semiconducting Carbon Nanotubes Network or Thin Film

Due to difficulty on precise control growth of dense, perfectly aligned arrays of SWNTs, solution processable random single-walled carbon nanotube networks provide an

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alternative option for transistor applications. The main advantages of solution processable CN-FETs comparing with dense, perfectly aligned arrays of SWNTs-FETs is scalable approach and highly compatible with the conventional silicon processing techniques. In general, such random single-walled carbon nanotubes network provides a great promise in making nanoscale electronic device. It has been widely discussed in section 2.5.1 that sorting semiconducting SWNTs is crucial to ensure random single-walled carbon nanotube network acted as semiconducting material. Recently, several research groups have explored various approaches for sorting semiconducting SWNTs from pristine SWNTs and demonstrated the feasibility of fabricating high performance CN-FETs device. Thus, the random semiconducting SWNTs networks may offer the most immediate opportunity for SWNTs to impact electronic applications.

Hersam's group has demonstrated that semiconductor-enriched SWNTs can be obtained with the aid of co-surfactant encapsulation by DGU which has been widely discussed in section 2.5.1.2. The fabricated CN-FET devices by transfer-print technique possess impressive electrical characteristic with its mobility and on-off ratio is $20 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and greater than 4 orders, respectively as shown in Figure 2-16 (41). In another study, the selective extraction of semiconducting SWNTs has been demonstrated by using polyfluorene as an extracting agent in toluene due to strongly specific interaction between polyfluorene and specific SWNTs (90-91). The electrical characteristic of the device exhibits p-type behaviour in ambient with on-off ratio and estimated hole mobility are up to 5 orders and $2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ respectively (92). In addition, the DNA generally possesses greater tendency on small diameter SWNTs and exhibits diameter selectivity. The DNA-SWNT hybrids further treat with size-exclusion chromatography (SEC) and ion-exchange

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chromatography (IEX) to further improve the chirality selectivity with only few (n,m) chiralities. After treating with chromatographic techniques, its average tube length is relatively short and such type of treated DNA-SWNT hybrids is suitable for nanoelectronics. Its device's performance with on-off current ratio up to 5 orders has been demonstrated under short channel device configuration, suggesting that abundance of semiconducting tubes exists in treated DNA-SWNT hybrids (93). Recently, the purification of single-chirality SWNTs has been reported by IEX separation of DNA-CNT hybrids owing to the unique ability of a particular DNA sequence for specific (n,m) species by Zheng's group (48). The fabricated short channel electronic devices exhibit high on-off current ratio up to 6 orders owing to single-chirality-enriched (10,5) tubes as shown in Figure 2-17 (94).

Figure 2-16: (a) A representative atomic force microscopy image of random SWNTs network and a schematic geometry of CN-FET with SiO_2 dielectric. (b) A plot for the transfer characteristic of semiconducting CN-FET (red) and metallic CN-FET (blue) in log scale. The inset shows linear scale transfer curve of semiconducting CN-FET. Reproduced from ref. 41.

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Figure 2-17: (a) A schematic physical structure of (10,5) tube. (b) a plot of Photoluminescence-vs-excitation (PLE) spectra of single-chirality-enriched (10,5) tube after IEX separation of DNA-SWNT hybrids. (c) A plot for the transfer characteristic of short channel device in log scale with various V_{ds} . Reproduced from ref. 94.

Figure 2-18: (a) Schematic of the SWNT TFT fabrication and structure. The SiO_2 dielectric is functionalized by either an amine-terminated (A) or phenyl-terminated (B) silane SAM. The SWNTs are deposited on modified substrate, followed by gold electrodes deposition for fabricating a top-contact device structure. AFM images ($10\text{ }\mu\text{m}$ by $10\text{ }\mu\text{m}$, z scale = 10 nm) of the nanotubes reveal the degree of density and alignment. (b) The top plot represents the maximum “on-current” for one typical wafer, and the bottom plot compares mobility and on/off ratio as a function of test location on the wafer. Reproduced from ref. 95.

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Bao's group recently demonstrates that the electrical characteristic of SWNT networks FET can be dramatically improved by selective absorption of amines or phenyl towards semiconducting or metallic SWNTs respectively via π - π stacking (95). Electronic structure separation, control of density and alignment of the self-sorted SWNT networks for diminishing intertube contacts can be achieved simultaneously in one step during device fabrication via spin-coating technique owing to highly specific interaction between SWNTs and silane compounds. The SWNT networks FETs fabricated on channel surface with amine-terminated silane attachment possess controllable topology and highest on-off ratio $\sim 900,000$ and effective field-effect mobility ranging from 0.5 to $6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ as plotted in Figure 2-18(b). Despite great promise, there are several factors such as stability of silane compounds in ambient, arrangement of silane compounds on substrate surface that directly affect the device's performance. In addition, the additional step of functionalization of substrate surface complicates the FET device fabrication process resulting in difficulty on scaling up the process.

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Figure 2-19: (a) Plot of I_{on} , I_{off} and linear mobility of fabricated devices with W (channel width) = 200 μm and L (channel length) = 20 μm at $V_{ds} = -0.1\text{V}$, together with the mean $\pm$ SD values as a function of PSEPVE/SWNT/molar concentration ratio c . The inset of I_{on} and I_{off} dependence on L for $c = 0.018$. (b) AFM images of pristine and PSEPVE functionalized SWNT at $c = 0.018$ and 0.038 . plot of transfer curve for (c) SWNT-PSEPVE and (d) SWNT-PFMDT TFTs at $c = 0.018$ and $V_{ds} = -0.1\text{V}$ and -0.01V , respectively. Reproduced from ref. 57.

Recently, cycloaddition of fluorinated olefins for functionalizing SWNTs has been reported to deactivate M tubes in commercially available HiPCO tubes (57). The concentration of the fluorination level is crucial for obtaining optimized mole ratio of fluorinated olefins to SWNTs. Its optimized fluorination level ($c \sim 0.018$) under controlled conditions is used for fabricating high electrical performance TFT devices. As plotted in Figure 2-19(c) & (d), the fabricated TFT devices from perfluoro-2(2-fluorosulfonylethoxy) propyl vinyl ether (PSEPVE) functionalized SWNTs and perfluoro (5-methyl-3,6-dioxanon-1-ene) (PMDE) functionalized SWNTs exhibit mobilities of 10

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$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and $104 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively and both with on/off ratio up to 5 orders. Overall, this method offers a promising route to produce S tubes inks used for printable electronics. However, the issue of reproducibility on fabricating such kind of S devices and its yield were not reported. Both of factors are extremely crucial to implement such method for realizing printable electronics based on SWNT networks or thin films.

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3. Experiments

In this chapter, several SWNT samples by different types of growth methods as starting materials were used for preparing SWNT aqueous dispersion with aid of surfactant. In order to obtain well-dispersed SWNT in aqueous solution, several methodologies such as ultrasonication, ultracentrifugation and density gradient ultracentrifugation are adopted. Characterization tools including absorption, photoluminescence and Raman spectroscopy are used for identifying the optical properties of the SWNTs. In addition, FET fabrication via drop casting method and characterization are also illustrated for assessing electrical performance of semiconducting CN-FET.

3.1 SWNT Samples

The SWNT samples with various diameters distribution and chiralities used in this thesis were purchased from various suppliers or supplied from collaborators' laboratories. In general, each SWNT growth technique produces distinct properties of SWNT in term of diameter and chirality distribution, proportion of M and S tubes and quality of SWNTs. The population of S and M tubes is approximately 67% and 33% respectively from conventional growth methods. In Table 3-1, the author lists several explored SWNT sample sources, which vary with (1) growth method such as arc-discharge and CVD method, and (2) diameter distribution from 0.7 nm to 1.4 nm. For instance, nanotubes produced by arc-discharge growth method from different collaborators' laboratories expect variation in chiralities, and composition of M and S tubes content. In contemporary CVD growth technique with appropriate catalyst in suitable size range

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under highly controlled and favourable growth parameters condition, as-grown SWNTs with specific properties can be synthesized for applications as extensively described in section 2.4.1.6. Therefore, the author specifically selected CoMoCat65 and CoMCM41 tube sample sources with major chiral tubes as (6,5) and (7,5),(6,5) respectively for exploring the effectiveness of separation techniques such as DGU and chemical functionalization. As far as this thesis is concern, the author has scarcely explored the electrical properties of SWNTs for realizing high electrical performance of FET based on its networks or thin films. The selection of appropriate SWNT sample sources is extremely crucial to determine the effectiveness of each particular separation technique as broadly illustrated in section 2.4.1.

Table 3-1: The explored SWNT samples in this thesis and their diameters distribution range based on the statistical measurements by TEM and Optical measurements.

Sample Code	Source	Description (Diameter distribution range)
ARC	Prof. Green's Group (Inorganic Chemistry, Oxford)	Produced by arc-discharge method (1.0 ~ 1.4nm)
P2	Carbon Solutions Inc.	Produced by arc-discharge method (1.0 ~ 1.4nm)
N-Arc	Dr. M. Glerup (Chemistry, Oslo)	Nitrogen-doped arc-discharged tubes (1.0 ~ 1.4nm)
BN-Arc	Dr. M. Glerup (Chemistry, Oslo)	Boron & Nitrogen-doped arc-discharged tubes (0.9 ~ 1.3nm)
CoMoCat 65	South West NanoTechnologies Inc.	Cobalt – Molybdenum catalyzed (0.7 ~ 0.9nm) (6,5) tube specie enriched
CoMCM41	Asst. Prof. Chen Yuan (School of Chemical & Biomedical Engineering, NTU)	cobalt-incorporated MCM-41 (Co-MCM-41) catalysts (< 0.9nm)

3.2 SWNT Aqueous Dispersion

SWNTs are one of most outstanding materials for a wide variety of applications owing to their unique properties. However, the low solubility of SWNTs in aqueous phase and tendency of forming bundle owing to van der Waals forces interaction with each other have hindered their applications. Thus, solubilization and dispersion of pristine SWNTs are primarily major issues in carbon nanotube research. The solubility of SWNTs can be enhanced by chemical modification (1). Despite improvement of SWNTs solubility, the chemical modification leads to disruption of their electronic structure owing to generation of defect sites on tube wall (2). O'Connell et al. have demonstrated that ultracentrifugation is an effective method for dispersing and separating individual and bundled tubes with the aid of surfactant encapsulation (3). The influence of surfactant encapsulation on its electronic structure is spectacularly weak compare to chemical modification. As a result, SWNT aqueous dispersion via ultracentrifugation with surfactant encapsulation is most popular method and initiates the wide variety of carbon nanotube researches on aqueous phase.

3.2.1 Ultrasonication & Ultracentrifugation

Dispersed SWNTs in aqueous suspensions in this thesis were prepared by ultracentrifugation method. Typically, 4 mg of SWNTs was dispersed in 10 ml H₂O solution with 2 wt % surfactant (SDS or SC) or co-surfactants (SDS-SC at 1:4 ratio) as encapsulation agent via ultrasonication for 30 mins. The ultrasonication was implemented by immersing an ultrasonic probe (Sonics & Materials Inc., Model: VCX 130) into the

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SWNT solution with co-surfactants for 20 to 30 minutes based on the dispersity of nanotubes. The SWNT suspension with encapsulating agent was placed in a bath of ice-water during ultrasonication to avoid heating and control the temperature of the SWNT suspension between 10 and 20⁰ C. After ultrasonication, ultracentrifugation with fixed angle rotor at 140,000 g-force for 2 hours was carried out at 20⁰ C for removal of insoluble materials in solution. Supernatant solution was extracted out from centrifuge tube via syringe after ultracentrifugation.

3.2.2 Density Gradient Ultracentrifugation (DGU)

The concentrated SWNT suspension is required for carrying out DGU. If the concentration of the SWNT suspension is not sufficiently high, the concentrated SWNT step is necessary via ultracentrifugation. 60% w/v iodixanol (density gradient medium, 1.32 g/cm³) with encapsulating agent added at the same concentration as the SWNT suspension was filled three quarters from the bottom of the centrifuge tube. The SWNT solution was added to almost fully fill up the centrifuge tube before ultracentrifugation. The ultracentrifugation with swing rotor was carried out at 207,000 g force for 12 hours at 20⁰ C. After ultracentrifugation, the concentrated SWNTs, with a buoyant density between 1.00 and 1.32 g cm⁻³, was sedimented to the interface between both layers. The concentrated SWNT solution was then withdrawn via syringe. Before injecting concentrated SWNT solution into the centrifuge tube with density gradient, the density gradient was prepared from the aqueous solutions of density gradient medium (iodixanol) in order to proceed DGU. A slope of the gradient from 7.5 % w/v iodixanol to 30 % w/v iodixanol was formed by utilizing linear density gradient maker. 7.5 % w/v

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iodixanol to 30 % w/v iodixanol with encapsulating agent added the same concentration as SWNT solution was prepared separately and added to the linear density gradient maker to create linear gradients in the centrifuge tube. The concentrated SWNT solution was inserted into the linear gradient via syringe at the point in which the density of concentrated SWNT solution matched with the performed gradient. The ultracentrifugation with swing rotor was carried out at 276,000g force for 12 hours at 20⁰ C for sorting the isolated SWNTs. After the density gradient ultracentrifugation, the isolated SWNTs layers were extracted via syringe layer by layer for characterization.

3.3 Characterization of SWNT Aqueous Dispersion

Chiralities of SWNT samples were characterized using UV-vis-NIR, PLE and Raman spectroscopy. Optical absorption measurements were performed in a Perkin Elmer Lambda 9 UV-Vis-Nir spectrometer using a 10mm light path quartz cuvette. PLE measurement was performed on a Jobin-Yvon Nanolog-3 spectrofluorometer with an InGsAs detector. Confocal Raman microscope (WITec CRM200) equipped with 633nm and 488nm of laser was used for Raman measurements.

3.3.1 Absorption Spectroscopy

Absorption spectroscopy is a basic optical experimental tool for determining the transition of Van Hove singularities (VHS) on both metallic and semiconducting SWNTs. Particularly, the energy gap of a SWNT is reversely proportional to its diameter.

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Therefore the absorption spectra can be used to estimate the diameter distribution in a first approximation. In addition, the identity of each chiral SWNT species is its discrete transitions of VHS. Based on the optical absorption spectrum, 1st, 2nd and even 3rd transition of VHS of individual chiral SWNT species could be identified for corroborating its existence.

3.3.2 Photoluminescence Spectroscopy

Photoluminescence spectroscopy is a useful optical instrument for determining band gap energy of a semiconductor material. The fundamental working principle of photoluminescence is that applying an excitation laser with the photon energy greater than the band gap (ES11) of a semiconductor, carriers (electrons) existing in the valence band of the semiconductor is excited to its conduction band. Subsequently, the excited electrons relax to the edge of the conduction band and typically recombine with holes in the valence band, associated with simultaneous emission of photons. The emitted photon energy corresponds to the band gap of the semiconductor. The near-infrared band gap photoluminescence of micelle isolated semiconducting SWNTs has been demonstrated and driven tremendous attention in carbon nanotubes research (3).

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Figure 3-1: A schematic diagram of density of electronic states for a SWNT structure. Solid arrows depict the optical excitation and emission transitions; dashed arrows denote nonradiative relaxation of the electron (in the conduction band) and hole (in the valence band) before emission. Reproduced from ref. 3.

The ES22($V_2 \rightarrow C_2$) transition by laser with photons energy generates an electron-hole pair which travels to the band edge and subsequently emits a distinct photon energy ES11, as illustrated in Figure 3-1. The luminescence information not only presents the electronic properties of SWNTs, but also provides the identification of the chiral vector indices (n,m) of semiconducting tubes and their relative abundance in an SWNT sample (4). The luminescence technique therefore is widely used for assigning chirality of chiral semiconducting SWNTs in this thesis.

3.3.3 Raman Spectroscopy

Resonant Raman spectroscopy is a powerful experimental tool for characterizing carbon nanotubes with specific diameters and chiral angles from several mode frequencies. Dresselhaus et al has comprehensively reviewed the Raman spectra and phonon modes for carbon nanotubes (5). The distinct Radial Breathing Mode (ω_{RBM}) Raman features of SWNTs with diameters ranging from 1 to 2 nm appear between 120 cm^{-1} and 250 cm^{-1} , corresponding to atomic vibration of the C atoms in the radial direction (6). The relationship between (ω_{RBM}) Raman features and nanotube diameters is obtained experimentally formulated as $\omega_{\text{RBM}} = A/d_t + B$, where the A and B parameters are determined experimentally and d_t is widely used for determining nanotube diameter. Kataura plot was applied to assess transition energies of SWNTs from a simple TB model as a function of their diameters (7-8). By comparing the experimental data with the Kataura (9) plot based on third-nearest neighbor TB calculations (10-11), Telg et al. plotted an extended Kataura plot as shown in Fig. 3-2. The extended Kataura plot exploits for determining electronic properties of SWNTs as well as estimating its diameter and chirality (n,m). The other distinct mode frequency of SWNTs is D mode appearing at $1330\text{-}1360\text{ cm}^{-1}$ as excited with a visible laser, which is widely attributed to existence of defects in the tubes.

Figure 3-2: Kataura plot from experimental results (filled circles) and third-neighbor tight-binding calculations (open circles). Gray and black indicate semiconducting (2nd and 3rd transitions) and metallic tubes, respectively. The plot consists of theoretical (right, top axes) and experimental data (left, bottom axes). Reproduced from ref. 9.

Besides ω_{RBM} Raman and D mode features of SWNTs, the other distinct frequency mode of SWNT is G-band, which is composed of several peaks owing to the phonon wave vector confinement along the SWNT circumferential direction as well as symmetry-breaking effects associated with SWNT curvature. The G-band frequency can be used for (1) diameter characterization, (2) distinguishing between M and S SWNTs via analyzing their Raman lineshapes (12-13); (3) probing the charge transfer arising from doping a SWNT; and (4) investigating the selection rules in the various Raman scattering processes and scattering geometries. Fig. 3-3(b) indicates that the G-band feature for

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SWNTs consists of two main components, which are at around 1590 cm^{-1} (G^+) and 1570 cm^{-1} (G^-). The G^+ feature is associated with carbon atom vibrations along the nanotube axis (longitudinal optic (LO) phonon mode) and its frequency ω_G^+ is sensitive to charge transfer from dopant additions to SWNTs(14-15). While, the ω_G^- feature is associated with vibrations of carbon atoms along the circumferential direction of the SWNT (transverse optic (TO) phonon mode), and its lineshape is highly sensitive to whether the SWNT is M (Breit–Wigner–Fano lineshape) or S (Lorentzian lineshape), as shown in Fig. 3-3(a) (16-17). Charge transfer to SWNTs can lead to an intensity increase or decrease of the BWF feature(18-19). Measurements on the G band at the single nanotube level show that the G-band is a first-order process(20-21), with the frequency ω_G^+ essentially independent of d_t or chiral angle θ , while ω_G^- is dependent on d_t and whether the SWNT is M or S, but not on chiral angle as illustrated in Fig. 3-3(c) (22).

Figure 3-3: (a) The G-band for highly oriented pyrolytic graphite (HOPG), S SWNT and M SWNT. (b) RBM and G-band Raman spectra for three S isolated SWNTs of the indicated (n, m) values. (c) Frequency vs. $1/d_t$ for the two most intense G-band features (ω_G^- and ω_G^+) from isolated SWNTs. Reproduced from Ref. 22.

3.4 FET Fabrication and its Electrical Characterization

The FETs were fabricated by drop-casting the obtained SWNT solutions in a bottom contact device geometry, where Au electrodes (as Au-SWNT contact) were patterned on top of SiO_2/Si substrates using standard lithography techniques as illustrated in Fig 3-4. The SiO_2 acts as dielectric layer. For the drop-cast procedure, 50 μL of SWNT suspension was added onto the devices, followed by drying and rinsing of de-ionized water. To improve the SWNT film uniformity, the devices were heated up when the same amount of SWNT dispersions were dropped in the middle of device channel for each device. The high evaporation rate at heated device surfaces helps to limit the coffering effect. The procedure was repeated until the network density is high enough to form a percolation path. All electrical measurements were carried out in ambient conditions using a Keithley semiconductor parameter analyzer Model 4200-SCS.

Figure 3-4: A scheme of typical single-walled carbon nanotube network or thin film field-effect transistor device in bottom-gate configuration.

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4. Effectiveness of Density Gradient Ultracentrifugation on Improving SWNTs Network Transistors' Performance for Arc-discharged Tubes

Single-walled carbon nanotube (SWNT) is widely described as a roll-up of graphene sheet into a hollow cylinder with nm scale diameter. Owing to its roll-up chirality, the electronic property of SWNTs exhibits either metallic (M) or semiconducting (S) behaviour. The ballistic electron transport in S SWNT manifests superior field-effect behavior and its incredibly high intrinsic carrier mobility anticipating as one of most promising S material candidate for electronic applications. However, precise positioning and alignment of SWNTs, inconsistency of its electrical properties due to variations of its chirality and diameter in SWNTs assembly, and the integration of single-tube devices as well as scalability of its fabrication process are remaining major technical hurdles for realizing its electronic applications. Therefore the development of field-effect transistor (FET) based on SWNT networks is necessary. In this chapter, the author focuses on the purification and preparation of carbon nanotubes and its solution for solution-processable SWNT network transistor devices as well as improvement on device's on-off ratio

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characteristic via density gradient ultracentrifugation (DGU). For arc-discharge SWNTs (its diameters 1.0-1.4 nm), drastic enrichment of S species is considerably achieved via DGU separation technique with assisted co-surfactants encapsulation (1:4 SDS-SC) leading to improvement of device's on-off ratio.

4.1 Introduction

Single-walled carbon nanotubes (SWNTs), which can be treated as rolled-up cylinders of graphite monolayer with ~1 nm diameter and tens of nanometers to several centimeters length, are widely regarded to be an outstanding candidate for field-effect transistors (FETs) owing to their unique physical properties. The electronic properties of SWNTs exhibiting either metallic (M) or semiconducting (S) strongly depend on their roll-up chirality. Owing to the nearly one-dimensional and defect-free electronic structure, electronic transport in SWNTs is ballistic, which pledges high current without heating. The maximum SWNT electrical current density is about $4 \times 10^9 \text{ A/cm}^2$ – which is about three orders of magnitude higher than that in a typical metal (*e.g.* Cu). In addition, the electron transport in S SWNTs manifests superior field-effect behavior (*I*). The intrinsic carrier mobility in SWNTs is about $100,000 \text{ cm}^2/\text{V.s}$ (2), incredibly superior compare to the $1 \text{ cm}^2/\text{V.s}$ typically achieved with amorphous-Si or other conducting polymers. Furthermore, SWNTs have excellent thermal, mechanical and chemical stability, bendability and unique optical properties. However, there are several technically challenging hurdles for realizing electronics based on single-tube devices such as precise positioning and alignment of SWNTs in current growth and assembly technology, inconsistency of its electrical properties due to variations of its chirality and diameter in

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SWNTs assembly, and the integration of single-tube devices into a circuit as well as scalability of device fabrication processes. By contrast, obtaining random SWNTs networks is relatively easy either by direct growth on a substrate with aid of catalyst or by deposition onto a substrate from a carbon nanotube suspension. The electrical properties of the random SWNTs networks are fundamentally governed by the percolation paths of the nanotubes in conduction channels, resulting in sample-to-sample variations are relatively small compared with the single-tube devices. Therefore there is a growing body of research in FETs based on SWNT networks or thin films (CN-FET) (3-10). The electrical property of the SWNT networks is likely dominated by the percolation path, thus the CN-FET variations are suppressed by averaging SWNTs ensemble with sufficiently large no. of nanotubes (4). Remarkably, the outstanding advantage of CN-FETs devices is printable, making low-cost ink-jet processing possible. Hence, random SWNTs networks or thin films are anticipated to be ideal S materials for low-cost carbon-based electronics. In addition, CN-FETs have been demonstrated as a potential candidate for gas (11-13) and biomolecular sensors (14-15) as well as photodetectors (16-18). The higher on-off ratio characteristics of CN-FETs are preferably for achieving better performance for these applications.

The deficiency of on-off ratio characteristics on CN-FETs is mainly due to coexistence of M and S SWNTs within its random networks. Therefore tremendous efforts have been dedicated from carbon nanotubes researchers for enriching semiconducting species and searching scalable separation methods to separate a given SWNT ensemble into its distinct species. Several methods have been reported to enrich semiconducting or metallic SWNTs such as octadecylamine assisted precipitation(19),

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oxidation(20) and selective chemical functionalization by nitronium ion(21), bromination(22) and fluorination(23). These methods involve chemical attachments onto SWNTs and therefore change the electronic structure of SWNTs. Direct electrical breakdown(9, 24) of M tubes on SWNT devices has also been reported to improve the on-off characteristics, where the reproducibility is still a challenge for SWNT random networks. Another attractive approach is by Deoxyribonucleic acid (DNA)-assisted dispersion (25-26) or polymer wrapping (27-28), where the removal of long-chain DNA or polymers needs to be further addressed. Dielectrophoresis (29-30) has demonstrated the possibilities towards non-destructive enrichment in M tubes, certain diameter or certain length of tubes. Interestingly, Arnold et al. has recently demonstrated that certain specific S SWNTs (6,5) and (7,5) have been significantly enriched using density gradient ultracentrifugation (31-32), which is a post-growth and scalable treatment process.

Traditionally, DGU has been broadly applied for sorting subcellular components in biochemistry as well as pharmaceutical field(33). Basically, the working principle of DGU is via utilizing trivial differences in buoyant density among the components. The materials of interest are injected to an aqueous solution with a known density gradient. Under ultracentrifugation, the materials diffuse and remain at their respective isopycnic points (i.e. the place where their density equivalent to prepared density gradient of the solution)(34). With appropriate selection of initial gradient, the materials can be separated by density and such process is known as fractionation.

In order to realize the success of DGU, the buoyant density of a SWNT must be directly correlated to its physical and electronic structure. As knowing that physical structure of a SWNT is a hollow cylinder, its mass is solely relied on mass of atoms,

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which present at its surface. The density (mass-to-volume ratio) of a SWNT should be proportional to the surface-to-volume ratio, thus the density is inversely proportional to the diameter. This inverse relationship between density and diameter is valid as DGU occurred in vacuum. However, in the case of DGU for sorting SWNTs is in aqueous solution and SWNTs are strongly hydrophobic in nature. Therefore, amphiphilic surfactants must be utilized to disperse the SWNTs and consequently, the actual buoyant density of an SWNT includes both of the SWNT geometry, and the thickness and hydration of the amphiphilic surfactant shell. The ideal assumption is that the surfactants uniformly and identically encapsulate SWNTs in solution, thus the buoyant density is only a function of the SWNT diameter. If a surfactant or co-surfactant system encapsulates SWNTs with electronic structure selectivity (e.g M versus S), DGU can sort SWNTs by properties beyond simple geometrical parameters. Ultimately, effective sorting SWNTs can be realized via combination of brilliant surfactant chemistry and DGU, which has been adopted in this chapter.

4.2 Experimental

Three sources of arc-discharge SWNTs have been studied including boron-mediated nitrogen-doped arc-discharge produced SWNTs (BN-Arc), nitrogen-doped arc-discharge produced SWNTs (N-Arc) and commercially available arc-discharge produced SWNTs P2 from Carbon Solutions, Inc. (USA). The synthesis of BN-Arc and N-Arc has been reported elsewhere (35). Graphite and Ni/Y catalyst were mixed with the desired amounts of boron nitride (99.8%, Matthey Reagents) and/or melamine powders ($C_3N_6H_6$, 99% from Aldrich) and packed into the drillings of the anode rods. Graphite with boron nitride

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powders corresponding to 1 at.% boron and 1 at.% nitrogen were used to produce the BN-arc materials. The nitrogen content in both BN-Arc and N-Arc was measured by electron energy loss spectroscopy (EELS) to be around 1 at.% (35). No boron was detected by EELS in BN-Arc within the detection limit of 0.05 at.%.

The preparation of the SWNT suspensions comprises of (i) surfactant encapsulation, (ii) concentration of SWNT solution and (iii) density gradient ultracentrifugation (DGU) (31). The detail of the (i) surfactant encapsulation is as follows: 4 mg of SWNTs was dispersed in 10 ml H₂O solution with 2 wt % co-surfactants which consists of sodium dodecyl sulfate (SDS) and sodium cholate hydrate (SC) with 1:4 ratio or 2 wt % SC as encapsulating agent via ultrasonication and ultracentrifugation, which have been extensively elaborated in chapter 3. After ultrasonication and ultracentrifugation, supernatant solution was drawn out from centrifuge tube. The following steps are (ii) concentration of SWNT solution and (iii) DGU, which have been widely discussed in chapter 3 as well, for sorting isolated SWNT layers. The isolated SWNTs layers were withdrawn via syringe layer by layer for characterization.

The CN-FETs were fabricated by drop-casting the obtained SWNT solutions in a bottom contact device geometry, where 200 nm thick of Au electrodes (as Au-SWNT contact) were patterned on top of SiO₂/Si substrates using standard lithography techniques. The gate dielectrics SiO₂ is 300 nm thick. The geometry of the investigated devices is around 200 μ m in channel length and 500 μ m in channel width for arc-discharge tubes. The detail of device fabrication procedure has been declared in chapter 3. Figure 4-1 illustrates the brief experimental procedure of this chapter as well as the device geometry. Prior doing conductivity measurement of the CN-FETs in the

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percolation region, it is necessary to verify that all the resistances are predominantly contributed to the network, where the result reveals that the Au-SWNT contributes 12% of the total resistance for the device with a 200 μ m channel length, similar to the system studied in Hu's network system (4). Optical absorption measurements were performed in a Perkin Elmer Lambda 9 UV-Vis-Nir spectrometer. All electrical measurements were carried out in ambient using a Kiethley semiconductor parameter analyzer Model 4200-SCS.

Figure 4-1: The schematic diagram of the brief experimental procedure as well as the device geometry for the chapter 4.

4.3 Results and Discussion

To explore the suitability of fabricating solution-processable CN-FETs from three arc-discharge produced SWNTs (BN-Arc, N-Arc and P2), the author evaluates the statistical on-off ratio characteristics of the drop-cast devices based on the networks. Typical transfer characteristics (I_d - V_g curves) and current-voltage characteristics (I_d - V_d) of S and M CN-FET devices fabricated these three various untreated arc-discharge produced SWNTs are presented in Figure 4-2. CN-FET exhibits M-like behaviour, which is no gate-dependence characteristic and low on-off current ratio revealing at its output characteristic and transfer characteristic, respectively as illustrated at Figure 4-2(c)& (d), as the M tubes bridge between source (S) and drain (D) electrode within its networks. Whereas the S-like CN-FET exhibits highly gate-dependent characteristic and high on-off current ratio as shown at Figure 4-2(a) & (b) respectively as there is only formation of S conductive paths within its networks. Owing to the coexistence of S and M, dominance of S conductive paths within its networks could be occurred if only the proportion of S tubes is notably greater than M tubes in pristine SWNTs as well as relatively low density of its network where the probability of forming M conductive path is low.

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Figure 4-2: (a) A typical output characteristics (I_d - V_d) of semiconducting SWNT device ranging from 30V to -2V with interval of -8V. (b) A typical transfer characteristic (I_d - V_g) of semiconducting SWNT device with on-off ratio greater than 4 orders. (c) A typical output characteristics (I_d - V_d) of metallic SWNT device ranging from 30V to -10V with interval of -8V reveals no gate-dependence behavior. (d) A typical transfer characteristic (I_d - V_g) of metallic SWNT device with on-off ratio lower than 1 order.

Figure 4-3(a) shows that the on-off ratio of the devices drop-cast from BN-Arc is significantly higher than those from N-Arc and P2. The commercial P2 is showing a moderate probability but the N-Arc is having very low probability to produce S devices (or higher on-off ratio devices). For both N-Arc and BN-Arc, sp_2 -type bonded nitrogen was nominally measured as 1 at.% (35). The low yield of S devices for N-Arc SNWTs may be resulted from two possible reasons: (1) the nitrogen doping may be unintentionally caused the stronger M behaviors, or (2) the N-doped tubes were strongly

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bundled (not easy to be dispersed in solution) (36), which would enhance the possibility to obtain M devices. Although in the BN-Arc tubes no incorporated boron was found above the electron energy loss (EEL) spectra detection limit of 0.05–0.1 at.%, the presence of boron during synthesis clearly has an appreciable effect on its growth mechanism. Previous reports on the Raman and optical absorption analysis for these BN-Arc and N-Arc SWNTs have already demonstrated that incorporation of boron during synthesis leads to reduction in diameter of SWNTs (36-37). In addition, the chirality distribution may be significantly changed. It is speculated that the relatively high S device yield for BN-Arc may be due to the change in chirality distribution and S-to-M ratio, resulted from the modification of catalyst surface by boron (38). Despite possibility of achieving high S CN-FET devices, the output current is relatively low resulting in low effective mobility which definitely underperforms comparing to single-tube transistor's performance. Figure 4-3(b) compares the optical absorption features for the three raw SWNTs dispersed in SDS-aqueous solution, where it shows that the average diameter of the BN-Arc is smaller than those of N-Arc and P2. Moreover, the ratio (M/S) of the integrated absorption peak areas between 1st-order van Hove absorption for M SWNTs (M11) and the second-order van Hove absorption for S SWNTs (S22) suggests that the content of metallic tubes in BN-Arc is relatively lower than those of N-Arc and P2. The author integrates the peak area for M11 and S22 in Figure 4-3(b) for three samples and estimates the relative M/S ratios for BN-Arc, N-Arc and P2 to be 0.134, 0.237 and 0.254 respectively with its accuracy approximately $\pm 5\%$.

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Figure 4-3: (a) Histograms of device percentages with various $I_{\text{on}}/I_{\text{off}}$ (on-off) ratios (x-axis) for devices made of N-Arc, P2 and BN-Arc SWNTs respectively. (b) The optical absorbance spectra of BN-Arc, N-Arc and P2 SWNTs show the different diameter distribution. In the optical absorbance spectra, the second- and third-order semiconducting and first-order metallic optical transitions are labeled as S22, S33 and M11 respectively.

N-Arc and BN-Arc SWNTs are therefore selected to undergo DGU separation technique with co-surfactant encapsulation (SDS-SC) for investigating the enhancement of the yield of high on-off ratio devices. DGU has been reported to provide a scalable and non-destructive approach for sorting SWNTs by diameter, band gap or electronic type depending on the composition of co-surfactant (SDS-SC)(31-32). In this study, the

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separation was performed using a fixed SDS/SC ratio (1:4) of co-surfactants. After DGU, the top layer of the SWNT solution was extracted out for examining the efficiency of DGU separation technique. Figure 4-4 compares the optical absorption features of N-Arc and BN-Arc SWNTs before and after DGU. There is a significant reduction in relative M/S ratio for BN-Arc SWNTs after DGU from 0.134 to 0.076 with its accuracy approximately $\pm 5\%$, suggesting that enrichment of S tubes has been achieved. The observed electronic type selectivity is consistent with the Arnold et al, where in their separation they used laser-ablation-grown SWNTs with similar diameter distribution (32). It is noted that the BN-Arc tubes used, which possesses very similar wavelength region of absorption to that of laser-ablation-grown tubes (diameter is mainly ranged from 1.0~1.6 nm)(32) despite produced by different method. A separate study on density gradient assisted separation for N-Arc SWNTs demonstrates a drastically different result, the M SWNTs after DGU is enriched to M/S ratio of 0.302 (shown in Fig. 4-4). It is therefore suggested that the selection of S and M tubes is strongly related to the tube diameters.

Arnold and his co-workers have speculated that the possible mechanism of surfactant-based separation using DGU is likely driven via surfactant arrangement and orientation surrounding SWNTs of different structures and electronic types. There are several critical factors such as the energetic equilibrium among nanotube-surfactant, water-surfactant and surfactant-surfactant interactions as well as the linear packing density of surfactant molecules along the length of the SWNTs, orientation, ionization and the resulting hydration of the surfactants on influence of its buoyant density as well as sorting effectiveness. In addition, differences in the arrangement of anionic-alkyl

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surfactants (such as SDS) and bile salts (such as SC) surrounding carbon nanotubes are anticipated according to previous studies of these amphiphiles on graphene, which possesses identical building block as SWNT. In the case of graphene, anionic-alkyl surfactants assemble into hemicylindrical micelles with liquid-like hydrophobic cores(39-40), whereas bile salts form well-organized monolayers with their less-polar terminals orienting to the hydrophobic surface(41) and well-defined host-guest structures around small hydrophobic molecules (42-43). Based on the rigidity and planarity of SC molecules (contrast with SDS surfactants), it is anticipated that the forming encapsulation layer is sensitive to subtle changes in the underlying SWNT, resulting in sorting SWNTs. Moreover, the observed metal-semiconductor selectivity indicates a coupling of the surfactant and/or its hydration with the electronic nature of the underlying SWNT. Lu and co-workers have suggested that interaction of M SWNTs with adsorbates is relatively stronger via π interactions compare to S SWNTs, owing to their larger electronic polarizability (44). Furthermore, the linear packing density of the surfactants and their hydration are likely to be sensitive to electrostatic screening by the underlying SWNT. Other effects, such as partial charge transfer between M SWNTs and surfactants induced by CH- π interactions could also be crucial on determining its diameter and/or electronic type separation. Despite the exact mechanism of separation-based separation using DGU is still under investigation, it is likely attributed from combination of several above effects leading the diameter and/or electronic type separation.

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Figure 4-4: Comparison of the optical absorbance spectra of N-Arc and BN-Arc SWNTs for before and after DGU separation.

The sorted BN-Arc discharge SWNTs solution after DGU was subsequently used for fabricating device by drop-casting method and measuring its electrical performance. Figure 4- 5(a) emerges the typical transfer characteristics of a device possessing 5-order magnitude of on-off ratio characteristic from BN-Arc discharge SWNTs after DGU. In order to effectively compare the effect of DGU on improving on-off ratio characteristics of devices, both of BN-Arc discharge SWNTs solutions before and after DGU were used to fabricate identical device geometry, which is illustrated at Figure 4-1. The author has summarized the histogram of device percentage with various on-off ratios for the devices made of BN-Arc discharge SWNTs before and after DGU. It is revealed that the on-off

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ratio of devices obtained after DGU is considerably higher than those before DGU, which evidently demonstrates that the DGU separation efficiently lowers the M/S ratio by enriching S tubes (shown in Figure 4-4). Hence, improvement on on-off ratio characteristic of device is achieved by adopting DGU separation technique with co-surfactant encapsulation (1:4 SDS-SC) for BN-Arc discharge SWNTs with its diameter ranging from 0.9 to 1.3 nm.

Figure 4-5: (a) The typical transfer characteristic of a device from BN-Arc discharge SWNTs after DGU reveals 5-order magnitude of on-off ratio, where the drain voltage was fixed at 2V. (b) Histograms of device percentages with various on-off ratios for devices before and after DGU.

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Despite significant improvement of device's on-off ratio characteristic after DGU, the typical current output is in the range of 10^{-7} A, which is far inferior compare to single-tube FET. The relatively low current output of CN-FET is possibly due to its network density. Therefore, it is essential to understand the relationship between the network density and the device's electrical performance. In addition, knowing that high tendency of forming bundled tubes in SWNT networks, it is interesting to study the effect of bundle state on the electrical performance of its networks. The above studies would be extensively investigated in the following chapter 5.

4.4 Conclusion

In summary, the author has initially used 3 various arc-discharged tubes and prepared their aqueous solution to form isotropic SWNT networks via drop-casting method as well as fabricated CN-FETs to evaluate their electrical performance. BN-Arc and N-Arc tubes were selected for purification via DGU technique. There is no detectable alteration in M/S ratio for N-Arc tubes after DGU, suggesting that DGU separation technique is not effective on N-Arc tubes. Whereas, BN-Arc discharge tubes reveal drastic enrichment of S species after DGU separation with co-surfactants encapsulation (1:4 SDS-SC), which is in line with the findings from Arnold et al (32), resulting in significant improvement on device's on-off ratio characteristic.

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4.5 References

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5. Towards High Performance Solution-Processable SWNTs Network Transistors by Removing Nanotube Bundles

Carbon nanotube based electronics are still far from practical reality owing to unsolved fundamental and technical challenges such as (1) coexistence of metallic (M) and semiconducting (S) SWNTs, normally resulting in low on-off ratio, (2) low effective field-effect mobility, and (3) low yield for production of FETs. Without separating S SWNTs out from as-grown SWNTs, the electrical performance of CN-FETs basically exhibits either high mobility but low on/off ratio or vice versa owing to the existence of M tubes. Consequently, low yield of S devices can be obtained from SWNT ensembles. Extending the achievement of S enrichment via DGU, the author demonstrate that removing the SWNT bundles using organic-aqueous interfacial trapping purification (ITP) can further enhance the electrical performance of CN-FET devices. The on/off ratio of CN-FET device is improved by ~ 1 order of magnitude and other characteristics such as subthreshold swing and off current are also improved. By adopting combination of DGU (to enrich S species) and ITP (to remove bundled tubes) methods, it is possible to achieve solution-processable CN-FET device with representative effective mobility $\sim 1.5 \text{ cm}^2/\text{V}\cdot\text{s}$ and on/off ratio $\sim 10^4$ at a promising yield without applying electrical

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breakdown. The effective mobility and on current of the CN-FET devices increase with the tube density in its networks regardless with existence of bundled tubes. In addition, SWNT network conductance extracted from on current is in an approximately good agreement with the percolation conduction theory.

5.1 Introduction

The electrical property of the single-walled carbon nanotube (SWNT) networks is dominated by the percolation path (1-2). These SWNT network devices can be printed, making low-cost ink-jet processing possible. Hence, SWNTs are potential semiconducting materials for printed electronics. SWNT networks have promising applications in gas detection (3-4), biomolecular sensors(5-6) and optoelectronics(7) despite solution-processable SWNT printed electronics are still far from realization due to unsolved challenges in device fabrication. The major challenges include: (1) low on-off ratio, (2) low effective field-effect mobility, and (3) low yield for production of FETs. The coexistence of S and M tubes in the available SWNTs ensembles is believed to be the key issue towards high performance device. Therefore many efforts have been dedicated towards the enrichment of S species or the development in purifying a given SWNT ensemble into its distinct species, such as selective chemical functionalization(8), dielectrophoresis(9), deoxyribonucleic acid (DNA)-assisted dispersion(10) or polymer wrapping(11). Direct electrical breakdown(12) of M tubes on SWNT devices has been reported to improve the on-off characteristics. Recently, Arnold et al. have made significant improvements in obtaining semiconductor-enriched SWNTs via DGU (13), which provides a scalable and non-destructive approach for sorting SWNTs. The author

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has demonstrated that DGU effectively enriches S species for BN-Arc discharge tubes with assisted SDS-SC co-surfactant encapsulation, resulting in improvement on its device's on-off ratio characteristic as presented in chapter 4. Existence of bundles tubes is generally occurred as forming isotropic SWNT network from its dispersion via drop-casting method. Therefore, it is necessary to understand the effect of bundling states on electrical performance of the network

High tendency on aggregation of tubes in bundle form is due to substantial van der Waals interaction forces (950 me/nm)(14) resulting in difficulty of obtaining individual SWNT in its dispersion. Conventionally, surfactants or polymers are widely used to stabilize individual SWNT via wrapping it, resulting in reducing its surface energy (15-16). Despite wrapping with surfactant, the stability of individual dispersed SWNTs is relatively low resulting in gradual aggregation forming bundled tubes. Thus, additional effort is required to deal with existence of bundled tubes in its dispersion. Recently, Ziegler's group has reported the viability of bundled SWNTs removal in its dispersion via organic-aqueous interfacial trapping purification (ITP) at toluene-water interfaces (17).

5.2 Experimental

The BN-Arc-discharge tubes were used as starting material. The preparation of its dispersion comprises of co-surfactant encapsulation, concentration of its dispersion and followed by DGU (13) which are identical to the experimental procedure described in chapter 4. In order to effective removing tube bundles, ITP (17) was adopted after DGU. The ITP procedure is as follows: 1mL of toluene was added to the 3mL of aqueous

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SWNT suspensions and the mixture was shaken vigorously for 30 s to increase interfacial area and remove SWNT bundles from its dispersion. The mixture of toluene and aqueous SWNT dispersion was left for 10 minutes to ensure the completion of the interface formation between toluene and aqueous SWNT dispersion. The aqueous SWNT dispersion was withdrawn carefully via syringe after interfacial trapping. The ITP treated SWNT dispersion was used immediately to fabricate CN-FET device via drop-casting method. The device configures back-gate bottom contact geometry, where 200 nm thick of Au electrodes (as Au-SWNT contact) were patterned on top of SiO₂/Si substrates using standard lithography techniques. The gate dielectrics SiO₂ is 300 nm thick. The geometry of the investigated devices is around 200 μ m in channel length and 500 μ m in channel width. The detail of device fabrication procedure has been declared in chapter 3. The entire brief experimental procedure of this chapter has been schematically illustrated at Figure 5-1. Prior doing conductivity measurement of the CN-FETs in the percolation region, it is necessary to verify that all the resistances are predominantly contributed to the network, where the result reveals that the Au-SWNT contributes 12% of the total resistance for the device with a 200nm channel length, similar to the system studied in Hu's network system (2).

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Figure 5-1: The schematic diagram of the brief experimental procedure for the chapter 5.

Optical absorption measurements were performed in a Perkin Elmer Lambda 9 UV-Vis-Nir spectrometer. All electrical measurements were carried out in ambient using a Kiethley semiconductor parameter analyzer Model 4200-SCS. Atomic force microscopy (AFM) measurement was carried out using an Asylum Research MFP-3D system to image the SWNTs. The estimation of number density of tubes and measuring of the tube length is based on the average of randomly selected 5 AFM images in a 1 $\mu\text{m} \times 1 \mu\text{m}$ dimension. Device channel isolation was performed in a focus ion beam (HELIOS Nanolab, FEI) using gallium source (Voltage = 30kV and Current = 0.46nA).

5.3 Results and Discussion

BN-Arc discharge tubes was selected to undergo DGU separation technique which has

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been corroborated effective enrichment of S species for this particular tube in chapter 4. Figure 5-2 summarizes the absorption spectra for the un-separated and separated BN-Arc discharge tubes. Multiple regions (layer 1 to layer 4) are visible throughout the density gradient as indicated in the photograph of Figure 5-2. By contrast to the black colors observed in layer 2 to layer 4, the layer 1 shows slightly brown color, indicating that the layer 1 is enriched with S tubes. This is further verified in the absorption spectra in Figure 5-2, where in layer 1 the S22 for S SWNTs is enhanced relative to the M11 for M SWNTs. After subtracting the baseline and calculating the integral intensities of the M11 and S22 peaks, the relative M/S ratio for BN-Arc SWNTs after DGU reduces from 0.134 to 0.076 with its accuracy approximately $\pm 5\%$. However, other layers do not show pronounced differences in comparison with their un-separated ensemble. Despite S enrichment in layer 1, Majority of tube species existing at 4 layers is similar with their un-separated ensemble. Therefore, the pattern of their absorption spectra as shown in Figure 5-2 look similar except difference in relative quantity of S and M tube species. The observed S enrichment is consistent with the Arnold et al, where in their separation they used laser-ablation-grown SWNTs with similar diameter distribution (13). It is noted that the BN-Arc discharge tubes used, which possesses very similar wavelength region of absorption to that of laser-ablation-grown tubes (diameter is mainly ranged from 1.0~1.6 nm)(13) despite produced by different method.

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Figure 5-2: Photograph BN-Arc discharge SWNTs separated in a co-surfactant solution (1:4 SDS-SC) via DGU and the corresponding optical absorbance spectra for each layer.

The ITP method to remove the bundled tubes has been suggested recently (17). The large bundled tubes are anticipated to lower the on-off ratio of the devices because the conduction of bundled SWNTs would be dominated by M species within its bundles. Therefore, the ITP method was adopted to remove the bundled SWNTs existing in the extracted Layer 1 after DGU in SDS-SC co-surfactant encapsulation. Figures 5-3(a) & (b) demonstrate the typical AFM images for the devices drop-cast with low and high density of purified (bundle-removed) layer 1, where no large bundles are found in AFM images. By contrast, relatively large bundles can be obtained in Figures 5-3(c) & (d), where the networks devices are prepared by the similar way from the layer 1 without ITP. These AFM images provide direct evidence that the ITP is able to effectively remove large bundled tubes.

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Figure 5-3: The typical atomic force microscope image on the device channel region for low density SWNT network (a) with ITP and (c) without ITP. The typical atomic force microscope image of high density SWNT network on device channel region (b) with ITP and (d) without ITP. Removal of bundled tubes is effective after adopting interfacial trapping method.

Figure 5-4(a) demonstrates the typical transfer characteristics, forward and reverse sweeps of drain current (I_d) vs. gate voltage (V_g), for a CN-FET drop-cast from the purified layer 1. The inset of Figure 5-4(a) shows the AFM images for the channel area and the tube density is estimated to be $64 \text{ tubes}/\mu\text{m}^2$. The on-off ratio shown in Fig. 5-4(a) is 1.68×10^4 . The author has summarized the histogram of device percentage with various on-off ratios for the devices made of SWNTs extracted respectively from layer 1, layer 2 and purified layer 1 (indicated as Layer1+ITP; after removal of bundles using interfacial trapping method). The number of measured devices for each type of SWNTs is

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60. It is revealed that the on-off ratio obtained from layer 1 is significantly higher than that from layer 2, which clearly demonstrates that the separation efficiently lowers the M/S of the layer 1 ensemble (Figure 5-2). It is also concluded that the on-off ratio of the device is detectably improved after removal of bundled tubes. In addition, revelation of gate hysteresis phenomenon, which is referred to the area under the forward and reverse gate sweeps at its transfer characteristic, is observed at Figure 5-4(a). As far as realization of electronic integrated circuits based on SWNT networks is concerned, the gate hysteresis (shown in Figure 5-4(a)) revealing in the Si backgate configuration is a remaining problematic issue. Such issue would be systematically addressed and discussed for understanding its possible root cause in chapter 7.

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Figure 5-4: (a) Transfer characteristic of the device sweeping from positive to negative and back to positive, where the drain voltage was fixed at 2V. Inset shows the atomic force microscope image on device channel region with possessing 4-order magnitude of on-off ratio. (b) Histograms of device percentages with various on-off ratios for devices made from layer 2 and layer 1 as well as layer 1+ITP.

To further examine the effect of bundle-removal, the transistor parameters for the devices with and without ITP every time were measured as increase in their network density by adding more drops. Figures 5-5(a), (b) & (c) summarize the effects of measured on-off ratio, off-current (I_{off}) and subthreshold swing respectively. It is noted

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that the networks in the channel region of the devices studied in Figures 5-5(a), (b) & (c) are not isolated from those outside the channel region. Therefore the conductance is overestimated by the fringe effect from the SWNT networks beyond the channel area. Even though, the effect of bundle-removal on these parameters is still valid. The standard percolation theory predicts that the conductivity (σ) is proportional to $(N-N_c)^\alpha$, where N is the density of conduction sticks (CS), N_c is the critical density of CS corresponding to the percolation threshold and α depends only on the dimensionality of the space for the networks. From the relation, the I_{on} is positively related to the density of CS. Therefore the results in Figure 5-5 suggest that the bundle tubes would lead to higher I_{off} , which may be attributed to the fact that the bundled tubes would effectively reduce the number of isolated S SWNTs in the networks. In addition, the subthreshold swing is decreased (improved) after bundle-removal probably due to that the bundled tubes are M in nature, which effectively reduces the gate coupling of SWNT networks.

Figure 5-5: comparison of device's electrical performance between layer 1 and layer1+ITP by plotting (a) on-off ratio, (b) off current and (c) subthreshold swing vs. on current.

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To extract the accurate effective mobility of the networks, the author separately prepared the devices with and without interfacial trapping and performed the isolation for these devices using focus ion beams (FIB), where the ion beams selectively etch off the carbon nanotubes at the edge of the channel area such that the network beyond the channel region is isolated. The effective field-effect mobility is then extracted from the experimental transfer curves for the devices based on the equation (1, 18), mobility $\mu = (dI_d/dV_g) / (\epsilon V_d W/L_{ox}L)$, where L_{ox} is the gate dielectric thickness, W and L represent channel width and channel length respectively, ϵ is the dielectric constant of gate dielectrics (thermal oxide = 3.9) and V_d is the source-drain bias. Figure 5-6(b) shows the on-extracted mobility versus the tube density for two typical samples prepared by drop-cast method. Isolation using FIB was performed after every drop-cast procedure. Each number density of SWNTs was obtained by averaging the number of tubes calculated based on five separate $1\mu\text{m} \times 1\mu\text{m}$ areas from AFM images. Based on the AFM images, it is nearly impossible to distinguish between bundled and individual tube. This method is heavily biased towards detection of bundled tube, and the detection of individual tubes may present a challenge. Therefore, both bundled and individual tubes are treated as single effective tube, and the tube density calculated based on AFM images could barely represent effective tube density regardless with bundled and individual tubes. The average tube length calculated from this method and its standard deviation is around 430 nm and 178 nm, respectively. The on-off ratio for these devices is shown in Figure 5-6(a), where the field effect mobility is increased but on-off ratio is decreased with the SWNT network density. For the solution processable random network transistors demonstrated here, its field effect mobility is able to go up to $1.5 \text{ cm}^2/\text{V.s}$ while the on-

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off ratio is still kept reasonably high ($\sim 10^4$). However, the effective mobility is not as superior as the highest reported (13) ($20 \text{ cm}^2/\text{V.s}$) probably due to several reasons (1) the device channel length is longer ($\sim 200 \text{ }\mu\text{m}$) which is suitable for macroelectronics, (2) The source of nanotubes is different, and (3) the average length of the SWNT in its dispersion is short. Nevertheless, the concrete conclusion can be drawn from the obtained results is that removing bundled tubes is critically important for improving device's electrical performance.

The field effect mobility obtained for the device with and without ITP in Figure 5-6(b) may be fitted with a universal curve, where no significant difference in field-effect mobility is observed for both cases. The reason is that for the tube density estimation from AFM images, a bundled tube is counted as only one effective CS which is the same as the individual tube. On the other hand, the percolation theory only considers CS in the networks and therefore the contributions of bundled or individual tubes to the conductivity are treated the same. Sheet conductance (G_σ) is defined as $1/R_\sigma$ for these devices as a function of tube density plotted at Figure 5-6(c), where R_σ is equal to the DC resistance between two electrodes (R) times (W/L). The matching of the measured sheet conductance at on states ($V_g = -10\text{V}$) for these two samples (with and without bundle removal) corroborates the conclusion drawn from the mobility plot (Figure 5-6(b)) and further validates the prediction from the percolation theory.

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Figure 5-6: (a) The on-off ratio, (b) the mobility, and (c) the sheet conductance vs. tube density of for the devices made from layer 1 and layer+ITP. (d) The fitting of the sheet conductance vs. tube density relations using the percolation theory, where the percolation threshold of the device is 30 tubes per μm^2 . The red dot and black square represent layer 1 and layer 1+ITP respectively.

It is noted that the SWNT density discussed in Figure 5-6 is at the same order of magnitude as the predicted percolation threshold density ($N_c = 4.236^2/\pi L_c^2$) therefore this discussion is within the low tube-density regime (close to percolation threshold or close to ideal two dimensional film). For the devices discussed in Figure 5-6, the predicted N_c are around 30 tubes/ μm^2 based on the measured average tube length (434 nm). The data

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points obtained in Figure 5-6(c) was fitted to the equation $G_{\sigma} \propto (N-N_c)^{\alpha}$, where N_c is set to 30 and the fitted curves is plotted in Figure 5-6(d). The fitted value of 1.21 for the dimensional factor α is slightly lower than the prediction (1.33) for an ideal two dimensional film (19). It is speculated that the variations are due to the underestimation of the number density of tubes in AFM. This obtained result suggests percolation theory can be used to adequately describe the conduction properties of the SWNT networks(1-2).

Despite obtaining decent electrical performance of CN-FET devices by adopting DGU and ITP methods for BN-Arc tubes (its diameter distribution 1.0 to 1.4nm), there is still approximately 30 percent of devices with on-off ratio lower than 3-magnitude likely owing to measurable miniature quantity of M tubes after DGU (shown in Figure 5-4). Knowing that the selection of S and M tubes is exceedingly sensitive with the tube diameters, it is therefore necessary to clarify the S enrichment efficiency of DGU for small diameter SWNTs. Based on the experimental results from M. C. Hersam's group, CoMoCAT SWNTs possessing a relatively narrow diameter distribution (0.7 to 1.1nm) can be sorted via DGU technique and fractionation (20). Therefore, the author would extensively study the S enrichment efficiency of DGU for narrow diameter distribution CoMCM41 (0.7-0.9 nm) tubes in the chapter 6. Another motivation of utilizing narrow small diameter CoMCM41 tubes to undergo DGU is that there is still a technical challenge to synthesize larger diameter tubes with narrow diameter distribution (BN-Arc, HiPCO are wider diameter distribution).

5.4 Conclusion

In summary, the author demonstrate that removing SWNT bundles via ITP method can further enhance the electrical performance of CN-FET devices. Its on/off ratio is promisingly improved by ~ 1 order of magnitude and other characteristics such as subthreshold swing and off current are also improved. By adopting combination of DGU (to enrich S species) and ITP (to remove bundled tubes) methods, it is possible to achieve solution-processable CN-FET device with representative effective mobility $\sim 1.5 \text{ cm}^2/\text{V.s}$ and on/off ratio $\sim 10^4$ at a promising yield without applying electrical breakdown. The effective mobility and on current of the CN-FET devices increase with the tube density in its networks regardless with existence of bundled tubes. In addition, SWNT network conductance extracted from on current is in an approximately good agreement with the percolation conduction theory.

5.5 References

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6. Assessment of (n,m) Selectively Enriched Small Diameter SWNTs via Density Differentiation

Uniformly semiconducting (S) SWNTs networks are ideal materials for large area electronics. With the aim of developing optimal enrichment in S tubes and evaluation its solution towards the large-scale, economical production of semiconductor-enriched SWNTs for electronics, the enrichment of specific SWNTs, which possess small diameters (<0.9 nm) and a narrow (n,m) distribution, can be achieved by synthesized on cobalt-incorporated MCM-41 catalysts. The (7,5) and (6,5) enriched SWNTs are produced by sodium cholate (SC) dispersion and cosurfactant mixture of sodium dodecyl sulfate (SDS) and SC (at 1 : 4 ratio) respectively. Density gradient ultracentrifugation (DGU) is adopted for further refining the separation. Enriched SWNTs via SC alone produced more devices with higher on-off ratio (I_{on}/I_{off}) (up to 10^6) compared to SWNTs obtained from SDS-SC cosurfactants. These result are different from previous results using BN-Arc SWNTs (1.0 – 1.4nm) and laser-ablation-grown SWNTs (1.1-1.4 nm), appealing for more comprehensive models to explain diameter dependent chirality selection using surfactants. In addition, small fraction of M tubes unavoidably existed in the treated SWNT solutions via DGU with surfactant encapsulation leads to impossibility of full yield S CN-FETs production despite exploitation of selectively narrow diameter and chirality distribution SWNTs as starting material.

6.1 Introduction

Single-walled carbon nanotubes (SWNTs) have many exceptional electronic properties (1-2). The use of individual SWNTs as functional elements could be significant for many applications in electronics, optoelectronics, sensors, nanomechanical devices and other areas (3-6). However, after 15 years' efforts, realistic applications of devices relied on individual SWNTs are hindered by their low current outputs, small active areas, and difficulties in integration of individual tube devices into scalable integrated circuits (7). The emerging applications of SWNTs are based on the two-dimensional network of SWNTs (8-14). The SWNT network can be regarded as a novel transparent electronic "material" with excellent and tunable electrical, optical and mechanical properties. SWNT network structures can be printed, making low-cost ink-jet processing possible and considered to be ideal semiconducting materials for low cost carbon-based electronics. Although properties of SWNT networks are expected to be dominated by their percolation paths; and the variation among individual tubes are suppressed by the ensemble averaging, the heterogeneously properties of SWNTs lead to significant variation in device performance and remain the major challenge in the device development. As demonstrated in chapter 4 and 5, despite decent device's electrical performance from BN-Arc tube, variation in device characteristic is notable especially existence of tiny fraction of M tubes in sorted SWNT dispersion resulting unfeasibility of full S SWNTs network FETs yield.

As-synthesized SWNTs vary in their diameters, and chiral angles which are characterized by the chiral indices (n,m) . These structural variations result in striking differences in their electronic behaviors, therefore often lead to low on-off ratios, low effective field-effect mobilities and low production yields (7). One of the key tasks to

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realize applications based on SWNT networks is to obtain SWNTs with well-defined structures and electronic properties. A recent review has summarized the progress towards monodisperse SWNTs which includes strategies from various aspects - including selective growth, enrichment by selective chemistry, electrical breakdown, electrophoretic separation, chromatography, and ultracentrifugation (15). The above SWNTs sorting techniques have been extensively reviewed at 2.4.1 section of chapter 2. Besides adopting post-growth treatment such as DGU for enriching S SWNTs species which has been explored in chapter 4 and 5, it is also crucial to investigate the selective growth approach for potential providing narrow diameter or chirality distribution SWNTs as starting material.

Currently, narrowly (n,m) distributed SWNTs can be grown from Co/Mo catalysts (16), Fe/Co catalysts (17), Fe/Ru catalysts (18) and Co-MCM-41 catalysts (19-21). Improved (n,m) selective enrichments were made by the combination of size-exclusion chromatography and ion-exchange chromatography (22), density gradient separation (23-24) and co-surfactant extraction (25). Analytical techniques including optical absorbance, photoluminescence excitation, Raman spectroscopy, atomic force microscopy have been employed by researchers to demonstrate improvements in SWNT monodispersity (26). Zhang et al. (26) recently measured field effect transistor (FET) performance using about 15 tubes in a 200 nm device channel to evaluate the chirality separation of DNA functionalized HiPco SWNTs. However results from those devices involving a small number of tubes in a short channel may not be feasible for macroelectronic applications which involve large amount of tubes. Arnold et al. have made thin-film FET electrical transport measurements for devices fabricated from density-gradient separated laser-ablation-growth SWNTs using co-surfactant mixtures of sodium cholate (SC) and sodium dodecyl sulphate (SDS), and

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an on-off ratio of 2×10^4 was achieved (23). However, they did not report the electrical transport measurements for smaller diameter tubes (<0.9 nm) which are the most predominant SWNTs produced by chemical vapor deposition (CVD). CVD is a more scalable synthesis approach compared to arc-discharge and laser ablation in obtaining high purity SWNTs in large-scale and economically. Therefore, it is necessary to investigate the enrichment efficiency of DGU separation technique for small diameter SWNTs from Co-MCM-41 (CoMCM41 tubes) with narrow diameter distribution (0.7 to 0.9 nm).

6.2 Experimental

Narrowly (n,m)-distributed SWNTs were obtained from cobalt-incorporated MCM-41 (Co-MCM-41) catalysts (19-20, 27). The precise control of cobalt reduction and nucleation through the MCM-41 template enable size uniform Co clusters for the SWNT structure control in CVD synthesis (28-30). As-synthesized tubes were purified by a mild, four-step purification procedure using NaOH reflux, HCl wash, and oxidation by 4 mol % molecular oxygen at 500 °C to remove contaminants and obtain bulk low-defect-density SWNTs (31). The purified SWNTs powders were supplied from the collaborators and carried out a series of treatments for obtaining enriched chiral SWNT suspensions. The preparation of enriched chiral SWNT suspensions including surfactant encapsulation, ultrasonication, ultracentrifugation, concentrating SWNT solution and subsequently density gradient ultracentrifugation has been described in detail in chapter 3. Figure 6-1 illustrates a schematic diagram for both sample A enriched in (7,5) SWNTs and sample B enriched in (6,5) SWNTs was obtained by dispersing purified SWNTs in 2 wt % SC and 2 wt% SDS-SC (1:4 wt

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ratio) cosurfactant encapsulation aqueous solution, respectively. After DGU, the upper two layers, which appear in faint pink and dark green color respectively, were characterized by optical spectroscopies, as well as utilized for FET device fabrication. Chiralities of SWNT samples were characterized using PLE, UV-vis-NIR and Raman spectroscopy, which has been introduced in chapter 3. SWNT thin film FETs were fabricated by the drop-casting method as depicted in chapter 3. The bottom device geometry, where Pt electrodes with Ti as adhesion layer were patterned on the top of SiO₂/Si substrates using standard lithography techniques and 300 nm thick SiO₂ as gate dielectric, as schematically illustrated in Figure 6-1. The geometry of the investigated devices is around 8 μm in the source-drain distance and 20 μm in the channel width. The concise experimental procedure on (n,m) selective enrichment as well as FET device fabrication has schematically exemplified in Figure 6-1. All electrical measurements were carried out in ambient using a Keithley semiconductor parameter analyzer Model 4200-SCS. Atomic force microscopy (AFM) was conducted using a MFP 3D microscope (Asylum Research, Santa Barbara, CA) with a cantilever (ArrowTM NC, Nanoworld) in ac mode. The scan rate was set to 1 Hz and scan sizes were 2 μm $\times$ 2 μm in FET device channels.

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Figure 6-1: Schematic diagram of the experimental procedure on (n,m) selective enrichment process as well as FET device fabrication in the chapter 6.

6.3 Results and Discussion

The PLE intensity map is widely used for identification of chiralities species. The PLE intensity map of SC dispersed SWNTs, which is denoted as sample A, exhibit (7,5) SWNTs with diameter of 0.829 nm as dominant species as shown in Figure 6-2. The selective enrichment of (6,5) and (8,3) SWNTs can be achieved through SDS-SC(1:4) co-surfactant extraction particularly enriching (6,5) SWNTs with diameter of 0.757 nm as illustrated in Figure 6-2 for sample B. There is not notably different from PLE intensity maps between SWNTs dispersed in SC (sample C) and SDS-SC (sample D), which are first layer after DGU, where the observation of peaks of (6,5) and (8,3) SWNTs indicates that smaller diameter SWNTs are enriched in the first pink layers of SWNT dispersions. The obtained result suggests preferential enriching

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smaller diameter SWNTs in first layer after DGU regardless with type of surfactant encapsulation. Whereby, Peaks of (7,5), (8,4), (7,6) and (9,4) SWNTs can be identified for sample E and sample F in Figure 6-2, suggesting that slightly larger diameter tubes are enriched in the second dark green layers. These diameter selective enrichment results are similar with CoMoCAT SWNTs as starting material with same treatment (23). It is possibly anticipated owing to similar diameter range (main species <0.9 nm) of SWNTs produced from both CoMo catalysts and Co-MCM-41 catalysts.

Figure 6-2: Photoluminescence excitation (PLE) intensity map as a function of excitation and emission wavelength for (n,m) selectively enriched SWNTs via surfactant extraction and density gradient ultracentrifugation. A to F correspond to sample A to F as denoted in Figure 6-1.

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Besides identification of chirality of SWNTs, PLE intensity map is also generally utilized for determining the relative abundance of S SWNT species. Previously, the quantum efficiency differences among various (n,m) tubes based on a single-particle electron phonon interaction model has been used (31). However, a recent experimental study showed that there is a deviation on abundance between a recent experimental data and theoretical predictions according to quantum efficiency difference among various tubes (32). In this chapter, the tube abundance is quantified by the intensity extracted from PLE intensity map. The results of two most dominant (n,m) species ((6,5) and (7,5)) are listed in Table 6-1. The co-surfactant extraction significantly enriches (6,5) SWNTs by comparing the (6,5) to (7,5) abundance ratio of sample A (0.41) to sample B (1.83). In addition, regardless with type of surfactant encapsulation, the first extracted layer after DGU reveals drastic rise in (6,5) to (7,5) ratio as shown in Table 6-1, suggesting high efficiency of smaller tubes enrichment via DGU.

Table 6-1: Abundance of two main (n,m) species determined from PLE intensity map depicted in Figure 6-2.

Sample	A		B		C		D		E		F	
(n,m)	(6,5)	(7,5)	(6,5)	(7,5)	(6,5)	(7,5)	(6,5)	(7,5)	(6,5)	(7,5)	(6,5)	(7,5)
Abundance,%	14.27	34.90	34.67	18.95	57.13	4.57	62.46	2.61	13.91	41.44	15.22	36.15
Standard uncertainty,±%	4	5	4	4	5	3	5	3	3	4	3	5
(6,5)/(7,5)	0.41		1.83		12.49		23.90		0.34		0.42	

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Figure 6-3: The optical absorption spectra of (n,m) selectively enriched SWNTs via surfactant extraction and density gradient ultracentrifugation. A to F correspond to sample A to F as denoted in Figure 4-6. The absorption peaks corresponding to metallic tubes are shaded blue below 500 nm wavelength.

Despite high sensitivity on S tubes in PLE spectroscopy, M tubes are basically invisible. Therefore, UV-vis-NIR absorption spectra is widely used for characterizing metallic tubes (23, 26). It is crucial to identify both S and M tubes in order to evaluate the effectiveness of DGU separation technique. Figure 6-3 reveals the optical absorption spectra of (n,m) selectively enriched SWNTs via surfactant extraction and DGU. The blue shaded area below 500 nm (shown in Figure 6-3) corresponds to the lowest electronic transition (M11) of M tubes for small diameter tubes (its diameter

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distribution $< 0.9\text{nm}$). Existence of absorption peaks below 500 nm wavelength suggests that there is presence of M tubes in all the samples. Similarly, the lowest electronic transition of S tubes (S11) and the second lowest electronic transition of S tubes (S22) are ranging from 900 nm to 1300 nm and 500 nm to 830 nm respectively. In Figure 6-3, the selective enrichment of various S tubes is confirmed in UV-vis-NIR absorption spectra and is a consistent trend as analyzing from PLE data.

Figure 6-4: Raman spectra of Sample A and Sample D obtained under (a) 633 nm and (b) 488 nm laser excitation. Spectrum of sample A is offset 30% in Y-axis for comparison.

Raman spectroscopy is another popular SWNTs characterization tool for distinguishing M and S SWNTs. Usually, two features on Raman spectra can provide such information: (1) the line shape for the lower frequency G-band feature for M

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tubes was broader, followed a Breit-Wigner-Fano line shape, and was downshifted in frequency from S tubes of similar diameter; (2) Raman intensity enhancement in radical breathing mode (RBM) of particular (n,m) SWNTs can be anticipated as the energy of the incident photons (E_{laser}) matching with optical transition energy (subject to selection rules for optical transitions) of particular (n,m) SWNTs. The two typical Raman spectra from all six SWNT thin film samples from both 633 nm and 488 nm laser excitation are presented in Figure 6-4. There is no detectable difference between sample A (alone SC) and D (first extracted layer after DGU in SDS-SC) on its G-band feature under 633 nm laser as shown in Figure 6-4(a). The line shape shown in Figure 6-4(a) suggests both samples are S SWNTs abundant. In addition, D-band features contributing from defects on SWNTs or amorphous carbon are trivial, indicating extremely high purity of SWNTs used in this study. The observation of a single sharp peak in the RBM feature indicates narrow (n,m) distribution. As known that 488 nm laser has strong resonance with smaller diameter M tubes, therefore it is necessary to perform Raman spectroscopy measurement with 488 nm laser for verifying the existence of M tubes. Figure 6-4(b) reveals there is slight change in the G-band features under 488 nm excitation, suggesting that sample D might have relatively higher concentration of M tubes compared to sample A. At the same time, the relative intensity of the Raman peak at 301 cm^{-1} possibly corresponding to (6,6) tubes increases, indicating relatively high metallic species content. However, the relative intensity is quite trivial and various specific Raman wavelengths are necessary to probe different species in resonance (33). Despite existence of M tubes, it is crucial to fabricate FET devices made from these 6 sample A to F and assess the improvement of its electrical performance in term of on-off ratio characteristic, which is extraordinarily sensitive to existence of M tubes within its networks or thin films, on

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effect of surfactant extraction and DGU separation technique. High on-off ratio could be obtained if low density networks below the M percolation threshold are applied (34). With the increase in M tube concentration, M tubes in SWNT networks can easily form continuous paths resulting in low on-off ratio (8). Ideally, SWNT networks with pure S tubes can achieve high on-off ratio.

Figure 6-5: (a) Schematic diagram of SWNT thin film FETs configuration as described in the Experimental Section. (b) Typical AFM image of a SWNT thin film device. The left side of the image refers to Au electrode. (c) 3D reconstruction of the AFM image in part B, showing the electrode and SWNT networks in the device channel. (d) Uniform SWNT networks observed in the device channel at a $5 \times 5 \mu\text{m}$ scan.

Figure 6-5(a) shows the schematic illustration of SWNT thin film FET configuration. SWNT networks lie on the top of Pt electrodes which permit the efficient testing of various SWNT samples. To monitor the SWNT film uniformity in the device channel, the detailed AFM characterization of SWNT films was performed. In Figure 6-5(b) & (c), AFM images show both the Pt electrode and SWNT networks.

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A $5 \times 5 \mu\text{m}^2$ scan of typical SWNT networks in the device channel is presented in Figure 6-5(d). The AFM sampling for the network structures on various devices show that the SWNT network is fairly uniform and quite dense with 30~50 tubes/ μm^2 . According to the findings in chapter 5 (35), the variation in on-off ratio caused by the network density difference is relatively not significant (a factor smaller than 5) compared with the difference reported later in this study.

Figure 6-6: (a) Transfer characteristics (I_d - V_g) of a typical semiconducting SWNT device, 54 devices have on-off ratio larger than 10^4 in the total 222 measured devices (b) Transfer characteristics of a typical metallic SWNT device, 56 device have on-off ratio less than 10 in the total 222 measured devices. (c) The typical current-voltage characteristics (I_d - V_d) of the semiconducting SWNT device at different V_g from 12 V to -20 V with intervals of -8 V. (d) The typical current-voltage characteristic of the metallic SWNT device exhibits no gate-dependence.

Large contact resistance between electrodes and SWNT networks may dominate FET device's electrical performance (13). A serial of devices with different source-

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drain distances ranging from 2 to 26 μm were fabricated. The network resistance versus the source-drain distance for SWNT networks of the same density was measured and resistances of these devices (8 μm in source-drain distance) have about 10-20% contributions from the electrode/nanotube interface at the contacts, similar as the result obtained in the chapter 4. At negative gate biases, SWNT networks exhibited similar sheet resistances of about 1 $\text{M}\Omega$ per square. 6 samples (sample A to F) from small diameter CoMCM41 tubes were utilized to fabricate FET device and its typical transfer characteristics (I_d - V_g curves) and output characteristics (I_d - V_d) of S-like and M-like SWNT networks devices are presented in Figure 6-6. Basically, existence of M tubes in these 6 samples is evidently confirmed based on their optical absorption spectra. Device exhibits S-like characteristic with higher on-off ratio (Figure 6-6(a) & (c)) as M tubes form fewer paths between source and drain electrode. Whereas, device exhibits M-like characteristic with low on-off ratio (Figure 6-6(b) & (d)) as the number of M conductive path rise and M tubes dominate the SWNT network conduction. Several other electrical properties of FETs for the (n,m) enriched samples (samples C-F) are listed in Table 6-2. Property values in Table 6-2 are the average for the specified number of devices from different (SWNT samples shown in Figure 6-7). In addition to the on-off ratio differences presented in Figure 6-7, the effective field effect mobility of devices from samples C and E (with higher on-off ratio) is lower than the effective mobility of devices from samples D and F (with lower on-off ratio). This result is consistent with the findings obtained in chapter 5 (35). It is because that conductance of SWNT network is proportional density of its network. Due to existence of M tubes, possibility of forming M conductive path bridging source and drain electrode rises with increase in its network density resulting in low on-off ratio but high effective field effect mobility owing to increase in its

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conductance. Another experimental observation is the pronounced gate hysteretic behaviors of devices fabricated from these enriched samples. Statistically, the gate hysteresis from samples C and D are relatively more pronounced than those of devices from samples E and F as presented in Table 6-2. The tremendous effort is necessary for further investigation on this fascinating experimental observation in order to figure out the literal reason. Such significantly obvious gate hysteresis in Si backgate configuration has been investigated and extensively discussed in chapter 8.

Table 6-2: Average Transistor properties for (n,m) Enriched SWNT samples

Sample	C	D	E	F
I _{off} (A)	9.03 X 10 ⁻⁹	1.75 X 10 ⁻⁸	1.72 X 10 ⁻⁸	6.30 X 10 ⁻⁹
I _{on} (A)	3.57 X 10 ⁻⁶	6.98 X 10 ⁻⁶	1.02 X 10 ⁻⁶	2.88 X 10 ⁻⁶
Threshold voltages forward (V _{th} ^f)	20.7	21.4	16.4	10.8
Threshold voltages reverse (V _{th} ^r)	0.6	-0.9	1.7	-1.0
Hysteresis ΔV _T (V)	20.1	22.2	14.7	11.8
Effective mobility (cm ² /(V-s))	1.73	2.83	0.81	2.61

Figure 6-7 reveals the histograms of device percentages with various on-off ratios for devices made from 6 samples (sample A to F). A-F correspond to samples A-F as described in Figure 4-6. The numbers of devices measured for each sample are indicated. Importantly, these 6 samples (sample A to F) were evaluated in terms of theirs on-off ratio characteristic for purity of S SWNTs on three aspects: (1) the effect of surfactant extraction without DGU, (2) the effect of DGU, and (3) the difference between SC and SDS-SC co-surfactant encapsulation with assisted DGU. Comparison between Figure 6-7(A) & (B) suggests that more residue M tubes exist in the cosurfactant extracted sample B. No device fabricated from sample B has on-off ratio larger than 10⁴, whereas 16% of devices obtained from sample A have on-off ratio

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greater than 10^4 . Comparison among Figure 6-7(A), (C) & (E) implies that DGU helps to improve the device performance. Devices from both samples C and E have higher on-off ratio, compared to those from sample A. When an individual surfactant (SC) is applied, sample C shows good enrichment of S tubes with >75% of its devices possessing on-off ratio larger than 10^3 . However, such a trend is not found among Figure 7-7(B), (D) & (F), which undergo SDS-SC cosurfactant encapsulation. After SDS-SC cosurfactant assisted DGU, sample D contains more metallic devices, > 70% of its devices possessing on-off ratio less than 100. Difference between samples C and D can also be observed between samples E and F. About 60% of devices from sample E possess on-off ratio greater than 10^4 compared to 20% of devices from sample F. Noticeably, the summation of sample C and sample E or sample D and sample F do not match with sample A or B as revealed in Figure 6-7. It is because after DGU only the upper two layers of dispersions with distinctive colors were extracted for device fabrication, and tubes/bundles in the lower portion of dispersions were discarded.

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Figure 6-7: Histograms of device percentages with various on-off ratios for devices made of (n,m) enriched SWNTs. A-F correspond to samples A-F as described in Figure 4-6. The numbers of devices measured for each sample are indicated in the figure.

Spectroscopic studies show that these 6 samples (sample A to F) are enriched with S SWNTs, yet characterization of SWNT thin film FETs fabricated from them reveal that trivial changes in their S SWNT purity lead to considerably detectable differences in device performance in term of on-off ratio. First, the author discusses effects of co-surfactant encapsulation without DGU. Without DGU, the enrichment of (n,m) tubes mainly is caused by the selective absorption of surfactants on SWNTs. It has been reported that the selection of (6,5) and (8,3) tubes (smaller diameter) is optimized when SDS-SC co-surfactant is at 1:4 wt ratio (25). The controversy of

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diameter selectivity from surfactant encapsulation has been demonstrated by looking the empirical data published from two separated research groups. McDonald et al.(36) has reported that SDS has a stronger binding to smaller-diameter nanotubes, whereas Li et al. has reported that SDS or SC alone has no selectivity toward smaller tubes (25). Despite the controversy, it is speculation that the nanotube diameter selectivity is caused by a particular surfactant shell arrangement of SDS and SC on SWNT surfaces at 1:4, but the exact mechanism of surfactant molecules adsorption on SWNT's surface still remains unclear (37). Therefore, this research currently undergoes intensive investigation worldwide and could eventually provide better understanding on its diameter selectivity. Nonetheless, by analyzing the statistical data as shown in Figure 6-7(B), the on-off ratio of FET devices fabricated from sample B further demonstrates the relatively high M tube concentration in sample B. The metallicity selection of SDS-SC (1:4) co-surfactant probably causes by the stronger interaction between SC and M tubes due to the proximity of the hydroxyl groups in the cholate molecule to the nanotube surface resulting in electronic polarization toward SWNTs (36). M tubes have delocalized electrons at the Fermi level and are more receptive to induced charges (38). However, metallicity selectivity is barely observed when a mixture of SDS-SC surfactants is used. Whereas SC alone (sample A) does not reveal metallicity selectivity. Therefore, it is likely that the observed M tube enrichment is due to as-synthesized SWNTs at diameter around 0.75 nm may contain higher M fractions compared to tubes at larger diameter around 0.81 nm. As shown in Figure 6-8, the (7,4) tube is M and located between the (6,5) and (8,3) tubes. It has been demonstrated that as-synthesized SWNTs are predominately in this same higher chiral-angle region (39). When smaller diameter (6,5) and (8,3) SWNTs are enriched from sample A to sample B, it is likely that (7,4) tubes or other M residues at the

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similar diameter are also enriched, leading to more M tubes in sample B. This is consistent with results obtained from chirality separated DNA functionalized HiPco SWNTs, where more residue M tubes exist in the fraction enriched with the (6,5) SWNTs (26).

Figure 6-8: Chirality maps of major (n,m) SWNT species concerned in this study. Pink hexagons are smaller semiconducting tubes identified in PLE spectroscopy of sample C or D; green hexagons are larger semiconducting tubes identified in PLE of sample E or F. Blue hexagons are possible metallic species which can not be observed in PLE.

For DGU effect, Hersam (15) has summarized that the extent of surfactant adsorption on nanotubes is not uniform for various chiralities, and creates assemblies with different buoyant densities. This facilitates their separation by isopycnic centrifugation, where particles migrate to regions with same density. DGU sorts SWNTs by their buoyant density resulting in layers in the centrifuge tube according to their buoyant density demonstrated with great success on BN-Arc-discharge SWNTs. Nair et al. (38) have proposed a hydrodynamic model to describe the motion of surfactant-suspended SWNTs in DGU, suggesting that 2.09 and 2.14 SC molecules adsorbed per nanometer along the length of the (6,5) and (7,5) nanotubes respectively.

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It is easy to comprehend the difference between sample A and sample E, as well as sample B and sample F owing to large diameter SWNTs with higher density can be removed by DGU. Removal of large diameter tubes helps to enhance the on-off ratio of devices as demonstrated in Figure 6-7.

However, the device's electrical performance difference between sample C and sample D, as well as sample E and sample F could not explain simply based on this hydrodynamic model. Despite obtaining almost identical spectra in PL, absorption and Raman spectroscopies from them, the device's electrical performance from them is considerably different. It is possibly due to less M residues existing in sample C and E using SC alone compared to sample D and F using SDS-SC (1:4) co-surfactant. From the obtained experimental results, there is notably different between smaller diameter tubes (<0.9 nm) in this chapter 6 and larger tubes reported in chapter 4 and 5. In addition, Arnold et al has demonstrated enrichment of S and M tubes by co-surfactant encapsulation with SDS-SC ratio =1:4 and 3:2 respectively assisted DGU for laser-ablation-grown SWNTs (1.1-1.4 nm) (23). The author has experimentally demonstrate that enrichment of S by SDS-SC (1:4) co-surfactant assisted DGU for arc-discharge SWNTs with its diameter distribution 1.0-1.4 nm in chapter 4 and 5, which is in line with the findings from Arnold et al. According to the hydrodynamic model, the affinity of SC molecules adsorbed on M tubes such as (7,4) should be higher. The first layer with SC assisted DGU should be M enriched. However, the obtained results from small diameter CoMCM41 tubes (0.7-0.9 nm) in Figure 6-6 suggest that both sample C and E contain less M tubes than sample A. Whereas SDS-SC (1:4) assisted DGU reveals a relatively high selection to M tubes than S tubes for smaller diameter tubes. To elucidate the observed results, an understanding of molecular level concerning the adsorption of surfactant on SWNTs and dynamics of

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SWNT-surfactant assemblies in DGU is required. Currently, it is still not available.

This study encourages further research on interactions between surfactants and various SWNT species.

In addition, small fraction of M tubes unavoidably existed in the treated SWNT solutions via DGU with surfactant encapsulation leads to impossibility of full yield S SWNT thin-film FETs production despite exploitation of selectively narrow diameter and chirality distribution SWNTs as starting material. Therefore, it is essential to prepare entire S SWNT dispersion in order to realize full yield of S CN-FET devices production and superior electrical performance device particularly effective mobility. In the following chapter 7, the author demonstrates how to achieve full yield of S CN-FET devices production by adopting adequate strategic approaches and further improve its effective mobility.

6.4 Conclusions

The (n,m) selective enrichment by both co-surfactant encapsulation and DGU for smaller SWNTs (<0.9 nm) obtained from Co-MCM-41 catalysts has been demonstrated. The enrichment of smaller diameter tubes such as (6,5) and (8,3) as well as M tubes with similar diameter can be achieved by cosurfactant encapsulation (SDS-SC). According to the statistical data of FET devices' on-off ratio collected from those enriched samples, the higher S fractions can be obtained from the first two layers after DGU with SC surfactant encapsulation. While relatively more M tubes exist in the first two layers after DGU with SDS-SC (1:4) cosurfactant encapsulation. Despite noticeable difference in device's performance in term of on-off ratio from after DGU with SC and SDS-SC surfactant encapsulation, feasibility of obtaining

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entire S CN-FET device yield is impossible owing to unavoidable small fraction of M tubes existed in the treated SWNT solutions via DGU regardless of type of surfactant.

6.5 References

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7. High Performance Solution Processable Semiconducting SWNTs Thin Film Transistors Devices

The author demonstrates that full semiconductor device yield can be achieved using SWNT solutions prepared by selective functionalization of SWNTs with diazonium reagents and followed by DGU to remove most of M species and impurities. CoMoCat SWNTs with appropriate diameter and chirality distribution were used and the major species present in the networks is (6,5) SWNT. M species are likely removed and the (6,5) species is enriched after treatment with 4-bromobenzene diazonium (BBDT) and DGU. By increasing the network thickness, the effective mobility of the devices can be raised to $\sim 10 \text{ cm}^2/\text{V}\cdot\text{s}$ while keeping the on-off ratio higher than 5000. According to the positive relationship between effective mobility and network thickness, it is possible to tune the mobility of solution processed SWNT transistors by controlling the thickness of SWNT films. The removal of impurities is found to be essential for achieving high on-off ratio devices. It is speculation that the achievement of the full semiconductor FET device yield using the CoMoCat SWNTs, which consist of small diameter tubes, is due to the differences between chiralities are significantly large in terms of the reactivity with diazonium salts.

7.1 Introduction

Single-walled carbon nanotube (SWNT) networks have been demonstrated as potential materials for transistor applications (1-5). The major hurdle to the scaling up of SWNT field-effect transistors (FETs) has been the difficulties in obtaining high mobility and full semiconductor device yield due to the presence of M along with S tubes in fabricated networks or films (6). In chapter 4 and 6, the author has demonstrated the possibility of achieving S SWNTs network or thin film FETs (CN-FETs) with moderate mobility and promising semiconductor device yield via DGU for arc-discharged produced SWNTs (its diameter 1.0 to 1.4 nm) as well as CVD produced SWNTs with Co-MCM-41 catalysts (its diameter <0.9 nm) respectively. However, a full semiconductor device yield is impossible due to detectable fraction of M tubes existed in the treated SWNT dispersion. Therefore, it is essential to suppress or remove the M species via other strategic approach in order to achieve the ultimate goal which is realization of full semiconductor device yield with decent mobility.

In literature, a variety of approaches including selective synthesis of S SWNTs (7-10), electrical breakdown of metallic M SWNTs (11-12) and selective elimination of M SWNTs by gas-phase (13) and selective chemical functionalization (14-16) has been developed to enhance the S behaviours of as-grown networks. Recent development of the method using photolithography-assisted stripping for as-grown SWNT random networks has enabled the fabrication of high yield semiconductor CN-FETs with mobilities as high as $80 \text{ cm}^2/\text{V}\cdot\text{s}$ (17). The advantage of SWNT random networks FET is ease of fabrication, which makes low-cost solution processing possible for realizing printable

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electronics. However, it is essential to separate M and S SWNTs for solution printing processes. Many different approaches have been attempted to separate M and S SWNTs or enhance the device semiconductor characteristics, including dielectrophoresis (18-19), selective oxidation (20), aromatic extraction (21-22), surfactant extraction (23), amine extraction (24), surface alignment (25-26), removal of bundles (27) and DNA or polymer wrapping (28-31). Most of the proposed methods may not easily achieve full semiconductor device yield or may involve substantial costs. Recent studies based on DGU (32), which is extensively exploited in the studies demonstrated in chapter 4 & 5, and gel-based separation techniques (33) have been shown to be efficient for sorting SWNTs. Suppression of metallic conductivity by cycloaddition has also been demonstrated (34). Moreover, highly selective reaction of diazonium reagents with M-SWNTs has been discovered and examined by optical measurements (35-39). Several groups have applied this process as a post-treatment to selectively eliminate M-SWNTs (14-15). The efficiency of post-fabrication treatments relies strongly on the composition and density of the networks. Up to date, there is not much success achieved in the preparation of high-quality SWNT inks for solution-processed FETs. The remaining technical challenge is to simultaneously achieve full semiconductor device yield and reasonably high carrier mobility. The author selected 4-bromobenzene diazonium tetrafluoroborate (BBDT) compounds, which is similar to the diazonium reagent used by Richard Smalley and his co-workers reported the highly selective reaction of diazonium reagents with M SWNTs(35), in this study. In addition, BBDT compound is aqueous soluble and can directly added into SWNT dispersion without further modification needed. In this chapter, the author demonstrates that full semiconductor device yield can

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be achieved using SWNT solutions prepared by selective functionalization of SWNTs with diazonium reagents and followed by DGU to remove most of metallic species and impurities. CoMoCat SWNTs with appropriate diameter and chirality distribution were used and the major species present in the networks is (6,5) SWNT. M species are likely removed and the (6,5) species is enriched after treatment with BBDT and DGU. The obtained effective mobility is increased with the network thickness and saturated at about $10 \text{ cm}^2/\text{V}\cdot\text{s}$.

7.2 Experimental

The starting materials, SWNT@SG 65 (CoMoCAT), were purchased from SouthWest Nanotechnologies (USA) and were used without further purification. The reason of selecting this type of CoMoCAT tubes as starting materials is due to high percentage of S species content in its initial stage and small diameter tube with narrower diameter distribution, which are beneficial for subsequent M-S separation. In addition, M. C. Hersam's group has demonstrated that CoMoCAT SWNTs possessing a relatively narrow diameter distribution (0.7 to 1.1nm) can be sorted out via DGU technique and fractionation (40). Thus, CoMoCAT tubes was selected in this chapter. The preparation of the SWNT suspensions for FET device fabrication consisted of (i) selective functionalization of SWNTs with diazonium reagents and (ii) density gradient ultracentrifugation. (i) SWNTs were selectively functionalized with diazonium reagent as follows: 4 mg of SWNTs was dispersed in 10 ml H_2O solution with 2 wt % co-surfactants consisting of sodium dodecyl sulfate (SDS) and sodium cholate hydrate (SC) with 1:4

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ratio as encapsulating agent via ultrasonication for 30 mins. The ultrasonication was implemented by immersing an ultrasonic probe (Sonics & Materials Inc., Model: VCX 130) into the SWNT solution with co-surfactants. During ultrasonication, 1mM of 4-bromobenzene diazonium tetrafluoroborate (BBDT) was added to obtain BBDT-treated SWNTs. The SWNT solution was placed in a bath of ice-water to control the temperature at around 15⁰ C during ultrasonication. After ultrasonication, centrifugation with fixed angle rotor at 140,000 g-force for 120 minutes at 20⁰ C was carried out for removal of insoluble materials. Some of the supernatant solution was applied to device fabrication and some was further processed with DGU. (ii) The experimental procedure of DGU has been described in chapter 3. After DGU, the top fractionated SWNTs layer, which was purple in color, was withdrawn via syringe for characterization by optical spectroscopies as well as for FET device fabrication. UV-vis-NIR and Raman spectroscopy were used for characterizing the treated SWNTs. SWNT network FETs (CN-FETs) were fabricated by drop-casting the obtained SWNT solutions on a bottom contact device geometry, on which 100 nm thick Au electrodes (as Au-SWNT contacts) had been patterned on top of SiO₂/Si substrates using standard lithography techniques. The gate dielectrics were 300 nm thick SiO₂. The geometry of the investigated devices is around 25 μ m in channel length and 25 μ m in channel width. The experimental procedure of device fabrication has been broadly elaborated in chapter 3. The schematic diagram of major experimental procedure in this study is presented in Figure 6-1. A confocal Raman microscope (WITec CRM200) equipped with 514nm and 488nm of laser was used for Raman measurements. Optical absorption measurements were performed with a Perkin Elmer Lambda 9 UV-Vis-Nir spectrometer. All electrical measurements were carried out

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in ambient conditions using a Keithley semiconductor parameter analyzer Model 4200-SCS.

Figure 7-1: Schematic diagram of the experimental procedure in the chapter 7.

7.3 Results and discussion

CoMoCat 65 nanotubes (SouthWest Tech.) were used as a starting material for preparing SWNT solutions. The experience gained from chapter 4 and 6 suggests that diameter distribution of SWNTs is exceptionally critical for achieving S enrichment via DGU. Therefore, SWeNT@SG 65 were selected in this study due to high percentage of S species content in its initial stage and the similar diameter distribution with CVD

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produced SWNTs with Co-MCM-41 catalysts (<0.9 nm in diameter) investigated in chapter 6 as well as highly selective dominance of (6,5) species, which are beneficial for subsequent M-S separation. Enrichment of (6,5) species has been demonstrated via DGU with SDS-SC cosurfactant encapsulation in chapter 6. As far as electronic application based on SWNTs network or thin film is concerned, achievement of full semiconductor device yield from almost semiconductor-enriched SWNTs dispersion is considered as an extraordinary breakthrough. Thus, removal of existed M species in starting SWNTs material is the primary task. In this chapter, the established approach of functionalization of SWNTs with diazonium reagent, which is favourably selective reacting with M species, was adopted to deliberately separate S species from M species. The SWNTs were dispersed in an aqueous solution with 2 wt % cosurfactants (1:4 ratio of sodium dodecyl sulfate (SDS) and sodium cholate hydrate (SC)) with the aid of probe sonication. 1mM of BBDT was added during the probe sonication process to accomplish selective reaction with M species. The schematic illustration for chemical functionalization of SWNTs by BBDT is shown in Fig. 7-2(a). Despite favourable reacting with M species, the concentration of the added BBDT plays a significant role for determining its effectiveness on auspiciously selective reaction with M species. Figure 7-2(b) shows the evolution of absorption spectra for the SWNTs after reacting with BBDT (from 0.45 to 4.97mM) together with the optical absorption spectra of the pristine SWNTs solely dispersing in co-surfactants system. According to the diameter distribution, differentiation of M and S species could be performed by analyzing its optical absorption spectra. In Figure 7-2(b), M11 represents the 1st van Hove electronic transitions for M species ranging from 350 nm to 500 nm. Whereas S11 corresponding the 1st van Hove

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transitions and S22 corresponding the 2nd van Hove transitions for S species are range from 500 nm to 900 nm and from 900 nm to 1200 nm respectively. Based on the obtained optical absorption spectra, the existence of detectable peaks between 350 nm to 500 nm with BBDT concentration <1mM suggests existence of M species as well as deficiency of minimum required BBDT amount for entire suppression of M species. On the other hand, the absorbance intensity of the major peaks appearing in S11 and S22 region gradually diminishes with rise in BBDT concentration, suggesting excess BBDT molecules begin to vigorously react with S species and reaction with S species results in loss of metallicity selectivity. Therefore, it is tremendously crucial to determine the optimized concentration which is the lowest to cause the loss of M peaks. After analyzing the BBDT concentration dependence study, the optimized BBDT concentration is determined to be ~1mM under favourable conditions in order to completely react with M species. Thus, the 1mM optimized BBDT concentration is selected for subsequent treatment process.

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Figure 7-2: (a) Schematic illustration for the chemical functionalization of SWNTs by 4-bromobenzene diazonium tetrafluoroborate compounds. (b) Absorption spectra for the CoMoCat tubes treated with various BBDT concentrations with the same reaction period (30 mins).

Despite ensuring complete reaction with M species at optimized BBDT concentration, the BBDT-treated SWNTs dispersion necessitates further purification for

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removing foreign substances such as impurities, residual BBDT and etc in order to fabricate FET devices. To further purify the BBDT-treated SWNTs, DGU was performed and the SWNTs remaining in the top fractionated layer were extracted and re-dispersed in a fresh aqueous co-surfactant solution. The DGU-extracted solution, purple in color, was used for FET device fabrication. Figure 7-3(a) shows the optical absorption spectra of pristine SWNTs, the SWNTs after treated with only BBDT (labeled as BBDT*), with only DGU (labeled as DGU*) and those with both BBDT and DGU (labeled BBDT+DGU*). The pristine tubes comprise several major S species ((6,5), (7,5), (7,6), (8,4), (6,4) and (5,4)) and M species ((6,6) and (5,5)) as assigned in Figure 6-3(a), where M11, S11 and S22 region is also indicated for comparison the difference among these 4 samples. Based on the optical absorption spectra of the pristine SWNTs, the estimation of S species proportion is approximately greater than 80 percent suggesting that high probability of revealing S behaviour from its network or thin film. In addition, according to the detectable SWNT species, the pristine SWNTs possess narrow diameter distribution ranging from 0.7 nm to 0.9 nm. After reacting with BBDT, the solution became brown in color as revealed in Figure 7-3(a). The optical absorption spectra of BBDT* sample shows that M species were selectively bleached. Simultaneously, Some of the peaks corresponding S species such as (7,5) and (7,6) were also preferentially suppressed by BBDT-treatment, suggesting that unambiguous reacting with M species is unlikely via BBDT-treatment despite selectively prioritized reacting with M species. Therefore, the optimization of BBDT concentration is necessarily crucial for preventing over-reaction resulting in deterioration of S species. In the contrary, the absorption peaks from M species (6,6) and (5,5) are noticeable present for the solution after treated with

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only DGU, suggesting that the adopted DGU process is not capable for efficient removing all the M species. Instead, DGU process is superior for diameter sorting for SWNT diameter less than 0.9 nm. The obtained experimental result is in line with result obtained from CoMCM41 tubes (diameter 0.7-0.9nm) as evidently demonstrated in chapter 4.

Figure 7-3: (a) optical absorption spectra of pristine SWNTs, the SWNTs after treated with only BBDT (labeled as BBDT*), with only DGU (labeled as DGU*) and those with both BBDT and DGU (labeled as BBDT+DGU*). Inset shows the visual appearance of the four solutions. (b) Raman D and G bands for pristine and BBDT+DGU* solutions excited with 515 nm (left) and 488 nm (right).

The preferential reaction of BBDT with M species is corroborated by the Raman spectra for both 488 and 515 nm laser as revealed in Figure 7-3(b). Knowing that both

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488 and 515 nm laser has strong resonance with smaller diameter M tubes which are targeted for verifying existence of these M species, the Raman spectra from both lasers are consistent and revealed suppression of longitudinal G bands of M SWNTs at $\sim 1544 \text{ cm}^{-1}$ as well as disappearance of the extended Breit-Wagner Fano line shape (characteristics of M species)(35, 39) after BBDT treatment. The Raman results are consistent with the findings from optical absorption spectra and further manifestly verify the preferential reaction of BBDT with M species. Interestingly, the D-band from SWNTs is obviously enhanced after reaction with BBDT. Knowing that D-band feature reflects the defects and perfection of SWNTs, therefore the observation of enhancement of D band is likely due to the conversion of an $\text{sp}^2 \text{ C}$ to an $\text{sp}^3 \text{ C}$ on the nanotube sidewalls during the BBDT functionalization (35). Furthermore, the Raman spectra of the samples BBDT* and BBDT+DGU* exhibit no detectable differences, suggesting that the quality of the SWNTs does not affect with DGU process. In Figure 7-3(a), the plasmonic background in the optical spectrum ($<600 \text{ nm}$) for DGU* or BBDT+DGU* is significantly reduced, indicating that the DGU is able to efficiently remove impurities (residual catalysts, amorphous carbon or other carbon nanostructures) (41-42). These impurities definitely influence the quality of the SWNTs dispersion. Noticeably, the onset of rise in absorbance at the wavelength $<400 \text{ nm}$ for DGU* and BBDT+DGU* is due to the absorption of degraded BBDT molecules. Separately, the intensity of absorbance at the wavelength $<400 \text{ nm}$ increases with the oxidation of the BBDT molecule itself in ambient, further verifying the absorption of degraded BBDT molecules interferes absorbance $<400 \text{ nm}$. Commendably, the loss of optical features such as SWNT absorption and Raman features may also be due to the Fermi energy shifts caused by

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BBDT reaction. Therefore, bleaching of the optical features of M species does not firmly conclude that the M tubes are physically removed from the BBDT* or BBDT+DGU*. Electrical characterizations are required to address this question.

Figure 7-4: Absorption spectra for the pristine HiPCO tubes, the SWNTs after treated with BBDT and with both BBDT+DGU treatments.

Interestingly, the experimental result of absorption spectra shed the light on the possibility to selectively attack M species for HiPCO tubes using both BBDT treatment and DGU separation as illustrated in Figure 7-4. The result suggests that BBDT treatment is applicable to large diameter tubes as well. Despite revealing preferentially attack M species, there is still present detectably trivial quantity of M species after BBDT treatment suggesting that such BBDT treatment is relatively effective to small diameter tube with great chiralities difference (e.g CoMoCat tube). In addition, there is nearly monodispersity with scarcely prominent (6,5) chiral species after BBDT+DGU treatment

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for CoMoCat65 tube as shown in Figure 7-3(a). The monodispersity of SWNTs dispersion likely leads to homogeneously electrical performance of its FET devices and reduce the variation in its device performance. Therefore, CoMoCat65 tube solution treated with both BBDT+DGU treatment is selected to carry out the subsequent study.

Figure 7-5: (a) Transfer characteristics for bottom-gated FETs drop-cast from the BBDT+DGU* solution. The channel length and width are 25 μm and 25 μm, respectively. Inset shows the AFM image for the SWNTs in the channel region. (b) Histogram of on-off ratios for devices constructed from BBDT-treated SWNTs (denoed BBDT*), DGU-extracted SWNTs (denoed DGU*) and those treated with both BBDT and DGU extraction (denoted BBDT+DGU*). The number x in x-axis represents 10^x .

Since DGU process efficiently removes impurities and the quality of SWNTs does not compromise after DGU based on the concrete experimental optical absorption spectra

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and Raman spectra. BBDT+DGU* solution was used to fabricate FET device for electrical characterization. Figure 7-5(a) shows the typical transfer characteristics, forward and reverse sweeps of drain current (I_d) vs. gate voltage (V_g), for bottom-gated FETs drop-cast from the SWNT solution after both BBDT-treatment and DGU-extraction. The channel length and width are 25 μm and 25 μm respectively and the gate dielectrics is a 300 nm SiO_2 layer. The device exhibits a typical p-type behavior and has effective carrier mobility $\sim 10 \text{ cm}^2/\text{V}\cdot\text{s}$ in the forward scan (V_g from positive to negative). The achieved mobility ($\sim 10 \text{ cm}^2/\text{V}\cdot\text{s}$) via these approaches is tremendously significant compare to the best mobility (1 to 2 $\text{cm}^2/\text{V}\cdot\text{s}$) reported in chapter 5 and 6. Mobility feature is one of most dominant factors for assessing the electrical performance of CN-FETs. Admirably, mobility with 10 $\text{cm}^2/\text{V}\cdot\text{s}$ is superior comparing to amorphous Si FET as well as organic FET which are in the range of 1 to 2 $\text{cm}^2/\text{V}\cdot\text{s}$. The inset of Figure 7-5(a) shows the atomic force microscopy (AFM) image of the device, where the device channel area is covered by a thick and film-like layer of SWNTs ($\sim 30 \text{ nm}$ thick), which is far beyond the predicted percolation threshold density ($N_c = 4.236^2/\pi \cdot L_c^2$ (43)) estimated to be ~ 2.5 to $\sim 23 \text{ tubes}/\mu\text{m}^2$ in this case. Therefore, the percolation conduction theory is not applicable to such thick SWNT films. However, the conductance of low density network from the BBDT+DGU* solution with its tube length (L_c) ranging from ~ 0.5 to $\sim 1.5 \mu\text{m}$ is in an approximately good agreement with the percolation conduction theory, suggesting that SWNT treated with BBDT and DGU is still similar to pristine SWNT in term of its nature. In addition, the AFM image of a low density network as presented in Figure 7-6 indicates the lengths of the tubes (L_c) range from ~ 0.5 to $\sim 1.5 \mu\text{m}$ from the BBDT+DGU* solution.

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Figure 7-6: AFM image of SWNTs drop-cast from the BBDT+DGU* solution.

Figure 7-5(b) is a histogram of the on-off ratios for the devices constructed with BBDT*, DGU* and BBDT+DGU* solutions. By looking at on-off ratio feature could effectively provide reliable and accurate information on purity of S SWNTs content (or existence of M SWNTs on its fabricated network). The relation between on-off ratios of the devices and the density of drop cast SWNTs network has been extensively discussed in chapter 5. Similarly, for this case that the on-off ratios for the devices also depend on the thickness of the drop cast SWNT films. Owing to the low controllable drop-cast technique in device fabrication such as droplet size, quantity of SWNTs in each droplet and etc, it is impossible to accurately determine the density of its film by simply accounting number of added droplets. Therefore, the statistical data presented here were obtained from the drop-cast devices without intentional thickness control, where the droplets were added on the channel area until the resistance of the device was smaller than $\sim 1 \text{ M}\Omega$ which ensures that the conductance of the devices dominates its network or film rather than contact resistance between electrode and SWNTs. The on-off ratios of

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devices from pristine SWNT solutions are generally very low (ratio ranging from 1.2 to 100) due to coexistence of M and S SWNTs. Amazingly, All the as-prepared devices made from the BBDT+DGU* solution exhibit on-off ratios ranging from 5000 to 10^7 and the typical effective mobility ranges from 6~10 $\text{cm}^2/\text{V}\cdot\text{s}$. The excellent electrical performance of CN-FETs in term of high on-off ratio and high mobility feature could be achieved from BBDT+DGU* solution with full semiconductor device yield. Surprisingly, after BBDT-modification (without DGU extraction), the devices obtained still have low on-off ratios (<1000) although the absorption features from M species are significantly bleached, suggesting that either M species are still present in the BBDT* solution or the impurities (associated with the plasmonic background in Figure 7-3(a)) may degrade the on-off ratios. On the other hand, the removal of plasmonic background is also observed for the DGU* (without BBDT treatment) but full semiconductor device yield is still not obtainable for the devices made from DGU*, where a significant proportion of the devices have on-off ratio below 1000. These results conclude that the removal of impurities may not be the dominating factor to achieve high semiconductor device yield. Instead, removal of M species is crucial for obtaining good on-off ratio characteristics.

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Figure 7-7: (a) Typical I_d - V_g characteristics for the device prepared from the discarded solution of BBDT+DGU* (b) Absorption spectra for the BBDT+DGU* and discarded solutions from the DGU process.

To understand whether M species are physically present in BBDT+DGU*, electrical measurements for the devices prepared from the solution discarded after DGU process were performed. Figure 7-7 shows the typical I_d - V_g curve for the devices prepared from the discarded solution and the device typically exhibits metallic behaviors (with almost no gate dependence), which is in clear contrast to those prepared from its counterpart solution BBDT+DGU*, suggesting that majority of M species remains in the discarded solution after DGU process. Moreover, it has been reported that the BBDT molecules attached on SWNTs can be removed from tube surfaces by thermal annealing at above 300°C (44). If the devices possess significant amounts of BBDT-attached M

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SWNTs in the conduction path, the M tubes shall be fully recovered and these devices are expected to become less gate-dependent after thermal annealing, evidenced by Figure 7-8(a) that the on-off ratio of the device made with BBDT* is largely reduced after thermal annealing (400°C H₂-annealing for 2hr). The proposed reaction scheme of H₂-annealing with BBDT* treated SWNT at 400⁰ C is shown in Figure 7-9. In addition, the observed I_d increase upon annealing is generally due to the perfection of the contact between SWNTs and electrodes. This suggested explanation is corroborated by annealing the device made with DGU*, where no on-off decrease but only increase in I_d is observed (Figure 7-8(b)). Similarly, the thermal annealing was carried out for at least 10 S devices prepared using BBDT+DGU*. Figure 7-8(c) shows no degradation in on-off ratio, indicating that the content of the M tubes is very low in the networks. This experiment evidently confirms that the proposed method BBDT+DGU* effectively remove the M tubes. In addition, it also suggests that the BBDT-reacted M SWNTs may be more distinguishable from S SWNTs in the DGU process resulting in exceptional separation of S and M SWNTs.

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Figure 7-8: Transfer curves of the device prepared from (a) BBDT* (BBDT-only), (b) DGU* (DGU only) and (c) BBDT+DGU* before and after thermal annealing at 400°C for 2hr (H₂-environment).

Figure 7-9: A proposed reaction scheme of H₂-annealing with BBDT* treated SWNT at 400°C

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The reactivity of BBDT towards M SWNTs may be caused by the degree of pre-existing defects, and the M tubes may be more prone to disorder induced by ambient conditions because of their available carriers/empty states for reactions (39). Instead of performing BBDT treatment prior DGU, the reverse approach, which is undergoing BBDT treatment after DGU, has been attempted. Unfortunately, the results show that all types of tubes react with BBDT even using a very low BBDT concentration (0.1mM). No obvious selectivity was observed. It is speculation that after initial dispersion and DGU, the SWNTs are decorated with more defects, which may promote the reaction with BBDT and thus suppress the selectivity.

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Figure 7-10: (a) The relation between extracted effective mobility and SWNT film thickness of the FET devices. The horizontal error bars represent the thickness measurement uncertainties. (b) The trend of on-off ratio with device mobility for the devices constructed from BBDT*, DGU* and BBDT+DGU* solutions.

Figure 7-10(a) shows the relationship between extracted effective mobility and SWNT film thickness of the FET devices. The thicknesses were measured with a surface profiler. Very thin films (just above the percolation threshold; ~1 to 2 nm thick experimentally) have effective mobility around 0.2 to 0.3 cm²/V·s, this value falls in the same order of magnitude with those obtained for the devices cast from solution-processed SWNTs with similar tube lengths (27, 33). Owing to efficient removal of most M

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SWNTs with BBDT and DGU treatments, it is possible to increase the density (thickness) of the networks without building up the M SWNT percolation path. By increasing the network thickness, the effective mobility of the devices can be raised to $\sim 10 \text{ cm}^2/\text{V}\cdot\text{s}$ while keeping the on-off ratio higher than 5000. Theoretically, the effective mobility is proportional to the density (or thickness) of its networks. However, Figure 7-10 presents this proportional relationship between mobility and density of its networks is valid as the thickness of its network is below 25 nm and the mobility seems saturated $\sim 10 \text{ cm}^2/\text{V}\cdot\text{s}$. Figure 7-10(b) shows that the on-off ratio decreases with increasing device mobility (or, equivalently, with film thickness) for devices from all solution including BBDT*, DGU* and BBDT+DGU*. This degradation of on-off ratio suggests the presence of trivial M-SWNTs content. However, in prospect of the high tube density in these device networks, it is anticipated that the M SWNT content must be fairly low. Also, these results demonstrate that it is possible to tune the mobility of solution processed SWNT transistors by controlling the thickness of SWNT films. Such tunability is expected to be immensely important in the future from the standpoint of device performance matching between p- and n-type transistors.

Another unsolved major issue for realizing high performance solution-processable CNT electronics is large gate hysteresis (shown in Figure 7-5(a)), which is widely observed on CN-FET device in Si-backgate configuration. The phenomenon of gating hysteresis could severely cause reliability and reproducibility issues on using CN-FET for electronic integrated circuits. Therefore, it is crucially essential to understand the problem of gate hysteresis by addressing its possible root causes, which are extensively discussed in the following chapter 8.

7.4 Conclusions

The author has demonstrated that the CoMoCat SWNTs treated with diazonium salts and purified by DGU can be used to fabricate solution-processable FET devices with a full semiconductor device yield. By increasing the network thickness, the effective mobility of the devices can be raised to $\sim 10 \text{ cm}^2/\text{V}\cdot\text{s}$ while keeping the on-off ratio higher than 5000. The removal of impurities is found to be essential for achieving high on-off ratio devices. It is speculated that successful achievement of full semiconductor device yield using the CoMoCat SWNTs, which possess relatively small diameters, is due to the differences between chiralities are significantly large in terms of the reactivity with diazonium salts.

7.5 References

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8. Gate Hysteresis of CN-FETs in Si-Backgate Configuration

The gate hysteresis in CN-FETs comprising Si-backgate (SiO_2 on doped Si) is normally attributed to either carrier injections from SWNTs to environmental dielectrics or the presence of charge traps at Si- SiO_2 interface. The author finds out that gate hysteresis in CN-FETs with a nearly trap-free Si-backgate is thermally-activated (activation energy $E_a \sim 129$ to 184 meV) in dark ambient. In addition, it is found that the gate hysteresis is attributed hole trappings at the SiO_2 surfaces proximate to SWNTs. Furthermore, the photon-illumination on CN-FET devices with thin SiO_2 dielectrics (80 nm) results in the on-current increase due to the effective gating from the photovoltage generated at Si- SiO_2 interface. The simultaneous enhancement of on-current and gate hysteresis suggest that the illumination-enhanced gate hysteresis is due to the photovoltage-activated hole trapping process on SiO_2 surfaces. Based on the experimental findings on gate hysteresis of CN-FETs in Si-backgate configuration, replacement of SiO_2 (gate dielectric layer) is reasonable remedy for solving the pronounced gate hysteresis.

8.1 Introduction

Gate hysteresis between forward and reverse gate bias sweeps is usually observed in the CN-FET devices. This raises concerns of using CN-FET for electronic integrated circuits. The gate hysteresis is a major issue on reliability and reproducibility for future electronic

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device applications. Therefore, it is essential to understand the origin of gate hysteresis in CN-FET and subsequently resolve it by embracing effectively strategic approach in order to practically utilize CN-FET as individual active component in future electronic applications. Conventionally, SiO₂, which is widely used as dielectric layer in CN-FET, is logically suspected as a main contributor for causing gate hysteresis due to its natural imperfections such as defects and charges existing within SiO₂ as well as abundance of dangling bonds. Generally, gate hysteresis in CN-FETs is attributed to injection of screening charges into/from traps in the gate oxide (1-3). Besides causing from gate oxide, Dai's group has proposed another mechanism of gate hysteresis based on experimental observation that the surface-bound water layer acted as charge trap or mediator contributes to gate hysteresis in CN-FET due to high environmental sensitivity of SWNT's nature resulting in water adsorption on its surface (4). However, the possibility of water molecules as charge traps has been questioned (5), along with the plausibility of ionic movements at low temperatures(6). In addition, another proposed explanation on the origin of gate hysteresis in CN-FETs is charge transfer between the SWNTs and charge traps at the silicon oxide/ambient interface involving surface silanol group as the main sources of screening charges(7). This explanation is agreeable with the experimental data on humidity dependence of gate hysteresis at room temperature(4, 8-9). With tremendous efforts putting in for searching the root cause of gate hysteresis in CN-FET, it is unlikely that the phenomenon of gate hysteresis is solely caused from single factor base on valuable experimental observation from various research groups.

Reduction in gate hysteresis is prioritized for demonstrating reproducible and stable operation mode of CN-FETs. In literature, there are several approaches for reducing gate

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hysteresis such as adoption of thin high-k dielectric top gates(10), electrolyte gating(11). Recently, the alternative approaches such as passivation of silicon oxide substrate with a self-assembled monolayer (SAM) (12), thermal annealing on a surfactant-covered device(13) and shortpulsed measurements(9) also pave the way for solving gate hysteresis issue. Moreover, J. Rogers's group has reported that a superior FET characteristic in low gating bias and small gate hysteresis can be successfully achieved by using thin high-k dielectric in Si backgate configuration (14-15).

In this chapter, the author focuses on investigating the hysteretic behaviors of transfer characteristics (drain current I_d vs. gate voltage V_g) of CN-FETs lying on a nearly trap-free backgate substrate (80 nm SiO_2 on Si) to exclude the hysteresis contributing from the underlying backgate. The hysteresis observed in the dark is thermally activated and with the extracted activation energy (E_a) $\sim$ 129-184 meV, indicating that the charge trapping/detrapping process is involved. The negative shift of threshold voltage (V_{th}) is attributed to the electric field (negative V_g)-driven hole trapping at SiO_2 surfaces proximate to SWNTs (7). Interestingly, the photon illumination on CN-FETs results in the simultaneous enhancement of ON-current and hysteresis. These results suggest that the illumination-enhanced hysteresis is due to the photovoltage-activated hole-trapping process on SiO_2 surfaces.

8.2 Experimental

The typical CN-FETs were fabricated in a bottom contact device geometry, where a p -doped silicon wafer (boron doped with resistivity 1~5 ohm-cm) with an 80 nm-thick

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thermal SiO₂ layer was used as the backgate and SWNT electrodes spaced by a channel length of 100 μ m were patterned on top of it as illustrated in Figure 8-1. SWNT or multi-walled carbon nanotube (MWNT) electrodes were used to replace the commonly used Au electrodes for transistor fabrications. SWNT or MWNT aqueous dispersion was sprayed onto Si substrate with mask attached for forming electrodes (16-18). 6 mg of SWNT or MWNT powders was dispersed in 10 mL aqueous sodium dodecylbenzene sulfate (SDBS) suspensions with 30 min probe sonication (Sonics & Materials Inc., model VCX 130), followed by ultracentrifugation at 53000g for 2 hours at 20⁰ C. The SWNT solutions were then sprayed on to the photoresist patterned substrates to form merely CNT electrodes for further transistor fabrication. The semiconductor-enriched tubes were obtained via DGU with aid of SDS-SC co-surfactant encapsulation (described in chapter 4 and 5) and then were applied to form its networks in channel areas for device fabrication. Subsequently, photon-illumination study was carried out to understand the root cause of gate hysteresis. The concise experimental procedure has been schematically demonstrated in Figure 8-1. All electrical measurements were carried out using a Kiethley semiconductor characterization system (Model 4200-SCS) or HP precision LCR METER (model 4284A) in ambient environment. A desired band of light was selected by using band-pass filters (+/-10nm) from a broadband light source (250W of W-lamp) and the desired light intensity was attenuated by using neutral density filters.

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Figure 8-1: The schematic diagram of the concise experimental procedure in the chapter 8.

8.3 Results and Discussion

The measurements of C-V loops were carried out for the SWNT electrode-SiO₂-Si MOS structure at 100Hz to characterize the traps existed in Si-backgate substrates. The voltage V_a is typically applied on the electrodes as illustrated in inset of Figure 8-2. As demonstrated in Figure 8-2, the C-V curves measured in dark (or with exposure to low intensity of light $\leq 0.03 \text{ nW/mm}^2$) are consistent with those observed in Si MOS capacitors (19), where the negative-to-positive V_a sweep results in a deep depletion state (20-21) and the small ledge appears in the positive-to-negative V_a sweep as a consequence of the recombination of captured minority carriers (electrons) at the SiO₂-Si interface with the majority carriers (holes) in Si (21). As expected, once stronger light is admitted ($\geq 0.94 \text{ nW/mm}^2$), depletion capacitance increases rapidly with the light

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intensity as a result of the decreased space-charge region by an effective decrease of the Si surface potential caused by illumination (22). No significant hysteresis is observed between forward and reverse C-V curves in both cases; with and without light exposure. This suggests that the Si-SiO₂ interface is trap-free and light-illumination does not induce trapped charges in it. It is noted that the observation is also valid for the MOS structures using Au or MWNTs as electrodes on the same Si-backgate substrate.

Figure 8-2: The capacitance-voltage (CV) loop characteristics at 100Hz for the SWNT electrode-80 nm SiO₂-Si capacitors with and without exposure of light. Inset shows its schematic structure.

Figure 8-3 shows the typical transfer curves for a CN-FET on a Si-backgate (80 nm of SiO₂) using SWNTs as electrodes with and without light exposure, where the light (4.69 nW/mm² at 632 nm with a spot size 100μm) was focused onto the channel area through optical objectives. A significant increase in drain current (I_d) is observed with photon-illumination at $V_g < 0$. This is attributed to a photovoltage which negatively gates

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CN-FET due to the redistribution of electrons and holes in Si and at the SiO₂-Si interface (16, 23). Interestingly, the gate hysteresis of CN-FETs is also greatly enhanced with photon-illumination. The forward threshold voltages (V_{th}^f), threshold voltage (V_{th}) extracted from forward sweeps (positive to negative V_g), measured in dark ambient were close to those measured with light exposure. By contrast, the reverse V_{th} (V_{th}^r) is largely shifted to a more negative value with photon-illumination comparing to the V_{th}^r in dark. Twenty devices have been characterized to understand the effect of the photon-illumination on CN-FET and all devices show consistent results. The FETs fabricated on Au or MWNT electrodes also exhibit consistent behaviors. To describe the evolution in transfer curves, the gate hysteresis is defined as a threshold voltage difference (ΔV_{th}), the difference between V_{th}^f and V_{th}^r as indicated in Figure 8-3. It is observed that the ΔV_{th} for this device with photon-illumination is $\sim 23V$, higher than the ΔV_{th} in dark ($\sim 7V$).

Figure 8-3: Typical transfer curves (I_d vs. gate voltage V_g) of CN-FETs with and without light exposure (632 nm). The gate hysteresis is defined as the difference between the forward threshold voltages (V_{th}^f) and reverse threshold voltage (V_{th}^r). The scheme illustrates the device structure of a CN-FET.

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Figure 8-4: (a) Typical transfer curves of CN-FETs at various temperatures (25, 60 and 90°C) in dark ambient. (b) The Arrhenius plot of ΔV_{th} for CN-FETs under dark and room light illumination over the temperature range from 18°C to 100°C.

First, the author examines the hysteresis for CN-FET in dark. It has been widely quoted that the gate hysteresis of individual SWNT FET is due to the charges injected from SWNTs into the surrounding dielectrics(6-7, 24-25). To reveal the causes of the observed gate hysteresis in CN-FETs, temperature dependence of the hysteretic behaviors is studied in ambient. Figure 8-4(a) shows the typical transfer curves at various temperatures for a selected device. By using nearly trap-free Si-backgate substrate according to C-V loop measurement, the observed hysteresis is unlikely due to the traps

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in Si-backgate. Thus, the negative shift of V_{th}^r with increasing temperature observed in Figure 7-4(a) is attributed to the electric field (negative V_g)-driven hole trapping at SiO_2 surfaces proximate to SWNTs (7). Figure 7-4(b) shows the Arrhenius plot of ΔV_{th} for five CN-FETs over the temperature range from 18°C to 100°C; the results for these five devices including four devices (D1 to D4) in dark and a device D1 under room light exposure are demonstrated for comparison. The ΔV_{th} measured in dark and ambient condition is thermally-activated and exhibits an $E_a \sim 129$ to 184 meV when temperature is $< 60^\circ C$, where the fitted E_a values corresponds well with the reported energy barrier for charge trapping/de-trapping (120~170 meV) (26) in SiO_2 dielectrics. This study provides direct evidence for the occurrence of charge trapping/de-trapping at ambient- SiO_2 interface, and is in line with the recent proposal that the non-zero hysteresis in dark is caused by the surface silanol groups (trapping centers for holes) on SiO_2 (7), where the hole injection is anticipated to take place from SWNT or moisture to silanol groups driven by a negative V_g .

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Figure 8-5: The plot of ON-state I_d (at $V_g = -20\text{V}$) and ΔV_{th} as a function of (a) light intensity (at 600 nm). (b) illumination wavelength.

Interestingly, the gate hysteresis of CN-FETs is greatly enhanced with light exposure compare to in dark condition. As depicted in Figure 8-4(b), the gate hysteresis for device D1 observed with room light exposure at room temperature is saturated at around the same maximum of hysteresis obtained in dark at high temperature. In addition, the hysteretic behaviors induced by photon-illumination (Figure 8-3) are similar to those induced by heating in dark (Figure 8-4(a)), indicating that photon-illumination

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could activate the similar hole trapping and saturate the hole traps at ambient-SiO₂ interfaces. Meanwhile, Figure 8-5(a) demonstrates that the hysteresis ΔV_{th} is abruptly increased as the light intensity is greater than 0.3 nW/mm² (600 nm of light) and reaches a saturation level. The ON-state I_d (at $V_g = 20V$) also exhibits a simultaneous increase with light intensity. Moreover, the wavelength dependence (from 600 up to 1400 nm) of gate hysteresis as shown in Figure 8-5(b) reveals that no photon-induced gate hysteresis is observed as the incident wavelength is longer than 1100nm (Si substrate absorption band-edge). These results indicate that the photon-induced gate hysteresis is likely related to optical absorption of Si. It is known that the direct consequence of photon absorption by Si is the generation of photovoltage, which negatively gates CN-FETs, thus resulting I_d -ON increase. The coincidence between I_d -ON and gate hysteresis in Figure 8-5(a) & (b) strongly suggests that the photovoltage is likely the root cause of photon-induced gate hysteresis. Therefore, the author proposes that the photon-induced hole-injection to SiO₂ is facilitated by the photovoltage owing to effective increase in negative V_g and the effective negative bias (from the photovoltage) is able to activate the hole-injection to SiO₂ surface.

8.4 Conclusions

In summary, the author reports the effects of photon-illumination on the gate hysteresis behavior of CN-FETs with Si-backgate. The gate hysteresis shows an activation energy of ~129 to 184 meV at temperature lower than 70°C in dark ambient condition. Moreover, the photon-illumination (≥ 0.3 nW/mm², 600nm) enhances the gate hysteresis significantly, possibly owing to hole trapping at SWNT-SiO₂ interface induced by the

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photovoltage. Based on the experimental findings on gate hysteresis of CN-FETs in Si-backgate configuration, replacement of SiO₂ (gate dielectric layer) is reasonable remedy for solving the pronounced gate hysteresis in order to realize electronics based on SWNT networks or thin films.

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9. Concluding Remarks

The author focuses on the purification and preparation of carbon nanotubes and its solution for solution processable S CN-FETs devices. Owing to coexistence of M and S tubes in its ensemble, Separation of SWNTs according to electronic type via adopting various strategic sorting approaches is most crucial task for realizing high performance solution processable S CN-FETs devices. Several optical spectroscopies including absorption, photoluminescence and Raman, are exploited for SWNT characterization on evaluating effectiveness of adopted strategic sorting approaches. Two-dimensional isotropic SWNT network or thin film is formed via conventional drop-casting method from its solution on patterned Si substrate for fabricating FET device.

1. The (7,5) and (6,5) enriched SWNTs are produced via alone SC and (1:4 SDS-SC) co-surfactant extraction respectively from small diameter CoMCM41 tubes (its diameter 0.7-0.9nm).
2. DGU is an effective separation technique for BN-Arc discharge (its diameter 1.0-1.4nm) and CoMCM41 tubes (its diameter 0.7-0.9nm), and effectively improve on-off ratio characteristic of its device.
3. Removing bundled tubes via ITP can drastically improve on-off ratio characteristic by ~1 order of magnitude as well as enhance other electrical characteristics such as subthreshold swing and off current.
4. Full semiconductor CN-FET device yield can be achieved using SWNT solutions prepared by selective functionalization of SWNTs with diazonium reagents and followed by DGU to remove most of M species and impurities. The obtained

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effective mobility is increased with an increase in the network thickness and saturated at $\sim 10 \text{ cm}^2/\text{V}\cdot\text{s}$ while keeping the on-off ratio higher than 5000.

5. The gate hysteresis in CN-FETs with a nearly trap-free Si-backgate is thermally-activated (activation energy $E_a \sim 129$ to 184 meV) in dark ambient. Under photon-illumination, the phenomenon of photon-enhanced gate hysteresis is likely due to the photovoltage-activated hole trapping process at SiO_2 surfaces proximate to SWNTs based on the experimental observation on simultaneous enhancement of I_{on} current and gate hysteresis.

9.1 Recommendations

This thesis principally focuses on realization of high performance solution processable S CN-FETs devices for electronic applications. Full semiconductor CN-FET device yield is realized via functionalizing SWNTs (its diameters $< 0.9 \text{ nm}$) with diazonium salts and subsequently purifying by DGU with aid of co-surfactant encapsulation (SDS-SC) as demonstrated in chapter 7. The obtained effective mobility is increased with an increase in the network thickness and saturated at $\sim 10 \text{ cm}^2/\text{V}\cdot\text{s}$ while keeping the on-off ratio higher than 5000. Despite having decent effective mobility from CN-FET device, its best effective mobility via above approach is still several orders lower than the intrinsic carrier mobility in SWNTs ($100,000 \text{ cm}^2/\text{V}\cdot\text{s}$). The inferior effective mobility of CN-FET compared to individual single-tube FET is likely due to the inter-tube contact resistance. Thus, it is crucial to understand the contact resistance of inter-tubes junction in order to further improve its effective mobility. Increase in

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individual tube length, which leads to reduction in quantity of inter-tube contact in its network or thin film at fixed area, could possibly improve its effective mobility. Furthermore, well alignment of SWNTs in its network or thin film drastically reduces quantity of inter-tube contact compare to random alignment leading to enhancement of effective mobility.

Another major issue on realization of high performance solution processable S CN-FETs devices is large gate hysteresis. It is commonly occurred in Si-backgate configuration with SiO₂ as gate dielectric, where its possible root cause has been extensively discussed in chapter 8. The replacement of conventional SiO₂ gate dielectric with high capacitance dielectric material as well as appropriate design of device configuration could be the promising remedies for resolving large gate hysteresis in CN-FETs. Therefore, more efforts should be dedicated to resolve large gate hysteresis in order to realize high performance solution processable S CN-FETs devices for electronic applications.

LIST OF PUBLICATIONS

Solution Processable Carbon Nanotubes for Semiconducting Thin Film Transistor Devices

C.W. Lee, X. Han, F. Chen, J. Wei, Y. Chen, M. B. Chan-Park and L.-J. Li
Advanced Mater. 22, 1278 (2010)

Illumination-enhanced Hysteresis of Transistors Based on Carbon Nanotube Networks

C.W. Lee, X. Dong, S. H. Goh, J. Wang, J. Wei and LJ Li
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C.W. Lee, CH Weng, L. Wei, Y. Chen, M. B. Chan, CH Tsai, KC Leou, C. H. Poa, J. Wang and LJ Li
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Solution-Processable Semiconducting Thin-Film Transistors Using Single-Walled Carbon Nanotubes Chemically Modified by Organic Radical Initiators

JW Zhao, **C. W. Lee**, X. Han, F. Chen, Y. Xu, Y. Huang, Chen, M. B. Chan-Park, P. Chen and L.-J. Li
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Assessment of (n,m) selectively enriched small diameter single-walled carbon nanotubes by density differentiation from cobalt-incorporated MCM-41 for macroelectronics

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YM Shi, X. Dong, H. Tangtang, F. Chen, **C.W. Lee**, K Zhang, Y. Chen, JL Wang, L J Li
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N-type Behavior of Ferroelectric-Gate Carbon Nanotube Network Transistor

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Applied Physics Letters. 93, 082103 (2008)

Appendix A

Effects of Substrates on Photocurrents from Photosensitive Polymer Coated Carbon Nanotube Networks

Y. Shi, H. Tintang, **C.W. Lee**, C-H Weng, X. Dong, L. J. Li, P. Chen

Applied Physics Letts. 92, 113310 (2008)