Morphology variation of single walled carbon nanotubes networks by lithography technology for improvement of field effect transistors

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**NANYANG
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**MORPHOLOGY VARIATION OF SINGLE WALLED
CARBON NANOTUBES NETWORKS BY
LITHOGRAPHY TECHNOLOGY FOR IMPROVEMENT
OF FIELD EFFECT TRANSISTORS**

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**A thesis submitted to the Nanyang Technological University
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List of Abbreviations

1-D	one-dimensional
2-D	two-dimensional
AFM	atomic force microscopy
ALD	atomic layer deposition
AMOLED	active-matrix organic light-emitting diode
APTES	(3-Aminopropyl)triethoxysilane
AP-SWNTs	as-produced single walled carbon nanotubes
CMOS	complementary metal-oxide-semiconductor
CNTs	carbon nanotubes
CVD	chemical vapor decomposition
DB71	direct Blue 71
DCB	dichlorobenzene
DGU	density gradient ultracentrifugation
DNA	deoxyribonucleic acid
DMF	dimethylformamide
FE-SEM	field-emission scanning electron microscopy
FET	field effect transistor
FT-IR	fourier transform infrared
HF	hydrofluoric
ITO	indium tin oxide
LED	light-emitting diode
MWNTs	multi walled carbon nanotubes
m-SWNTs	metallic single walled carbon nanotubes
NAND	not-AND
NOR	not-OR
PANI	polyaniline
PC	polycarbonate
PEI	polyetherimide
PET	polyethylene terephthalate
PGMEA	methoxyl propyl acetate
PMMA	polymethyl methacrylate
PTFE	polytetrafluoroethylene
RBM	radio breathing mode
RF	radio frequency
RFID	radio frequency identification
SDS	sodium dodecylsulfate
SWNTs	single walled carbon nanotubes
s-SWNTs	semiconducting single walled carbon nanotubes
TEM	transmission electron microscope
UV-vis-NIR	ultraviolet-visible-near infrared

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Summary

MORPHOLOGY VARIATION OF SINGLE WALLED CARBON NANOTUBES NETWORKS BY LITHOGRAPHY TECHNOLOGY FOR IMPROVEMENT OF FIELD EFFECT TRANSISTORS

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Single walled carbon nanotubes (SWNTs) are potential candidate of channel material instead of Si in field effect transistors due to their small diameter, high carrier density and flexibility. Two major obstacles to application of SWNT networks in field effect transistors (FETs) are the existence of metallic SWNTs (m-SWNTs) and contact resistance between tubes. To solve these problems, the stripping of SWNT networks and partial alignment of SWNTs has been developed for increasing on/off ratio and mobility of the FETs. This thesis focuses on the design and fabrication of a series of micron pattern to break the metallic percolation pathway and a new partial alignment method to reduce the tube-tube contact resistance in SWNT networks. The stripping-*cum*-sorting method and the solution-based immersion-*cum*-shake method were developed to pattern the SWNT networks in the FET channel. They are easy and effective ways to reduce both the influence of m-SWNTs in the networks and the film resistance between electrodes.

We have studied the effect of stripping on pristine and partially enriched semiconducting single walled carbon nanotubes (s-SWNTs). Although some techniques such as density gradient ultracentrifugation (DGU) can produce ultrahigh purity (~99%) s-SWNTs, the yield is usually low so that large-scale implementation

of SWNT FET is still in the research stage. Unsorted as-produced SWNTs (AP-SWNTs, 79% semiconducting) and also partially sorted s-SWNTs (88% semiconducting) are employed as starting materials. We fabricate FETs on SiO₂/Si wafers with channel width (W) of 20 μ m and 50 μ m, varying channel lengths (L) of 2 – 50 μ m and strip width (W') of 2 – 10 μ m.). On the SiO₂/Si wafer, when on/off ratio of the FETs is $> 10^4$, mobility of the best FETs with but stripped AP-SWNTs is $3.7 \pm 1.25 \text{ cm}^2/\text{V-s}$; by stripping of partially sorted s-SWNTs, the mobility of the best FETs increase to $15.8 \pm 2.92 \text{ cm}^2/\text{V-s}$. However, the on-current is still low at $0.219 \pm 0.037 \text{ }\mu\text{A}$. When the HfO₂ dielectric layer was also applied instead of SiO₂ layer, the on-current improved to $3.43 \pm 1.86 \text{ }\mu\text{A}$, the mobility of FETs with the stripped s-SWNT networks could reach $21.9 \pm 8.72 \text{ cm}^2/\text{V-s}$ when the on/off ratio is $8.16 \times 10^4 \pm 3.04 \times 10^4$. This combination of stripping and solution based sorting technique can achieve fully switchable devices without the need for ultrahigh purity SWNTs.

Furthermore, a partially aligned SWNT thin films was deposited on silicon wafers of 500 nm thick SiO₂ using a novel parallel solution-based immersion-*cum*-shake method and ultrahigh (99%) purity s-SWNTs. Superior FET devices with on/off ratio of $\sim 3.2 \times 10^4$ and mobility of $46.5 \text{ cm}^2/\text{V-s}$ are achieved with suitable choice of linear SWNT density and channel dimension. The shear force which generated by rotary fluid of the SWNT solution partially oriented the SWNTs as they were absorbed onto the substrate. The alignment direction of SWNTs was confirmed along the fluid flow direction but with an angular distribution of FWHM of

about 15 degrees by AFM images. The partial alignment was corroborated by polarized Raman spectra. AFM images at multiple locations over the whole wafer surface ($20 \times 20 \text{ mm}^2$) confirmed that the alignment is uniform. This large-scale method provides a facile way of depositing partially aligned nanotubes with controllable density to enhance FET performance. As expected from the first principles, partial alignment has the effect of reducing tube-tube contacts while preserving percolation to maximize on-current.

Chapter 1 Introduction

1.1 Background

SWNTs are one-dimensional (1D) materials which are thought to be cylinders of one carbon atom thick layer with very high length to diameter aspect ratio. The electronic properties of SWNTs are determined by chiralities which indicate the orientation of the symmetry direction of the carbon hexatomic ring with respect to the SWNT cylinder axis. According to the chiralities, SWNTs can be classified into semiconducting and metallic species. Semiconducting SWNTs (s-SWNTs) are known to have excellent on/off ratios while metallic SWNTs (m-SWNTs) can support currents as high as 4×10^9 A/cm². [1] Due to their high intrinsic current carrier mobility of 10^5 cm²/V-s and high lateral flexibility, s-SWNTs are considered to be excellent candidates in nanoelectronic transistor channels in place of current semiconducting materials such as amorphous silicon, semiconducting polymers and small molecules. [2, 3] However, if the as-produced SWNTs (AP-SWNTs) are directly deposited on the device channels, the resulting nanotube-based FETs are unswitchable because of the existence of m-SWNTs in the AP-SWNTs. One technique to achieve the switchable SWNT-based FETs even with the presence of m-SWNTs is to carefully control of the density of SWNT networks to avoid the m-SWNT percolating between the source and drain electrodes. [4, 5] By adopting this technique, a low areal density is needed to avoid m-SWNTs bridging the source and drain, which finally leads to relative low mobility and on-current of the switchable devices.

In order to enrich s-SWNT from as-prepared samples sufficiently for use in

active circuits, post-synthesis methods have been considered necessary. Thus far, most separation methods reported in the literature have respective drawbacks in scaling to industrial production.[6-8] The commercial DGU process can achieve ultrahigh purity (96% – 99%), but has a low yield due to the slow differential migration of SWNTs through the dense, viscous gradient medium.[6, 9] Simultaneous ultrahigh purity and high yield solution-based enrichment of s-SWNTs remains an aspirational goal.

Various methods to convert the morphology of SWNT networks that are lying on the wafer substrates have also been investigated to improve SWNT networks devices. Current burning of the m-SWNTs in the active channel and post-channel-deposition treatment with chemicals which preferentially destroy m-SWNTs or convert them into s-SWNTs has been studied.[10-12] These methods are somewhat effective in improving on/off ratio of device. However, these m-SWNT etching and conversion methods are tube diameter dependent and the tube density of SWNT network on the substrate should be strictly controlled. Cao *et al.* have reported a new striping method for SWNT networks are synthesized by Chemical Vapor Deposition (CVD) method. due to the fairly length of $\sim 10\text{ }\mu\text{m}$, the strips of $5\text{ }\mu\text{m}$ are formed to achieve mobility of $80\text{ cm}^2/\text{V-s}$ and on/off ratio of 10^5 .[13] However, for generally shorter solution-processed SWNTs whose length is usually less than $5\text{ }\mu\text{m}$, the width of strips should go down to sub-micron dimension and the resultant short nanotubes may likely result in poor on-current and mobility. We combine the striping technique with simple solution-based separation to improve the performance of the FETs.

The tube-tube resistance limits the performance of FETs with high purified

SWNTs. To reduce the impact of tube-tube resistance to SWNT network transistors, the techniques for the alignment of carbon nanotubes have attracted much attention recently.[14-17] With the co-synthetic horizontal SWNT alignment techniques in which the SWNTs are aligned during their growth, the FETs show extremely high on-current, but poor on/off ratio due to the m-SWNTs in the as-grown SWNT arrays.[18, 19] Post-growth SWNT alignment techniques, such as shear force alignment, micro-fluidic assembly, electric-/magnetic-field alignment, blow bubble film, Langmuir-Blodgett self-assembly *etc*, could effectively align the SWNTs after dispersion in solution.[20-22] However, most of reports on the post-synthesis alignment do not demonstrate their application for FETs. For FET applications, the SWNT networks need to control the density in SWNT networks, which are not easily achieved. The intrinsic anisotropic electronic property of SWNTs indicates that alignment could effectively support an enhancement of conductivity along the orientation of SWNTs. Optimization of nanotube orientation, the channel dimension of FETs and materials of dielectric layer can potentially result in high performance FETs with the solution-based alignment techniques.

1.2 Objectives of thesis

The overall objective of this thesis is to develop an effective method of changing the morphology of the SWNT networks in FET channel to enhance the performance of SWNT FETs. The parameters of this study include the SWNTs purity and channel dimensions. The sub-objectives in this thesis are introduced below.

The first sub-objective is to etch the uniformly deposited SWNT networks into

strips with lithography technique, so as to improve the on/off ratio of the FETs SWNT networks. We compare the effect of stripping two different SWNT purities (78% and 88% purity) on the SWNT FETs performance. The pristine SWNTs used here are the as-produced SWNTs (AP-SWNTs) which are bought from Carbon Solutions and have removed the amorphous carbon and catalysts. We also employ our previously reported selective dye, Direct Blue 71 (DB 71) to enrich the s-SWNTs. The channel stripping method cut the SWNT networks into parallel strips of different widths (2 μm , 5 μm and 10 μm) by lithographic technique. By fabrication FETs with different channel dimensions (with widths of 20 μm and 50 μm and lengths of 2 μm to 50 μm) on both SiO_2/Si and HfO_2/Si substrates, the improvements on on/off ratio, on-current and mobility were investigated. This combination method makes it feasible to fabricate high performance SWNT-network-based FETs without the need for highly enriched s-SWNTs.

The second sub-objective of the thesis is to develop a new method for the parallel assembly of the large-scale SWNTs from their suspension to enhance the performance of the SWNT FETs. SWNTs are about 1nm in diameter and up to tens of microns in length so that the electron transport is highly anisotropic. This immersion-cum-shake method could orient them into defined direction at desired position, therefore the electron transport along the aligned arrays has a significantly improvement. It has also been theoretically predicted that partial alignment of the SWNTs along the transistor channel can achieve optimum transistor device performance. With our newly developed method, ultrapure s-SWNTs (99% enriched

bought from NanoIntegris) were partially aligned on the aminosilane treated wafer surface on a rotary shaker. By adjusting the nanotube concentration in the solution, the tube density of the partially aligned SWNT arrays could be controlled. Through controlling of the linear SWNT density and channel length, the optimum SWNTs-based FET is achieved. The partial alignment was uniform over an area of $20 \times 20 \text{ mm}^2$ and confirms that the orientation of the SWNTs is mostly along the flowing direction of the SWNTs suspension. This large-scale partially alignment process that exploits the anisotropic properties of the SWNTs presents a viable path for the industrial adoption of SWNTs in electronic devices.

1.3 Organization of thesis

This thesis is divided into 6 chapters. Chapter 1 covers the background and objectives of this work. Chapter 2 presents a literature review on intrinsic properties, self-assembly of SWNTs and SWNT FETs. Chapter 3 describes the experimental details. In Chapter 4, the improvement of on/off ratio of SWNT FETs by stripping of the metallic-percolated SWNT networks into semiconducting SWNT strips are investigated. The influence of channel dimension, strip width and thickness are also studied. Chapter 5 describes a technique to achieve uniform aligned SWNT film on the wafer surface directly and the performance of FETs with different channel dimension has been discussed. Chapter 6 presents the conclusions of this thesis and recommendations for future work.

Chapter 2 Literature Review

Carbon nanotubes (CNTs)

Carbon, one of the most common elements on the earth, is a cornerstone of human lives. It exists in many different kinds of allotropes, including diamond, graphite, buckyballs, graphene and carbon nanotubes because one atom could form four chemical bonds. Both the multi walled carbon nanotubes (MWNTs) and single walled carbon nanotubes (SWNTs) show excellent and unique mechanical, chemical, optical and electronic properties, which have attracted lots of experiments to improve and displace the existent materials. The unique properties of SWNTs are attributed to the one-atom thickness of their sidewall. Depending on the chiralities of SWNTs, the SWNTs could be sorted into metallic and semiconducting groups. Due the intrinsic properties of SWNTs, they are the potential candidate of substitute for silicon material in minimization and performance improvement of integrated circuits. The around 1 nm diameter and sp^2 hybridization of atoms in the tubes give SWNTs both a ballistic quantum channel for electrons and high current density. Beside the circuits, CNTs also have potential application in transparent film, super-capacitor and sensor due to their larger area surface and flexibility. Then the controllable deposition techniques which include selective growth and alignment become important.

In this chapter, the recent studies about mechanism and application of aligned CNTs are reviewed. It is started with a simple introduction of basic properties of CNTs. The alignment processes are mainly divided into vertical alignment and horizontal alignment parts. In the vertical alignment process, the CNTs are oriented

perpendicularly on the substrate with different as-synthetic and post-synthetic methods. In the horizontal alignment process, the processes were also divided into as-synthetic and post synthetic alignments. During as-synthetic alignment, the uniform and dense catalyst is important to achieve CNT forests and the gas flow and substrate directed tube growth. Normally the pre-treatment of CNTs are necessary for post-synthetic alignment, including purification, separation and dispersion into solution. Then the alignment process continued on substrate or in composite with external shear force. The alignment technique could enhance the thermal conductivity, electron transport and tensile strength in the oriented arrays, compared with random CNT networks. The controllable, exact positioning and alignment methods show a possible way to apply CNTs in electronic devices, such as transistors, sensors, batteries and capacitor. Many studies about morphology transformation of CNT networks on soft and transparent substrate have been done in these five years. Then the advantages, techniques and application of CNT alignment are summarized.

2.1 Properties of CNTs

In 1991, CNTs with structure of several coaxial graphite sheets were reported.[23] They were produced on the negative electrode with an arc-discharge method and were discovered under transmission electron microscopy (TEM). In 1993, monolayer tubes of diameter range, 0.7 nm to 1.6 nm, were synthesized with iron catalyst. They were speculated as the early development stage of multi-layer tubes.[24] These multiple and single cylindrical carbon tubules of the fullerene structured family are named as MWNTs and SWNTs. Both of them have a larger length to diameter ratio which is

over $10^6:1$ than the aspect ratio of other materials.[25] The MWNTs which have from double to tens of concentric layers could be considered as a set of several nesting SWNTs (Figure 2.1 (A)). The distance between each layer is 0.34 nm, which is nearly equals to the gap between carbon atom sheets in graphite (Figure 2.1 (B)).[26] Although the individual layer could be metallic or semiconducting, MWNTs are normally conductive material.[27]

Figure 2.1 (A) TEM images of MWNTs with different layers.[23] (B) Schematic structure of MWNTs and the distance between each layer.[26]

2.1.1 Mechanical property

The MWNTs which have a cylinder structure show different mechanical property in axial and radial direction. Along the axial direction, Young's modulus of CNTs could reach 100 GPa and the tensile strength is around 10-60 GPa.[28] Young's modulus of the SWNTs could also reach ~1 TPa. But in the radial direction, van der Waals force could easily bend them.[29] So the alignment of CNTs could improve the mechanism property along the stretched direction.

2.1.2 Optical property

Optical absorption spectrum, band-gap fluorescence spectroscopy and Raman spectroscopy are accurate and reliable to characterize the concentration, chirality and defects of SWNTs. Optical absorption spectra of SWNTs originates from electronic transitions from the corresponding level to conduction band.[30, 31] The significant peaks in S_{11} , S_{22} and M_{11} regions could identify the m- and s-SWNTs. The 2D fluorescence spectroscopy could characterize SWNT chiralities with recording both excitation and emission energy. Due to the absence of electron-hole pair, m-SWNTs have no light excitation. Raman spectroscopy is sensitive to the diameter, chirality and chemical modification of both SWNT and MWNT. When the power of laser source matches the electronic transition energy between conduction and valence band of SWNTs, the spectra has corresponding Raman intensity peak. The peaks in RBM region varies inversely with the diameter of SWNTs. Relative intensity of the G-band (G^-/G^+) peak are different with electronic properties of SWNTs.[32] So the Raman scattering techniques with different laser wavelength was used to characterize the m-/s- SWNTs after sorting. Raman spectra with polarized laser source also could characterize the alignment condition of CNTs. Because the intensity of G peak depends on the angle between tube orientation and laser polarization.

2.1.3 Electrical property of an individual SWNT

The one-atom-thick sidewalls of SWNTs are made up of sp^2 hybridized carbon atoms. SWNTs show metallic or semiconducting behavior because of the band gap of different SWNTs that ranges from 0 to around 2 eV. According to the chiral angle

distribution, around one third of the tubes should be metallic and the balance is semiconducting. As shown in Figure 2.2 (A), a couple of integers (n, m) are used to describe the chirality of the SWNTs and a vector $C = na_1 + ma_2$ is used to describes the rolling orientation and diameter of SWNTs, where a_1 , a_2 are unite vectors of graphene.[33] The chirality map of SWNTs is shown and more details of the SWNTs properties could be estimated in Figure 2.2 (B). The tubules are formed by overlaying the original point and end point along vector and the chiral angle of SWNTs are from 0 to 30°.

Figure 2.2 (A) Schematic illustration of lattice vector a_1 and a_2 . (B) Map of Chiral vectors of SWNTs (Small dots represent s-SWNTs while encircled dots are for m-SWNTs).[33]

In 2000, the intrinsic electrical transport study of m-SWNTs was reported by Zhen *et al.*[34] The current density of m-SWNTs could reach as high as 10^9 A/cm². Kong *et al.* reported the conductance of an individual metallic or semiconducting SWNT which was synthesized with the CVD method.[35] The resistance of the s-SWNT is around 250 kΩ at room temperature and the current density could reach 10^8 A/cm². With application of ± 6 V gate voltage, the variation in on-off current ratio is 10^6 . The positive gate voltage reduced the hole-density in the s-SWNT, because the valence band is excluded from the Fermi level. Maki *et al.* had studied electrical

properties of an individual SWNT with superconductive contact.[36] In the strong coupling regime without Coulomb blockade effect, the zero-voltage conductance enhancement and the multi-Andreev reflection processes were observed. In weak coupling regime, the Kondo effect was observed in normal state.

2.2 Alignment of CNTs

Self-assembly techniques could order the molecules and nanoparticles in to a required pattern or structure at different dimension. Lots of studies have been done about CNTs in recent years due to their classical 1D structure. Their thermal conductivity and charge transport are more superior along the axis direction. Alignment of CNTs means orient the tubes into the uniform arrays which have a desired direction. After alignment, the unique properties of CNT get enhanced in the required direction. The alignment techniques that include both vertical and horizontal methods are reviewed here.

2.2.1 Vertical alignment of CNTs

The vertically aligned CNT forests are normally synthesized on the metal layer with CVD method.[37] The e-beam deposited uniform metal layer is important for preparation of vertically standing SWNT films. These CNT forests have great potential application in composites to enhance mechanism, electrical and thermal property and in electronic devices to improve the conductance.[38-40]

Vertical growth of CNTs

The individual SWNT is more flexible than MWNTs due to their one atom thick wall. Compared with synthesis of MWNTs forests, there are more challenges to

achieve vertically aligned SWNTs during growth. The SWNTs should form stronger bundles to stand up during synthesis. Therefore, the gap between catalysts should be very small to prevent random orientation. In 2004, Hata *et al.* successfully synthesized a millimeter high SWNT forest on an iron layer with CVD method (Figure 2.3 (A)).[41] During synthesis, the water could remove amorphous carbon and keep the catalyst layer active. This water assisted CVD method could produce long, highly pure SWNT forests and show the potential of industrial production. Recently a series of works about the optimization of growth parameters have been reported to synthesis vertically aligned SWNTs. In the synthesis of SWNT forests, the preparation of catalysts is important. The diameters, orientation and types of SWNTs depend largely on the catalyst preparation.[42, 43] By using a nanolaminate technique, a thin catalyst film was achieved from three layers of Al_2O_3 , Fe and Al_2O_3 after plasma treatment.[44] The area density of the SWNT forest could reach as high as 1.5×10^{13} tubes/ cm^2 . An *et al.* has synthesized aligned SWNTs with dip-coating patterned catalysts.[45] The tube length and density could be exactly controlled by adjustment of catalysts concentration and pretreatment time, growth temperature. A temperature gradient CVD process was studied to produce the vertical SWNT forest.[46] The temperature history of carbon source acetylene plays an important factor to achieve SWNT forests. The results confirmed that this temperature gradient CVD method could be applied to control the gas phase reaction during the forest growth. A low temperature process to prepare vertical SWNTs was also reported by Lee *et al.*[47] The vertical SWNTs could be synthesized at 450 °C on the alumina supported iron

layer with the water plasma CVD method. Beside all the parameter above, the alumina layer is very important for the preparation of vertically aligned SWNTs. The morphology of this alumina buffer layer is important to control the wall numbers of the aligned nanotubes.[48] The SWNT forest could be achieved on iron film which was deposited on the sputtering produced γ -Al₂O₃ buffer layer and the MWNTs forest was achieved on the thermal evaporated buffer film which had poor thermal stability.

With several homocentric walls, the MWNT forest is easier to synthesis. Now many researchers focus on the production of MWNT forests in the industrial grade. Fei Wei's group has published a series of works about large-scale preparation of MWNTs with fluidized-bed reactor.[49-51] In their works, the yield of MWNT forests could reach 3 kg/h after optimization and the diameter distribution is narrow.[52] The synthesis was carried out in a fluidized bed reactor with lamellar vermiculite as catalysts supporter (Figure 2.3 (B)). To achieve the well aligned MWNTs, the temperature, reduction of catalysts and different types of fluidizations were also investigated. The impact of roughness of catalyst layer on the vertical growth of MWNTs was reported by Oye *et al.*[53] The carbon precursor absorption and rearrangement was affected by the surface roughness of the catalyst layer. Therefore, vertically aligned MWNTs were achieved only at the smooth area and the MWNTs formed a thick random layer at the rough area. With patterned catalysts, the position and morphology of MWNTs forest could be controlled exactly.[54, 55] The technique shows a possible way to apply the vertically aligned MWNTs in micron devices.

Figure 2.3 (A) SEM image of the vertically aligned SWNTs (scale bar, 1 μm ; insert is image of millimeter high SWNT forest).[41] (B) SEM image of MWNTs forest (insert is the diameter distribution).[52]

Both the SWNT and MWNT forests could be successfully synthesized on the catalyst layer. After optimization, the density, diameter and length could be controlled. These perfect aligned CNT film have a potential application in field emission devices, supercapacitors and solar cells.[56-58]

Post vertical alignment

The CNT forests could effectively improve the performance of composites, field-emitters in display, biosensors, and batteries.[59-61] In all these applications, the orientation of CNTs is important. Compared with growth method, it is harder to achieve vertically aligned SWNTs on the substrate after growth because of their wire-like structure. To ensure they could stand on the substrates, normally the SWNTs are cut into short tubes and functionalized with carboxyl groups on the end before vertical deposition.

The vertical alignment method was firstly reported by Liu *et al.* to vertically deposit SWNTs on gold layer.[62] After refluxing in the acid, SWNTs were cut into short tubes and were functionalized with carboxyl groups at the end of tubes. Then the

mercapto chemical groups were induced onto the ends of these SWNTs. With Au-S bond, the SWNTs finally deposit on the gold surface to form a monolayer forest. The Figure 2.4 (B) shows the AFM image of the vertical alignment of SWNTs on gold layer. In the self-assembly procedure, SWNTs should attach to each other with $\pi - \pi$ interaction to be strong enough for free standing. This work shows a successful way to achieve perpendicular SWNTs with the solution-based process.

Subsequently, other methods to prepare vertical CNT film on various substrates with different reactions were reported. [63, 64] It was a simple way to modify the surface of quartz or glass slides with amino groups using APTES. After acid treatment, the carboxyl groups functionalized SWNTs could be immobilized on the substrate with amide bond. Figure 2.4 (C) shows AFM image of the vertically standing SWNTs on silicon wafer surface. From the Figure 2.4 (D), the tube density of forests on surface was higher than the tube density on gold film in Figure 2.4 (B). This result confirms that the efficiency of amidation reaction was higher than the Au-S reaction. Compared with Au-S bond, the amide bond was more stable and the chemical reactions between amide and carboxyl group are easier to induce on most of substrate. Similar results were reported on several substrates, such as silicon, quartz and PET.[65-67] Recently, this technique was applied to improve the performance of solar cell.[68] In this paper, the esterification reaction between hydroxyl and carboxyl groups was also used to vertically immobilize SWNTs on the tin oxide electrodes. After modification with vertical SWNT film, the transmittance kept as high as 97% and the conversion efficiency of the solar cell reached 4.7%. The results confirmed

that vertical SWNTs could be used as a substitute for Pt as transparent electrode material in solar cell.

Figure 2.4 (A) Schematic structure of vertically aligned SWNTs on gold layer by Au-S bond.[62] (B) AFM images vertically aligned SWNTs on gold layer at 24 h assembling times.[62] (C) AFM image of vertically aligned SWCNTs on silicon.[63] (D) AFM micrographs of vertical MWNTs on gold surfaces (inset is SEM image).[64]

Beside covalent bond, other forces, such as coulombs force and π - π interaction, were also applied to prepare the perpendicular standing SWNT forests.[69, 70] A metal-assisted layer by layer process to fabricate both mono- and multi- layer of vertical SWNT film was reported (Figure 2.5 (A)).[69] When the carboxyl group functionalized SWNTs were dispersed into DMF by sonicating, a glass substrate of which the surface was an iron hydroxides film was immersed into the SWNT dispersion. With electrostatic interaction, the SWNTs were attracted onto the surface and then they were immobilized on the surface by reaction between iron atom and carboxyl groups (Figure 2.5 (B)). The iron ions could be deposited onto the vertical SWNT film again by immersing into the aqueous solution of Fe^{3+} , the multi-layer of vertically aligned SWNTs could be achieved with same process. Ferri *et al.* reported a

reversible strategy to vertically assemble SWNTs on gold surface with π - π interaction (Figure 2.5 (C)).[70] After modification the gold layer with 4,4'-dithiobipyrindine (DTBPY), a SWNT forest with high tube density and maximum height of 60 nm could assembled on the gold surface. The formation of vertical SWNT film was sensitive to the pH value of solution so that the adjustment of protonation could control the releasing of SWNTs from substrate. This method showed a possible way to utilize SWNTs for controllable drug delivery.

Figure 2.5 (A) Schematic structure of vertically aligned SWNTs on $\text{Fe}(\text{OH})_x^{(3-x)+}$ -functionalized wafer surface.[69] (B) AFM images vertically aligned SWNTs on silicon wafer.[69] (C) AFM images of vertically aligned SWNT film on DTBPY modified gold layer at different pH value.[70] (D) Fluorescence image of SWNT film before and after immersing in acid solution.[70]

Compared with coulombs force and π - π interaction, an electronic field could support a stronger interaction to oriented SWNTs in solution.[71, 72] With the parallel electrodes, a high voltage could effectively oriented SWNTs in the space between the adjacent electrodes. The carboxyl group modified SWNTs which had negative charges in solution will migrate to the positive electrode and vertically immobilized on the electrodes under the voltage of 150V (Figure 2.6 (B)).[72] In order to increase the

tube density on the electrode surface, the sonication could remove the unfixed tubes. When the SWNTs reached the positive electrodes surface, the single tube aggregated together to form a small bundles which were strong enough to stand up.

Figure 2.6 (A) SEM images of MWNTs forests on the positive electrodes. (B) Schematic of DC electrophoresis cells.[72]

In this section, the recent methods to prepare vertically aligned CNT film are reviewed. Compared with directly growth methods, the post-growth processes are normally simple, solution-based and low-cost. But before alignment, the CNTs should be cut into shorter ones and they are also functionalized with different chemical groups which could support charges in solution and fixing point on substrate surface. During functionalization, the defects are induced on the side walls of CNTs. After modification with different groups, the mass/charge ratio is still too large. In the electronic field, the movement of CNTs is too slow and high voltage is necessary. These post-synthetic methods also show potential applications of vertically aligned CNTs in sensor and supercapacitor.

2.2.2 Horizontal alignment of CNTs

Compared with vertical alignment, horizontal alignment means the CNTs arrays

are parallel deposited on the substrate. The horizontal alignment technique receives lots of attention because of its widely application in transistors, sensors and transparent film. The horizontal growth method could prepare perfectly aligned arrays on silicon and quartz substrates. With transfer technique, the aligned SWNTs could be fabricated into micron or nanosize devices. The purification and separation of SWNTs could be carried out before post-synthetic horizontal alignment. Then the transistors with high on/off ratio and mobility could be achieved. Both methods could convert the random networks into the well oriented arrays which is the cornerstone of the SWNT-based circuits.

Horizontal growth of aligned CNTs

The horizontal orientation of SWNTs attracts lots of attentions in self-assembly research. In the integrated circuits, the locating and patterning of an individual SWNT are necessary. The large-scale horizontally aligned SWNTs show many advantages in application. Lots of methods have been reported to grow aligned CNTs on different kind of substrates. The alignment depends on the production environment, such as substrate, catalysis, gas flow direction and so on.

With parallel aligned catalysts, the conductive self-aligned SWNT bundles and MWNTs on the silicon wafer were synthesized.[73, 74] Though the alignment of CNTs was reported, it just existed in polymer matrix and not controllable. Zhang *et al.* had applied an electric field to orient the tube along the electric field lines during growth.[16] During the recent 10 years, lots of methods have been developed to control the orientation, linear tube density and tube length, including the external

electric/magnetic field, the gas flow, the crystalline pattern of substrate, the catalyst pretreatment and the carbon source.[75-77] The external electric/magnetic field could support an effective force to align the SWNTs during growth in the sealed and high temperature CVD system. In 2010, under a weak magnetic-field, the scalable horizontally aligned SWNTs that were synthesized with arc-discharge method were first fabricated.[78] This method broke the limitation on the thermal stability of the substrates and the aligned SWNT film could be deposited on different kinds of substrates, including the polyethylene terephthalate (PET) film, the polymethyl methacrylate (PMMA) film, the glass slides and the quartz slides (Figure 2.7 (A)). The Raman spectra confirmed the alignment of SWNTs on those substrates, where the intensity of G Peak varies with the angle between the alignment direction of SWNTs and the polarized laser. The application of an electric field could selectively increase the content of the m-SWNTs after synthesis. Under the electric field of 200 V/m during CVD synthesis, the m-SWNTs which are more polarized than s-SWNTs were enriched to 80%.[79] The electric field could force the m-SWNTs into laminar flow for a longer time so that the length of m-SWNTs is larger than the s-SWNTs.

Without the external fields, the gas flow also could order the SWNTs direction during the synthesis. By adjustment of flow rate, the alignment of SWNTs along flow direction could be achieved. The mechanism of gas flow orientation had been reported.[80] In this paper, the Reynolds number and Richardson number was used to estimate the dynamic property of gas flow. To achieve ultra-long aligned SWNTs, the fluidic should be adjusted with small Reynolds number and large Richardson number.

With gas flow assistance, a 100 μm long nanotube with the triple sidewalls was reported.[81] This nanotube showed semiconducting behavior and the water could increase the grow rate. Because the catalysts were flying in the gas during growing of nanotube, the mechanism of gas flow-assisted growth was named as kite mechanism which could be confirmed by the suspend array of the SWNTs suspending over a several microns wide channel.[82, 83] This results show that both the catalysts and growing SWNTs itself could be lifted up from the substrate and oriented by the flow. In these experiments, the steady and laminar gas flow played a crucial role in the SWNTs orientation. The aligned SWNT arrays were long, clean and uniform and the direction of tubes could be easily changed by rotating of substrate. For research on an individual SWNT, the gas flow assisted CVD method is better. However, the low linear tube density ($< 1 \text{ tube}/\mu\text{m}$) became the limitation on the other applications.

Beside the gas flow orientation, the crystalline of substrate could be used as the mold to orient the SWNTs along the crystalline steps. The Inoue *et al.* have investigated the influence of gas pressure on the tube density of aligned SWNTs during CVD growth.[84] It is confirmed that the gas pressure strongly affected the tube density in parallel arrays (Figure 2.7 (B)). Under the lower partial pressure of the source gas and long synthesis time, the oriented and dense SWNT arrays ($\sim 10 \text{ tubes}/\mu\text{m}$) could be prepared on the quartz substrate. The tube length and diameter were limited by the gap distance of the parallel patterned catalysts.[85] The catalysts were an important factor in growth of SWNTs. A controllable diameter distribution of parallel aligned SWNT arrays by adjustment of diameter of gold catalysts with

thermal annealing method was reported.[77] After annealing in Ar and H₂ mixture, the gold catalysts were smaller than 2 nm. In the aligned SWNTs, the diameter of tubes is around 0.9 nm. The horizontally aligned SWNTs with 1.3-1.4 nm diameter were achieved on sapphire after annealing in ultrahigh vacuum. After annealing in ultrahigh vacuum, the size of ~76% iron catalysts ranged from 1.3 to 1.4 nm so that the diameter distribution was narrow. Many different kinds of catalysts were used to control the diameter distribution, such as SiO₂ nanoparticles, fullerenes.[86, 87] Figure 2.7 (C) shows the SWNTs which used the oxidized fullerenes as catalysts that were oxidized in air at 300 °C, 400 °C, 450 °C and 500 °C to achieve the cages with the opening of the different sizes.[87] If the pre-oxidization temperature is lower than 300 °C or is higher than 500 °C, the SWNT density became low. When the pre-oxidization is at 450 °C, the opened fullerenes were the most effective catalyst for the SWNT growth.

Figure 2.7 (A) Images of aligned SWNT film on different substrates (insert is polarized Raman spectra at different angles).[78] (B) SEM images of horizontally aligned SWNTs grown on r-cut quartz substrates at 29, 144, and 1300 Pa.[84] (C) SEM images of SWNTs synthesized on fullerene dione which were pre-oxidized at

different temperatures.[87] (D) SEM image of aligned SWNT film after single growth and double growth.[88]

Various CVD processes had been developed to achieve horizontally aligned SWNTs on the different substrates.[89-92] Aligned SWNTs had lots of potential applications in electronic devices. Many techniques to improve the linear density on crystalline substrate, such as the multiple growths on same substrate and the multiple transfer onto the substrate, were reported (Figure 2.7 (D)).[88, 93, 94] The radio frequency with this ultra-high aligned SWNT arrays showed high current density and frequency.

Post horizontal alignment of CNTs

In the post horizontal alignment process, the CNTs are normally dispersed in solution. Then an external force is applied to orient the tubes in suspension. After alignment, the CNT arrays are deposited onto to a substrate by transfer or by evaporating the solvent. With the post alignment technique, CNTs should be purified to remove the amorphous carbon and the metal catalysts. The post alignment is easier to scale up while the shortcoming is the defects on the SWNTs during the long time sonication.

The parallel CNT arrays were firstly observed on the cross-section of composites (Figure 2.8 (A)).[95] Similar results were reported in MWNTs/polymer composite after mechanical stretching or electro-spinning process.[96, 97] After alignment, the Young's modulus and elongation got improvement along the oriented direction due to the parallel oriented MWNTs. Yu *et al.* aligned the MWNTs in the polymer matrix with blow film extrusion method.[98] Both the nanowires and MWNTs could be well

aligned in the expanding polymer film and they could be transferred to various substrates (Figure 2.8 (B)). Recently, the SWNTs in aqueous solution could also be oriented with the same technique.[99] Due to the low bubble strength, the size of sample from aqueous solution was small and alignment of tubes was not uniform. The composites with aligned CNTs successfully extended their enhancement of electric and mechanism properties on macro-scale.[100-102]

Figure 2.8 (A) TEM image of aligned SWNTs on the sliced section surface (the arrows shows the cutting direction).[95] (B) Optical image of aligned MWNTs in dark-field (scale bar, 25 μm ; Inset image is schematic of blown extrusion procedure).[98]

In CNT alignment, the stretchable polymer is necessary in these mechanical alignment methods. But the aligned polymer wrapped CNTs could not be applied in electronic devices because of the large tube-tube resistance. Magnetic or electric fields were applied to orient the SWNTs with no direct contact. In magnetic field, CNTs had diamagnetic/paramagnetic and ferromagnetic anisotropies in the field direction.[103] As a result, the CNTs could be aligned with a magnetic field. However, the magnetic field should be quit strong to keep a stable alignment because of the Brownian movement. To improve the interaction with magnetic field, the CNTs were modified with iron nanoparticles. The iron nanoparticle modified CNTs showed

ferromagnetic behavior in magnetic field. The ratio of iron nanoparticles/CNTs appeared important in obtaining the well aligned MWNTs arrays.[104, 105] Similarly, with an external electric field, CNTs could also be polarized and move along the electric field strength gradient. Both DC and AC electric field was applied to orient the CNTs between the two electrodes.[106, 107] Allen *et al.* have achieved a gel suspension of SWNTs and rrP3DDT mixture.[108] The uniform alignment is easily fabricated with this mixture at high concentration. After removing of the redundant rrP3DDT, it is possible to make conductive electrodes for devices. This technique is widely used in transistor fabrication using aligned s-SWNTs to achieve a high mobility and a large on/off ratio.[109, 110] The AC electric field could align the CNTs more uniformly and is more stable. The SWNT suspension is dropped on the electrodes and an AC electric field of 10 V was applied for 1 min. Figure 2.9 shows the alignment of tubes between the two electrodes. Due to various polarizations of s- and m-SWNTs, this technique could enrich the s-SWNTs, too.

Langmuir-Blodgett (LB) film is another widely used technique to assemble monolayer of dense 1D material. In the LB process, the CNTs should be dispersed into a kind of solution which could float onto the supporting liquid (Figure 2.9 (C)). The two barriers move at a controlled rate to force the CNTs into a parallel and dense film. Then after transfer, monolayer or multilayers of aligned CNTs on different surface could be achieved.[111, 112] As shown in Figure 2.9 (D), The aligned SWNT film could be patterned onto PET substrate after LB fabrication.[113] The alignment and density of SWNT film was controlled by LB method. Then the patterned

polydimethylsiloxane (PDMS) mode was used to transfer the aligned tubes onto PEF film or silicon wafer surface. This method controls the position and shapes of the horizontally aligned SWNTs on substrate to fabricate flexible transistor and solar cell. Although the LB method is simple and easier to scale-up, the Langmuir film is too sensitive to vibration from the environment.

Figure 2.9 (A) Schematic image of alignment with AC electric field. (B) SEM images of aligned SWNTs between two electrodes (scale bar, 1 μm).[109] (C) Schematic image of LB process.[113] (D) SEM image of aligned SWNT film on silicon wafer (scale bar, 1 μm)[113]

Microfluidic technique shows an effective way to assemble CNTs on a desired area with a controllable pattern.[114-116] The CNTs was dispersed into aqueous solution and the substrate was patterned with the micron channels. The moving of gas-liquid-solid contact line could orient the tubes along the axis of channels. To improve the alignment condition, the PDMS microfluidic channels were designed into a funnel-shape of which the narrowest part of channels is only 1 μm wide (Figure 2.10 (A)).[117] When the SWNT solution went into the funnel-shape channels, a gas blow was used to improve the SWNT orientation. After gas-spinning, the width of aligned SWNT arrays could reach as narrow as 20 nm on the APTES functionalized silicon

wafer surface. The well aligned SWNTs were deposited on the silicon wafer surface from the SWNT suspension (Figure 2.10 (C)). The wafer that was covered with micron channel pattern was dipped into the SWNT suspension. With water evaporation, the aligned SWNTs were deposited on the channel bottom (Figure 2.10 (C)). The aligned strips which had perfect resistivity ($2.2 \times 10^{-3} \Omega \text{cm}^{-1}$) were a potential channel material in radio frequency FETs (RF-FETs). Kim *et al.* developed a capillary-driven technique to achieve aligned SWNT pattern with nano-channels.[115] The opening end channels were fabricated by sealing PEG mold on a gold layer with electrostatic attraction. After dropping the SWNT suspension at one end of 50 nm and 200 nm wide channels, the solution entered the channels under surface tension. Then the highly oriented SWNT arrays were achieved along the flowing direction. The microfluidic alignment technique plays an important role to accurately pattern SWNTs on the desire location of various substrates.

Figure 2.10 (A) Schematic outline of the SWNT alignment procedure with funnel-shape channel. (B) FESEM image of the aligned SWNTs in the narrowest part of funnel-shape channel.[117] (C) Schematic process of the SWNT alignment with the micro-channels. (D) FESEM images of aligned SWNTs.[118]

Besides the horizontal alignment methods mentioned above, many works to

achieve the uniformly oriented SWNT arrays have been reported, such as gas-flow assisted alignment, acoustic waves alignment method, selective laser-ablation and blow-bubble method.[98, 119-121] Yamada *et al.* applied aligned SWNT film in fabrication of stretchable devices which were sensitive and durability.[122] During stretching, the resistance of aligned SWNT arrays became large due to the existence of gaps in the aligned film. After electrodes deposition on the ends of film, the devices could be used as sensor of human motion. Normally, to achieve a perfectly aligned SWNT array, the multiple techniques were employed simultaneously. The alignment techniques were important in nano-devices fabrication and the aligned SWNTs could improve the stability of the electronic circuit.

2.3 SWNT-based FETs

In the integrated circuits, billions of FETs are fabricated on the silicon wafers every year. Silicon is a semiconducting material which could be controlled by the gate voltage in the FET channels. A quantum tunneling occurs when the thickness of isolated layer is smaller than 2 nm so that the leakage current of FETs become larger. S-SWNTs are considered to be a potential channel material instead of silicon in FETs due to the ballistic transport and the nanosize diameter (Figure 2.11).[123] The SWNT-based FETs are widely used in bio/chemical sensors, transparent and soft logic circuit and radio-frequency (RF) devices.[124-128] The individual s-SWNT shows an excellent on/off ratio and high intrinsic current density.[35] By the gate voltage sweeping from positive to negative, the variation of the drain current could reach several orders ($\sim 10^5$).[129]

Figure 2.11 Schematic cross section of FET with individual s-SWNT.[123]

2.3.1 Single s-SWNT FETs

The FETs with single s-SWNT have lots of advantages, including high mobility and excellent on/off ratio, negligible hysteresis, stable performance, no quantum tunneling.[130] So the FETs with a single s-SWNT is a candidate to substitute the silicon based devices for next generation. As the channel material, the s-SWNTs shows both high on-current and large on/off ratio because of the sp^2 hybridization of carbon atoms. Since the SWNTs are flexible, their application in FETs on a soft and stretchable substrate attracts lots of attention. These properties satisfy the demand of many applications such as the artificial skin, the camber complementary metal oxide semiconductor (CMOS) and the soft display in which all the circuits are fabricated on the polymer films.

In 1998, Martel *et al.* successfully fabricated the FETs with an individual s-SWNT or an individual MWNT to investigate the intrinsic properties of CNTs respectively.[131] As the gate voltage increased over the positive threshold voltage, the drain current was around 10^{-10} A. The results confirmed that the s-SWNT was *p*-type. With the individual MWNT, the gate voltage could not tune the drain current, which meant the multi walled tubes are metallic. To improve the performance of FET with individual s-SWNT, the contact metals, dielectric layers and channel dimensions were investigated. Franklin *et al.* fabricated single s-SWNT FET with gap length of

only 10 nm.[132] At 0.5 V drain voltage, the diameter normalized on-current (2.41 mA/ μm) was four times of the one in silicon-based FETs. With on/off ratio 10^4 , the FETs showed a possibility of minimizing the logic circuits and the improvement in the electron transport at the contact between metal and CNT. Then the transport characterization from the individual s-SWNT FETs of which the channel ranged from 15 nm to 3 μm showed that there is no short channel effect (Figure 2.12 (A)).[133] When the channel length is 15 nm, the on-current reached 25 μA at drain voltage of 0.4 V with on/off ratio was around 10^5 . The relationship between metal-CNT contact and performance of transistors were firstly confirmed by the experiments. As shown in Figure 2.12 (B), the metal-CNT contact length affected the on-current more seriously than the off-current, because the small contact length decreased the conductance of metal-CNT contact. The results provided an evidence to reduce the cost of FET fabrication.

Figure 2.12 (A) FESEM image of the individual s-SWNT FET and the transconductance curve of FET with 15 nm, 300 nm and 3 μm long channels. (B) FESEM image of FETs with different metal-CNT contact length and the transconductance curve of FET with metal-CNT contact length of 20 nm, 30 nm, 50 nm, 70 nm and 100 nm, when the channel length is 40 nm.[133]

Due to the excellent properties of the s-SWNTs, they received a lot of application as sensors in logic circuits. The individual s-SWNT was fabricated into piezoresistive pressure sensor. The size of sensor was minimized to 25 μm and the consuming also had a significant decreasing ($< 40 \text{ nW}$). The sensitivity of this device increased to $0.25 \Delta R/R^{-1}$ and resolution kept as 50 mBar. In 2010, Mueller *et al.* reported an light emission from the p - n diodes of an individual SWNT.[134] In this single SWNT LED, The p - n junction was formed by electrostatic doping through application of positive and negative biased voltage on gate electrode respectively. This LED had a low driving power and high conversion efficiency, but had no threshold and heating.

2.3.2 Aligned SWNT array FETs

Although the devices with an individual CNT show a remarkable performance, it is hard to position it one by one on large scale due to the small diameter. The dense, well-aligned SWNT arrays could provide a super large current density and uniformity on wafer scale.

Rogers and co-workers have published many works of the devices with aligned SWNT arrays.[15, 18, 135] A horizontally aligned SWNTs were synthesized on the ST-cut quartz surface using CVD method.[18] Then high performance FETs were obtained with these aligned SWNT arrays in which the linear tube density was controlled by the catalyst concentration. The highest mobility of the FETs was 125 $\text{cm}^2/\text{V}\cdot\text{s}$ and each individual SWNT supported a mobility of 9000 $\text{cm}^2/\text{V}\cdot\text{s}$. This method shows a possible way to improve the FET mobility. Two years later, Kang *et al.* firstly fabricated transistors with dense, non-overlapping and aligned SWNT

arrays.[136] With the lithographic technique, a matrix of top-gate transistors were fabricated on the quartz wafer directly and a 1.5 μm thick epoxy was used as the dielectric layer. The arrays could provide a large current ($\sim 1\text{ A}$) due to direct connection of source and drain electrodes and there was only metal-CNT resistance. The on/off ratio had a significant increasing when m-SWNTs were removed. The aligned arrays were then used to fabricate SWNT-FETs for application in a radio.[137] In this radio, the amplifiers and transistors (which are the most important parts) are all produced using the aligned SWNT arrays. Three FETs with SWNT arrays were adequate to give 20 dB power gains a common speaker. The results showed a possible way to fabricate flexible, paper thick radio. As shown in Figure 2.13 (A), the highly pure s-SWNTs ($> 99\%$) was fabricated into well aligned SWNT film with tube density of 500 tubes/ μm with LB method.[138] When they were fabricated into FETs, the current density of the devices could reach 120 $\mu\text{A}/\mu\text{m}$ and on/off ratio of 1×10^3 . Because of the small average tube length after separation, the dense and aligned arrays could effectively increase the mobility of the FETs whose channel was longer than tube. Besides the post alignment, Wang *et al.* reported the CMOS fabrication with as-synthesized SWNT arrays.[139] In the *p*-type transistor, Pd source and drain electrodes were deposited on the aligned arrays and Gd electrodes were deposited on the arrays as electrodes in *n*-type FETs. The conversion from *p*-type to *n*-type using low work function metal was proved air-stable. The technique that was reported in this paper solved the absence of *n*-type FET in CMOS integrated circuit. For RF-FETs, the aligned SWNT arrays could fulfill the demand of high current (Figure 2.13 (E)).

The extrinsic current gain cut-off frequency of the FETs with dense aligned s-SWNTs on channel could reach 7 GHz.[140] Compared with RF-FETs with graphene, the FETs with the aligned s-SWNTs had a lower power consuming and a higher power gain. With as-synthetic aligned SWNT arrays, the circuit frequency could reach as high as 40 GHz.

Figure 2.13 (A) SEM image of aligned SWNTs (Inset is transfer characterization curve). (B) Plot of mobility and on/off ratio versus channel length.[138] (C) Schematic image of CMOS with Pd for *p*-type part, and Gd for *n*-type part. (D) Transfer characteristics of CMOS.[139] (E) SEM image of the FET with double channels and aligned SWNT arrays (F) Transfer characterization (I_d - V_g) and transconductance (g_m) of the FETs.[140]

Although devices with aligned SWNT arrays have shown lots of attractive properties, the research in the device with the aligned SWNT arrays is still at a primary stage. The large-scale transfer, the removing of m-SWNTs in the arrays and the controllable-chirality growth are some major limitations which must be overcome in order to utilize these SWNT arrays in the industries.

2.3.3 S-SWNT network FETs

The coexistence of m-SWNTs in s-SWNTs limits their application in transistors due to their no responding to the variation of the gate voltage. It is obligatory to

enrich the s-SWNTs which have a large on/off ratio to fabricate reasonable FETs. After enrichment with various methods such as the density gradient ultracentrifugation (DGU), the DNA-assisted chromatography and the selective adsorption, the highly enriched s-SWNTs (>95%) could be successfully obtained.[141, 142] As the enriched s-SWNTs are still a mixture of chiralities and the performances of FETs with an individual s-SWNT are not stable. Therefore, the fabricating of FETs with the thin s-SWNT film on a large scale is necessary. Compared with silicon, the thin film of s-SWNTs is flexible, transparent and could be deposited on the soft substrates. Compared with the organic semiconducting materials, the thin s-SWNT film shows a significant enhancement in the mobility of the FETs. To achieve the stable and good performance, the uniform s-SWNT film fabrication is important.

There are many techniques to fabricate a thin SWNT film on the various substrates, such as the vacuum filtration, the evaporation-assisted self-assembly, the spin- and dip-coating spray techniques and the inkjet printing.[143-146] Normally the substrates are functionalized with amine groups.[144] After uniform modification, the s-SWNTs could be effectively adsorbed onto the surface with the methods mentioned above. The thin s-SWNT film transistors show both a large mobility and a good on/off ratio ($> 10^4$). Subsequently, the metal electrodes and the dielectric layer were deposited in the sequential order and the isolation step was used to remove the s-SWNTs from unwanted areas.

Zhou's group has published a series of works about FETs with the thin s-SWNT films.[147-151] In addition, Wang *et al.* have fabricated the wafer-scale FETs with a

uniform thin film of the s-SWNTs (95 %) for controlling of the organic light-emitting diode (AMOLED).[148] After functionalization of silicon wafer with APTES, the uniform s-SWNT film of which the tube density was around 28 tubes/ μm^2 was formed onto the surface by immersing into the SWNT suspension. The 50 nm thick silicon dioxide was used as dielectric layer and Ti/Pd (0.5/70 nm) were used as a source and drain electrodes using lift-off procedure. The mobility of the FET was 52 $\text{cm}^2/\text{V}\cdot\text{s}$ and the on/off ratio was larger than 4 orders, which could fulfill the requirement of AMOLED manipulation. In the paper, the research group had successfully solved the problem in fabrication of the uniform s-SWNT film on a large scale and had also realized a potential application in the logic circuit. One year later, the application of FETs with a thin s-SWNT film in a macro electronic circuit was reported. [152] In FET fabrication, the 95% and 98% s-SWNTs were respectively used as semiconducting material in the channel of FETs which showed stable performance. With the same channel length, the on-current density of 95% SWNTs is around 5 times higher than that of 98% SWNTs. The highest mobility could reach 67 $\text{cm}^2/\text{V}\cdot\text{s}$, which was suitable for high frequency application. It was found that with just 3% more m-SWNTs, the film resistance decreased significantly and these m-SWNTs does not bridge the source and drain electrodes because the average length of SWNT is less than 1 μm . However, the FETs with 98% s-SWNTs showed better on/off ratio than the FETs with 95% s-SWNTs, especially on small gap. The inverter, not-AND (NAND) gate and not-OR (NOR) gate which were fabricated with the 98% s-SWNTs also showed a stable performance. In 2011, the printed FETs with s-SWNTs (98%) in the

OLED control circuit was reported by Chen *et al.* (Figure 2.14 (E)).[151] The electrodes were printed with silver ink and the 98% s-SWNTs were printed in the FET channel. Then the PEI/LiClO₄ mixture was printed on the s-SWNT film as the dielectric layer to form a totally printed thin film transistor. With this printing technique, the mobilities of the printable s-SWNT FETs were found to be in the range of 10 to 30 cm²/V-s and the on/off ratios were from 10⁴ to 10⁷, which were the potential block in flexible circuit. A single OLED could be turn on and off in this printed logic circuit. This technique showed an attractive prospect of s-SWNTs in the macro electronic application.

Figure 2.14 FESEM images of (A) 95% and (B) 98% enriched s-SWNT networks (C) On current density of FETs with 95% (black) and 98% (red) s-SWNT networks in different long channels. (D) On/off ratio of FETs with 95% (black) and 98% (red) s-SWNT networks in different long channels.[148] (E) Schematic process of the fully

printed SWNT TFT fabrication (F) Images of OLED which is controlled by SWNT TFT at different data and drain voltage (Inset is OLED circuit).[151]

Bao's group has also published many papers about FETs with the s-SWNT film which are enriched by amine absorption or polythiophene.[153-159] LeMieu *et al.* found that different groups functionalized substrate surface could selectively adsorb SWNTs.[153] Amine modified wafer surface selectively adsorbs s-SWNTs and phenyl modified wafer surface adsorbs m-SWNTs. Using spin coating of the SWNT suspension, the self-sorted s-SWNT film was achieved on the wafer. The on/off ratio of FETs with the thin s-SWNT (70%) film which was fabricated on the amine modified wafer was over 10^4 and the mobilities of these FETs were from 0.5 to 6 $\text{cm}^2/\text{V}\cdot\text{s}$. On the contrary, the on/off ratio of FETs with the SWNT film which was adsorbed on the phenyl functionalized wafer surface was only 2 and both the on- and off-current of these FETs are much higher than the on- and off-current of FETs on amine modified wafer. The Raman spectra at 633 and 785 nm also confirmed that the amine group prefers the s-SWNTs and the phenyl group selectively adsorbed the m-SWNTs. This work supported an effective way to separated SWNTs during the SWNT network fabrication. To optimize the performance of FETs and stability of s-SWNT absorption by the amine group, LeMieux *et al.* reported the relation between topology of s-SWNT film and performance of FETs.[154] When 150 μL was dropped on the wafer at 4000 rpm, the on/off ratio of FETs with s-SWNT film of which the density was $\sim 15 \text{ tubes}/\mu\text{m}^2$ could reach 10^5 and the mobility was 2 $\text{cm}^2/\text{V}\cdot\text{s}$. When the tube density was more than 18 tube/ μm^2 , the mobility significant increases to 17 $\text{cm}^2/\text{V}\cdot\text{s}$ and the on/off ratio dropped dramatically ($\sim 10^2$). Although the tube density

increased, these incoming SWNTs were not adsorbed by amine groups on wafer surface but by the nascent s-SWNT networks, which resulted in a loss of selectivity. The m-SWNTs which existed in the networks decreased the on/off ratio.

Besides these two groups, many papers about the performance of transistors with SWNT film had been published.[160-163] The on/off ratio and mobility of FET with a s-SWNT film were attributed to the density, the average tube length and the electric purity. Takahashi *et al.* reported a technique to fabricate flexible FETs with s-SWNTs.[164] By controlling the immersion time, the s-SWNT films with the different tube densities were deposited on the polyimide substrate (Figure 2.15). As shown in Figure 2.15 (B), when the tube density increased, the on-current became larger while the on/off ratio decreased. Although there were only 1% m-SWNTs in the suspension, some conductive bundles and a direct carrier path in channel were formed at the higher tube density. Then the off-current shows an obviously increasing. For application in FETs, the on/off ratio was important to prevent power wastage. For RF-FETs, the s-SWNT film with higher tube density could afford a higher current. After optimization, the mobility of the FETs could reach $30 \text{ cm}^2/\text{V}\cdot\text{s}$ and the on/off ratio was 10^4 . These FETs were built into the pressure sensitive matrix backplane circuit.

Figure 2.15 (A) AFM images of SWNT networks with different tube concentration on the PI substrates. (B) Drain current versus gate voltage of the TFTs with SWNT networks of three different dense.[164]

Using the roll-to-roll and the inkjet printing techniques, a printed radio frequency identification (RFID) reader and ring oscillator were fabricated directly on PET film, where the SWNTs was printed in the FET channels.[165] The printed devices show 13.56 MHz- operated 1 nit FR task that generated 102.8 Hz of clock signal. This technique shows a simple way to fabricate flexible RFID tags and FETs on polymer film for particular application. The dense networks of highly purified s-SWNTs are necessary to obtain high performance of devices.

2.3.4 N-type SWNT FETs

The metal-oxide semiconductor is widely used in logic circuits, due to its large signal reliability and high power utilization. One CMOS requires both *n*-type and *p*-type FETs which cannot be turned on at the same time to minimize the static power consumption. Fabricating symmetrical pairs of *p*-type and *n*-type FETs with silicon-based material is a mature technology, but this technique is hard to directly apply in the fabrication of the SWNT FETs. The SWNT FETs in air show *p*-type behavior due to the O₂ doping at the contacts between SWNTs and metal. To convert the *p*-type FET into an *n*-type one, many methods have been tried, including the O₂

desorption in vacuum, the organic chemical/metal doping and the electrostatic gating.[166-171] The air stability and process reliability are important to the *n*-type conversion methods for the large-scale application.

Klinke *et al.* reported a charge transfer behavior between the SWNT and the hydrazine molecule which could convert the *p*-type FET into the *n*-type one.[168] By immersing the FETs into the hydrazine solution, the SWNTs in the FET channel were highly doped by amine groups. After doping, the FETs showed a classic *n*-type behavior which confirmed that the hydrazine donate the electrons to the SWNTs. The on-current showed a 3 orders increasing because of the reduction of the resistance between the SWNTs and the electrodes. The redox-active polyaniline (PANI) was used to cover the SWNTs in FET channel to confirm the amine group charge donating ability. As a result, the *p*-type FET is converted into the *n*-type one. After oxidation of the imine groups in PANI, the FETs went back to the *p*-type behavior. The FETs with the HfO₂ covered SWNT networks showed *p*-type or *n*-type behavior by respective annealing in O₂ or N₂. [172] O₂ and N₂ could form the donor and the acceptor trap in the SWNT networks after annealing. Figure 2.16 showed the classic *p*-type transport characterization of the O₂ doped SWNT FET. With the annealing period, both on-current and on/off ratio became larger. The results confirmed that O₂ molecules could pass through the HfO₂ layer and finally absorbed onto the SWNTs. The FET was gradually converted into *n*-type ones in N₂. The N₂ doping could increase the electrons conductance in the SWNT networks and the on/off ratio was also increased. The holes conduction in device was suppressed at the interface between the SWNT

networks and HfO_2 layer during N_2 annealing. The PEI n-doped SWNTs were fabricated into the p-n junctions with *p*-type substrate in the solar cell.[173] The air-stable PEI, which contained lots of electron donating amine groups, could convert the SWNTs that were used as both the photo-generator site and the transport layer into the *n*-type behavior. This technique provided a possible way to fabricate flexible carbon-based solar cell.

Figure 2.16 Transport characteristic of SWNT FETS which are annealed in (A) O_2 gas or (B) N_2 gas.[172]

Due to the O_2 molecules in the environment, the stability of the *n*-type FETs is not the same as the *p*-type ones, although *n*-type devices exhibit significant improvements, such as the reproducibility and the uniformity in the lab-scale experiments. Nonetheless, industrial application of the SWNT FETs in the logic circuit is still a big challenge.

2.4 Other application with aligned SWNT

As the channel material in transistors, the alignment could significantly improve the mobility and on-current of devices. CNTs also have excellent mechanical, thermal and electrical properties. Both vertically and horizontally aligned CNTs have wide application in different scientific fields, including composites, transparent conductive films, supercapacitors and batteries. The alignment technique could also enhance the

properties of CNTs at desired direction.

Due to the large surface area and the perfect conductivity, the vertically aligned SWNTs were normally used into the supercapacitors and the batteries to improve the power density and stability.[174-176] After growth, the vertically aligned MWNTs were attached onto the indium tin oxide (ITO) electrode which was used as the cathode in a Zinc-oxygen battery.[177] The power density could reach as high as $275 \mu\text{W}/\text{cm}^2$. In the flexible supercapacitor, the vertically aligned CNTs were patterned as the finger electrodes on the polycarbonate (PC) film.[178] With an ionic liquids electrolyte, the bending of 1000 cycles had no decreasing in capacitance of $430 \mu\text{F}/\text{cm}^2$ at a scan rate of 0.1 V/s. The vertically aligned CNTs were used to improve the flux and fouling of membranes in water purification.[179] With the CNT forest, the water flux was three times higher and the water transport was 70,000 times faster than ultrafiltration membrane. The results confirmed the potential applications of the CNT forest in water purification. In biosensors, the vertically aligned SWNTs could improve the sensitivity of the sensor. They were patterned on the finger electrodes in biosensor to detect cancer cell.[180]

The horizontally aligned CNTs are normally applied into the sensors, the transparent conductive film and the logic circuits due to their perfect electron transport. Li *et al.* fabricated two types of strain sensor with horizontally aligned CNTs.[181] With the aligned CNT film, the two sensors showed both positive and negative gauge factors of 20 and 40 magnitude respectively due to the different structures. The aligned SWNT arrays were fabricated into a pH sensor using dielectric

field.[182] The resistance of the aligned SWNT arrays linearly responded to the pH values of 5-9 and the response time was smaller than 25 s. The gold nanoparticles were deposited on horizontally aligned SWNT arrays using electrochemical method.[183] Each aligned SWNT were used as an individual microelectrodes and the sensitivity could reach as low as 6 DNA molecules (10 base) in 1 mL solution. The horizontally aligned SWNTs were patterned as electrodes in the organic FETs using a dielectric field. [184] The aligned SWNT arrays were used to enhance the efficiency of hybrid solar cells.[185] A drop of the chlorosulfonic acid and SWNT mixture is added between the two slides of glass. Then the two pieces of glass were separated into opposite directions to orient the random SWNTs into aligned arrays. With this aligned, transparent and conductive SWNT film, the fill factor and power conversion efficiency of the solar cell could reach 73.8% and 11.5% respectively. In printed FETs of soft substrate, the aligned SWNTs could also enhance the stability of bending test.[186]

Many scientists and engineers in IBM Research Center have paid much attention to apply SWNTs into logic circuits due to their high carrier mobility, large on/off ratio and extremely small diameter. A breakthrough of simple CPU which was based on the SWNT FETs has been reported, including the enrichment of the s-SWNTs, the self-assembly of SWNTs, the fabrication of the air-stable n-type SWNT FETs and the fabrication of the logic circuits.[187-191] Due to the pristine SWNTs were mixture of m-SWNTs and s-SWNTs, the enrichment technique is necessary to achieve stable performance of SWNT FETs. Tulevski *et al.* developed a simple and scalable column

chromatography process to enrich the 99.9% s-SWNTs.[187] This is method solved a critical problem for the SWNT circuits. Although the purity of s-SWNTs could reach as high as 99.9%, the dense, uniform and aligned s-SWNT film in the FET channel was also important to support high power output in the circuits. Therefore, Lobez *et al.* reported a one-step self-assembly method to deposit SWNT film with high density on SiO₂ wafer surface.[188, 189] Then Cao *et al.* used the Langmuir-Schaefer method to fabricate a aligned s-SWNT film with a tube density of 500 SWNT/ μm .[138] This aligned s-SWNT film could support the on-current density of 120 $\mu\text{A}/\mu\text{m}$ and the on/off ratio of 10^3 which were good enough to build into the logic circuits. Now, the challenge of preparing air stable n-type FETs appear. Several contact metals, such as Er, La and Y, have been investigated on the performance of n-type FETs. The erbium oxide layer between the surface of electrodes and the protect layer had no effects on the performance of the SWNT FETs.[190] With Er electrodes and protection of Bis(trimethylsilyl)amine (HMDS) shows stable n-type characteristics. This working showed a possible way to fabricate air-stable n-type s-SWNT FETs with good performance. SWNT FET with gates and dielectric layers that wrap the tubes was reported by Franklin *et al.*[191] This work successfully fabricated p- and n-type FETs with a scalable self-aligned gate, which was a remarkable breakthrough in application of integration circuit. The suspending channels of FETs were achieved by wet etching away the top silicon layer of silicon-on-insulator (SOI) wafer after the SWNT networks transfer and the source/drain electrodes deposition. Then the adhesion layer/dielectric layer (AlO_xN_y/Al₂O₃ for the p-type FETs and AlO_xN_y/HfO₂ for the

n-type ones) and the gate metal were deposited with atomic layer deposition (ALD) machine. The uniformity of surrounding layers was confirmed by TEM machine. This technique opened a possible way to apply n- and p-type FETs with the aligned s-SWNT arrays into the logic circuits.

2.5 Summary and outlook

In this chapter, both the vertical and the horizontal alignment techniques and their applications were reviewed. In the transistor, the well aligned, dense and highly purified s-SWNT arrays are necessary to achieve a good performance. Recently, the co-synthesis and post-synthesis methods have a rapid development. In the co-synthesis alignment process, the parameters such as the catalyst, the gas flow rate and direction, the crystalline of the substrate and the growth temperature have been fully studied. Both the vertically and the horizontally aligned CNTs could be successfully synthesized and these co-synthesis aligned SWNT film could be deposited on the soft substrates with the transfer techniques. The advantage of the post-synthesis methods includes the pre-purification and pre-separation, the low energy requirement and the easy scale-up. The post-synthesis methods normally start with the SWNT dispersion. So it is hard to achieve perfect vertically aligned SWNTs on the substrate due to their flexibility. After cutting into short tubes, they could be anchored on the various substrates to increase the specific surface. The horizontally aligned SWNTs are more useful for minimizing the logical circuits. It shows well performance on a soft substrate. The selective growth, in-situ separation and conversion between m-SWNT and s-SWNT are urgently required. Then the aligned

arrays could be easily built into a logic circuit as both conductive wire and semiconducting channel material directly. Both the exact positioning and the orienting techniques are very useful to fabricate the SWNT-based devices, including FETs, sensors and solar cells.

Chapter 3 Experimental Details

In this chapter, the common information of the chemicals, the repeat experiments and the characterization techniques in this thesis are summarized. All other experimental details for specific research are listed in Chapter 4 and 5.

3.1 Materials

SWNTs

The as-produced SWNTs (AP-SWNTs, Lot# AP-W101; CO# 1347) that were synthesized with the arc-discharge method were purchased from Carbon Solutions Inc. (USA); the distribution peak of the SWNT diameters is 1.4 nm; The SWNT lengths ranges from 1 μm to 5 μm ; the bundle diameter is 2 – 10 nm and the purity of these SWNTs is around 30 – 40%. (More information is shown in Appendix A.)

The semiconducting enriched SWNTs were purchased from NanoIntegris Inc. The content of s-SWNTs is 99%. The diameters of the s-SWNTs range from 1.2 nm to 1.7 nm and the lengths ranges from 100 nm to 4 μm (The mean length is 1 μm .). They were dispersed in the 1% ionic surfactant aqueous solution and the concentration is 0.01 mg/mL. (More information is shown in Appendix B)

Silicon dioxide wafer

The *p*-type silicon and silicon dioxide wafers were purchased from Bonda Technology Pte Ltd. The wafer size is 4 inch in diameter and thickness is 500 ± 5 μm . The silicon dioxide wafers have a thermally annealed 500 nm silicon dioxide layer. The silicon was highly boron doped and the resistivity is around 0.005 $\text{ohm}\cdot\text{cm}$.

Photoresist AZ 5124E

AZ 5214E is a kind of positive photoresist which contains the novolak resin and the naphthoquinone diazide as the photoactive. In the image reversal process, it could form a negative pattern of the mask. The solvent is the methoxyl-propyl acetate (PGMEA) and the maximum water content is 0.5%. It has the viscosity of 24.0 cSt, absorptivity (at 377 nm) of $0.76 \text{ g}^{-1}\text{cm}^{-1}$ and the spectral sensitivity of 310 – 420 nm.

Other chemicals

Sodium dodecyl sulfate (SDS), potassium bromide (KBr), 3-aminopropyltriethoxy silane (APTES) and dimethylformamide (DMF) were purchased from Sigma-Aldrich. Acetone and ethanol were purchased from VWR International Pte Ltd.

3.2 SWNT purification, enrichment and pattern fabrication

SWNT purification

The 10 mg AP-SWNTs (Lot# AP-W101; CO# 1347, purchased from Carbon Solutions, Inc.) were heated in a tubular furnace at 400 °C in air (open the two ends) for 2 h to remove the amorphous carbon present in the AP-SWNTs from the arc-discharge method. After baking, the residual SWNTs were refluxed in 5 M hydrochloric acid (HCl) at 80 °C overnight to remove the metal Ni/Y catalysts. The acid treated SWNTs were collected by vacuum filtration using the PTFE membrane with pore size of 0.45 μm (Merck Millipore) and were washed with deionized (DI) water to remove the trapped acid. The solid SWNT powder were dried in 80 °C oven and collected for characterization.

Carboxyl functionalization of purified SWNTs

The 2 mg purified SWNTs were refluxed in the 50 mL 2 M HNO₃ at 80 °C overnight to induce the carboxyl groups on the ends. The acid treated SWNTs were collected by the vacuum filtration using a PTFE membrane with pore size of 0.45 µm and were washed with DI water to remove the trapped acid. The solid SWNT powders were freeze dried and were collected for characterization.

DB71 enrichment of s-SWNTs

The 1.6 mg purified SWNTs were added into the 50 mL 1 mM DB71 aqueous solution in a blue-gap bottle. The bottle was covered with a tinfoil to exclude light and was kept at 60 °C for 46 min in an oil bath. Then the solution was sonicated for 1 h at 70% amplitude (5 s on and 2 s off) in an ice-water bath. After sonication (Vibra-Cell CVX130, Sonics & Material, Inc., USA), the bottle was kept in darkness for 48 h at room temperature. After this step, the solution was centrifuged for 1 h at 20,000 g with a fixed angle rotor and the 60 % supernatant was collected. The supernatant was vacuum filtered through a PTFE membrane (pore size 0.45 µm) and the solids were washed successively with DMF and ethanol to remove the DB71. The chemical structure of DB71 which contains the naphthalene-based azo groups was shown in Figure 4.4 a). The DB71 prefers to suspend s-SWNTs due to the four naphthalene groups. The sulfonate groups improve the dispersing ability. The naphthyl-based radicals which are decomposition from DB71 during sonication selectively react with m-SWNTs. Then these modified m-SWNTs become sediment after centrifugation.[192]

Dielectric layer deposition

The back-gate FETs were fabricated on the SiO₂/Si wafers. Most of the FETs were fabricated on the gate dielectric layer of SiO₂ and the balance ones were fabricated on the HfO₂ dielectric layer to achieve higher on-current. The SiO₂ (500 nm) /Si wafer was purchased from Bonda Technology Pte Ltd and the HfO₂ layer was deposited on the silicon wafer with e-beam machine (BAK501, Evatec process system, base pressure of 1.5×10^{-6} torr). Firstly, the silicon wafers were washed into 4.8% hydrofluoric (HF) acid at room temperature for 10 min to remove the thin oxide layer on the polish side. After drying in N₂, a HfO₂ film of 50 nm was deposited on the silicon wafer by e-beam evaporation at 1 Å/s deposition rate. After the e-beam deposition, to cover the pinholes in the e-beam deposited HfO₂ film, a 30 nm HfO₂ layer was immediately deposited by atomic layer-deposition (ALD S100, Cambridge Nanotech Inc.) process from the precursor tetrakis(diethylamido) hafnium (IV) (from Sigma-Aldrich) and H₂O at 150 °C.

APTES modification

The FET substrate (SiO₂/Si or HfO₂/ Si) wafer surface was modified with APTES to support a strong interaction with SWNTs. The wafer was immersed into Piranha solution (H₂SO₄/H₂O₂ 3:1) for 30 min, rinsed with DI water and dried under nitrogen gas. Then it was immersed in isopropanol with 0.5% APTES in for 2 h. After the mono-layer formation, the wafer was rinsed in isopropanol to remove residual APTES, dried with nitrogen blast and baked on a 100 °C hotplate for 10 min.

Micro-pattern fabrication

The 1-2 mL AZ 5124E photoresist was spin coating on the SiO₂ wafers (20 mm ×

20 mm) at 4,000 rpm for 30 s. Then they were baking on a 105 °C hot plate for 105 s. After cooling, the mask with the electrodes patterns (with the channel lengths of 2 µm, 5 µm, 10 µm, 20 µm and 50 µm and the channel widths of 20 µm and 50 µm) was covered onto the samples with the mask aligner (SUSS MJB4). The exposure time is 2.5 s at 10 mW/cm² and the post exposure baking is carried out in a 110 °C oven for 7.5 min. When the temperature of the samples went down to the room temperature, the time of flood exposure is 25 s at 10 mW/cm². After flood exposure, the electrodes pattern was achieved by developing into the AZ developer which is diluted by DI water (1:2). The wafer with patterned resist was rinsed in DI water for 30 s and dried with a nitrogen blast. In isolation process, the photoresist is used as the positive tone. After the spin-coating and the soft baking with same parameters in the negative step above, the alignment was done under optical microscope of the mask aligner machine and the exposure time was set as 22 s at 10 mW/cm². Without baking in oven, the developing was carried out on the top of exposure step with AZ developer which is diluted by DI water (1:2). The wafer with patterned resist was rinsed in DI water for 30 s and dried with a nitrogen blast. Then the hard baking is at 105 °C for 2 min.

SWNT film fabrication

The surface of the wafer with 500 nm SiO₂ or 80 nm HfO₂ was modified with APTES. The purified and DB71-sorted SWNTs were dispersed into *o*-dichlorobenzene (DCB) respectively with tip sonication (Vibra-Cell CVX130, Sonics & Material, Inc., USA) at 100 W for 30 min. Finally, after the centrifugation at 10,000 g for 1 h with a fixed angle rotor, the supernatant was collected for

characterization and FET fabrication. The wafer was clipped onto the dip-coater and a 100W infrared lamp (from Philips) was used to warm the environment to about 50 °C. The speed was set at 8 mm/min and the 50 dip repetitions were performed. After dip-coating, the wafer was annealed at 200 °C in vacuum (3.85×10^{-5} mbar) for 1 h to improve the tube-tube reattachment.

Network stripping

These parallel stripes were imposed by cutting the SWNT film to create the electrically isolated strips in the active channels of the FETs. The strips were masked with the standard lithography techniques and the unprotected portions of SWNTs were removed by oxygen plasma (100 W, 2 min and 10 ccm; PECVD_PlasmaTherm790). The widths of these strips were 2 µm, 5 µm and 10 µm. Between the strips, the width of space (S') is approximately the same width as the strips.

FET fabrication

The electrode patterns with various channel lengths and widths were deposited on the SWNT film using lithographic lift-off technique. After electrode fabrication, the individual FET were electrically isolated. Six FETs were fabricated in each channel geometry (length/width/sub-channel width) with the dielectric layer (SiO₂ and HfO₂) and the channel material (purified or DB71-sorted SWNTs). The electrodes were patterned on the SWNT film by the lift-off technique. The 5 nm Ti and 45 nm Au layers were deposited using an e-beam evaporator (HHV Auto 306 Turbo). During deposition, the pressure is around 5×10^{-7} mbar. The deposition rate of Ti is set as 0.2

nm/s and the deposition rate of gold is 0.6 nm/s. After metal deposition, the wafer was immersed in acetone to remove the photoresist mask and the overlying metal. Then the devices were electrically isolated. A protective mask pattern covers the channel regions of the FETs and the unprotected SWNTs were removed with plasma RIE system (PECVD_PlasmaTherm790) for 1 min. The flow rate of O₂ was 20 sccm and the power was set as 100 W. After the isolation, the protective masks were removed.

3.3 Characterization techniques

Raman spectra

Raman spectra were measured using a Renishaw Raman microscope with a 0.45 mW He-Ne laser operated at 633 nm with a spot size of around 20×20 μm². The integration time was 10s in a single scan and the scan times are 3.

The polarized Raman spectra was measured using a Renishaw Raman microscope with a 0.45 mW He-Ne laser operated at 785 nm. A fixed polarizer was used to polarize the laser light, and the Raman spectra were taken at ~22° rotation intervals. The integration time was 15s in a single scan.

Ultraviolet-visible-near infrared (UV-vis-NIR)

UV-vis-NIR absorption spectra was used to characterize the purification and the electronic property of SWNTs. The spectra was tested using a Varian Cary 5000 UV-vis-NIR spectrophotometer and the scan scale was set as 400 – 1200 nm with step as 2 nm.

Atomic force microscope (AFM)

The thickness and the morphology of the SWNT films were characterized with

AFM machine. The height image and height curves were recorded on the MFP 3D microscope in AC mode. All the SWNTs were deposited on the SiO₂ wafer surface whose thickness of the oxide layer which formed by thermal oxidation is 500 nm and the crystal plane of the silicon wafer is <1-0-0>.

Field-emission scanning electron microscope (FESEM)

To confirm the morphology of the SWNT films, FESEM images were taken with a JEOL JSM-6700F microscope and the operation voltage is 5 kV. Some samples were sputtered platinum in JEOL JFC-1600 Auto Fine Coater at 10 mA for 80 s to achieve high quality images.

FET performance measurement

The transport characterization of FETs with both the SWNT strips and the aligned arrays was accomplished with Keithley 4200-SCS electrometer at room temperature. Both the drain current versus gate voltage curves and the drain current versus drain voltage curve were obtained.

Mobility calculation

In Chapter 4, the effective mobility of FETs with the SWNT strips was calculated from the conventional relation:

$$\mu = \frac{L}{W_{sum}C_{ox}V_d} \frac{dI_d}{dV_g} \quad (3.1)$$

Where W_{sum} is the sum of the width of strips for devices with portioned channels and L is respectively channel and channel length, V_d is source-drain bias voltage (For devices on SiO₂/Si wafer, $V_d = 0.5$ V; for devices on the HfO₂/Si wafer, $V_d = 0.2$ V), dI_d/dV_g is the transconductance (g_m) extracted from the slope of the forward transfer

curve and C_{ox} is gate capacitance per unit area. For SWNT-based FETs, the electrostatic coupling between tubes and planar gate electrodes on gate capacitance estimation affect the performance of devices. The following equation is used to calculate capacitance, when the electrostatic coupling between sparse SWNTs and planar gate electrodes happens.[193, 194]

$$C_{ox} = \left(C_Q^{-1} + \frac{1}{2\pi\epsilon_0\epsilon_Q} \ln \left[\frac{\Lambda_0}{R} \cdot \frac{\sinh(2\pi t_{ox}\Lambda_0^{-1})}{\pi} \right] \right)^{-1} \cdot \Lambda_0^{-1} \quad (3.2)$$

Where $C_Q = 4 \times 10^{-10}$ F/m is the SWNT quantum capacitance, Λ_0 is density of nanotubes, $R = 1.0$ nm is average tube radius, $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the vacuum permittivity and $\epsilon = 3.9$ is relative permittivity of SiO_2 . The capacitance of 80 nm thick HfO_2 layer is ~ 139 nFcm⁻² at 100k Hz. With HfO_2 deposition process which is mentioned above, the relative static permittivity of HfO_2 is 12.[193]

In Chapter 5, the electrical performance of the FETs was measured at room temperature in the back-gated configuration using a Keithley semiconductor parameter analyzer. All devices were tested at $V_d = 0.5$ V. Device mobility was computed using the standard equation (2):

$$\mu = \frac{L}{WC_i V_d} \cdot \frac{dI_d}{dV_g} \quad (3.3)$$

Where dI_d/dV_g is the transconductance extracted from the slope of the backward transfer curve (from -20 V to 20 V), L is the channel length, W is the channel width, and C_i is the specific capacitance per unit area of the active channel. C_i is given by

$$C_i = \frac{D}{C_Q^{-1} + \left(\frac{1}{2\pi\epsilon_0\epsilon} \right) \ln \left[\sinh \left(\frac{2\pi\tau_{ox}D}{\pi D \Gamma} \right) \right]} \quad (3.4)$$

Where $C_Q = 4 \times 10^{-10}$ F/m, the nanotube quantum capacitance, $t_{ox} = 500$ nm, the thickness of the oxide layer, $\epsilon = 3.9$, the dielectric constant of silicon dioxide, ϵ_0

$=8.85 \times 10^{-12}$ F/m, the permittivity of free space, $r = 0.7$ nm is the average radius of the nanotubes and D is the SWNT linear density on the channel of FETs (which is the reciprocal of tube-tube separation).[195]

Chapter 4 Stripping of SWNT-based Networks for Improved FET Performance

4.1 Introduction

As discussed in Section 2.1, SWNTs are cylinders of graphene with very high length/diameter ratio.[24, 196] The electronic properties of SWNTs are determined by the details of their orientation of the graphene symmetry direction with respect to the SWNT axis. These details determine whether a particular SWNT species is semiconducting or metallic in its electronic properties. The SWNT synthesis methods, including arc-discharge and chemical vapor deposition (CVD), produce populations of diverse chiral species, of which about one third are metallic and the balance are semiconducting. The s-SWNTs have excellent carrier mobility and high on/off ratio and are potentially excellent active channel materials in FETs.

The SWNT networks that comprise the rigid long nano-sticks that cross-cross each other will give high mobility. The networks with the shorter tubes will result in more tube-tube junctions and higher network resistance. Further, the performance of a random stick network transistors can be controlled by the semiconducting species purity as well as the physical characteristics of the channel-percolation of the metallic tubes as opposed to semiconducting tubes and also the channel geometric dimensions. Sorting of SWNTs has attracted much research effort and a wide range of separation methods such as DGU separation, DNA sequence assisted sorting and size-exclusion chromatography enrichment have been explored.[6, 7, 197] However, to date, only DGU is being employed in commercial production of highly purified s-SWNTs, and

this process is batch-based and is rather slow due to the slow differential migration of SWNTs through the dense, viscous gradient medium.[9]

Alternative methods of FET performance enhancement, involving channel fabrication processing of the active channel, have been explored to improve the effective s-SWNT content of network devices fabricated using as grown SWNTs.[198-200] Current burning of the m-SWNTs in the active channel network and post-channel-deposition treatment with chemicals which preferentially destroy m-SWNTs or convert them into s-SWNTs has been studied.[10, 201] These methods are somewhat effective in improving device performance, but the etching and conversion of m-SWNTs are tube diameter dependent and the tube density of the SWNT networks on the substrate should be strictly controlled.

SWNT samples, regardless of their synthesis method, tend to be dominated by semiconducting species, and even in networks produced with un-sorted SWNTs, the m-SWNTs are sparser than the s-SWNTs and consequently its current capacity is more limited by the percolation effects in the random SWNT networks. It is well known that the switchability of the unsorted SWNT networks increases with the channel length's increasing. Long channel devices have limitations in many applications, but a similar effect can be achieved in shorter channel devices by patterning the SWNT networks into strips with large length/width ratio. A simple geometrical stripping method has been developed for active channel deposition which in principle ought to significantly improve the switchability of SWNT-network devices.[13] Cao Qing has reported this method for CVD grown devices but used

fairly wide strips of 5 μm for the fairly long tubes, to achieve mobility of 80 $\text{cm}^2/\text{V}\cdot\text{s}$ and on/off ratio of 10^5 . Solution-processed sorted nanotubes are shorter and percolate less well than CVD tubes at a given areal density, which makes it difficult to simultaneously achieve high on/off ratio and high mobility. Active channels made with shorter tubes need even narrower strip width that will significantly increase the network resistance and decrease the mobility.

The work reported in this paper is motivated by the hypothesis that solution enrichment of s-SWNTs combined with the simple sub-channel stripping with standard lithography methods can achieve high device performance (on/off ratio, mobility and on-current). Unsorted as-produced SWNTs (AP-SWNTs, 79% semiconducting) and also semiconducting-enriched (DB-71 sorted, 88% purity) SWNTs were employed as active channel materials.[192] We fabricated FETs on SiO_2/Si wafers with channel width (W) of 20 μm and 50 μm and varying channel lengths (L) and strip width (W') (L varies from 2 μm to 50 μm and W' varies from 2 μm to 10 μm). On the SiO_2/Si wafer, for FETs with on/off ratio $> 10^4$, the mobility of the best FETs with unsorted SWNTs but stripped channels is $3.7 \pm 1.25 \text{ cm}^2/\text{V}\cdot\text{s}$; the mobility of the corresponding FETs made with DB71-sorted AP-SWNTs was much higher, $15.8 \pm 2.92 \text{ cm}^2/\text{V}\cdot\text{s}$. However, the on-current was low at $10.9 \pm 1.85 \times 10^{-3} \mu\text{A}/\mu\text{m}$. When the HfO_2 dielectric layer was employed, improving the on-current to $17.2 \pm 9.30 \times 10^{-2} \mu\text{A}/\mu\text{m}$, the mobility of FETs with DB71-sorted AP-SWNT stripped network could reach $21.9 \pm 8.72 \text{ cm}^2/\text{V}\cdot\text{s}$, with on/off ratio of $8.16 \times 10^4 \pm 3.04 \times 10^4$. This combination method makes it feasible to fabricate good performance

SWNT-network-based FETs with widely available and low-cost unsorted SWNTs.

4.2 Experiment Section

Materials

The AP-SWNTs (Lot# AP-W101; CO# 1347) and P2-SWNTs were purchased from Carbon Solutions Inc. (Riverside, CA, USA). The difference between AP-SWNTs and P2-SWNTs was introduced in Appendix A. (3-aminopropyl)triethoxysilane (APTES, 99%), tetrakis(diethylamido) hafnium (IV), DB71 and HCl were purchased from Sigma-Aldrich (Singapore). The PTFE membranes with pore size 0.45 μm were purchased from Merk Millipore and were used for the SWNT collection.

SWNT purification

Figure 4.1a) shows the steps employed for SWNT purification. The AP-SWNTs were heated in a tubular furnace at 400 $^{\circ}\text{C}$ in air for 2 h to remove the amorphous carbon present in the AP-SWNTs from the Arc-discharge synthesis process. After oxidation, the SWNTs were refluxed in 10% hydrochloric acid (HCl) at 80 $^{\circ}\text{C}$ for 48 h to remove the metal Ni/Y catalysts. The acid treated SWNTs were collected by vacuum filtration using PTFE membrane with pore size 0.45 μm and washed with DI water to remove the trapped acid. The SWNT powder was freeze-dried and re-dispersed into *o*-dichlorobenzene (DCB) with tip sonication at 100 W for 0.5 h. The supernatant was collected for dip-coating after 20, 000 g for 1 h.

Figure 4.1 The SWNT purification process and the schematic process of the forming SWNT strips and FETs fabrication. **a)** SWNT purification process; **b)** Schematic process of SWNT strips formation and FET fabrication

DB71 enrichment of s-SWNTs

1.6 mg purified SWNTs (per above procedure) were added to 50 mL of 1 mM DB71 aqueous solution in a glass bottle. The bottle was covered with tinfoil to exclude light and was warmed at 60 °C for 46 min in an oil bath. After sonication (Vibra-Cell CVX130, Sonics & Material, Inc., USA) for 1 h at 70% amplitude (5 s on and 2 s off), the bottle was kept in darkness for 48 h at room temperature. After this period, the solution was centrifuged (Sigma 3K30) for 1 h at 20,000 g with a fixed angle rotor and the supernatant was collected. The supernatant was vacuum filtered through a PTFE membrane and the solids were washed successively with DMF and ethanol to remove the DB71.[192]

HfO₂ dielectric deposition

Firstly, 50 nm HfO₂ film was deposited on the silicon wafer by e-beam evaporation (BAK501, Evatec process system, base pressure 1.5×10^{-6} torr) at a deposition rate of 1 Å/s. After e-beam evaporation, a 30 nm HfO₂ layer was immediately deposited, to cover any pinholes in the e-beam evaporated HfO₂ film, by

atomic layer-deposition (ALD, Savannah S100 Cambridge Nanotech Inc.) process from a precursor of tetrakis(diethylamido) hafnium (IV) and H₂O at 150 °C.

SWNT film fabrication

The wafer surface with 500 nm SiO₂ or 80 nm HfO₂ was modified with APTES. The wafer was cleaned in Piranha solution (H₂SO₄/H₂O₂ 3:1) for 30 min, rinsed with DI water and dried under nitrogen gas. Then it was immersed for 2h in a isopropanol solution containing 0.5% APTES. After mono-layer formation, the wafer was rinsed in isopropanol to remove residual APTES, dried with nitrogen gas and baked on a 100 °C hotplate for 10 min. The purified and DB71-sorted AP-SWNTs were dispersed in DCB with tip sonication (Vibra-Cell CVX130, Sonics & Material, Inc., USA) at 100 W for 30 min. Finally, after centrifugation (10,000 g for 1 h) with a fixed angle rotor, the supernatant was collected for characterization and FET fabrication. As shown in Figure 4.1b), the wafer was clipped onto the dip-coater and a 100W infrared lamp (from Philips) was used to warm the environment to about 50 °C. The speed was set at 8 mm/min and 50 dip repetitions were performed. After dip-coating, the wafer was annealed at 200 °C in vacuum (3.85×10^{-5} mbar) for 1 h to improve the tube-tube contacts.

Network stripping

As shown in Figure 4.1b), patterns of parallel stripes were imposed on the film to create electrically isolated strips within the active channels of the FET devices. The strips were masked with standard lithography techniques and SWNTs in the unprotected portions of the FET channels were removed by oxygen plasma (100 W, 2

min and 10 ccm; PECVD_PlasmaTherm790). As shown in Figure 2, the strips widths (W) in these patterns were 2 μm , 5 μm and 10 μm . The inter-strip gap width (S') was approximately the same as the strip width (W').

Electrodes deposition

Bottom-gated FETs were fabricated on SiO_2/Si and HfO_2/Si wafers. Metal electrodes were formed on the patterned SWNT film by lithographic lift-off technique. An electrodes pattern mask (with channel lengths (L) of 2 μm , 5 μm , 10 μm , 20 μm and 50 μm and channel widths (W) of 20 μm and 50 μm was fabricated by lithographic method on the SWNT film. Figure 4.2 showed the schematic structure of FET channel. Then 5 nm Ti and 45 nm Au layers were deposited by e-beam evaporation. The wafer was immersed in acetone to remove the electrodes mask and the overlying metal. Six devices were fabricated in each chosen combination channel geometry (L/W/W'), dielectric (SiO_2 and HfO_2), and channel material (unsorted SWNTs or DB71-sorted s-SWNTs). After electrodes deposition, a protective mask pattern covering the channel regions of the devices was formed by standard lithography method and the unprotected SWNTs were removed with oxygen plasma treatment. After device isolation, the protective masks were removed by acetone rinsing.

Figure 4.2 Schematic structure of FET channel area after stripping, electrodes deposition and isolation.

Sample characterization and mobility calculation

The SWNT strips on the FETs channel were measured with a MFP3D AFM microscope in tapping mode and with field emission scanning electron microscopy (FESEM, JOEL 6700). UV-vis-NIR absorption spectra were measured using a Varian Cary 5000 UV-vis-NIR spectrophotometer. Raman spectra were measured using a Renishaw Raman microscope with a 0.45 mW He-Ne laser operated at 633 nm and with a spot size of around $20 \times 20 \mu\text{m}^2$. The integration time was 10s in a single scan. Electrical performance of the fabricated devices was measured at room temperature in back-gated FET configuration using a Keithley semiconductor parameter analyzer Model 4200-SCS. The effective mobility of the FETs was calculated from the conventional relation:

$$\mu = \frac{L}{W_{\text{sum}} C_{\text{ox}} V_d} \frac{dI_d}{dV_g} \quad (4.1)$$

Where W_{sum} is the sum of the width of strips for devices with partitioned channels and L is channel length, V_d is source-drain bias voltage (For devices on SiO_2/Si wafer,

$V_d = 0.5$ V; for devices on the HfO_2/Si wafer, $V_d = 0.2$ V.), dI_d/dV_g is the transconductance (g_m) extracted from the slope of the forward transfer curve and C_{ox} is gate capacitance per unit area. For SWNT-based FETs, the electrostatic coupling between tubes and planar gate electrodes affects the gate capacitance estimate and consequently the implied device performance. The following equation was used to calculate capacitance, taking into account the electrostatic coupling between sparse SWNTs and planar gate electrodes.[193, 194]

$$C_{ox} = \left(C_Q^{-1} + \frac{1}{2\pi\epsilon_0\epsilon_Q} \ln \left[\frac{\Lambda_0}{R} \cdot \frac{\sinh(2\pi t_{ox}\Lambda_0^{-1})}{\pi} \right] \right)^{-1} \cdot \Lambda_0^{-1} \quad (4.2)$$

where $C_Q = 4 \times 10^{-10}$ F/m is the SWNT quantum capacitance, Λ_0 is area nanotube density, $R = 1.4$ nm is average tube radius, $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the vacuum permittivity and ϵ is the relative permittivity (static) of the gate dielectric (3.9 for SiO_2 and 12 for HfO_2).[194]

4.3 Results and Discussion

High on-current in SWNT-based FETs requires high SWNT network density. Due to the character of percolative conduction and its dependence on network density, the minority class of SWNTs (m-SWNTs) forms a network and the conductivity of which is more sensitive to changes in network density than is the majority SWNT (s-SWNTs) network. A workaround to this problem is to reduce the fraction of m-SWNTs in the material used to create the FET active channels. Improvement of the on/off ratio can also be achieved through manipulation of the channel geometry. It is well known that in FET channels formed from SWNT networks which are predominantly semiconducting, the on/off ratio improves as the channel is

lengthened.[155] The reason for this is that the conductive network is more nearly percolation limited than is the semiconducting network. It may not be desirable in practice to have very long channel devices, but a similar effect can be achieved at fixed channel length by making the channel width smaller. Increasing the aspect ratio of the channel will decrement the conduction of the more nearly percolation limited conductive network more than of the semiconducting network. In order to keep the on current high, the channel could be partitioned into a parallel circuit of high aspect ratio sub-channels.

4.3.1 Characterization of purified and BD71-sorted AP-SWNTs

The presence of amorphous carbon and metal catalysts in the as-received SWNTs complicates the deposition of a uniform SWNT networks on the substrate surface (SiO_2/Si or HfO_2/Si wafer surface), necessitating oxidation and acid treatments to remove these impurities. SEM imagery confirms that the oxidation and acid treatment have removed most of the synthesis-related impurities (Figure 4.3).

Figure 4.3 The FESEM images of pristine SWNTS and purified SWNTs. **a)** The FESEM image of pristine SWNTs; **b)** The FESEM image of purified SWNTs.

Figure 4.4 a) shows the chemical structure of DB71 which contains the naphthalene-based azo groups. The DB71 prefers to suspend s-SWNTs due to the four naphthalene groups and the sulfonate groups improve the dispersing ability. The

naphthyl-based radicals which are decomposition from DB71 selectively react with m-SWNTs. Then these modified m-SWNTs become sediment after centrifugation.[192] The DB71 enrichment of s-SWNTs is confirmed by UV-vis-NIR absorption spectra of unsorted SWNTs (black) and DB71-sorted AP-SWNTs (red) (Figure 4.4a)). (The AP-SWNTs and P2-SWNTs are synthesized with arc-discharge method. P2-SWNTs are the AP-SWNTs after removing impurities. The AP-SWNTs in this chapter are the ones after purification in our lab. The details of AP-SWNT purification procedure have been introduced in Section 3.2. The AP-SWNTs are much cheaper and the details of purification could be controlled. After purification, the AP-SWNTs here are longer than P2-SWNTs used in Figure S2.[202] In Dr. Ashok's paper, a small quantity of P2-SWNTs was used as starting material to achieve s-SWNTs by treatment of DB71 in the ~10 mL aqueous solution.[192]. To fabricate FETs arrays, much more DB71-sorted SWNTs should be suspended into > 50 mL DBC for dip coating, so that we use the AP-SWNTs instead of P2-SWNTs. The differences in purification and tube length maybe the reason that the s-SWNTs in DB71-sorted AP-SWNTs is only 89%.) The solid lines are measured absorption data and the dotted lines are the spectra normalized to unit absorption at short wavelength. Both samples were dispersed in 1% SDS aqueous solution. The absorption spectra are used to estimate the relative proportions of m- and s-SWNTs contained in the samples. The characteristic absorption feature (M_{11}) of metallic arc-discharge SWNTs is a broad peak from 600 to 850 nm and the semiconducting absorption features (S_{22} and S_{33}) are at 900–1270 nm and 450–630 nm respectively. The scaled peak area ratio of

$S_{22}/(S_{22}+M_{11})$ is used as an estimate of the fraction of s-SWNTs in the samples.[192]

The s-SWNTs fraction of the total AP-SWNT population is estimated to be 79% and 88% before and after DB71 enrichment respectively.

Figure 4.4 The UV-vis-NIR absorption and Raman spectra of the purified and DB71-sorted AP-SWNTs. **a)** chemical structure of DB71; **b)** UV-vis-NIR spectra; **c-d)** Raman spectra at 633 nm.

Raman spectroscopy with 633nm excitation (He/Ne laser) was used to characterize the vibrational and radial breathing mode (RBM) features of the purified and DB71-sorted SWNT samples. The peaks in the region 100–170 cm⁻¹ (S₃₃, S₄₄) are from s-SWNTs and the absorption at 175–225 cm⁻¹ (M₁₁) is due to m-SWNTs. Figure 4.4b) shows the RBM of purified and DB71-sorted AP-SWNTs. The M₁₁ peak of DB71-sorted AP-SWNTs decreases compared with purified SWNTs. There is also an apparent shift in the s-SWNT RBM peaks toward higher frequency (around 4 cm⁻¹), implying that in addition to enriching the s-SWNT content, the DB71-sorted preferentially suspends s-SWNTs with smaller diameter. The G⁻ and G⁺ peaks, which

arise from the tangential mode vibrations of SWNTs, are located from 1450 cm^{-1} to 1700 cm^{-1} . The peak position of G^+ which shows the vibrations of carbon atom along the tube axis is sensitive to charge transfer from dopant to SWNTs, while the peak position and shape of G^- (due to vibrations of carbon atom along the circumferential direction) varies depending on whether the SWNTs are metallic or semiconducting. The G^- lineshape of m-SWNTs is of Breit-Wigner-Fano lineshape and that of s-SWNTs is Lorentzian.[203, 204] As shown in Figure 4.4c), the G^- peak of the DB71-sorted AP-SWNTs is significantly narrower and lower than that of the purified SWNTs, indicating that the DB71-sorted sample is depleted in m-SWNTs compared to the input purified SWNTs.

4.3.2 Morphology of SWNT strips in FET channels

The stripping method was firstly applied on the CVD grown SWNT networks.[13] After striping the uniform SWNT network into $5\text{ }\mu\text{m}$ parallel strips, the on/off ratio of FET have a significant increasing ($\sim 10^5$) and the mobility is as high as $80\text{ cm}^2/\text{V}\cdot\text{s}$. Our works also starts from the $2\text{-}5\text{ }\mu\text{m}$ long unsorted SWNT network which is formed with dip-coating method. Figure 4.5 shows the tapping mode AFM images of with $2\text{ }\mu\text{m}$, $5\text{ }\mu\text{m}$ and $10\text{ }\mu\text{m}$ wide strips of both unsorted SWNTs and DB71-sorted AP-SWNTs in the SiO_2 and HfO_2 FETs channel. According to the height curve, the height of DB71-sorted AP-SWNT strips is about 8 nm and the height curves of unsorted strips are 5 nm . With DB71-sorted AP-SWNTs, the thickness of strips could be larger than the unsorted one due to the removing of m-SWNTs. The increasing of strips height directly causes the mobility increasing of DB71-sorted

AP-SWNTs based FET.

Figure 4.5 The AFM image and height curves of the **a)** 2 μm , **b)** 5 μm and **c)** 10 μm strips of unsorted and DB71-sorted AP-SWNTs on SiO_2/Si and HfO_2 wafer surface.

After Ti/Au electrodes deposition, Figure 4.6 shows the FESEM images of complete FETs (after Ti/Au electrode deposition and device isolation) without channel stripping and with channels stripped into 2 μm , 5 μm and 10 μm via photolithography in channel ($L = 20 \mu\text{m}$ and $W = 20 \mu\text{m}$). (The width of the gaps between the network strips (S') is approximately the same as the width of the strips.) In this figure, the substrate is HfO_2 (80 nm)/Si wafer. FESEM images of FETs with different gap geometries ($W = 20 \mu\text{m}$, 50 μm and $L = 2 \mu\text{m}$, 5 μm , 10 μm , 20 μm and 50 μm) on both SiO_2 and HfO_2 wafer are shown in the Appendix A **Figures S5-S7**.

Figure 4.6 The FESEM images of different width SWNT strips in FET channels: channel length (L) is 50 μm and channel width is 20 μm . **a)** no strips in the FET channel; **b)** 2 μm strips on the FET channels; **c)** 5 μm strips on the FET channels; **d)** 10 μm strips in the FET channels; (Substrate is SiO_2/Si wafer) (The FESEM images of other FETs with both unsorted and DB71-sorted AP-SWNTs on SiO_2/Si and HfO_2/Si wafer are all tested and the results are not put inside.)

4.3.3 Performance of FETs with strips of unsorted and DB71-sorted AP-SWNTs

After isolation, the performance of FETs with DB71-sorted AP-SWNTs was tested. Figure 4.7a) shows the typical transfer characteristics (drain current versus gate voltage, I_d - V_g) of the FETs made from DB71-sorted s-SWNTs on the HfO_2/Si wafer substrate. These devices were tested under 0.2 V drain voltage and the gate voltage was swept from -4 V to 4 V. The FETs show on-current at negative gate voltage and were turned off at positive gate voltage. The FET without stripping shows low on/off ratio of 10.1 ± 3.45 and on-current of $8.9 \pm 2.31 \mu\text{A}$. As the strip width decreases from 20 μm ($S' = 0 \mu\text{m}$) to 2 μm , the on current decreases somewhat from $8.9 \pm 2.31 \mu\text{A}$ to $2.52 \pm 1.69 \mu\text{A}$ (current per total channel strips width is nearly

constant), while the on/off ratio significantly increases from 10 to 10^4 ($W'=2\text{ }\mu\text{m}$ and $5\text{ }\mu\text{m}$). For a fixed channel length, as the strip width decreases, the network becomes more switchable as demonstrated by the increasing on/off ratio, although the on-current is also slightly decreased. Other devices with channel lengths of $20\text{ }\mu\text{m}$ and $50\text{ }\mu\text{m}$ show similar trends of increasing on/off ratio with almost constant on-current. Figure 4.7b) shows the corresponding typical output characteristic (I_d - V_d) of the devices with V_g ranging from -6 V to 6 V with 2 V steps. At low drain voltage ($-0.2\text{ V} < V_d < 0.2\text{ V}$), the linear rising curve indicates ohmic contact between SWNTs and source and drain electrodes. This figure also shows that our devices have no observable current leakage. Hence, the stripping method can greatly improve the on/off ratio of FETs with small loss of on-current.

Figure 4.7 The characterization of the FETs with various SWNT strips ($W'=2\text{ }\mu\text{m}$, $5\text{ }\mu\text{m}$ and $10\text{ }\mu\text{m}$) using channel width (W) of $20\text{ }\mu\text{m}$ and channel lengths (L) of $20\text{ }\mu\text{m}$ and DB 71 sorted SWNTs on HfO_2/Si wafer surfaces. **a)** the I_d - V_g curve of the FETs with no strips (black), $2\text{ }\mu\text{m}$ wide strips (red), $5\text{ }\mu\text{m}$ wide strips (blue) and $10\text{ }\mu\text{m}$ wide strips (green); **b)** the I_d - V_d curve for FET with $2\text{ }\mu\text{m}$ wide strips (The transfer characterization of other FETs with both unsorted and DB71-sorted AP-SWNTs on SiO_2/Si and HfO_2/Si wafer are all tested and the results are not put inside.)

The on/off ratio, on-current and mobility of FETs with unsorted and DB71-sorted AP-SWNTs on SiO_2/Si and HfO_2/Si wafer are summarized in Figure 4.8-4.10. The effect of combining stripping process with moderately DB71-sorted AP-SWNTs is

discussed below. Figure 4.8 shows the variation of device performance (on/off ratio, on-current and mobility) of FETs fabricated using unsorted SWNTs on SiO₂/Si wafer substrates for channel width (W) of 20 μm (Figure 4.8a)) and 50 μm (Figure 4.8b)) respectively. For each channel width, the effect of different strip widths of 2 μm , 5 μm and 10 μm was also investigated. Figure 4.8i) shows that for a fixed channel length, particularly for the larger channel length, as the strip width is reduced, the on/off ratio increases. Also, at a fixed strip width, reducing the channel length leads to an increase of the on/off ratio. Increasing the channel length and decreasing the strip width both result in decreased number of percolating m-SWNT paths between the source and drain.

Figure 4.8 The statistical study of FETs on SiO_2 wafer with different width unsorted AP-SWNT strips. **a)** Channel width (W) = $20 \mu\text{m}$. Plot of average on/off ratio ($I_{\text{on}}/I_{\text{off}}$), average current density (I_{on}) and average devices mobility (μ) versus channel length (L) for FETs with strips width (S') of $2 \mu\text{m}$, $5 \mu\text{m}$ and $10 \mu\text{m}$; **b)** Channel width (W) = $50 \mu\text{m}$. Plot of average on/off ratio ($I_{\text{on}}/I_{\text{off}}$), average current density (I_{on}) and average devices mobility (μ) versus channel length (L) for FETs with strips width (W') of $2 \mu\text{m}$, $5 \mu\text{m}$ and $10 \mu\text{m}$;

Figure 4.8ii) shows the average on-current of FETs with different channel lengths and strip widths. Due to the finite resistance of the semiconducting network in the “on” state, the on-current decreases with increased channel length. Also, after

stripping, the resistance of the SWNT networks increase. With narrower strips, the on-current of FETs decreases; in the stick-like SWNT networks, as the channel narrowed to 2 μm and 5 μm , some electron transporting paths have been removed and fewer m-SWNTs are able to form continuous pathways. The on-current decreases with decreased strips width and with increased channel length. Both the longer channel and narrower strips increases the resistance between the two electrodes.

In addition to on/off ratio and on-current, mobility is another important parameter to evaluate FET performance. Figure 4.8iii) shows the effect of channel length and strip width on effective mobility. For the 20 μm wide channels, the mobility of the devices increases as channel length increases from 2 μm to 10 μm and then decreases when the device channel increases to 20 μm and 50 μm . For the 50 μm wide channel width (W), the mobility generally decreases with increased channel length. For high on/off ratio $> 10^4$ (shaded areas in Figure 7i), the corresponding highest device mobility achievable is $3.7 \pm 1.25 \text{ cm}^2/\text{V-s}$ (marked by * in Figure 7iii)) with 5 μm wide strips on the 50 $\mu\text{m} \times 50 \mu\text{m}$ (length x width) channel. Mobility is calculated from Equation (4.1), and is a function of channel length and the transconductance ($g_m = dI_d/dV_g$). However, the transconductance is also dependent on channel length. The trend of mobility versus channel length is a composite effect.

The DB71 treatment and centrifugation step reduces the metallic content from 21% in pristine SWNTs to 12% in the treated SWNTs. Figure 4.9 shows, for FETs fabricated with SWNTs enriched in semiconducting species through the DB71-treatment and centrifugation process, the variation of the device on/off ratio,

on-current and mobility with various strip width and channel length. Figure 4.9i) shows a similar trend of on/off ratio with channel length as Figure 4.8i): the on/off ratio generally increases as channel length increases or strip width decreases. Figure 4.9ii) also shows a similarly trend as Figure 4.8ii) that on current decreases with increased channel length or decreased strip width. However, with DB71-sorted AP-SWNTs, after channel stripping, the best mobility (with $> 10^4$ on/off ratio shaded in Figure 4.8i) is $15.8 \pm 2.92 \text{ cm}^2/\text{V-s}$ (marked by * in Figure 4.9i) is $15.8 \pm 2.92 \text{ cm}^2/\text{V-s}$ (marked by * in Figure 4.9iii)); specifically, these devices have on/off ratio of $2.27 \times 10^4 \pm 7.45 \times 10^3$ and on-current of $10.9 \pm 1.85 \times 10^{-3} \text{ } \mu\text{A}/\mu\text{m}$. Compared to stripping of unsorted tubes, the optimum FETs with DB71-sorted AP-SWNTs can achieve higher mobility ($15.8 \pm 2.92 \text{ cm}^2/\text{V-s}$ versus $3.7 \pm 1.25 \text{ cm}^2/\text{V-s}$) with shorter channel lengths (20 μm versus 50 μm) when both sets of devices have switchable with on/off ratio kept at around 10^4 . Shorter channel length is important for device miniaturization.

Figure 4.9 The performance of FETs on SiO₂/Si wafer using DB71-sorted AP-SWNTs. **a)** Channel width (W) = 20 μm . Plot of average on/off ratio ($I_{\text{on}}/I_{\text{off}}$), average current density (I_{on}) and average device mobility (μ) versus channel length (L) for FETs with strip width (S') of 2 μm , 5 μm and 10 μm ; **b)** Channel width (W) = 50 μm . Plot of average on/off ratio ($I_{\text{on}}/I_{\text{off}}$), average current density (I_{on}) and average device mobility (μ) versus channel length (L) for FETs with strips width (W') of 2 μm , 5 μm and 10 μm ;

Although the on/off ratio and mobility are improved by stripping combined with enrichment of the s-SWNT content, the on-currents of the FETs achievable with DB71-sorted AP-SWNT stripped network are still of the order of 0.1 μA which is too

low for some applications, such as driving LEDs in logic circuits.[205, 206] The above devices in Figure 4.8-4.9 were fabricated on SiO₂ (500 nm)/Si substrates. The on-current of these FETs can be improved by use of a material with higher dielectric constant (K), such as HfO₂ (K= 25), compared with the one of SiO₂ (K= 3.9).[207]

Figure 4.10 shows the variation with channel length and strip width of the on/off ratio, on-current and mobility using DB71-sorted AP-SWNTs on HfO₂/Si substrates. It is observed that with HfO₂/Si wafer and DB71-sorted AP-SWNTs could achieve an on-current of $10.9 \pm 1.85 \times 10^{-3} \mu\text{A}/\mu\text{m}$, and high mobility and on/off ratio of $21.9 \pm 8.72 \text{ cm}^2/\text{V-s}$ and $8.16 \times 10^4 \pm 3.04 \times 10^4$ respectively. The combination of stripping and s-SWNT enrichment on HfO₂ dielectric substrates results in significantly improved performance over the unsorted and DB71-sorted AP-SWNTs on SiO₂ dielectric devices. On the HfO₂/Si wafer, the best device (marked by * in Figure 4.10iii)) can support 4 orders on/off ratio and mobility as high as $21.9 \pm 8.72 \text{ cm}^2/\text{V-s}$ with on current of $17.2 \pm 9.30 \times 10^{-2} \mu\text{A}/\mu\text{m}$ and channel length of 20 μm . This type of devices can be potentially applied into logic circuits to drive LED.[206] The devices in Figure 4.9 can potentially be used in bio- and gas sensors which do not require high on current.[208, 209]

Figure 4.10 The performance of FETs on HfO₂ wafer with DB71-sorted AP-SWNT strips. **a)** Channel width (W) = 20 μm. Plot of average on/off ratio (I_{on}/I_{off}), average current density (I_{on}) and average device mobility (μ) versus channel length (L) for FETs with strip width (S') of 2 μm, 5 μm and 10 μm; **b)** Channel width (W) = 50 μm. Plot of average on/off ratio (I_{on}/I_{off}), average current density (I_{on}) and average device mobility (μ) versus channel length (L) for FETs with strips width (W') of 2 μm, 5 μm and 10 μm;

An additional consideration is the relative scales of the SWNT lengths (2-5 μm) and the channel strip widths. From Figure 4.10i), it is found that the strip width of 2 μm and 5 μm, which is comparable to SWNT length, is generally more effective for

increasing the on/off ratio than the strip width of 10 μm . It appears that the strip width should be comparable to the nanotube length to increase the on/off ratio. Our nanotubes are about 2–5 μm in length which is similar to the shorter channel lengths ($L = 2\ \mu\text{m}$ and $5\ \mu\text{m}$) investigated. Shorter channel lengths increase the likelihood of bridging between source and drain electrodes and likelihood of percolation of the conductive lower-density networks so that even with stripping, the on/off ratio remains low; this effect is demonstrated by the low on/off ratios (< 100) of the shorter devices ($L < 20\ \mu\text{m}$). Also, our stripping is also somewhat limited by the resolution of contact photolithography although even smaller strip width is likely to increase tube-tube resistance and decrease on-current.

By etching SWNTs into strips, the metallic percolation pathways are reduced. The percolation of m-SWNTs depends on the individual m-SWNT length and tube density. For the unsorted SWNTs, there are around 21% m-SWNTs in the network but they are still the minor components. After stripping, the continuity of some metallic pathways is broken and the strip which has mixed paths of m- and s-SWNTs shows more predominant semiconducting behavior.

In this chapter 4, a facile method is reported to improve the on/off ratio and mobility of the FETs by stripping the networks of the DB71-sorted SWNTs. Most methods of sorting reported to date can achieve some degree of purification but cannot achieve high purity close to 98-99% needed for reproducible network devices.[210, 211] One method that can achieve high purity sorting is DGU method but the yield is low so that the price of sorted nanotubes is extremely high.[9] For the

first time, we demonstrate that the combination of inexpensive solution-based SWNT sorting and active channel patterning – stripping – can achieve high performance devices with good on/off ratio ($> 10^4$) and mobility (around $20 \text{ cm}^2/\text{V-s}$) that opens up the path for the large-scale application of such inexpensive solution-sorted nanotubes. Cao *et al.* have applied stripping on CVD grown nanotubes to improve FET on/off ratio.[13] Due the longer tube ($> 5 \text{ }\mu\text{m}$) and low tube-tube resistance of the networks of CVD growth SWNTs, it is easier to achieve switching; their strip width is $5 \text{ }\mu\text{m}$ to achieve on/off ratio of 10^5 and mobility of $80 \text{ cm}^2/\text{V-s}$, when the channel length is as long as $100 \text{ }\mu\text{m}$. For solution processed tubes, the tubes are relatively short (around $2 \text{ }\mu\text{m}$) and so if the strip width is even smaller than around $1 \text{ }\mu\text{m}$ or so, the tube-tube resistance becomes significant so that we cannot achieve as high mobility as with stripped CVD nanotubes. So, starting with shorter nanotubes, there is a limit with stripping. By combining stripping with solution-based sorting available via various reported high yield techniques, we can achieve high on/off ratio and mobility simultaneously.

The approach presented here, of device performance improvement through stripping, is relatively inexpensive compared with highly enriched s-SWNTs that would be required to produce similar switching ratio ($>10^4$) with high on-current ($>1 \text{ }\mu\text{A}$) in conventional geometry FETs. Firstly, the AR-SWNTs have larger mean diameter ($\sim 1.4 \text{ nm}$) than HiPCO SWNTs ($\sim 1.0 \text{ nm}$) and CoMoCAT SWNTs ($\sim 0.8 \text{ nm}$). In the FETs whose channel dimension is same, the on-current of the FET with arc-discharge SWNT networks is 5 times higher than the FET with HiPCO SWNT

networks and is 17 times higher than the one with CoMoCAT SWNT networks.[142]

So the arc-discharged SWNT FETs could support enough current to drive and control the OLED in the logic circuit, although the on/off ratio of 10^4 – 10^5 is relative lower.

Secondly, the cost of AR-SWNTs is lowest due to their easy and large-scale production. Finally, the DB71 sorting with DB71 is diameter depended. Our previous results show that DB71 combined with DGU, a combination technique, can produce 98% purity. However, with normal centrifugation, a lower purity of about 93% can be produced. We extend the normal centrifugation-DB71 technique to AP-SWNTs (Appendix A) instead of P2-SWNTs here as AP-SWNTs is about 1/8 the price of P2-SWNT (the purified grade from AP-SWNTs from Carbon Solutions). Also, the AP-SWNTs are statistically longer (1–5 μm) compared to P2-SWNTs (~ 1 μm) which will in general be more optimal to achieve lower network junction resistance but are generally thought to be more challenging to suspend in solution. Our novel combination approach of combining selective dispersion/normal centrifugation with stripping to SWNT-network-based FET fabrication should permit widespread applications of unsorted and DB71-sorted s-SWNTs in many applications which require good FET performance parameters.

4.4 Conclusion

We have fabricated FETs on SiO_2/Si and HfO_2/Si substrates using unsorted and DB71-sorted as-produced SWNTs. The FET active channels were stripped into narrow strips of varying widths (2 μm , 5 μm and 10 μm) to assess the utility of stripping to improve the performance of SWNT-network-based FETs. The stripping of

the active channel into narrow strips can increase the on/off ratio of SWNT-network-based FETs by orders of magnitude but the mobility remains somewhat low ($< 5 \text{ cm}^2/\text{V-s}$) and the channel length is long ($50 \text{ }\mu\text{m}$); the best device achieved with $2 \text{ }\mu\text{m}$ wide stripped unsorted SWNTs has on/off ratio, on-current and mobility of $1.65 \times 10^4 \pm 5.79 \times 10^3$, $3.9 \pm 1.28 \times 10^{-3} \text{ }\mu\text{A}/\mu\text{m}$ and $3.7 \pm 1.25 \text{ cm}^2/\text{V-s}$, respectively. By increasing the content of s-SWNTs from 79% to 88%, stripping can improve the device mobility to $15.8 \pm 2.92 \text{ cm}^2/\text{V-s}$ and decreased the channel length to $20 \text{ }\mu\text{m}$ while keeping the on/off ratio and on-current at $2.27 \times 10^4 \pm 7.45 \times 10^3$ and $10.9 \pm 1.85 \times 10^{-3} \text{ }\mu\text{A}/\mu\text{m}$. With 80 nm HfO_2 as dielectric layer, the on-current could reach $17.2 \pm 9.30 \times 10^{-2} \text{ }\mu\text{A}/\mu\text{m}$, while the on/off ratio is $8.16 \times 10^4 \pm 3.04 \times 10^4$ and mobility is $21.9 \pm 8.72 \text{ cm}^2/\text{V-s}$.

4.5 Declaration

Part of the work presented in this chapter was in submission.

Chapter 5 High Performance Partially Aligned Semiconducting Single Walled Carbon Nanotubes Transistors Achieved with a Parallel Technique

5.1 Introduction

In this chapter, a horizontal alignment technique is applied to improve the mobility of FETs with 99% enriched s-SWNT film as semiconductor in the FETs channel. CNTs are classic 1D materials and the anisotropic current carrying capacity can be exploited to achieve higher performance FETs in nanotube networks fabricated with a degree of alignment among the nanotubes. When most m-SWNTs are removed from s-SWNTs, the tube-tube resistance limits the performance of FETs. The alignment technique could effectively reduce the resistance of s-SWNT network along axis direction. Techniques for the alignment of carbon nanotubes have been reviewed in Section 2.2. The post-synthetic horizontal SWNT alignment techniques can be applied to FET devices and can generally be further classified as co-synthetic or post-synthetic techniques. Post-synthetic alignment techniques which include shear force alignment, micro-fluidic assembly, electric-/magnetic-field alignment, blow bubble film, Langmuir-Blodgett self-assembly could be applied after s-SWNTs enrichment.[20-22, 212] For FET application, the nanotubes network needs to have controllable density with minimal contamination and these properties are not easily achieved. Partial alignment of the SWNTs effectively minimizes contacts in the network while maximizing the network continuity and current. Thus far, there is no

report on a suitable technique for parallel assembly of sorted nanotubes to achieve partial alignment and controllable nanotube density for optimum FET performance.

In Chapter 4, the conductive film of unsorted and DB71 sorted SWNTs could be converted into semiconducting strips by lithography process. In this method, the thin, uniform SWNT film plays a key role in the conversion of electronic property. Due to the minor content of m-SWNTs in raw production, the fabrication of parallel aligned segments from uniform SWNT film could effectively break the electron transport pathways which are formed by m-SWNTs. When the m-SWNTs are eliminated, some semiconducting ones are also broken at the same time. Therefore the on/off ratio of the FET has a significantly increasing from 10 to 10^4 ; the highest mobility is only $21.9 \pm 8.76 \text{ cm}^2/\text{V-s}$ which is made on HfO_2/Si wafer at certain channel dimension. If the SWNTs are highly enriched, there is no need to sacrifice any SWNTs in device channel.

In this chapter, we present an immersion-*cum*-shake method for partial alignment of s-SWNTs (99% enriched) by immersion of APTES treated wafer in nanotube solution on a rotary shaker. The repetitive oriented flow of nanotube solution over the SiO_2/Si wafer surface promotes partial alignment of the nanotubes after they attach on the wafer surface. By controlling the nanotube aqueous concentration, the linear density of the SWNT network deposited on the wafer surface is readily controllable with linear densities varying from ~ 5 to $\sim 45 \text{ SWNTs}/\mu\text{m}$ produced in the networks reported here. The alignment of the nanotubes was characterized by atomic force microscopy (AFM) and polarized Raman spectroscopy. FETs with varying channel

lengths of 2 μm , 5 μm , 10 μm , 20 μm and 50 μm (with fixed channel width (W) of 10 μm) were fabricated over the partially aligned *s*-SWNT network and their on/off ratio and mobility metrics were measured. The SWNTs outside the channel regions were removed by O_2 plasma. The transistor device performance metrics vary significantly with deposited linear SWNT density and channel length. The devices with the optimal combination of fabrication parameters show excellent performance with mobility of $46.5 \text{ cm}^2/\text{V}\cdot\text{s}$ and on/off ratio of 3.2×10^4 .

5.2 Experiment section

Materials

The SWNT solution (99% pure *s*-SWNTs aqueous dispersion with 1 % sodium dodecyl sulfate (SDS) surfactant) was supplied by NanoIntegris, Inc. CNT concentration in the original solution is 1%. The 99% (3-aminopropyl)triethoxysilane (APTES) was purchased from Sigma-Aldrich. The SiO_2 wafer (*p*-type, 4" diameter with 500 nm $\pm 5\%$ thick oxide as dielectric layer) was purchased from Bonda Technology Pte Ltd.

Nanotube Alignment Procedure and FET fabrication

Prior to use in the alignment experiments, the original CNT solution was diluted to 0.5%, 0.2%, 0.1% and 0.05% using 1% SDS aqueous solution (see Table 5.1). The different CNT concentrated solutions were sonicated by probe sonicator (Vibra-Cell CVX130) at 91 W for 10 min before use. The SiO_2 wafer was cut into $20 \times 20 \text{ mm}^2$ pieces and immersed in Piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ 3:1) for 2 h, rinsed with DI water and dried under nitrogen gas. The substrates were then treated with 0.5%

(3-aminopropyl)triethoxysilane solution in isopropanol for 2 h. After self-assembly, the substrates were rinsed with isopropanol to remove the residual APTES, dried under nitrogen gas and baked at 100 °C on a hot plate for 30 min. Solution-based alignment of s-SWNTs on the substrates were performed with a Certomat® rotary shaker which was purchased from Sartorius. The amino functionalized silicon substrates were attached at the periphery of a glass crystallizing dish (diameter, $\Phi = 12$ cm) bottom and the substrates with 25 mL solution were shaken at 120 rpm for 36 hours to align the SWNTs. After shaking, the substrates were baked vertically in an oven at 60 °C for 2 min to prevent coffee ring effect. After drying, the substrate surface was rinsed with DI water to remove the surfactant. The substrates with aligned SWNT networks were annealed at 200 °C in vacuum (3.35×10^{-5} mbar) for 2 hours. Then 5 nm Ti and 45 nm Au layers were deposited on the partially aligned *semi*-conductive carbon nanotubes film, after which an electrodes pattern (with channel lengths of 2 μm , 5 μm , 10 μm , 20 μm and 50 μm) was fabricated on the deposited metal layer by photolithography. The unprotected gold layer was removed with standard gold etchant (Sigma-Aldrich) and the uncovered Ti layer was removed with 0.8 % HF solution. Then a protective device isolation pattern was lithographically fabricated on the channel region of each pair of electrodes. After development and drying, the nanotubes outside the FET channels were removed with oxygen plasma (100 W, 2 min).

Table 5.1 FET fabrication parameters: SWNT suspension and channel gap length

		s-SWNT density of suspension [mg/mL]				
		0.05 %	0.1 %	0.2 %	0.5 %	1 %
Gap Length of FET [μm]		1	2	3	4	5
2	a	(1,a)	(2,a)	(3,a)	(4,a)	(5,a)
5	b	(1,b)	(2,b)	(3,b)	(4,b)	(5,b)
10	c	(1,c)	(2,c)	(3,a)	(4,c)	(5,c)
20	d	(1,d)	(2,d)	(3,d)	(4,d)	(5,d)
50	e	(1,e)	(2,e)	(3,e)	(4,e)	(5,e)

Sample Characterization

The linear SWNT density on the device channel was measured with a MFP3D AFM microscope under tapping mode. Raman spectra was measured using a Renishaw Raman microscope with a 0.45 mW He-Ne laser operated at 785 nm and the spot size of around $20 \times 20 \mu\text{m}^2$. A fixed polarizer was used to polarize the laser light, and the Raman spectra were taken by rotating the substrate with aligned SWNT network at a $\sim 22^\circ$ rotation interval. The integration time was 15s in a single scan. Electrical performance of the fabricated devices with different nanotube densities and channel lengths were measured at room temperature in back-gated FET configuration using a Keithley semiconductor parameter analyzer Model 4200-SCS. All devices were tested at $V_d = 0.5 \text{ V}$. Device mobility was computed using the standard equation (5.1):

$$\mu = \frac{L}{WC_i V_d} \cdot \frac{dI_d}{dV_g} \quad (5.1)$$

Where dI_d/dV_g is the transconductance extracted from the slope of the backward transfer curve (from -20 V to 20 V), L is the channel length, W is the channel width,

and C_i is the specific capacitance per unit area of the active channel. C_i is given by equation (5.2):

$$C_i = \frac{D}{C_Q^{-1} + \left(\frac{1}{2\pi\epsilon_0\epsilon}\right) \ln\left[\sinh\left(\frac{2\pi t_{ox} D}{\pi D r}\right)\right]} \quad (5.2)$$

Where $C_Q = 4 \times 10^{-10}$ F/m, the nanotube quantum capacitance, $t_{ox} = 500$ nm, the thickness of the oxide layer, $\epsilon = 3.9$, the dielectric constant of silicon dioxide, $\epsilon_0 = 8.85 \times 10^{-12}$ F/m, the permittivity in the free space and $r = 0.7$ nm is the average radius of the nanotubes, D is the SWNT linear density on the channel of FETs (which is the reciprocal of tube-tube separation).[195]

5.3 Results and Discussion

Figure 5.1 B shows details of the alignment procedure. The SWNT aqueous dispersion used contains 1% sodium dodecyl sulfate (SDS) surfactant. The hydrophobic alkyl chain of SDS adsorbs onto the SWNT surface by van der Waals interaction and the hydrophilic SO_4^{2-} end orients towards the aqueous phase.[213-215] When the SiO_2/Si wafer is immersed in the SWNT solution, the SWNTs settle onto the amine-functionalized wafer surface. After an SWNT partially anchors to the wafer surface, it is oriented by the shear force caused by the circumferential fluid motion in the glass dish and eventually attaches to the wafer at multiple points along its length.[216] The first SWNTs to deposit and align do so on pristine wafer surface; these early-deposited SWNTs in turn attach and align the subsequently deposited SWNTs, since SWNTs strongly interact with each other via π - π stacking. Nanotubes which attach at more than one point along their length before becoming well aligned will be less readily aligned by the fluid flow; this is likely to occur more frequently

for later-deposited SWNTs since they encounter a complex “terrain” of previously deposited SWNTs with which they may strongly interact. As this process proceeds, a partially-aligned SWNT film is built up on the wafer surface.

Figure 5.1 Schematic depiction of the SWNT alignment procedure using *immersion-cum-shake* method (A) overall SWNT alignment process survey. (B) micro-details of the 3rd step.

Figure 5.2 (A-E) shows Atomic Force Microscopy (AFM) images ($20 \times 20 \mu\text{m}^2$) and orientation angle histograms of aligned SWNTs with different densities resulting from different solution concentrations.

Figure 5.2 The AFM images of partially aligned networks. AFM images ($20 \times 20 \mu\text{m}^2$, z-scale is $\pm 20 \text{ nm}$) of aligned SWNTs with CNT concentrations described in Table 6.1; FWHM is from the Gaussian fit to the orientation histograms. (A) 0.05% CNT (0-5 SWNTs/ μm); (B) 0.1% CNT (5-15 SWNTs/ μm); (C) 0.2% CNT (15-25 SWNTs/ μm); (D) 0.5% CNT (25-35 SWNTs/ μm); (E) 1.0% CNT (35-45 SWNTs/ μm).

The AFM images show that the nanotubes are partially aligned. The orientation distributions of the nanotubes are approximately Gaussian in shape and the low and intermediate density films have quite tight angular distributions, with fitted Full Width at Half Maximums (FWHMs) less than 15° . The highest density film has a wider but still reasonably aligned orientation, with FWHM $\sim 35^\circ$. It appears that angular distribution tends to increase with increasing deposited SWNT density as the aminosilane surface gets depleted. Also, with increase in SWNT density, more residuals are present in the network leading to larger scatter in the alignment orientation. After the alignment process and DI water cleaning and drying, the substrates with aligned SWNT network were thermally annealed to reduce the amount of residuals. However, it is difficult to completely remove all the surfactants. AFM images of the channel regions confirm that the nanotubes are aligned in the source-drain direction (Figure 5.3).

Figure 5.3 AFM images of aligned SWNTs in FET channels of length (A) 2 μm , (B) 5 μm , (C) 10 μm , (D) 20 μm and (E) 50 μm . (Others are put into Appendix.)

Figure 5.4 (A) shows the polarized Raman spectra of the aligned SWNT networks.

The intensity of the G band increases as the angle between the laser polarization direction and aligned nanotube direction varies from 0° to 90° . The variation of the G band intensity with angle corroborates that the SWNTs are oriented. Figure 6.4 (B) shows AFM images of the SWNTs aligned on different positions of the wafer ($20 \times 20 \text{ mm}^2$) using the 1.0% s-SWNT solution. At various positions on the wafer, the SWNT network is uniformly aligned mostly along the fluid flow direction.

Figure 5.4 (A) Raman spectra of the G-line of partially aligned s-SWNT networks measured at different angles (ϕ) between the laser polarization and alignment direction. The linear SWNT density of this sample is 5~15 SWNTs/ μm . (B) AFM images of SWNT alignment at different wafer surface positions using 1.0% CNTs.

Figure 5.5 (A-E) show the typical transfer characteristics (drain current versus gate voltage, I_d - V_g) of FETs with varying channel lengths (of $L = 2 \mu\text{m}$, $5 \mu\text{m}$, $10 \mu\text{m}$, $20 \mu\text{m}$ and $50 \mu\text{m}$) and nanotube densities (5-15 SWNTs/ μm to 35-45 SWNTs/ μm) at the fixed channel width (W) of $10 \mu\text{m}$. These devices were tested under 0.5 V drain voltage and the gate voltage was swept from 20 V to -20 V (forward). All the devices show *p*-type semiconducting behavior with on/off ratio in the range ~ 10 to $\sim 10^5$. For a particular channel length, as the SWNT density decreases, the network becomes more switchable as demonstrated by the increasing on/off ratio, although the conductance is sacrificed at the same time. For example, in the $20 \mu\text{m}$ channel length devices (Figure

5.5 (D)), as the areal density decreased from ultra-high (35-45 SWNTs/ μm) to low linear density (5-15 SWNTs/ μm), the on/off ratio of the device increased from ~ 10 to $\sim 10^4$ but the on-current decreased from $1.8 \mu\text{A}/\mu\text{m}$ to $6.5 \times 10^{-3} \mu\text{A}/\mu\text{m}$. The devices with other channel lengths (Figure 4A-E) show similar trends. Figure 5.5 (F) shows the corresponding typical output characteristic (I_d - V_d) of a representative device ($L=50 \mu\text{m}$, 25~35 SWNTs/ μm) with V_g ranging from -20 V to 20 V in 5 V steps. At low drain voltage ($-0.2 \text{ V} < V_d < 0.2 \text{ V}$), the linear curve indicates ohmic contact between SWNTs and source and drain electrodes.

Figure 5.5 Transfer characterization (I_d - V_g) of the aligned SWNT FETs with channel width (W) of 10 μm and channel lengths (L) of (A) 2 μm , (B) 5 μm , (C) 10 μm , (D) 20 μm and (E) 50 μm ; (F) the output (I_d - V_d) characteristics of the FET (L = 50 μm and W = 10 μm , 25~35 SWNTs/ μm) in triode region

Figure 5.6 and Table 6.2 summarize the variation of the normalized on- and off-current density, mobility and on/off ratio for different SWNT density devices with different channel length and fixed channel width (W = 10 μm). Each data point represents measurements of fifteen FETs. (In Figures 5.6 (B) and (D), the dotted lines

indicate that the measured values do not represent the true device performance because the current is at or below the detection limit of the measuring instrument.) Figure 5.6 (A) shows the variation of average on-current density (I_{on}/W) with channel length of the devices tested at $V_d = 0.5$ V and $V_g = -20$ V. Short channel ($L < 10\mu m$) devices exhibit a rapid decline in on-current density as the channel length increases. When channel length is larger than $10\mu m$, the current density decreases gradually. As reported by Kumar *et al.*, for non-ohmic transport simulation, the conductance of the film changes more rapidly with channel length for small channel devices.^[217] Also, at a fixed channel length, the on-current increase with SWNT density shows that the linear SWNT density is well controlled by this flow induced alignment method. The variation of average off-current density (I_{off}/W) with channel length is shown in Figure 5.6 (B). The off-current decreases exponentially with the reduction of SWNT density at each fixed channel length. Also, we found that the off-current decreases with increase in channel length at fixed SWNT density. The off-current decreases more rapidly with channel length than the on-current does. The m-SWNT species constitute approximately 1% of the nanotube samples. The on-current is due largely to the almost continuous semiconducting network. The off-current is due to the percolating m-SWNTs and consequently is more sensitive than the on-current to network density variations along the channel length.

Figure 5.6 Property correlations of FETs with different SWNT densities and channel length (L). A) Average current density (I_{on}/W) versus channel length (L). B) Average off-current density (I_{off}/W) versus channel length (L). C) Average devices mobility (μ) versus channel length (L). D) Average on/off ratio (I_{on}/I_{off}) versus channel length. (Dotted lines show the measured values which are lower than what they should be because the detection limit of the machine is reached.)

Figures 5.6 (C) and 5.6 (D) show respectively the variation of mobility (μ) and the on/off ratio with channel length. Figure 5.6 (C) shows that regardless of network density, the mobility varies more slowly with channel length at high channel length ($> 10 \mu\text{m}$) than at low channel length. For the small channel lengths of $2 \mu\text{m}$ to $10 \mu\text{m}$, the mobility increases in general with channel length, except for the ultra-high density (black line) network. Also, the mobility increases with linear SWNT density. High mobility (shaded in Figure 5.6 (C)) is desirable in transistors, but for applications in many practical electronic circuits, the minimum requirement of on/off ratio is at least 10^4 (this region is shaded in Figure 5.6 (D)). Figure 5.6 (D) shows that the variation of

on/off ratio with SWNT density depends on both the linear SWNT density and the channel length. For 2 μm channel length, none of the devices tested can satisfy the switching requirement. For the devices with 10 μm channel length, the low density network (5~15 SWNTs/ μm) could fulfill the on/off ratio requirement. For the 20 μm channel length devices, the network with low and medium network densities (5~15 SWNTs/ μm and 15~25 SWNTs/ μm) could fulfill the switching requirement. Finally for the 50 μm channel length, the medium, high network and ultra-high densities (15~25 SWNTs/ μm , 25~35 SWNTs/ μm and 35~45 SWNTs/ μm) could fulfill that. The standard deviation of the mobility and on/off ratio (about 30%, see Table 5.2) corroborates that our alignment technique is robust and reproducible.

Table 5.2 Average value of FET's mobility, on/off ratio and on-current

		Linear SWNT Density			
	Gap Length [μm]	35-45 [tubes/ μm]	25-35 [tubes/ μm]	15-25 [tubes/ μm]	5-15 [tubes/ μm]
I_{on}/W [$\mu\text{A}/\mu\text{m}$]	2	5.72 $\pm$ 36.5%(10)	0.788 $\pm$ 26.6%(15)	0.182 $\pm$ 34.6%(15)	0.0574 $\pm$ 44.8%(15)
	5	4.30 $\pm$ 27.9%(10)	0.529 $\pm$ 24.6%(15)	0.126 $\pm$ 25.4%(15)	0.0482 $\pm$ 47.7%(15)
	10	2.01 $\pm$ 35.8%(10)	0.251 $\pm$ 32.6%(15)	0.12 $\pm$ 38.3%(15)	0.0294 $\pm$ 54.1%(15)
	20	1.13 $\pm$ 25.6%(10)	0.167 $\pm$ 26.3%(15)	0.0312 $\pm$ 26.9%(15)	0.00617 $\pm$ 42.8%(15)
	50	0.18 $\pm$ 32.2%(10)	0.0524 $\pm$ 30.5%(15)	0.00645 $\pm$ 31.0%(15)	0.00058 $\pm$ 44.8%(15)
On/Off ratio	2	2.73 $\pm$ 26.0%(10)	5.96 $\pm$ 32.9%(15)	53.36 $\pm$ 50.2%(15)	4421.83 $\pm$ 68.3%(15)
	5	5.09 $\pm$ 20.4%(10)	30.47 $\pm$ 32.3%(15)	104.38 $\pm$ 38.6%(15)	6086.28 $\pm$ 49.4%(15)
	10	36.55 $\pm$ 24.8%(10)	140.53 $\pm$ 30.5%(15)	1166.6 $\pm$ 44.0%(15)	29820.3 $\pm$ 55.3%(15)
	20	177.63 $\pm$ 24.0%(10)	6086.28 $\pm$ 49.1%(15)	84175.8 $\pm$ 35.7%(15)	32500 $\pm$ 32.1%(15)
	50	32,250 $\pm$ 30.9%(10)	410,330.6 $\pm$ 44.3%(15)	16,463.7 $\pm$ 46.5%(15)	2542.86 $\pm$ 62.3%(15)
Mobility [$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$]	2	209.4 $\pm$ 18.3%(10)	10.8 $\pm$ 30.7%(15)	2.9 $\pm$ 31.4%(15)	1.6 $\pm$ 58.8%(15)
	5	128.6 $\pm$ 29.9%(10)	20.5 $\pm$ 27.2%(15)	3.8 $\pm$ 27.9%(15)	2.9 $\pm$ 45.5%(15)
	10	62.6 $\pm$ 28.2%(10)	22.6 $\pm$ 33.0%(15)	5 $\pm$ 39.4%(15)	1.9 $\pm$ 60.0%(15)
	20	57.4 $\pm$ 27.5%(10)	20.8 $\pm$ 25.7%(15)	4.8 $\pm$ 38.3%(15)	1.7 $\pm$ 57.6%(15)
	50	46.5 $\pm$ 27.6%(10)	24.7 $\pm$ 27.0%(15)	7.8 $\pm$ 36.2%(15)	1.2 $\pm$ 75.0%(15)
mobility/ tube [$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ /tube]	2	5.235 $\pm$ 18.3%(10)	0.360 $\pm$ 30.7%(15)	0.145 $\pm$ 31.4%(15)	0.16 $\pm$ 58.8%(15)
	5	3.215 $\pm$ 29.9%(10)	0.667 $\pm$ 27.2%(15)	0.19 $\pm$ 27.9%(15)	0.29 $\pm$ 45.5%(15)
	10	1.565 $\pm$ 28.2%(10)	0.753 $\pm$ 33.0%(15)	0.25 $\pm$ 39.4%(15)	0.19 $\pm$ 60.0%(15)
	20	1.435 $\pm$ 27.5%(10)	0.693 $\pm$ 25.7%(15)	0.24 $\pm$ 38.3%(15)	0.17 $\pm$ 57.6%(15)
	50	1.1625 $\pm$ 27.6%(10)	0.823 $\pm$ 27.0%(15)	0.39 $\pm$ 36.2%(15)	0.12 $\pm$ 75.0%(15)

The variation of the mobility with channel length and network linear density (Figure 5.6 (C)) for the partially aligned *s*-SWNT networks can be explained in terms of the percolating network and the contributions of the various resistances. When the channel length is longer than the nanotube length, the resistance of the partially aligned network is $R_{\text{total}} = R_{\text{cnt-cnt}} + R_{\text{intrinsic-cnt}} + R_{\text{cnt-metal}}$, where $R_{\text{cnt-cnt}}$ is the sum of SWNT contact resistance, $R_{\text{intrinsic-cnt}}$ is the sum of intrinsic resistance of the SWNTs themselves on the device channel and the $R_{\text{cnt-metal}}$ is the sum of the contact resistance

between metal electrodes and the SWNTs.[218] From Figure 5.6 (C), when the linear SWNT density is generally low to high (from 5 to 35 SWNTs/ μm), the mobility increases with channel length at lower channel length range ($L < 10\mu\text{m}$) since small channel length implies that the electrode/nanotube resistance is significant. As L increases, the effect of electrode/nanotube resistance becomes negligible so that mobility rises. With ultrahigh linear SWNT density (black line, Figure 5.6 (C)), the tube-tube resistance becomes significant instead, and larger L indicates higher tube-tube resistance so that mobility decreases with increasing L .

The variation of on/off ratio with channel length (Figure 5.6 (D)) can be explained by the presence of small (but not zero) amounts of m-SWNTs. For the $2\mu\text{m}$ long channel length devices, the on/off ratio increases monotonically with linear SWNT density reduction. The length range of the *s*-enriched SWNTs is $0.1\text{-}4\mu\text{m}$ and the mean length is $\sim 1\mu\text{m}$ (from Carbon Nanotube Technical Data Sheet, NanoIntegris). The individual m-SWNTs which have excellent on-current density of $\sim 4 \times 10^9\text{ A/cm}^2$ are not field-effect switchable and the on/off ratio of the device is usually lower than 10.^[1] The $2\mu\text{m}$ channel length devices have channels short enough that some of the m-SWNTs (1% of the SWNT content) can bridge the Source and Drain electrodes. At high linear SWNT density ($> 15\text{ SWNTs}/\mu\text{m}$, or 150 SWNTs across the width of the channel), there will usually be one or more m-SWNTs bridging the electrodes, with consequent low on/off ratio ($< 10^2$). As the linear SWNT density declines, the sample average on/off ratio increases. When the density reaches about $5\text{-}15\text{ SWNTs}/\mu\text{m}$, the on/off ratio of the FETs is $\sim 10^3$. At lower linear SWNT

density, the probability that a m-SWNT directly bridges the source and drain decreases and the off-current (population average) is correspondingly lower. As the channel length becomes larger ($L \geq 10 \mu\text{m}$) than the m-SWNT length, electron transport in the channel is by percolation through the network rather than by direct bridging. Longer channel lengths reduce the chance of m-SWNTs forming a percolating path so that on/off ratio increases with channel length.

The variation of on/off ratio with network density (Figure 5.6 (D)) is further illuminated by the observations of Fuhrer *et al.* who tested the resistances of individual SWNT junctions.^[54] The metallic/metallic and the semi/semi junctions have good tunnel contacts; the resistance of metallic/metallic junction is only $5-10h/e^2$.^[219] The resistance between semi-/s-SWNTs is also small. But the metallic/semi junctions function as *p*-type Schottky diodes. With varying chiralities, the Schottky barriers also depend differently on the gate bias. In high density network (or with shorter L), we have a higher density of Schottky barrier and so lower on/off ratios. The high density network needs a higher negative gate voltage to turn on all the Schottky diodes; with a fixed negative gate voltage, not all the metallic/semi junctions will be turned on. Figure 5.7 (A) shows that the on-current density varies with $1/L$. For the partially aligned network density which is from 5 SWNTs/ μm to 45 SWNTs/ μm , the shape of the curve shows nonohmic conduction. This is the same as the simulation results which are reported by Kumar Murthy.^[217] The decline of the on-current is steeper for sparser than for denser networks, but are generally close to $1/L$, with a little curvature. In the Kumar *et al.* paper, a doubling of the areal density

produces about a 4-fold increase in current.[217] Our dependence of on-current on areal density is much stronger than that of the simulations. From our experiments, an about 40% increase in areal density produces 10-fold increase in current. The alignment effectively reduces the tube-tube contact points of which the resistance is much higher than it of the SWNTs self during unit channel length. The rapid increasing of the on-current/tube corresponds that the partially aligned *semi*-SWNT network serves a percolative material.

Figure 5.7 Channel length and network density dependence of FET properties. (A) Average on-current density (I_{on}/W) versus channel length (L). (B) Average on-current/tube ($I_{on}/tube$) versus $1/L$. (C) Average off-current/tube ($I_{off}/tube$) versus channel length (L). (D) Average device mobility/tube ($\mu/tube$) versus channel length (L). (E) Average device on-current/tube ($I_{on}/tube$) versus channel length (L)

The best properties were found in the longest channel devices ($L = 50 \mu\text{m}$) with the higher SWNT densities: either device 1) (25-35 SWNTs/ μm) with on/off ratio $\sim 4 \times 10^5$ and mobility of $24.7 \text{ cm}^2/\text{V-s}$, or device 2) (35-45 SWNTs/ μm) with on/off ratio $\sim 3.2 \times 10^4$ and mobility of $46.5 \text{ cm}^2/\text{V-s}$. Our partially aligned nanotubes devices are superior to other aligned nanotubes devices. LeMieux *et al.* have reported the performance of devices with aligned semiconducting enriched SWNTs prepared on modified SiO_2/Si wafer surface.[153] The SWNTs were oriented by fluidic forces during high speed spin coating. The average on/off ratio of the aligned SWNT network TFTs was greater than 10^5 but the average mobility of the devices was $2 \text{ cm}^2/\text{V-s}$. Engel *et al.* fabricated SWNT-TFTs using 99% s-SWNTs aligned on the substrate with a water evaporation driven self-assembly method.[220] The on/off ratio of the devices could reach 10^4 and the corresponding mobility was $10 \text{ cm}^2/\text{V-s}$. However, the width and the SWNT density of the self-assembly SWNT networks are hard to control.

Pimparkar *et al.* predicted that partial alignment results in better network current-carrying capacity than either random orientation or near-perfect parallel alignment.[221] The on-current would increase by around 20%-40% (above that of a randomly network) for an optimally partially aligned network with long-channel devices (channel length is larger than the nanotube length). Kocabas *et al.* used the stick-percolation model to study the characteristic of anisotropic networks which are partially aligned.[222] From the stick-percolation model, the partially aligned networks could carry more current than perfectly or non-aligned networks, when the

channel length is longer than the tube length. The higher mobility of our devices, compared to other aligned nanotube networks, can be explained in terms of fewer tube-tube contacts within the contiguous network. The alignment affects the R_{total} of the SWNT network by reducing the number of tube-tube contacts along the electron transport path between the source and drain electrodes, which improves the on-current and device mobility. After alignment, the SWNTs are oriented somewhat parallel along the source to drain electrodes direction. The reduction of the tube-tube contacts numbers effectively decreases the $R_{\text{cnt-cnt}}$. Our method results in consistent partial alignment as shown by AFM and polarized Raman spectroscopy and superior performance. This is the first report of partial alignment with sorted nanotubes to produce superior FETs. Various groups have previously shown that micro-fluidic assembly and electric field could fabricate partially aligned networks but have not demonstrated device applications using the resulting networks.[223-226]

Our ultrahigh linear SWNT density (35~45 SWNTs/ μm) deposited in shorter channels (2 μm) exhibit high normalized on-current of 5.72 $\mu\text{A}/\mu\text{m}$ and mobility of 209.4 $\text{cm}^2/\text{V-s}$ but with the low on/off ratio of 2.7. Based on the 2-D stick model, the percolation density should be $N = \frac{1}{\pi} \left(\frac{4.236}{l} \right)^2$ where l is the average tube length. [227] The average length of these s-SWNTs (99%) is 1 μm . To form a conductive percolation pathway with m-SWNTs (1%), the total tube density should be around 570 SWNTs/ μm^2 . Obviously, our tube density could not reach this value. But this equation works only when the channel length of FETs should be much large then the tube length. If the channel length of the FET is only 2 μm , the 1% m-SWNTs could

also form a conductive percolation pathway between the two electrodes, when the tube concentration is too high (35~45 SWNTs/ μm). The $\sim 1\ \mu\text{m}$ m-SWNTs have a large probability to meet and form a conductive pathway, when the channel length is only $2\ \mu\text{m}$. Therefore, the off-current increased sharply and the on/off ratio was very small. The on/off ratio of the FETs is small. The results also confirm the importance of s-SWNT purity for fabrication of the SWNT-based FETs with uniform and good performance in a large scale. After partial alignment, the SWNT network has lower tube-tube contacts between source and drain electrodes than a random network would have. The decreased tube-tube junction decreases the contribution to the resistance per unit channel length of the network. Many of the superior (randomly aligned) devices reported by other groups have been made with more effective dielectrics such as HfO_2 or Al_2O_3 which are usually vacuum deposited and may not be feasible for printed devices.[228, 229] Wang *et al.* used $50\ \text{nm}$ SiO_2 as the dielectric and achieved performance similar to ours here: mobility of about $30\ \text{cm}^2/\text{V}\cdot\text{s}$ and on/off ratio of 10^5 with same channel length, $L = 50\ \mu\text{m}$, and similar nanotube purity (98% semiconducting enriched).[230] We have also previously used HfO_2 (dielectric constant = 12 compared to 3.9 for SiO_2 here) and achieved similar device performance.[231] It appears that partial alignment can improve device performance, to a degree comparable to that achieved by use of a superior dielectric. Solution processable dielectric materials *e.g.* cross-linked polyvinylphenol and poly(styrene-block-ethylene oxide-block-styrene) have been applied in printed device fabrications.[232-234] However, these dielectrics may not be as effective as

vacuum-deposited HfO_2 and partial alignment reported here offers another route towards achieving high performance FETs. Our alignment process can be accelerated by increasing the temperature of the deposition (Figure 5.8). Possibly, increase in the amine concentration through use of self-assembled monolayers may also accelerate the deposition process.

Figure 5.8 AFM images of SWNT networks formed with different solution temperatures and shaking time. The concentration of SWNT solution is 0.5%. The yellow arrow indicates the aligned direction of SWNT networka. A) 20 °C solution and 6, 12 and 24 h deposition/shaking. B) 40 °C solution and 6, 12 and 24 h deposition/shaking.

The technique reported here is one of a few methods that can produce partially aligned nanotubes with controllable SWNT density, both of which are important in nanotube electronics. Our method employs immersion with a gentle oriented fluid motion (120 rpm shaking) and the nanotubes are slowly partially aligned on the APTES-pretreated surface with controllable SWNT density.

5.4 Conclusions

We have successfully produced partially aligned SWNT thin films on silicon wafers (with 500 nm thick SiO_2 as gate dielectric) using a novel parallel

solution-based immersion-*cum*-shake method. With suitable choice of linear SWNT density and channel length, superior FET devices with on/off ratio of $\sim 3.2 \times 10^4$ or higher and mobility of $46.5 \text{ cm}^2/\text{V-s}$ or higher were achieved. The directional fluid flow provided by rotary shaking of the SWNT solution partially aligns the SWNTs as they settle onto and attach to the substrate. AFM images show that the nanotubes are aligned mostly along the fluid flow direction but with an angular distribution of FWHM of about 15 degrees (or at most 35 degrees for the densest films). The partial alignment is corroborated by polarized Raman spectroscopy. AFM images at multiple locations over a wafer region ($20 \times 20 \text{ mm}^2$) confirm that the alignment is uniform. This parallel method provides a facile way of depositing partially aligned nanotubes with controllable density for enhanced FET performance and wide-scale and/or large area applications. Partial alignment has the effect of reducing tube-tube contacts while preserving percolation as expected from first principles - to maximize on-current.

5.5 Declaration

Part of the work presented in this chapter has been published in the *Small*.

Wang, Y., S.K.R. Pillai, and M.B. Chan-Park, High-Performance Partially Aligned Semiconducting Single Walled Carbon Nanotube Transistors Achieved with a Parallel Technique. **Small**, 2013. 9(17): p. 2960-2969.

Chapter 6 Conclusions and Recommendations

6.1 Conclusions

In this thesis, two different methods were designed to form different kinds of the morphologies of the SWNT networks to improve the performance of SWNT-FETs. Stripping was exploited to convert metallic-percolated SWNT networks into semiconducting strips and it increased the on/off ratio of FETs successfully. The influences of the SWNT purity, the dielectric layers, the tube density in the SWNT networks and the dimension of the electrode and strip patterns were studied. We also showed that with partial alignment of ultra-pure (99%) s-SWNTs, the electron transport of the resulting FETs was increased. The relationship between the channel dimension, the tube density and the mobility, the on/off ratio was elaborative studied.

Firstly, we demonstrated that the optimization of the stripping widths and the FET channel dimensions could convert the non-switchable networks (defined as having low on/off ratios of $<10^2$) made of unsorted or DB71-sorted AP-SWNTs to highly switchable networks (with on/off ratios $> 10^4$). The SWNT networks were fabricated on both the SiO₂/Si wafers and the HfO₂/Si wafers and then they were stripped into different narrow strips of 2 μm , 5 μm and 10 μm . The stripping of the networks into the narrow strips can increase the on/off ratio of the SWNT-network-based FETs by orders of magnitude (up to $\sim 10^4$). With stripping of unsorted AP-SWNTs ($\sim 79\%$ semiconducting), the FETs had the on/off ratio of $1.65 \pm 0.579 \times 10^4$, but got relatively poor mobility and on-current of $3.7 \pm 1.25 \text{ cm}^2/\text{V}\cdot\text{s}$ and $3.9 \pm 1.28 \times 10^{-3} \mu\text{A}/\mu\text{m}$ respectively. By stripping DB71-sorted s-SWNTs ($\sim 88\%$),

with similar on/off ratio ($> 10^4$), the respective mobility and on-current increased to $15.8 \pm 2.92 \text{ cm}^2/\text{V-s}$ and $10.9 \pm 1.85 \times 10^{-3} \text{ }\mu\text{A}/\mu\text{m}$ respectively. Further, the channel of the switchable FETs decreased from $50 \text{ }\mu\text{m}$ (AP-SWNTs) to $20 \text{ }\mu\text{m}$ (DB71-sorted SWNTs). Further, with the 80 nm dielectric layer of HfO_2 whose dielectric constant was much higher than the one of SiO_2 , the mobility and on-current increased to $21.9 \pm 8.72 \text{ cm}^2/\text{V-s}$ and $17.2 \pm 9.30 \times 10^{-2} \text{ }\mu\text{A}/\mu\text{m}$ respectively, where the on/off ratio was still above 10^4 . This combination method made it feasible to fabricate good performance SWNT-network-based FETs without ultra-pure s-SWNTs.

Finally, a solution-based immersion-*cum*-shake technique to produced partially aligned SWNT thin films on silicon wafers with 500 nm thick SiO_2 dielectric layer using the highly pure s-SWNTs (99%) was reported. The on/off ratio and mobility of the superior FETs could reach $\sim 3.2 \times 10^4$ and of $46.5 \text{ cm}^2/\text{V-s}$. After attachment to the substrate, the SWNTs were partially oriented by the directional fluid flow provided by rotary shaking of the SWNT solution. The angular distribution of FWHM ranged from 15 degrees to 35 degrees and alignment of SWNTs were mostly along the fluid flow direction, which was shown in AFM images. The partial alignment was corroborated by the polarized Raman spectroscopy. This parallel method provided a facile way to deposit partially aligned nanotubes with controllable density for enhancement of the FET performance on a large scale. The partial alignment had the effect of reducing tube-tube contacts and finally maximized the on-current of the FETs.

6.2 Recommendations for future work

From the observation of SWNTs, many works have carried out to apply the

SWNTs into the logic circuits because of their bullet transport and small diameter as introduced above. The SWNTs based logic circuits could definitely bring a revolution in the electronic industry. From lab to factory, there are still some hurdles, including the low yield of highly pure s-SWNTs after separation, large diversity of FETs' outputs on wafer scale and high tube-tube and tube metal resistance. These problems limits the experiment results become the revolutionary power to change the electronic industry.

However, there are still some ways to overcome these difficulties. To achieve highly pure s-SWNTs, the synthesis of SWNTs in a single chirality is the perfect way. Until now, no SWNTs with a single chirality could be massively synthesized by adjustment of the catalysts, the growth temperature and the carbon sources. The SWNTs of certain chirality could only be enriched after synthesis. DGU is an effective method to sort SWNTs by the electronic property, the chirality and even the length. A new kind of water-soluble polymer which has large viscosity could be used as a substitute of the iodixanol which is the density media in DGU. The column chromatography and extraction method are the potential techniques to enrich s-SWNTs on a large scale. The molecules which could enrich s-SWNTs could be connected onto the fillers and then the m-SWNTs would be collected at the outlet of the column. It is urgent to develop a process to continuously sorting s-SWNTs with high purity.

To deposit SWNTs on desired position is a critical technique to reduce the variety of the FETs' output in the logic circuits. Because of the 1D structure, the

orientation and the density of SWNTs in the arrays are a key challenge. As reviewed techniques in Section 2.2, the alignment techniques should control the density of SWNTs which are deposited on device channel exactly on the wafer scale. The self-assembly process with molecules modified patterns are necessary to place the sorted s-SWNTs which are normally dispersed in a solution on a substrate. If the chirality of SWNT could be controlled during the synthesis, the *in-situ* alignment is also a competitive way to deposit s-SWNTs on the desired substrate.

After semiconducting sorting, the length of the s-SWNTs are normally smaller than 5 μm due to the strong sonication. The tube-tube resistance strongly affects the on-current of the SWNT FETs when the channel length is much longer than average tube length because it is hundreds times of the one in SWNT. The alignment could reduce the numbers of tube-tube contacts between the source and drain electrodes. A polymer which could assist to disperse SWNTs in solution could be totally removed by the thermal annealing at temperature of $< 350\text{ }^{\circ}\text{C}$ in vacuum or air. It is easier to control the length of SWNT on substrates with CVD synthesis but it is hard to control the tube density. The resistance between SWNT and metal electrode are also affects the mobility of FETs. If the contact length of SWNT-metal is different, the outputs of FETs with the same SWNT varies. The exactly positioning SWNTs and lithography technique are the only way to control the SWNT-metal contact length.

6.2.1 Sensor fabrication with striped pristine SWNTs

In chapter 4, we have successfully converted the conductive SWNT networks into semiconducting strips by micro-fabrication. It is believed that this technique

could be applied in the FET-based sensor fabrication. Due to one-atom thick sidewall of SWNTs, they are a most potential material in many sensors. To transform the FET into sensors, photoresist should be washed as clear as possible after isolation step. Then the SWNT strips could be modified by covalent bond or π - π interaction.[235, 236] With functionalization, semiconducting strips could show responding to certain chemicals which is shown in the variation of current and on/off ratio. These SWNT-based sensors which have both a high sensitivity and a good selectivity could satisfy the real-time detection of the objective chemical.

6.2.2 *N*-type FET conversion and CMOS fabrication on soft substrate

The high mobility and on/off ratio of *p*-type FETs with aligned SWNTs are reported in Chapter 5. But the CMOS which is composed of both *n*-type and *p*-type FETs is the basic device in the logic circuits. It is difficult to apply SWNTs to fabricate *n*-type FETs directly due to its *p*-type behavior from the O₂ doping in air. It is reasonable to find a way to convert *p*-type FETs into air stable *n*-type one. Though many doping chemicals, such as K, Cs and PANI have been reported, the *n*-type conversion is still a challenging.[166, 168, 170, 173] Due to the charge donating ability of the amine, bromine and iodine groups, polymers with these groups could be used to convert the transport behavior. Before dispersion, all the solutions are degased and SWNTs are mixed with these polymers by tip sonication under protection of N₂/Ar gas. Finally the alignment process also should carried out in inter gas environment. For the micro-fabrication, the top-gate process is preferred to fabricate *n*-type FET due to the cover of a dense dielectric layer could prevent the O₂

re-doping.

Appendix A

In our thesis, the single walled carbon nanotubes were purchased from Carbon Solutions, Inc. The main parameters were listed below. Besides the data in chapter 4, the AFM images of strips, FESEM images of devices, corresponding transport curve of devices and the tablets of average mobility, on/off ratio and on-current were shown here.

1. AP-SWNT and P2-SWNT parameters

PRODUCT	DESCRIPTION	CARBONACEOUS PURITY	METAL CONTENTwt% from TGA in air	PRICE**	MINIMUM ORDER
AP-SWNT	As prepared	60-70%	< 30	\$35/g	2 grams
P2-SWNT	Purified, low functionality	>90%	4-8	\$280/g	0.5 grams

AP-SWNT: EA-SWNTs synthesized using Ni/Y catalyst, with a narrow diameter distribution peaked at 1.4 nm. This material has the highest purity of any commercially available AP-EA-SWNTs (NanoLetters, 2003, 3, 309-314). Our tests of AP-EA-SWNTs from other suppliers with advertised purities of 60-90% show measured purity values in the range of 10-35%. The SWNTs can be dispersed in DMF at concentrations up to 0.05 mg/ml, and can be dispersed in water by using surfactants.

P2-SWNT: AP-SWNT are purified by air oxidation and subsequently treated to remove the catalyst. The purified material closely approximates the pristine state with low functionality and low chemical doping.

2. Supporting information

Figure S1 The AFM images and corresponding height curves of the **a)** 2 μm, **b)** 5 μm and **c)** 10 μm strips of unsorted SWNTs on SiO₂/Si wafer surface.

Figure S2 The AFM image and corresponding height curves of the **a)** 2 μm, **b)** 5 μm and **c)** 10 μm strips of DB71-sorted AP-SWNTs on SiO₂/Si wafer surface.

Figure S3 The FESEM images of the FETs with unsorted SWNT strips on the SiO_2/Si channel and the characterization of the FETs with 2 μm , 5 μm and 10 μm SWNT strips.

Figure S4 FESEM images of the FETs with DB-sorted SWNT strips on the SiO_2/Si channel and the characterization of the FETs with 2 μm , 5 μm and 10 μm wide SWNT strips.

Figure S5 FESEM images of the FETs DB sorted SWNT strips on the HfO_2/Si channel and the characterization of the FETs with 2 μm , 5 μm and 10 μm wide SWNT strips. (As the thickness of HfO_2 layer is only 80 nm, the gate voltage could be reduced to ± 4 V.)

Figure S6 The transconductance (g_m) of FETs on SiO_2/Si wafer using unsorted SWNTs **a)** $W=20\mu\text{m}$. Plot of average transconductance (g_m) versus channel length for FETs with strip width of $2\mu\text{m}$, $5\mu\text{m}$ and $10\mu\text{m}$ SWNTs; **b)** $W=50\mu\text{m}$. Plot of average transconductance (g_m) versus channel length FETs with strip width of $2\mu\text{m}$, $5\mu\text{m}$ and $10\mu\text{m}$.

Figure S7 The transconductance (g_m) of FETs on SiO_2/Si wafer using DB71 sorted SWNTs **a)** $W=20\mu\text{m}$. Plot of average transconductance (g_m) versus channel length for FETs with strip width of $2\mu\text{m}$, $5\mu\text{m}$ and $10\mu\text{m}$ SWNTs; **b)** $W=50\mu\text{m}$. Plot of average transconductance (g_m) versus channel length FETs with strip width of $2\mu\text{m}$, $5\mu\text{m}$ and $10\mu\text{m}$.

Figure S8 The transconductance (g_m) of FETs on HfO_2/Si wafer using DB71 sorted SWNTs **a)** $W=20\mu\text{m}$. Plot of average transconductance (g_m) versus channel length for FETs with strip width of $2\mu\text{m}$, $5\mu\text{m}$ and $10\mu\text{m}$ SWNTs; **b)** $W=50\mu\text{m}$. Plot of average transconductance (g_m) versus channel length FETs with strip width of $2\mu\text{m}$, $5\mu\text{m}$ and $10\mu\text{m}$.

Table S1 The statistical mobility, on-current and on/off ratio of the FETs with different wide unsorted SWNT strips on the SiO₂/Si channel

Channel Width 20 um								
Average Mobility (cm ² /V-s)								
channel length	No Strips	yEr±	10 um strips	yEr±	5 um strips	yEr±	2 um strips	yEr±
2 um	6.9	0.89	7.8	1.85	4.4	1.44	2.8	1.64
5 um	12.9	1.36	4.8	0.99	4.9	1.08	5.6	1.5
10 um	16.6	1.54	7.8	1.4	7	1.71	6.4	1.42
20 um	3.9	0.98	5	1.89	7.2	2.04	2.6	1.03
50 um	3.9	1.38	3.5	1.14	3.9	1.62	2.2	0.84
On-Current (A)								
channel length	No Strips	yEr±	10 um strips	yEr±	5 um strips	yEr±	2 um strips	yEr±
2 um	3.24E-05	4.90E-06	2.02E-05	4.60E-06	1.03E-05	4.70E-06	5.19E-06	3.25E-06
5 um	2.43E-05	3.90E-06	5.96E-06	1.29E-06	5.32E-06	1.22E-06	4.70E-06	1.25E-06
10 um	6.96E-06	7.74E-07	3.38E-06	6.80E-07	2.02E-06	5.71E-07	1.05E-06	3.04E-07
20 um	1.02E-06	4.30E-07	7.64E-07	2.27E-07	6.83E-07	2.44E-07	2.74E-07	1.18E-07
50 um	3.50E-07	4.53E-08	4.58E-08	1.65E-08	6.34E-08	2.41E-08	3.08E-08	1.29E-08
On/Off Ratio								
channel length	No Strips	yEr±	10 um strips	yEr±	5 um strips	yEr±	2 um strips	yEr±
2 um	1.30E+00	9.00E-01	1.24E+00	9.00E-01	1.32E+00	7.00E-01	1.76E+00	8.00E-01
5 um	1.28E+00	9.30E-01	1.97E+00	1.02E+00	1.88E+00	1.02E+00	2.44E+00	7.30E-01
10 um	3.74E+00	7.00E-01	2.96E+00	8.40E-01	1.75E+01	6.84E+00	3.16E+01	9.42E+00
20 um	2.41E+00	1.03E+00	6.94E+00	2.08E+00	1.38E+02	4.02E+01	7.70E+02	2.83E+02
50 um	2.80E+01	1.36E+01	7.85E+03	2.88E+03	8.85E+03	3.01E+03	9.69E+03	3.88E+03
Channel Width 50 um								
Average Mobility (cm ² /V-s)								
channel length	No Strips	yEr±	10 um strips	yEr±	5 um strips	yEr±	2 um strips	yEr±
5 um	7.3	0.94	3.7	0.98	7.6	1.22	3.8	0.88
10 um	6.2	0.82	5.2	0.83	4	0.72	2.3	0.54
20 um	1.2	0.44	0.6	0.33	0.7	0.44	0.71	0.42
50 um	1.1	0.52	2.5	0.8	3.7	1.25	2.3	1.19
On-Current (A)								
channel length	No Strips	yEr±	10 um strips	yEr±	5 um strips	yEr±	2 um strips	yEr±
5 um	3.68E-05	6.23E-06	1.06E-05	1.80E-06	8.15E-06	1.44E-06	4.02E-06	8.64E-07
10 um	7.04E-06	1.01E-06	3.36E-06	6.00E-07	2.14E-06	4.34E-07	1.02E-06	2.89E-07
20 um	6.88E-07	1.65E-07	1.08E-07	2.89E-08	1.22E-07	1.32E-08	9.40E-08	2.58E-08
50 um	3.18E-07	1.01E-07	1.24E-07	3.06E-08	1.95E-07	6.40E-08	9.20E-08	2.74E-08
On/Off Ratio								
channel length	No Strips	yEr±	10 um strips	yEr±	5 um strips	yEr±	2 um strips	yEr±
5 um	1.51E+00	8.00E-01	1.48E+00	6.80E-01	4.94E+00	2.00E+00	9.86E+00	3.30E+00
10 um	4.23E+00	2.20E+00	5.28E+00	2.10E+00	6.57E+00	3.40E+00	2.27E+01	5.80E+00
20 um	8.85E+00	3.50E+00	1.22E+02	5.69E+01	1.43E+02	6.05E+01	5.84E+04	8.35E+03
50 um	3.21E+00	1.26E+00	3.18E+03	6.09E+02	1.65E+04	5.79E+03	1.37E+04	6.98E+03

Table S2 The statistical mobility, on-current and on/off ratio of the FETs with different wide DB71-sorted AP-SWNT strips on the SiO₂/Si channel

Channel Width 20 μm								
Average Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
2 μm	3.9	0.8	2	0.36	2.3	0.45	3	0.6
5 μm	5.6	0.98	6.4	1.02	5.2	1.25	7.2	1.58
10 μm	3.6	0.86	1.3	0.34	1.9	0.41	3.7	0.96
20 μm	0.9	0.23	5.3	1.02	8.5	3.34	15.8	2.92
50 μm	2.6	0.78	1.4	0.54	8.4	2.02	9.7	2.7
On-Current (A)								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
2 μm	1.92E-05	4.20E-06	7.72E-06	1.52E-06	4.70E-06	1.62E-06	3.21E-07	6.90E-08
5 μm	8.91E-06	1.25E-06	5.52E-06	1.05E-06	5.94E-06	1.80E-06	3.68E-06	8.80E-07
10 μm	4.85E-06	1.22E-06	2.15E-06	2.60E-07	1.28E-06	2.70E-07	1.26E-06	4.50E-07
20 μm	4.02E-07	1.02E-07	1.83E-07	4.10E-08	2.95E-07	7.50E-08	2.19E-07	3.70E-08
50 μm	3.85E-07	1.68E-07	8.14E-08	3.01E-08	4.89E-08	1.19E-08	9.20E-08	1.90E-08
On/Off Ratio								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
2 μm	1.20E+00	8.40E-01	1.50E+00	1.22E+00	1.60E+00	1.09E+00	6.80E+00	3.81E+00
5 μm	1.30E+00	7.30E-01	1.80E+00	8.60E-01	2.80E+00	1.82E+00	4.10E+00	2.46E+00
10 μm	1.10E+00	6.20E-01	9.00E-01	5.90E-01	1.50E+00	1.06E+00	8.00E+00	5.02E+00
20 μm	3.20E+00	2.13E+00	3.50E+00	2.64E+00	1.78E+03	6.70E+02	2.27E+04	7.45E+03
50 μm	2.30E+00	1.48E+00	2.37E+01	1.09E+01	8.13E+03	3.21E+03	1.59E+04	4.89E+03
Channel Width 50 μm								
Average Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
5 μm	3.1	0.64	2.7	0.62	4.2	0.8	2.5	0.46
10 μm	1.9	0.52	0.86	0.52	2.2	0.52	9	2.02
20 μm	1.1	0.24	0.9	0.24	8.6	1.98	9.4	1.96
50 μm	4.7	0.91	4.7	1.45	7.6	2.1	9.5	2.59
On-Current (A)								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
5 μm	1.37E-05	3.80E-06	8.50E-06	2.26E-06	6.28E-06	1.22E-06	3.44E-06	6.40E-07
10 μm	2.95E-06	8.70E-07	8.80E-07	5.40E-07	1.08E-06	3.20E-07	1.46E-06	3.60E-07
20 μm	7.31E-07	1.28E-07	7.30E-07	2.16E-07	4.84E-07	1.06E-07	1.61E-07	4.00E-08
50 μm	2.85E-07	5.80E-08	1.57E-07	5.50E-08	1.18E-07	3.60E-08	1.26E-07	5.80E-08
On/Off Ratio								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
5 μm	2.30E+00	1.08E+00	2.00E+00	9.40E-01	3.40E+00	1.18E+00	3.20E+00	1.43E+00
10 μm	3.30E+00	1.22E+00	2.40E+00	1.13E+00	1.20E+01	5.45E+00	3.80E+02	1.06E+02
20 μm	5.20E+00	2.45E+00	7.50E+00	3.66E+00	1.65E+04	5.02E+03	5.24E+03	2.15E+03
50 μm	1.95E+02	6.80E+01	2.45E+02	9.20E+01	2.16E+04	5.78E+03	2.35E+04	8.95E+03

Table S3 The statistical mobility, on-current and on/off ratio of the FETs with different wide DB-sorted SWNT strips on the HfO₂/Si channel

Channel Width 20 μm								
Average Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
2 μm	5.89	1.79	8.31	3.22	14.5	4.94	12.6	4.25
5 μm	9.16	3.56	5.67	3.37	14.2	4.42	7.8	2.54
10 μm	10.38	3.12	9.3	2.91	11.2	3.93	10.2	4.98
20 μm	15.11	3.92	13.3	5.58	21.9	8.72	14.4	8.83
50 μm	20.56	5.66	16.9	7.57	20.6	6.55	20.1	6.89
On-Current (A)								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
2 μm	3.76E-05	1.15E-05	2.53E-05	9.80E-06	2.14E-05	8.30E-06	1.66E-05	5.90E-06
5 μm	2.62E-05	1.02E-05	2.16E-05	1.29E-05	1.77E-05	5.45E-06	1.02E-05	3.31E-06
10 μm	1.53E-05	4.60E-06	1.29E-05	4.05E-06	8.09E-06	2.83E-06	3.88E-06	2.26E-06
20 μm	8.90E-06	2.31E-06	4.87E-06	2.04E-06	3.43E-06	1.86E-06	2.52E-06	1.69E-06
50 μm	5.98E-06	2.03E-06	2.46E-06	1.13E-06	1.67E-06	1.24E-06	1.43E-06	1.01E-06
On/Off Ratio								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
2 μm	3.15E+00	1.62E+00	3.22E+00	2.07E+00	5.43E+00	3.62E+00	6.17E+00	3.96E+00
5 μm	2.89E+00	1.72E+00	4.08E+00	2.55E+00	2.55E+01	9.62E+00	9.05E+01	3.06E+01
10 μm	3.93E+00	1.59E+00	1.68E+01	5.94E+00	1.46E+02	5.93E+01	3.27E+03	1.93E+03
20 μm	1.01E+01	3.45E+00	8.01E+03	2.97E+03	8.16E+04	3.04E+04	7.03E+04	3.68E+04
50 μm	2.17E+01	8.62E+00	2.27E+03	1.40E+03	1.37E+04	4.30E+03	6.63E+04	3.00E+04
Channel Width 50 μm								
Average Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
5 μm	4.52	0.66	8.6	2.92	9.5	2.73	8.7	3.25
10 μm	8.43	2.34	7.8	2.71	11	3.2	10.9	4.26
20 μm	14.05	5.08	9.5	3.35	16.9	4.82	17.4	5.42
50 μm	10.29	5.86	16.15	8.01	18.3	9.4	19.6	8.05
On-Current (A)								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
5 μm	7.37E-05	1.08E-05	4.03E-05	1.10E-05	3.56E-05	1.03E-05	2.69E-05	1.15E-05
10 μm	4.03E-05	1.12E-05	2.13E-05	7.35E-06	1.96E-05	5.66E-06	1.48E-05	5.76E-06
20 μm	2.04E-05	6.60E-06	1.09E-05	4.74E-06	8.97E-06	2.59E-06	7.73E-06	3.50E-06
50 μm	1.23E-05	7.84E-06	5.87E-06	3.65E-06	4.58E-06	3.08E-06	3.50E-06	2.15E-06
On/Off Ratio								
channel length	No Strips	yEr $\pm$	10 μm strips	yEr $\pm$	5 μm strips	yEr $\pm$	2 μm strips	yEr $\pm$
5 μm	2.12E+00	9.20E-01	1.51E+01	6.08E+00	5.14E+01	2.39E+01	3.37E+02	1.78E+02
10 μm	2.72E+00	1.81E+00	8.04E+00	4.95E+00	2.13E+01	1.07E+01	2.84E+03	1.63E+03
20 μm	6.62E+00	3.95E+00	2.47E+01	1.27E+01	4.28E+04	2.89E+04	1.66E+04	6.09E+03
50 μm	9.27E+00	4.87E+00	1.22E+03	3.83E+02	1.50E+03	5.65E+02	8.16E+04	3.49E+04

Appendix B

In our thesis, the 99% semiconducting single walled carbon nanotubes were purchased from Carbon Solutions, Inc. The main parameters were listed below. Besides the data in chapter 5, the AFM images of strips, FESEM images of devices, corresponding transport curve of devices and the tablets of average mobility, on/off ratio and on-current were shown here.

1. Main parameters of 99% s-SWNTs

Property	IsoNanotubes-M	IsoNanotubes-S	PureTubes	Measurement	Set Figure	Solution	Powder
Nanotube Type	Arc discharge	Arc discharge	Arc discharge	Manufacturer data	n/a	✓	✓
Diameter Range	1.2 - 1.7 nm	1.2 - 1.7 nm	1.2 - 1.7 nm	Manufacturer data	n/a	✓	✓
Mean Diameter	1.4 nm	1.4 nm	1.4 nm	Manufacturer data	n/a	✓	✓
Length Range	100 nm – 4 µm	100 nm – 4 µm	100 nm – 4 µm	AFM	6	✓	✓
Mean Length	~0.5 micron	~1 micron	~1 micron	AFM	6	✓	✓
Catalyst Impurity	~1% by mass	~1% by mass	~0.5% by mass	NAA, TGA	3, 4	✓	✓
Carbonaceous Impurity	< 5% by mass	< 5% by mass	< 5% by mass	TGA, Raman	4, 5	✓	✓
Semiconducting CNT Content	n/a	90%, 95%, 98%, or 99+%	n/a	Optical absorbance	2	✓	✓
Metallic CNT Content	70%, 95%, 98% or 99%	n/a	n/a	Optical absorbance	2	✓	✓
Shelf Life	6 months	6 months	6 months	n/a	n/a	✓	n/a
Nanotube Concentration	0.01 mg/mL	0.01 mg/mL	0.25 mg/mL	n/a	n/a	✓	n/a
Surfactant Concentration	1% w/v	1% w/v	1% w/v	n/a	n/a	✓	n/a
Surfactant Type	Ionic (proprietary mixture)	Ionic (proprietary mixture)	Ionic (proprietary mixture)	n/a	n/a	✓	n/a

2. Supporting information

Table S1. Device properties (sample averages)

	Gap Length [μm]	Linear SWNT Density			
		35-45 [tubes/ μm]	25-35 [tubes/ μm]	15-25 [tubes/ μm]	5-15 [tubes/ μm]
I_{on}/W [$\mu\text{A}/\mu\text{m}$]	2	5.72 $\pm$ 36.5%(10)	0.788 $\pm$ 26.6%(15)	0.182 $\pm$ 34.6%(15)	0.0574 $\pm$ 44.8%(15)
	5	4.30 $\pm$ 27.9%(10)	0.529 $\pm$ 24.6%(15)	0.126 $\pm$ 25.4%(15)	0.0482 $\pm$ 47.7%(15)
	10	2.01 $\pm$ 35.8%(10)	0.251 $\pm$ 32.6%(15)	0.12 $\pm$ 38.3%(15)	0.0294 $\pm$ 54.1%(15)
	20	1.13 $\pm$ 25.6%(10)	0.167 $\pm$ 26.3%(15)	0.0312 $\pm$ 26.9%(15)	0.00617 $\pm$ 42.8%(15)
	50	0.18 $\pm$ 32.2%(10)	0.0524 $\pm$ 30.5%(15)	0.00645 $\pm$ 31.0%(15)	0.00058 $\pm$ 44.8%(15)
On/Off ratio	2	2.73 $\pm$ 26.0%(10)	5.96 $\pm$ 32.9%(15)	53.36 $\pm$ 50.2%(15)	4421.83 $\pm$ 68.3%(15)
	5	5.09 $\pm$ 20.4%(10)	30.47 $\pm$ 32.3%(15)	104.38 $\pm$ 38.6%(15)	6086.28 $\pm$ 49.4%(15)
	10	36.55 $\pm$ 24.8%(10)	140.53 $\pm$ 30.5%(15)	1166.6 $\pm$ 44.0%(15)	29820.3 $\pm$ 55.3%(15)
	20	177.63 $\pm$ 24.0%(10)	6086.28 $\pm$ 49.1%(15)	84175.8 $\pm$ 35.7%(15)	32500 $\pm$ 32.1%(15)
	50	32,250 $\pm$ 30.9%(10)	410,330.6 $\pm$ 44.3%(15)	16,463.7 $\pm$ 46.5%(15)	2542.86 $\pm$ 62.3%(15)
Mobility [$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$]	2	209.4 $\pm$ 18.3%(10)	10.8 $\pm$ 30.7%(15)	2.9 $\pm$ 31.4%(15)	1.6 $\pm$ 58.8%(15)
	5	128.6 $\pm$ 29.9%(10)	20.5 $\pm$ 27.2%(15)	3.8 $\pm$ 27.9%(15)	2.9 $\pm$ 45.5%(15)
	10	62.6 $\pm$ 28.2%(10)	22.6 $\pm$ 33.0%(15)	5 $\pm$ 39.4%(15)	1.9 $\pm$ 60.0%(15)
	20	57.4 $\pm$ 27.5%(10)	20.8 $\pm$ 25.7%(15)	4.8 $\pm$ 38.3%(15)	1.7 $\pm$ 57.6%(15)
	50	46.5 $\pm$ 27.6%(10)	24.7 $\pm$ 27.0%(15)	7.8 $\pm$ 36.2%(15)	1.2 $\pm$ 75.0%(15)
mobility/ tube [$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ / tube]	2	5.235 $\pm$ 18.3%(10)	0.360 $\pm$ 30.7%(15)	0.145 $\pm$ 31.4%(15)	0.16 $\pm$ 58.8%(15)
	5	3.215 $\pm$ 29.9%(10)	0.667 $\pm$ 27.2%(15)	0.19 $\pm$ 27.9%(15)	0.29 $\pm$ 45.5%(15)
	10	1.565 $\pm$ 28.2%(10)	0.753 $\pm$ 33.0%(15)	0.25 $\pm$ 39.4%(15)	0.19 $\pm$ 60.0%(15)
	20	1.435 $\pm$ 27.5%(10)	0.693 $\pm$ 25.7%(15)	0.24 $\pm$ 38.3%(15)	0.17 $\pm$ 57.6%(15)
	50	1.1625 $\pm$ 27.6%(10)	0.823 $\pm$ 27.0%(15)	0.39 $\pm$ 36.2%(15)	0.12 $\pm$ 75.0%(15)

A

B

C

D

Figure S1. AFM images of aligned SWNTs in FET channels of length A) 2 μm, B) 5 μm, C) 10 μm, D) 20 μm and E) 50 μm.

Figure S2. Channel length and network density dependence of FET properties. A) Average on-current density (I_{on}/W) versus channel length (L). B) Average on-current/tube ($I_{on}/tube$) versus $1/\text{channel length}$ ($1/L$). C) Average off-current/tube ($I_{off}/tube$) versus channel length (L). D) Average devices mobility/tube ($\mu/tube$) versus channel length (L). E) Average device on-current/tube ($I_{on}/tube$) versus channel length (L).

Reference

1. Hong, S. and S. Myung, *Nanotube electronics: A flexible approach to mobility*. Nature Nanotechnology, 2007. **2**(4): p. 207-208.
2. Niimi, K., et al., *Dianthra[2,3- b:2',3'- f]thieno[3,2- b]thiophene (DATT): Synthesis, characterization, and FET characteristics of new π -extended heteroarene with eight fused aromatic rings*. Journal of the American Chemical Society, 2011. **133**(22): p. 8732-8739.
3. Shim, M., et al., *Functionalization of Carbon Nanotubes for Biocompatibility and Biomolecular Recognition*. Nano Letters, 2002. **2**(4): p. 285-288.
4. Okimoto, H., et al., *Tunable carbon nanotube thin-film transistors produced exclusively via inkjet printing*. Advanced Materials, 2010. **22**(36): p. 3981-3986.
5. Beecher, P., et al., *Ink-jet printing of carbon nanotube thin film transistors*. Journal of Applied Physics, 2007. **102**(4).
6. Arnold, M.S., et al., *Sorting carbon nanotubes by electronic structure using density differentiation*. Nature Nanotechnology, 2006. **1**(1): p. 60-65.
7. Tu, X., et al., *DNA sequence motifs for structure-specific recognition and separation of carbon nanotubes*. Nature, 2009. **460**(7252): p. 250-253.
8. Peng, X., et al., *Improved optical enrichment of SWNTs through extraction with chiral nanotweezers of 2,6-pyridylene-bridged diporphyrins*. Journal of the American Chemical Society, 2007. **129**(51): p. 15947-15953.
9. NanoIntegrisInc., <http://www.nanointegris.com/en/semiconducting>.
10. Asheghali, D., P. Vichchulada, and M.D. Lay, *Conversion of Metallic Single-Walled Carbon Nanotube Networks to Semiconducting through Electrochemical Ornamentation*. Journal of the American Chemical Society, 2013. **135**(20): p. 7511-7522.
11. Zheng, G., et al., *Transition of Single-Walled Carbon Nanotubes from Metallic to Semiconducting in Field-Effect Transistors by Hydrogen Plasma Treatment*. Nano Letters, 2007. **7**(6): p. 1622-1625.
12. Zheng, F.z., et al., *Sorting single-walled carbon nanotubes by strain-based electrical burn-off*. Carbon, 2010. **48**(8): p. 2169-2174.
13. Cao, Q., et al., *Medium-scale carbon nanotube thin-film integrated circuits on flexible plastic substrates*. Nature, 2008. **454**(7203): p. 495-500.
14. Li, X., et al., *Improved efficiency of smooth and aligned single walled carbon nanotube/silicon hybrid solar cells*. Energy & Environmental Science, 2013. **6**(3): p. 879-887.
15. Kocabas, C., et al., *Experimental and theoretical studies of transport through large scale, partially aligned arrays of single-walled carbon nanotubes in thin film type transistors*. Nano Letters, 2007. **7**(5): p. 1195-1202.
16. Zhang, Y., et al., *Electric-field-directed growth of aligned single-walled carbon nanotubes*. Applied Physics Letters, 2001. **79**(19): p. 3155-3157.
17. Huang, S., et al., *Ultralong, Well-Aligned Single-Walled Carbon Nanotube Architectures on Surfaces*. Advanced Materials, 2003. **15**(19): p. 1651-1655.

18. Kocabas, C., et al., *Guided Growth of Large-Scale, Horizontally Aligned Arrays of Single-Walled Carbon Nanotubes and Their Use in Thin-Film Transistors*. Small, 2005. **1**(11): p. 1110-1116.
19. Kang, S.J., et al., *High-performance electronics using dense, perfectly aligned arrays of single-walled carbon nanotubes*. Nat Nano, 2007. **2**(4): p. 230-236.
20. Kong, X.H., et al., *Surface acoustic wave mediated dielectrophoretic alignment of rolled-up microtubes in microfluidic systems*. Applied Physics Letters, 2010. **96**(13).
21. Yan, X., et al., *The gluing of a Langmuir-Blodgett bilayer*. Journal of the American Chemical Society, 2003. **125**(27): p. 8094-8095.
22. Tang, G., et al., *New confinement method for the formation of highly aligned and densely packed single-walled carbon nanotube monolayers*. Small, 2010. **6**(14): p. 1488-1491.
23. Iijima, S., *Helical microtubules of graphitic carbon*. Nature, 1991. **354**(6348): p. 56-58.
24. Iijima, S. and T. Ichihashi, *Single-shell carbon nanotubes of 1-nm diameter*. Nature, 1993. **363**(6430): p. 603-605.
25. Huang, S., et al., *Ultralong, Well-Aligned Single-Walled Carbon Nanotube Architectures on Surfaces*. Advanced Materials, 2003. **15**(19): p. 1651-1655.
26. Li, C. and T.-W. Chou, *Elastic moduli of multi-walled carbon nanotubes and the effect of van der Waals forces*. Composites Science and Technology, 2003. **63**(11): p. 1517-1524.
27. Yang, D.J., et al., *Thermal and electrical transport in multi-walled carbon nanotubes*. Physics Letters A, 2004. **329**(3): p. 207-213.
28. Peng, B., et al., *Measurements of near-ultimate strength for multiwalled carbon nanotubes and irradiation-induced crosslinking improvements*. Nature Nanotechnology, 2008. **3**(10): p. 626-631.
29. Ruoff, R.S., et al., *Radial deformation of carbon nanotubes by van der Waals forces*. Nature, 1993. **364**(6437): p. 514-516.
30. Sinnott, S.B. and R. Andrews, *Carbon nanotubes: Synthesis, properties, and applications*. Critical Reviews in Solid State and Materials Sciences, 2001. **26**(3).
31. Kataura, H., et al., *Optical properties of single-wall carbon nanotubes*. Synthetic Metals, 1999. **103**(1-3): p. 2555-2558.
32. Saito, R., et al., *Raman intensity of single-wall carbon nanotubes*. Physical Review B - Condensed Matter and Materials Physics, 1998. **57**(7): p. 4145-4153.
33. Saito, R., et al., *Electronic structure of chiral graphene tubules*. Applied Physics Letters, 1992. **60**(18): p. 2204-2206.
34. Yao, Z., C.L. Kane, and C. Dekker, *High-Field Electrical Transport in Single-Wall Carbon Nanotubes*. Physical Review Letters, 2000. **84**(13): p. 2941-2944.
35. Kong, J., et al., *Synthesis, integration, and electrical properties of individual single-walled carbon nanotubes*. Applied Physics A, 1999. **69**(3): p. 305-308.

36. Shimizu, M., H. Akimoto, and K. Ishibashi, *Electronic transport of single-wall carbon nanotubes with superconducting contacts*. Japanese Journal of Applied Physics, 2011. **50**(3).
37. Ago, H., et al., *Dispersion of metal nanoparticles for aligned carbon nanotube arrays*. Applied Physics Letters, 2000. **77**(1): p. 79-81.
38. Yang, Z., et al., *Improvement in mechanical and thermal properties of phenolic foam reinforced with multiwalled carbon nanotubes*. Journal of Applied Polymer Science, 2013. **130**(3): p. 1479-1488.
39. Hu, R., et al., *Harvesting Waste Thermal Energy Using a Carbon-Nanotube-Based Thermo-Electrochemical Cell*. Nano Letters, 2010. **10**(3): p. 838-846.
40. Tay, C.Y., et al., *Cellular behavior of human mesenchymal stem cells cultured on single-walled carbon nanotube film*. Carbon, 2010. **48**(4): p. 1095-1104.
41. Hata, K., et al., *Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes*. Science, 2004. **306**(5700): p. 1362-1364.
42. Sakurai, S., et al., *Role of Subsurface Diffusion and Ostwald Ripening in Catalyst Formation for Single-Walled Carbon Nanotube Forest Growth*. Journal of the American Chemical Society, 2012. **134**(4): p. 2148-2153.
43. Hasegawa, K. and S. Noda, *Moderating carbon supply and suppressing Ostwald ripening of catalyst particles to produce 4.5-mm-tall single-walled carbon nanotube forests*. Carbon, 2011. **49**(13): p. 4497-4504.
44. Zhong, G., et al., *Growth of Ultrahigh Density Single-Walled Carbon Nanotube Forests by Improved Catalyst Design*. ACS Nano, 2012. **6**(4): p. 2893-2903.
45. An, J., et al., *Growth condition mediated catalyst effects on the density and length of horizontally aligned single-walled carbon nanotube arrays*. Chemical Engineering Journal, 2014. **237**(0): p. 16-22.
46. Youn, S.K., et al., *Temperature gradient chemical vapor deposition of vertically aligned carbon nanotubes*. Carbon, 2013. **54**(0): p. 343-352.
47. Lee, I.H., et al., *Low temperature growth of single-walled carbon Nanotube forest*. Bulletin of the Korean Chemical Society, 2010. **31**(10): p. 2819-2822.
48. Ohashi, T., et al., *Understanding the stability of a sputtered Al buffer layer for single-walled carbon nanotube forest synthesis*. Carbon, 2013. **57**(0): p. 401-409.
49. Zhao, M.Q., et al., *Advanced materials from natural materials: Synthesis of aligned carbon nanotubes on wollastonites*. ChemSusChem, 2010. **3**(4): p. 453-459.
50. Zhang, Q., et al., *Comparison of vertically aligned carbon nanotube array intercalated production among vermiculites in fixed and fluidized bed reactors*. Powder Technology, 2010. **198**(2): p. 285-291.
51. Zhao, M.Q., et al., *Large scale intercalated growth of short aligned carbon nanotubes among vermiculite layers in a fluidized bed reactor*. Journal of Physics and Chemistry of Solids, 2010. **71**(4): p. 624-626.
52. Zhang, Q., et al., *Mass production of aligned carbon nanotube arrays by*

- fluidized bed catalytic chemical vapor deposition*. Carbon, 2010. **48**(4): p. 1196-1209.
53. Oye, M.M., et al., *Surface smoothness effect for the direct growth of carbon nanotubes on Bulk FeCrAl metal substrates*. Journal of Nanoscience and Nanotechnology, 2010. **10**(6): p. 4082-4088.
 54. Parker, J.M. and H.S.P. Wong, *Synergetic carbon nanotube growth*. Carbon, 2013. **62**(0): p. 61-68.
 55. Copic, D., et al., *Fabrication, densification, and replica molding of 3D carbon nanotube microstructures*. Journal of Visualized Experiments, 2012(65).
 56. Li, D., et al., *Uniform arrays of carbon nanotubes applied in the field emission devices*. Science China: Physics, Mechanics and Astronomy, 2013. **56**(11): p. 2081-2084.
 57. Cui, K., et al., *Self-Assembled Microhoneycomb Network of Single-Walled Carbon Nanotubes for Solar Cells*. The Journal of Physical Chemistry Letters, 2013. **4**(15): p. 2571-2576.
 58. Arun, A., et al. *Micro-electro-mechanical capacitors based on vertical carbon nanotube arrays*. 2009.
 59. Dong, Z., et al., *Carbon nanotube–nanopipe composite vertical arrays for enhanced electrochemical capacitance*. Carbon, 2013. **64**(0): p. 507-515.
 60. Sameera, I., et al., *High emission currents and low threshold fields in multi-wall carbon nanotube-polymer composites in the vertical configuration*. Journal of Applied Physics, 2012. **111**(4): p. -.
 61. Arun, A., et al., *Carbon nanotube vertical membranes for electrostatically actuated micro-electro-mechanical devices*. Microelectronic Engineering, 2010. **87**(5–8): p. 1281-1283.
 62. Liu, Z., et al., *Organizing Single-Walled Carbon Nanotubes on Gold Using a Wet Chemical Self-Assembling Technique*. Langmuir, 2000. **16**(8): p. 3569-3573.
 63. Shearer, C.J., et al., *Improved field emission stability from single-walled carbon nanotubes chemically attached to silicon*. Nanoscale Research Letters, 2012. **7**.
 64. Zuaznabar-Gardona, J.C., et al., *Vertical self-assembly of modified multiwalled carbon nanotubes on gold surfaces induced by chitosan and Tween*. Chemical Communications, 2012. **48**(13): p. 1910-1912.
 65. Huang, X.-J., et al., *Electrochemical behavior of needle-like and forest-like single-walled carbon nanotube electrodes*. Journal of Electroanalytical Chemistry, 2006. **594**(1): p. 27-34.
 66. Constantopoulos, K.T., et al., *Carbon Nanotubes Anchored to Silicon for Device Fabrication*. Advanced Materials, 2010. **22**(5): p. 557-571.
 67. Shearer, C.J., et al., *Chemically Grafted Carbon Nanotube Surface Coverage Gradients*. Langmuir, 2010. **26**(23): p. 18468-18475.
 68. Seo, S.H., et al., *High electrocatalytic activity of low-loaded transparent carbon nanotube assemblies for CoII/III-mediated dye-sensitized solar cells*. Journal of Materials Chemistry A, 2014. **2**(8): p. 2592-2598.

69. Chattopadhyay, D., I. Galeska, and F. Papadimitrakopoulos, *Metal-Assisted Organization of Shortened Carbon Nanotubes in Monolayer and Multilayer Forest Assemblies*. Journal of the American Chemical Society, 2001. **123**(38): p. 9451-9452.
70. Ferri, T., et al., *Spatially Oriented and Reversible Surface Assembly of Single-Walled Carbon Nanotubes: A Strategy Based on π - π Interactions*. Angewandte Chemie International Edition, 2011. **50**(31): p. 7074-7078.
71. Kim, S.-K., et al., *Vertical Alignment of Single-Walled Carbon Nanotube Films Formed by Electrophoretic Deposition*. Langmuir, 2008. **24**(22): p. 12936-12942.
72. Santhanagopalan, S., F. Teng, and D.D. Meng, *High-Voltage Electrophoretic Deposition for Vertically Aligned Forests of One-Dimensional Nanoparticles*. Langmuir, 2010. **27**(2): p. 561-569.
73. Thess, A., et al., *Crystalline Ropes of Metallic Carbon Nanotubes*. Science, 1996. **273**(5274): p. 483-487.
74. Terrones, M., et al., *Controlled production of aligned-nanotube bundles*. Nature, 1997. **388**(6637): p. 52-55.
75. Huang, L., S.J. Wind, and S.P. O'Brien, *Controlled Growth of Single-Walled Carbon Nanotubes from an Ordered Mesoporous Silica Template*. Nano Letters, 2003. **3**(3): p. 299-303.
76. Ismach, A., et al., *Atomic-Step-Templated Formation of Single Wall Carbon Nanotube Patterns*. Angewandte Chemie International Edition, 2004. **43**(45): p. 6140-6143.
77. Kazuki, Y., K. Hiroki, and H. Yoshikazu, *Narrow Diameter Distribution of Horizontally Aligned Single-Walled Carbon Nanotubes Grown Using Size-Controlled Gold Nanoparticles*. Japanese Journal of Applied Physics, 2013. **52**(3R): p. 035105.
78. Wang, B., et al., *Facile and Scalable Fabrication of Well-Aligned and Closely Packed Single-Walled Carbon Nanotube Films on Various Substrates*. Advanced Materials, 2010. **22**(28): p. 3067-3070.
79. Peng, B., et al., *Enrichment of metallic carbon nanotubes by electric field-assisted chemical vapor deposition*. Carbon, 2011. **49**(7): p. 2555-2560.
80. Peng, B., Y. Yao, and J. Zhang, *Effect of the Reynolds and Richardson Numbers on the Growth of Well-Aligned Ultralong Single-Walled Carbon Nanotubes*. The Journal of Physical Chemistry C, 2010. **114**(30): p. 12960-12965.
81. Wen, Q., et al., *100 mm Long, Semiconducting Triple-Walled Carbon Nanotubes*. Advanced Materials, 2010. **22**(16): p. 1867-1871.
82. Liu, K., et al., *Intrinsic radial breathing oscillation in suspended single-walled carbon nanotubes*. Physical Review B - Condensed Matter and Materials Physics, 2011. **83**(11).
83. MuothM, et al., *Hysteresis-free operation of suspended carbon nanotube transistors*. Nat Nano, 2010. **5**(8): p. 589-592.
84. Inoue, T., et al., *Effect of Gas Pressure on the Density of Horizontally Aligned*

- Single-Walled Carbon Nanotubes Grown on Quartz Substrates*. The Journal of Physical Chemistry C, 2013. **117**(22): p. 11804-11810.
85. Hong, S.W., T. Banks, and J.A. Rogers, *Improved Density in Aligned Arrays of Single-Walled Carbon Nanotubes by Sequential Chemical Vapor Deposition on Quartz* (vol 22, pg 1826, 2010). Advanced Materials, 2010. **22**(45): p. CP30-CP30.
 86. Chen, Y. and J. Zhang, *Diameter controlled growth of single-walled carbon nanotubes from SiO₂ nanoparticles*. Carbon, 2011. **49**(10): p. 3316-3324.
 87. Yu, X.C., et al., *Cap Formation Engineering: From Opened C60 to Single-Walled Carbon Nanotubes*. Nano Letters, 2010. **10**(9): p. 3343-3349.
 88. Hong, S.W., T. Banks, and J.A. Rogers, *Improved density in aligned arrays of single-walled carbon nanotubes by sequential chemical vapor deposition on quartz* (Advanced Materials (2010) 22 (1826) DOI:10.1002/adma.200903238). Advanced Materials, 2010. **22**(45): p. 5081.
 89. Lim, S.H., et al., *Efficient Growth of Horizontally Aligned Single-Walled Carbon Nanotubes by Chemical Vapor Deposition Over MgO-Supported Bimetallic Co-Based Catalysts*. Journal of Nanoscience and Nanotechnology, 2011. **11**(1): p. 143-147.
 90. Chen, L.S., *Modification of well-aligned carbon nanotubes grown on AAO template by chemical vapor deposition*, 2013. p. 39-42.
 91. Zhang, C., et al., *Complementary metal-oxide-semiconductor-compatible and self-aligned catalyst formation for carbon nanotube synthesis and interconnect fabrication*. Journal of Applied Physics, 2012. **111**(6): p. 0643101-0643106.
 92. Ibrahim, I., et al., *Growth of catalyst-assisted and catalyst-free horizontally aligned single wall carbon nanotubes*. Physical Status Solidi B, 2011. **248**(11): p. 2467-2470.
 93. Shulaker, M.M., et al., *Linear Increases in Carbon Nanotube Density Through Multiple Transfer Technique*. Nano Letters, 2011. **11**(5): p. 1881-1886.
 94. Zhou, W., et al., *Synthesis of high-density, large-diameter, and aligned single-walled carbon nanotubes by multiple-cycle growth methods*. ACS Nano, 2011. **5**(5): p. 3849-3857.
 95. Ajayan, P.M., et al., *Aligned Carbon Nanotube Arrays Formed by Cutting a Polymer Resin-Nanotube Composite*. Science, 1994. **265**(5176): p. 1212-1214.
 96. Jin, L., C. Bower, and O. Zhou, *Alignment of carbon nanotubes in a polymer matrix by mechanical stretching*. Applied Physics Letters, 1998. **73**(9): p. 1197-1199.
 97. Ning, N., et al., *Dramatically improved dielectric properties of polymer composites by controlling the alignment of carbon nanotubes in matrix*. RSC Advances, 2014. **4**(9): p. 4543-4551.
 98. Yu, G.H., A.Y. Cao, and C.M. Lieber, *Large-area blown bubble films of aligned nanowires and carbon nanotubes*. Nat Nano, 2007. **2**(6): p. 372-377.
 99. Tang, G.L., et al., *New Confinement Method for the Formation of Highly Aligned and Densely Packed Single-Walled Carbon Nanotube Monolayers*. Small, 2010. **6**(14): p. 1488-1491.

100. Felisberto, M., et al., *Influence of filler alignment in the mechanical and electrical properties of carbon nanotubes/epoxy nanocomposites*. Physical Review B - Condensed Matter and Materials Physics, 2012. **407**(16): p. 3181-3183.
101. Kumar, S., et al., *Effect of Electric Field Alignment of MWCNT in PMMA Matrix for Hydrogen Gas Purification*. AIP Conference Proceedings, 2011. **1349**(1): p. 1061-1062.
102. Yu-Hsien, L., et al., *Carbon nanotube alignment driven rapid actuations*. Nanotechnology, 2013. **24**(46): p. 465501.
103. Lu, J.P., *Novel Magnetic Properties of Carbon Nanotubes*. Physical Review Letters, 1995. **74**(7): p. 1123-1126.
104. Shaver, J., et al., *Alignment Dynamics of Single-Walled Carbon Nanotubes in Pulsed Ultrahigh Magnetic Fields*. ACS Nano, 2008. **3**(1): p. 131-138.
105. Younes, H. and H. Hong. *Alignment of different functional single wall carbon nanotubes using Fe₂O₃ nanoparticles under external magnetic field*. 2013.
106. Yamamoto, K., S. Akita, and Y. Nakayama, *Orientation of carbon nanotubes using electrophoresis*. Japanese Journal of Applied Physics Part 2, 1996. **35**(7 SUPPL. B): p. L917-L918.
107. Zhou, Z., et al., *Postgrowth alignment of SWNTs by an electric field*. Carbon, 2006. **44**(1): p. 170-173.
108. Ranulfo, A., B. Zhenan, and G.F. Gerald, *Oriented, polymer-stabilized carbon nanotube films: influence of dispersion rheology*. Nanotechnology, 2013. **24**(1): p. 015709.
109. Toda, T., et al. *Thin-film transistor using dielectrophoretic assembly of single-walled carbon nanotubes*. 2012.
110. Shekhar, S., P. Stokes, and S.I. Khondaker, *Ultrahigh Density Alignment of Carbon Nanotube Arrays by Dielectrophoresis*. ACS Nano, 2011. **5**(3): p. 1739-1746.
111. Krstic, V., et al., *Langmuir–Blodgett Films of Matrix-Diluted Single-Walled Carbon Nanotubes*. Chemistry of Materials, 1998. **10**(9): p. 2338-2340.
112. Guo, Y., J. Wu, and Y. Zhang, *Manipulation of single-wall carbon nanotubes into aligned molecular layers*. Chemical Physics Letters, 2002. **362**(3–4): p. 314-318.
113. Choi, S.-W., et al., *Patterning of Hierarchically Aligned Single-Walled Carbon Nanotube Langmuir–Blodgett Films by Microcontact Printing*. Langmuir, 2010. **26**(19): p. 15680-15685.
114. Hedberg, J., L. Dong, and J. Jiao, *Air flow technique for large scale dispersion and alignment of carbon nanotubes on various substrates*. Applied Physics Letters, 2005. **86**(14): p. 1-3.
115. Kim, P., S. Baik, and K.Y. Suh, *Capillarity-Driven Fluidic Alignment of Single-Walled Carbon Nanotubes in Reversibly Bonded Nanochannels*. Small, 2008. **4**(1): p. 92-95.
116. Wang, L., et al. *Fluidic assembly of single-walled carbon nanotubes on SiO₂/Si substrates*. 2010.

117. Sai, L., et al., *Aligned single-walled carbon nanotube patterns with nanoscale width, micron-scale length and controllable pitch*. Nanotechnology, 2007. **18**(45): p. 455302.
118. Lee, D., et al., *Suspended and highly aligned carbon nanotube thin-film structures using open microfluidic channel template*. Sensors and Actuators A: Physical, 2012. **188**(0): p. 434-441.
119. Xin, H. and A.T. Woolley, *Directional Orientation of Carbon Nanotubes on Surfaces Using a Gas Flow Cell*. Nano Letters, 2004. **4**(8): p. 1481-1484.
120. Strobl, C.J., et al., *Carbon nanotube alignment by surface acoustic waves*. Applied Physics Letters, 2004. **85**(8): p. 1427-1429.
121. Kocabas, C., et al., *Aligned Arrays of Single-Walled Carbon Nanotubes Generated from Random Networks by Orientationally Selective Laser Ablation*. Nano Letters, 2004. **4**(12): p. 2421-2426.
122. Yamada, T., et al., *A stretchable carbon nanotube strain sensor for human-motion detection*. Nat Nano, 2011. **6**(5): p. 296-301.
123. Tans, S.J., et al., *Individual single-wall carbon nanotubes as quantum wires*. Nature, 1997. **386**(6624): p. 474-477.
124. Wanekaya, A.K., et al. *Fet based conducting polymer coated carbon nanotube bio/chemical sensor*. 2005.
125. Dwyer, C., M. Cheung, and D.J. Sorin. *Semi-empirical SPICE models for carbon nanotube FET logic*. in 2004 4th IEEE Conference on Nanotechnology. 2004.
126. Rutherglen, C., D. Jain, and P. Burke, *Nanotube electronics for radio frequency applications*. Nature Nanotechnology, 2009. **4**(12): p. 811-819.
127. Kim, D.-H., et al., *Dissolvable films of silk fibroin for ultrathin conformal bio-integrated electronics*. Nat Mater, 2010. **9**(6): p. 511-517.
128. Osman, B. and K. Coskun, *High frequency performance of individual and arrays of single-walled carbon nanotubes*. Nanotechnology, 2012. **23**(24): p. 245202.
129. Chico, L., et al., *Pure Carbon Nanoscale Devices: Nanotube Heterojunctions*. Physical Review Letters, 1996. **76**(6): p. 971-974.
130. Wei, Y., et al., *Stability of carbon nanotubes under electric field studied by scanning electron microscopy*. Applied Physics Letters, 2001. **79**(27): p. 4527-4529.
131. Martel, R., et al., *Single- and multi-wall carbon nanotube field-effect transistors*. Applied Physics Letters, 1998. **73**(17): p. 2447-2449.
132. Franklin, A.D., et al., *Sub-10 nm Carbon Nanotube Transistor*. Nano Letters, 2012. **12**(2): p. 758-762.
133. Franklin, A.D. and Z. Chen, *Length scaling of carbon nanotube transistors*. Nat Nano, 2010. **5**(12): p. 858-862.
134. Mueller, T., et al., *Efficient narrow-band light emission from a single carbon nanotube p-n diode*. Nat Nano, 2010. **5**(1): p. 27-31.
135. Kocabas, C., et al., *High-Frequency Performance of Submicrometer Transistors That Use Aligned Arrays of Single-Walled Carbon Nanotubes*.

- Nano Letters, 2009. **9**(5): p. 1937-1943.
136. Kang, S.J., et al., *High-performance electronics using dense, perfectly aligned arrays of single-walled carbon nanotubes*. Nature Nanotechnology, 2007. **2**(4): p. 230-236.
 137. Kocabas, C., et al., *Radio frequency analog electronics based on carbon nanotube transistors*. Proceedings of the National Academy of Sciences of the United States of America, 2008. **105**(5): p. 1405-1409.
 138. Cao, Q., et al., *Arrays of single-walled carbon nanotubes with full surface coverage for high-performance electronics*. Nat Nano, 2013. **8**(3): p. 180-186.
 139. Wang, C., et al., *Metal Contact Engineering and Registration-Free Fabrication of Complementary Metal-Oxide Semiconductor Integrated Circuits Using Aligned Carbon Nanotubes*. ACS Nano, 2011. **5**(2): p. 1147-1153.
 140. Steiner, M., et al., *High-frequency performance of scaled carbon nanotube array field-effect transistors*. Applied Physics Letters, 2012. **101**(5): p. 05312301-05312304.
 141. Green, A.A. and M.C. Hersam, *Nearly single-chirality single-walled carbon nanotubes produced via orthogonal iterative density gradient ultracentrifugation*. Advanced Materials, 2011. **23**(19): p. 2185-2190.
 142. Zhang, J., et al., *Comparative study of gel-based separated arc-discharge, HiPCO, and CoMoCAT carbon nanotubes for macroelectronic applications*. Nano Research, 2013. **6**(12): p. 906-920.
 143. Sun, D.M., et al., *Flexible high-performance carbon nanotube integrated circuits*. Nature Nanotechnology, 2011. **6**(3): p. 156-161.
 144. Liu, Z., et al., *SMALL-Hysteresis Thin-Film Transistors Achieved by Facile Dip-Coating of Nanotube/Polymer Composite*. Advanced Materials, 2012. **24**(27): p. 3633-3638.
 145. Minho, J., et al., *Spray-coated carbon nanotube thin-film transistors with striped transport channels*. Nanotechnology, 2012. **23**(50): p. 505203.
 146. Kang, S.H., et al., *Evaporative self-assembly of single-walled carbon nanotubes for field effect transistor*. Korean Journal of Materials Research, 2013. **23**(8): p. 453-461.
 147. Zhang, D., et al., *Transparent, conductive, and flexible carbon nanotube films and their application in organic light-emitting diodes*. Nano Letters, 2006. **6**(9): p. 1880-1886.
 148. Wang, C., et al., *Wafer-scale fabrication of separated carbon nanotube thin-film transistors for display applications*. Nano Letters, 2009. **9**(12): p. 4285-4291.
 149. Ishikawa, F.N., et al., *Importance of Controlling Nanotube Density for Highly Sensitive and Reliable Biosensors Functional in Physiological Conditions*. ACS Nano, 2010. **4**(11): p. 6914-6922.
 150. Zhang, J., et al., *Air-Stable Conversion of Separated Carbon Nanotube Thin-Film Transistors from p-Type to n-Type Using Atomic Layer Deposition of High- κ Oxide and Its Application in CMOS Logic Circuits*. ACS Nano,

2011. **5**(4): p. 3284-3292.
151. Chen, P., et al., *Fully printed separated carbon nanotube thin film transistor circuits and its application in organic light emitting diode control*. Nano Letters, 2011. **11**(12): p. 5301-5308.
 152. Wang, C., J. Zhang, and C. Zhou, *Macroelectronic integrated circuits using high-performance separated carbon nanotube thin-film transistors*. ACS Nano, 2010. **4**(12): p. 7123-7132.
 153. LeMieux, M.C., et al., *Self-sorted, aligned nanotube networks for thin-film transistors*. Science, 2008. **321**(5885): p. 101-104.
 154. LeMieux, M.C., et al., *Solution Assembly of Organized Carbon Nanotube Networks for Thin-Film Transistors*. ACS Nano, 2009. **3**(12): p. 4089-4097.
 155. Roberts, M.E., M.C. LeMieux, and Z. Bao, *Sorted and Aligned Single-Walled Carbon Nanotube Networks for Transistor-Based Aqueous Chemical Sensors*. ACS Nano, 2009. **3**(10): p. 3287-3293.
 156. Opatkiewicz, J.P., M.C. LeMieux, and Z. Bao, *Influence of Electrostatic Interactions on Spin-Assembled Single-Walled Carbon Nanotube Networks on Amine-Functionalized Surfaces*. ACS Nano, 2010. **4**(2): p. 1167-1177.
 157. Wang, Q., et al., *The effects of CNT alignment on electrical conductivity and mechanical properties of SWNT/epoxy nanocomposites*. Composites Science and Technology, 2008. **68**(7-8): p. 1644-1648.
 158. Lee, H.W., et al., *Selective dispersion of high purity semiconducting single-walled carbon nanotubes with regioregular poly(3-alkylthiophene)s*. Nat Commun, 2011. **2**: p. 541.
 159. Liyanage, L.S., et al., *Wafer-Scale Fabrication and Characterization of Thin-Film Transistors with Polythiophene-Sorted Semiconducting Carbon Nanotube Networks*. ACS Nano, 2011. **6**(1): p. 451-458.
 160. Toda, T., H. Frusawa, and M. Furuta, *Thin-film transistors using uniform and well-aligned single-walled carbon nanotubes channels by dielectrophoretic assembly*. Japanese Journal of Applied Physics, 2013. **52**(3 PART 2).
 161. Mistry, K.S., B.A. Larsen, and J.L. Blackburn, *High-Yield Dispersions of Large-Diameter Semiconducting Single-Walled Carbon Nanotubes with Tunable Narrow Chirality Distributions*. ACS Nano, 2013. **7**(3): p. 2231-2239.
 162. Li, H., et al., *Designing large-plane conjugated copolymers for the high-yield sorting of semiconducting single-walled carbon nanotubes*. Chemical Communications, 2013. **49**(89): p. 10492-10494.
 163. Sukjae, J., et al., *Flexible, transparent single-walled carbon nanotube transistors with graphene electrodes*. Nanotechnology, 2010. **21**(42): p. 425201.
 164. Takahashi, T., et al., *Carbon Nanotube Active-Matrix Backplanes for Conformal Electronics and Sensors*. Nano Letters, 2011. **11**(12): p. 5408-5413.
 165. Noh, J., et al., *Integrable single walled carbon nanotube (SWNT) network based thin film transistors using roll-to-roll gravure and inkjet*. Organic Electronics, 2011. **12**(12): p. 2185-2191.
 166. Derycke, V., et al., *Carbon Nanotube Inter- and Intramolecular Logic Gates*.

- Nano Letters, 2001. **1**(9): p. 453-456.
167. Liu, X., et al., *Carbon nanotube field-effect inverters*. Applied Physics Letters, 2001. **79**(20): p. 3329-3331.
 168. Klinke, C., et al., *Charge Transfer Induced Polarity Switching in Carbon Nanotube Transistors*. Nano Letters, 2005. **5**(3): p. 555-558.
 169. Mistry, K.S., et al., *n-Type Transparent Conducting Films of Small Molecule and Polymer Amine Doped Single-Walled Carbon Nanotubes*. ACS Nano, 2011. **5**(5): p. 3714-3723.
 170. Shearer, C.J., et al., *Highly resilient field emission from aligned single-walled carbon nanotube arrays chemically attached to n-type silicon*. Journal of Materials Chemistry, 2008. **18**(47): p. 5753-5760.
 171. Joo, M.K., et al., *Static and low frequency noise characterization of N-type random network of carbon nanotubes thin film transistors*. Journal of Applied Physics, 2013. **114**(15): p. 15450301-15450310.
 172. Jeng, B.S., et al., *Fabrication of high performance SWNT film FETs in unipolar p-type, n-type or ambipolar characteristics*. Journal of the Electrochemical Society, 2011. **158**(12): p. H1297-H1304.
 173. Li, Z., et al., *Polymer functionalized n-type single wall carbon nanotube photovoltaic devices*. Applied Physics Letters, 2010. **96**(3): p. -.
 174. Welna, D.T., et al., *Vertically aligned carbon nanotube electrodes for lithium-ion batteries*. Journal of Power Sources, 2011. **196**(3): p. 1455-1460.
 175. Wu, Y., et al., *Conformal Fe₃O₄ Sheath on Aligned Carbon Nanotube Scaffolds as High-Performance Anodes for Lithium Ion Batteries*. Nano Letters, 2013. **13**(2): p. 818-823.
 176. Yuan, Y., et al., *Platinum decorated aligned carbon nanotubes: Electrocatalyst for improved performance of proton exchange membrane fuel cells*. Journal of Power Sources, 2011. **196**(15): p. 6160-6167.
 177. Zloczewska, A., et al., *Vertically aligned carbon nanotube film electrodes for bioelectrocatalytic dioxygen reduction*. Electrochimica Acta, 2011. **56**(11): p. 3947-3953.
 178. Ben, H., et al., *Highly flexible, all solid-state micro-supercapacitors from vertically aligned carbon nanotubes*. Nanotechnology, 2014. **25**(5): p. 055401.
 179. Baek, Y., et al., *High performance and antifouling vertically aligned carbon nanotube membrane for water purification*. Journal of Membrane Science, 2014. **460**(0): p. 171-177.
 180. Abdolahad, M., et al., *A vertically aligned carbon nanotube-based impedance sensing biosensor for rapid and high sensitive detection of cancer cells*. Lab on a Chip, 2012. **12**(6): p. 1183-1190.
 181. Li, S., et al., *Working mechanisms of strain sensors utilizing aligned carbon nanotube network and aerosol jet printed electrodes*. Carbon, 2014. **73**(0): p. 303-309.
 182. Li, P., et al., *Dielectrophoresis aligned single-walled carbon nanotubes as ph sensors*. Biosensors, 2011. **1**(1): p. 23-35.
 183. Li, L., et al., *Electrochemical growth of gold nanoparticles on horizontally*

- aligned carbon nanotubes: A new platform for ultrasensitive DNA sensing.* Biosensors and Bioelectronics, 2012. **33**(1): p. 279-283.
184. Sarker, B.K. and S.I. Khondaker, *High-performance short channel organic transistors using densely aligned carbon nanotube array electrodes.* Applied Physics Letters, 2012. **100**(2): p. -.
 185. Li, X., et al., *Improved efficiency of smooth and aligned single walled carbon nanotube/silicon hybrid solar cells.* Energy and Environmental Science, 2013. **6**(3): p. 879-887.
 186. Pham, D., et al. *Bending tests of carbon nanotube thin-film transistors on flexible substrate.* 2010.
 187. Tulevski, G.S., A.D. Franklin, and A. Afzali, *High Purity Isolation and Quantification of Semiconducting Carbon Nanotubes via Column Chromatography.* ACS Nano, 2013. **7**(4): p. 2971-2976.
 188. Lobez, J.M. and A. Afzali, *Surface-Selective Directed Assembly of Carbon Nanotubes Using Side-Chain Functionalized Poly(thiophene)s.* Chemistry of Materials, 2013. **25**(18): p. 3662-3666.
 189. Lobez, J.M., et al., *Surface Selective One-Step Fabrication of Carbon Nanotube Thin Films with High Density.* ACS Nano, 2014. **8**(5): p. 4954-4960.
 190. Shahrjerdi, D., et al., *High-Performance Air-Stable n-Type Carbon Nanotube Transistors with Erbium Contacts.* ACS Nano, 2013. **7**(9): p. 8303-8308.
 191. Franklin, A.D., et al., *Carbon Nanotube Complementary Wrap-Gate Transistors.* Nano Letters, 2013. **13**(6): p. 2490-2495.
 192. Sundramoorthy, A.K., et al., *Scalable and effective enrichment of semiconducting single-walled carbon nanotubes by a dual selective naphthalene-based AzO dispersant.* Journal of the American Chemical Society, 2013. **135**(15): p. 5569-5581.
 193. Lee, C.W., et al., *High-performance Inkjet Printed Carbon Nanotube Thin Film Transistors with high-k HfO₂ Dielectric on Plastic Substrate.* small, 2012.
 194. Cao, Q., et al., *Gate capacitance coupling of singled-walled carbon nanotube thin-film transistors.* Applied Physics Letters, 2007. **90**(2).
 195. Stokes, P., et al., *Solution processed large area field effect transistors from dielectrophoretically aligned arrays of carbon nanotubes.* Applied Physics Letters, 2009. **94**(11).
 196. Wang, X., et al., *Fabrication of ultralong and electrically uniform single-walled carbon nanotubes on clean substrates.* Nano Letters, 2009. **9**(9): p. 3137-3141.
 197. Zheng, M. and E.D. Semke, *Enrichment of Single Chirality Carbon Nanotubes.* Journal of the American Chemical Society, 2007. **129**(19): p. 6084-6085.
 198. Yu, B., et al., *Selective removal of metallic single-walled carbon nanotubes by combined in situ and post-synthesis oxidation.* Carbon, 2010. **48**(10): p. 2941-2947.
 199. Ford, A.C., et al., *Physical removal of metallic carbon nanotubes from nanotube network devices using a thermal and fluidic process.*

- Nanotechnology, 2013. **24**(10).
200. Gomez, L.M., et al., *Scalable Light-Induced Metal to Semiconductor Conversion of Carbon Nanotubes*. Nano Letters, 2009. **9**(10): p. 3592-3598.
 201. Li, J., et al., *In situ charge-transfer-induced transition from metallic to semiconducting single-walled carbon nanotubes*. Chemistry of Materials, 2013. **25**(22): p. 4464-4470.
 202. CarbonSolutionInc. <http://www.carbonsolution.com/faq>.
 203. Pimenta, M.A., et al., *Raman modes of metallic carbon nanotubes*. Physical Review B - Condensed Matter and Materials Physics, 1998. **58**(24): p. R16016-R16019.
 204. Brown, S.D.M., et al., *Origin of the Breit-Wigner-Fano lineshape of the tangential G-band feature of metallic carbon nanotubes*. Physical Review B - Condensed Matter and Materials Physics, 2001. **63**(15): p. 1554141-1554148.
 205. Roy, S. and Z. Gao, *Nanostructure-based electrical biosensors*. Nano Today, 2009. **4**(4): p. 318-334.
 206. Wang, S., et al., *High-Performance Carbon Nanotube Light-Emitting Diodes with Asymmetric Contacts*. Nano Letters, 2010. **11**(1): p. 23-29.
 207. Robertson, J., *High dielectric constant oxides*. EPJ Applied Physics, 2004. **28**(3): p. 265-291.
 208. Wei, L., et al., *Gas sensors based on single-walled carbon nanotube field-effect transistor*. Sensors and Materials, 2014. **26**(1): p. 9-17.
 209. Allen, B.L., P.D. Kichambare, and A. Star, *Carbon Nanotube Field-Effect-Transistor-Based Biosensors*. Advanced Materials, 2007. **19**(11): p. 1439-1451.
 210. Chattopadhyay, D., I. Galeska, and F. Papadimitrakopoulos, *A Route for Bulk Separation of Semiconducting from Metallic Single-Wall Carbon Nanotubes*. Journal of the American Chemical Society, 2003. **125**(11): p. 3370-3375.
 211. Tang, M.S.Y., et al., *Separation of single-walled carbon nanotubes using aqueous two-phase system*. Separation and Purification Technology, 2014. **125**(0): p. 136-141.
 212. Li, S., et al., *Transfer printing of submicrometer patterns of aligned carbon nanotubes onto functionalized electrodes*. Small, 2007. **3**(4): p. 616-621.
 213. Kang, Y. and T.A. Taton, *Micelle-encapsulated carbon nanotubes: A route to nanotube composites*. Journal of the American Chemical Society, 2003. **125**(19): p. 5650-5651.
 214. Maynor, B.W., et al., *Supramolecular Nanomimetics: Replication of Micelles, Viruses, and Other Naturally Occurring Nanoscale Objects*. Small, 2007. **3**(5): p. 845-849.
 215. Vaisman, L., H.D. Wagner, and G. Marom, *The role of surfactants in dispersion of carbon nanotubes*. Advances in Colloid and Interface Science, 2006. **128-130**: p. 37-46.
 216. Ma, Y., et al., *The production of horizontally aligned single-walled carbon nanotubes*. Carbon, 2011. **49**(13): p. 4098-4110.
 217. Kumar, S., J.Y. Murthy, and M.A. Alam, *Percolating conduction in finite*

- nanotube networks*. Physical Review Letters, 2005. **95**(6).
218. Bachtold, A., et al., *Scanned probe microscopy of electronic transport in carbon nanotubes*. Physical Review Letters, 2000. **84**(26): p. 6082-6085.
 219. Fuhrer, M.S., et al., *Transport through crossed nanotubes*. Physica E, 2000. **6**(1): p. 868-871.
 220. Engel, M., et al., *Thin film nanotube transistors based on self-assembled, aligned, semiconducting carbon nanotube arrays*. ACS Nano, 2008. **2**(12): p. 2445-2452.
 221. Pimparkar, N., et al., *Limits of performance gain of aligned CNT over randomized network: Theoretical predictions and experimental validation*. IEEE Electron Device Letters, 2007. **28**(7): p. 593-595.
 222. Kordás, K., et al., *Magnetic-Field Induced Efficient Alignment of Carbon Nanotubes in Aqueous Solutions*. Chemistry of Materials, 2007. **19**(4): p. 787-791.
 223. Ye, Z., et al., *Thermally enhanced single-walled carbon nanotube microfluidic alignment*. Microelectronic Engineering, 2011. **88**(9): p. 2919-2923.
 224. Lee, P., et al., *Microfluidic alignment of collagen fibers for in vitro cell culture*. Biomedical Microdevices, 2006. **8**(1): p. 35-41.
 225. Banerjee, S., et al., *Precise positioning of single-walled carbon nanotubes by ac dielectrophoresis*. Journal of Vacuum Science and Technology B, 2006. **24**(6): p. 3173-3178.
 226. Vijayaraghavan, A., et al., *Metal–Semiconductor Transition in Single-Walled Carbon Nanotubes Induced by Low-Energy Electron Irradiation*. Nano Letters, 2005. **5**(8): p. 1575-1579.
 227. Pike, G.E. and C.H. Seager, *Percolation and conductivity: A computer study. I*. Physical Review B, 1974. **10**(4): p. 1421-1434.
 228. Rinkiö, M., et al., *High-speed memory from carbon nanotube field-effect transistors with high-k gate dielectric*. Nano Letters, 2009. **9**(2): p. 643-647.
 229. Ryu, K., et al., *CMOS-analogous wafer-scale nanotube-on-insulator approach for submicrometer devices and integrated circuits using aligned nanotubes*. Nano Letters, 2009. **9**(1): p. 189-197.
 230. Walters, D.A., et al., *In-plane-aligned membranes of carbon nanotubes*. Chemical Physics Letters, 2001. **338**(1): p. 14-20.
 231. Lee, C.W., et al., *Solution-processable carbon nanotubes for semiconducting thin-film transistor devices*. Advanced Materials, 2010. **22**(11): p. 1278-1282.
 232. Gan, Y., et al., *Solution-Prepared Hybrid-Nanoparticle Dielectrics for High-Performance Low-Voltage Organic Thin-Film Transistors*. ACS Applied Materials & Interfaces, 2009. **1**(10): p. 2230-2236.
 233. Cai, Q.J., et al., *Solution-processable barium titanate and strontium titanate nanoparticle dielectrics for low-voltage organic thin-film transistors*. Chemistry of Materials, 2009. **21**(14): p. 3153-3161.
 234. Cho, J.H., et al., *Printable ion-gel gate dielectrics for low-voltage polymer thin-film transistors on plastic*. Nature Materials, 2008. **7**(11): p. 900-906.
 235. Wei, L., et al., *Highly sensitive detection of trinitrotoluene in water by*

- chemiresistive sensor based on noncovalently amino functionalized single-walled carbon nanotube*. *Sensors and Actuators B: Chemical*, 2014. **190**(0): p. 529-534.
236. Banerjee, S., T. Hemraj-Benny, and S.S. Wong, *Covalent Surface Chemistry of Single-Walled Carbon Nanotubes*. *Advanced Materials*, 2005. **17**(1): p. 17-29.

List of Publications

1. **Y. Wang**, S. K. R. Pillai, M. B. Chan-Park, *High-Performance Partially Aligned Semiconductive Single-Walled Carbon Nanotube Transistors Achieved with a Parallel Technique*. Small, 2013. **9**(17): p. 2960-2969.
2. **Y. Wang**, X. Luan, A. K. Sundramoorthy, S. K. R. Pillai, M. B. Chan-Park, *Stripping of SWNT-based networks for improved FET performance*. Nanoscale, Submitted.
3. A. K. Sundramoorthy, **Y. Wang**, J. Wang, J. Che, Y. X. Thong, A. C. W. Lu, M. B. Chan-Park, *Lateral Assembly of Oxidized Graphene Flakes into Large-scale Transparent Conductive Thin Films with Calix[4]arene surfactant*. Nanoscale, Submitted. (co-first author)
4. J. Yang, **Y. Wang**, J. Wang, M. B. Chan-Park, *Reducing Graphene Oxide with Modified Birch Reaction*, RSC Advance, Submitted.
5. C. W. Lee, S. K. R. Pillai, X. Luan, **Y. Wang**, C. M. Li, M. B. Chan-Park, *High-performance Inkjet Printed Carbon Nanotube Thin Film Transistors with high-k HfO₂ Dielectric on Plastic Substrate*. Small, 2012.
6. J. Shi, M. B. Chan-Park, **Y. Wang**, H. Yang, C. M. Li., *A micropatterning technique to fabricate organic thin-film transistors on various substrates*. Journal of Materials Chemistry, 2011. **21**(40): p. 16184-16189.
7. S. Mesgari, Y. F. Poon, **Y. Wang**, Y. X. Thong, J. Wang, M. B. Chan-Park, *Polymer removal from electronic grade single-walled carbon nanotubes after gel electrophoresis*. Journal of Materials Chemistry C, 2013. **1**(41): p. 6813-6823.
8. H. Yang, G. H. Guai, C. Guo, Q. Song, S. P. Jiang, **Y. Wang**, W. Zhang, C. M. Li, *NiO/Graphene Composite for Enhanced Charge Separation and Collection in p-Type Dye Sensitized Solar Cell*. The Journal of Physical Chemistry C, 2011. **115**(24): p. 12209-12215.
9. Y. Zhang, S. S. Ng, **Y. Wang**, H. Feng, W. N. Chen, M. B. Chan-Park, C. Li, V. Chan, *Collective Cell Traction Force Analysis on Aligned Smooth Muscle Cell Sheet between Three Dimensional Microwalls*. Interface Focus, accepted.