Development of High-rate SWNTs Assembly

for Large-scale SWNTs-based Functional Device Applications

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This dissertation is dedicated to my beloved parents, family, and friends.

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ABSTRACT

Carbon nanotubes (CNTs) are promising building blocks for nanoscale devices due to its intrinsic small dimensions and remarkable electronic properties. At the nanoscale, it has been an unsolved problem to place CNTs at the desired locations with targeted shapes, directions, and densities for manufacturing CNTs-based functional devices. To date, development of CNT-based device applications has been impeded by a lack of abilities of CNTs control techniques and manufacturing processes.

In this thesis, I have focused on CNTs assembly techniques and nanotemplate manufacturing for single-walled carbon nanotubes (SWNTs)-based functional device applications. A template-guided fluidic assembly method has been utilized because it is directed, robust, and precisely controllable over other assembly methods. Since the fluidic assembly uses capillary force at the interface of the surface, however, it is a diffusion-limited process; the SWNTs are slowly attached on the surface while the solution is evaporated. Hence, a significantly progressive assembly technique is destined to meet all the integration requirements of precise control of the desired location, density, large area and alignment simultaneously. Therefore, I developed an electric-assisted template-guided fluidic assembly technique for high-rate SWNTs assembly accurately to assemble highly aligned SWNTs arrays with high density. The introduced method allows the reliable and well-controlled fabrication process of SWNTs-based devices and could provide control over the electrical properties of the fabricated nanotube assemblies.

As an increase of the demand for nanoscale electronic devices, it is required to realize
nanoscale manufacturing techniques to scale down the size of the devices. To assemble SWNTs onto nanoscale electronic device, nanotemplate is required to guide accurately the nanotubes at desired location. I developed a new nanolithography technique for the nanoscale template manufacturing using DODE process.

Finally, SWNTs-based functional devices were fabricated using the developed assembly methods for electrical, chemical, and biological applications. SWNTs thin film transistor is fabricated and the percolation transport properties are investigated. Large-scale SWNTs-based antenna is developed for energy harvesting application. I have fabricated densely packed and aligned SWNTs bundles for gas sensing applications. The site-selective fluidic assembly technique is used for controlled assembly of SWNTs with high density network architectures for in-vivo D-glucose biosensor application.
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CHAPTER 1: INTRODUCTION

1.1 Outline of Dissertation

Carbon nanotubes (CNTs) were discovered from fullerene-like material using high-resolution transmission electron microscopy (HRTEM) by Iijima in 1991. The observation heralded the beginning of the CNTs era in nanotechnology. Subsequently, synthesis method has been developed for large-quantity and high-quality CNTs so that paved the way for worldwide scientific and engineering research of efforts. The most unique aspects of the CNTs structure are high aspect ratio, high mechanical strength and electrical conductivity, thermal conductivity, and nanoscale one dimensionality. The remarkable size- and structure dependent properties have attracted intense research interests as numerous theoretical and experimental studies on CNTs structures. CNTs have been used as active components of nanodevices such as transistor or sensing elements. Especially, the CNTs-based devices have attracted intensive research interest for their possible technological applications in various files of science due to its excellent electrical and mechanical properties such as highest Young’s modulus, highest thermal conductivity, ballistic electron transport, and unique one-dimensional nanostructure with high aspect ratio. In particular, the outstanding high current carrying capacity and mechanical stability properties exhibit applications in electronic devices. Furthermore, the applications of CNTs in the field of chemical and biological sensors have started to emerge because of their unique geometry and amazing feature of being all surface reacting and large specific surface area. The thermoelectric properties of CNTs are sensitive to chemicals in contact with the nanotube walls.
The physical and chemical properties of CNTs are dependent on their one dimensionality of nanotube structures for various applications. Single-walled carbon nanotubes (SWNTs) is a \( \text{sp}^2 \)-bonded graphene sheet which is rolled into a seamless hollow cylinder and capped at each end with half of a fullerene molecule, while a multi-walled carbon nanotubes (MWNTs) is a collection of several concentric SWNTs.\(^8\) Even though there are no difference in any doping or an additional functionalization and the chemical bonding, SWNTs can behave as well-defined metallic, semiconducting or mixture of semi-metallic nanotubes depending on their diameter and chirality.

For CNTs-based functional device applications, CNTs assembly methods have been developed for alignment and / or patterning of CNTs into hierarchical arrays over large-scale areas with precisely controllable orientation, shape and density of the nanotubes at the desired location. The scientific and engineering efforts have been made to address for this CNTs assembly on the electronic device. The CNTs assembly techniques can be categorized into the two rubrics of direct synthesis and post-synthesis assembly. In this dissertation, I have focused on the post-synthesis approach and developed the high-rate SWNTs assembly method over large-area using fluidic assembly techniques for SWNTs-based functional device applications. I also demonstrate the development of nanolithography technique for the challenging task of the nanoscale assembly of the SWNTs.

In Chapter 1, I introduce the outline of my dissertation and research significance and objective goals. I aimed to develop SWNTs assembly techniques for SWNT-based functional device applications. There are four main parts of my research: 1) development of large-scale
SWNTs assembly using template-guided fluidic assembly method, 2) development of high-rate SWNTs assembly using electric-assisted template-guided fluidic assembly for highly-aligned SWNTs, 3) development of nanolithography technique using isotropic thin film deposition and anisotropic dry etching processes for nanotemplate fabrication, and 4) fabrication and characterization of SWNTs-based functional devices for electrical, chemical and biological applications.

In Chapter 2, I introduce the atomic and electronic structure of CNTs, and establish the basic nanotube properties that will be utilized in the nanotube devices. CNTs have a cylindrical one-dimensional nanostructure. The electronic properties of CNTs are strongly affected by the unique symmetry nanostructure. To implement CNTs onto electronic device applications, lots of techniques have been studied for assembly of CNTs into hierarchical arrays. I reviewed the development of CNTs synthesis and assembly methods under two categories of direct synthesis assembly and post synthesis assembly of CNTs, with emphasis given to the post-synthetic approach. The electronic properties of SWNTs thin film are affected by the alignment of SWNTs. I showed the results of percolation path of SWNTs on transistor performance and assembly techniques for aligned SWNTs networks. For SWNTs-based functional device applications, I have introduced of SWNTs-based functional devices for thin film transistor, antenna, chemical and biological sensors applications.

In Chapter 3, I demonstrate the large-scale SWNTs assembly using template-guided fluidic assembly. I investigated the surface energy and humidity effects on assembly efficiency. For highly organized SWNTs networks, surface energy control process is developed by surface
treatment process. Large-scale SWNTs networks are fabricated on a plastic substrate and characterized for flexible electronic device applications. It has been a challenge to harness the highly efficient electronic transport in CNTs because of difficulties in manipulating individual CNTs from a mixture of metallic and semiconducting nanotubes separately. I have achieved SWNTs assembly down to 50 nm of channel width for topological transition in SWNTs networks via nanoscale confinement process. SWNTs networks become geometrically aligned along the channel as decreasing topological channel width. Therefore, the alignment of CNTs driven by nanoscale confinement shifts the transitions to higher networks densities and shows marked reduction in metallic transport.

In Chapter 4, I illustrate the development of high-rate SWNTs assembly using electric-assisted template-guided fluidic assembly for highly aligned SWNTs networks. It utilized directed assembly strategies by integration of electrophoresis and fluidic assembly methods to enhance the assembly efficiency and orientation of the template-guided fluidic assembly. The applied electric-field not only increases partial concentration of the individual nanotubes suspended in solution, but also enable orientation of the electrically-driven SWNTs on the electrode surface in a desired direction to align along the assembly direction. The fluidic assembly process speed has been improved by 1000 times and the density and scale can be controlled through assembly pulling speed adjustment.

In Chapter 5, I have developed a new nanolithography method using isotropic thin film deposition and anisotropic dry etching processes for nanotemplate fabrication. The double oxide deposition and etching (DODE) lithography method - an integration of thin film deposition and
plasma etching process – has been developed as a novel nanolithography technique for overcoming the limitations of optical and alternative lithography methods. The nanopatterning was obtained by integrating CVD (chemical vapor deposition) attributes with a dry etching process on a microstructure. Moreover, the nanostructures fabricated by the DODE lithography method do not use a polymeric resin as a masking layer for high aspect-ratio nanostructure manufacturing. Thus, I could produce periodic arrays of nanostructures over a large area with high resolution by the DODE method with an aspect-ratio that is greater than 20:1.

In Chapter 6, I present SWNTs-based functional devices for electrical, chemical, and biological applications. SWNTs-based functional devices have fabricated using the developed assembly methods. SWNTs thin film transistor is fabricated using the developed assembly techniques. Large-scale SWNTs-based antenna is developed using the template-guided fluidic assembly for energy harvesting application. Highly dense and aligned SWNTs bundles have been fabricated using the electric-assisted fluidic assembly for gas sensing applications. For biosensor application, the site-selective fluidic assembly technique is used for controlled assembly of SWNTs with high density network architectures for in-vivo D-glucose biosensor.
1.2 Research Significance and Objectives

Objective: The goals of this thesis are 1) investigation of surface energies for large-scale SWNTs assembly using template-guided fluidic assembly, 2) development of high-rate SWNTs assembly using electric-assisted template-guided fluidic assembly for highly aligned assembly, 3) development of new nanolithography technique using isotropic oxide deposition using plasma enhanced chemical vapor deposition (PECVD) and anisotropic dry etching using ICP (inductively coupled plasma) processes for large-scale nanotemplate fabrication, and 4) characterization of the SWNTs-based devices for electronic, chemical and biological applications.

The specific goals are:

- Investigation of surface energies on assembly efficiency for large-scale SWNT assembly.
- Study of the humidity effects on SWNTs assembly efficiency.
- Development of surface energy control process using plasma treatment and self-assembled monolayers (SAMs) coating for highly dense SWNTs assembly.
- SWNTs assembly on PEN plastic substrate for flexible electronic applications.
- Sub-100 nm nanoscale SWNTs assembly using nanoscale confinement process.
- Development of high-rate SWNTs assembly using electric-assisted template-guided
fluidic assembly technique.

- Study of electrically polarized SWNTs assembly for highly aligned SWNTs assembly.
- Investigation of electrical percolation transport properties of the aligned SWNTs thin film networks.
- Development of sub-100 nm nanopatterning technique using oxide deposition process.
- Investigation of plasma etching process for high aspect ratio nanostructure manufacturing.
- Achievement of large scale nanolithography method using oxide deposition and etching processes for high aspect ratio nanostructures.
- Fabrication and characterization of SWNTs thin film transistor using SWNTs assembly techniques.
- Fabrication of large-scale assembly of SWNTs-based antenna for energy harvest application.
- Achieve high current carrying SWNTs assembly of NO₂ gas sensor for highly sensitive chemical sensor applications.
- Fabrication and characterization of SWNTs biosensors for D-glucose detection.
CHAPTER 2: BACKGROUND and LITERATURE REVIEW

2.1 Carbon Nanotubes for Integration into Electronic Devices

Carbon nanotubes (CNTs) have attracted considerable attention from both scientific and technological research areas for a whole host of applications. CNTs is a cylindrical nanostructure as a rolled-up graphene sheet which is symmetry and unique electronic structure so that the electrical properties of the CNTs are strongly affected by the nanostructures. In this chapter, I will illustrate the electronic properties of CNTs according to its size and structures.

2.1.1 Carbon Nanotubes Basics

Carbon element can form a variety of structures by sp² hybridization so the carbon can build honeycomb atomic arrangement with open and closed cages. First structure discovered by Kroto et al. was the C₆₀ molecule. Then, Iijima observed first time tubular carbon structures, multi-walled carbon nanotubes (MWNTs), which consisted of up to several tens of graphitic shells in 1991. Two years later, single-walled carbon nanotubes (SWNTs) were independently synthesized by Iijima and Ichihashi and Bethune et al. The MWNTs and SWNTs are produced by arc-discharge, laser-ablation, and catalytic growth.

The synthesized carbon nanotubes (CNTs) have a unique geometry of high aspect ratio hollow cylinders with diameters ranging from one to tens of nanometers and with lengths up to centimeters. The CNTs are composed entirely of carbon, and the elemental carbon in the sp²
hybridization can represent a variety of amazing structures. Structures that carbon adopts in the solid state include diamond, graphite, and buckyballs. These many different forms have emerged because of the ability of carbon to achieve relatively stable structures with different bonding configurations by forming hybridized orbitals. Such a unique and special properties of CNTs suggest great potential solution for interconnect metals and electronic devices of future integrated circuits. The excellent mechanical properties of the CNTs such as high Young’s modulus and tensile strength have led to speculations for their use in composite materials.\textsuperscript{14} In the field of electronic devices, the CNTs can be used as an active layer due to their high electrical conductivity, structural perfection, and chemical stability.\textsuperscript{15} MWNTs have shown electro-catalyze and oxygen reduction reaction for fuel cells\textsuperscript{16} and SWNTs have been used to large irreversible capacities and voltage hysteresis for battery electrodes.\textsuperscript{17} Moreover, the SWNTs have been proposed as a subject of extensive research because of their unique structure – dependent electrical, thermal and mechanical properties. Especially, SWNTs received increasing attention as central elements of multifunctional flexible electronic devices including field-effect transistors, energy harvesting antenna, chemical and biological sensors.
2.1.2 Atomic Structure and Electronic Properties of Single-Walled Carbon Nanotubes

Electronic properties, metallic and semiconducting, of CNTs are predicted depending on their diameter and the helicity of the arrangement of graphitic rings in their walls. The diameter of the most SWNTs is close to 1 nm and the tube length can be many millions of times longer. SWNTs structure can be considered as a wrapped one-atom-thick layer of a graphene sheet into a seamless cylinder. The way the graphene sheet is wrapped is indicated by a pair of indices \((n, m)\). The integers denote the number of a unit vector along two directions in the honeycomb crystal lattice of graphene. Once \((n, m)\) is specified, other structure properties, such as diameter \((d)\) and chiral angle \((\Theta)\) of the SWTNs can be calculated from the \((n, m)\) indices as follows

\[
d = \frac{\sqrt{3}a_{cc}}{\pi} \sqrt{(m^2 + nm + n^2)}
\]

and

\[
\theta = \tan^{-1}\left(\frac{\sqrt{3}m}{2n + m}\right)
\]

where \(a_{cc}\) corresponds to the nearest-neighbor carbon atom distance of 0.142 nm in the graphite sheet. The helicity of a defect-free SWNTs that connects crystallographically equivalent sites on a two-dimensional graphene sheet can be characterized by the roll-up vector as follows

\[
C_h = na_1 + ma_2 \equiv (n, m)
\]

where \(a_1\) and \(a_2\) are the graphene primitive lattice vectors as illustrated in Fig. 1. The magnitude
of the translation vector, $T$, which is directed along the SWNTs axis and perpendicular to $C_h$ corresponds to the length of SWNTs unit cell.

Figure 1. The honeycomb lattice and schematic model of single-walled carbon nanotubes: (a) Schematic of a two-dimensional graphene sheet illustrating lattice vectors $a_1$ and $a_2$, and the roll-up vector $c_h = na_1 + ma_2$. The limiting cases of (n, n) armchair (b), (n, 0) zigzag (c), and (n, m) chiral nanotubes (d) are indicated with dashed lines. As represented here, the angle between the zigzag configuration and $c_h$ is negative. Reproduced with permission from ref. 9 (Copyright 1998 Nature Publishing Group).
While the local carbon-carbon bonding remains constant, the electronic properties of the SWNTs depend only on diameter and chirality without doping. The integers, $n$ and $m$, determine the electronic band structures of SWNTs whether it is metallic or semiconducting behavior.\textsuperscript{20} Zigzag nanotubes are $n = 0$, armchair nanotubes are $n = m$. Otherwise, they are chiral nanotubes. The SWNTs with zigzag structure have two distinct types of behavior; if $n / 3$ is an integer, the nanotubes are metallic and otherwise semiconductors.\textsuperscript{21} The electronic properties of the chiral structure of SWNTs can be determined similar to the zigzag nanotubes; when $(2n + m) / 3$ is an integer the SWNTs are metallic, and otherwise semiconducting behavior.\textsuperscript{22} When the $C_6$ rotates away from zigzag $(n, 0)$ about $30^\circ$, the armchair $(n, n)$ nanotubes are expected to be truly metallic behavior SWNTs as illustrated in Fig. 2.

\textbf{Figure 2.} Possible vectors specified by the pairs of integers $(n, m)$ for general carbon nanotubes, including zigzag, armchair and chiral nanotubes. Reproduced with permission from ref. 9 (Copyright 1998 Nature Publishing Group).
The intrinsic electronic properties of SWNTs are studies using scanning tunneling microscopy (STM) for investigating fundamental one-dimensional (1D) physics simultaneously and for exploring nanoelectronics and molecular electronics. Since the nanotubes have finite curvature of the structure, the basic electronic band structure can be derived from a graphene sheet. Graphene is a zero-gap semimetal material and their π valence and π* conduction bands degenerate at only six corners (\(K, K'\)) of the Brillouin zone. Band structure of graphene near the Fermi level is shown in Fig. 3. The energy can be calculated by the measured wave vector \(\mathbf{\kappa}\) from the \(K\) points as follows:

\[
\varepsilon(\mathbf{\kappa}) = \pm \hbar v|\mathbf{\kappa}| = \pm \hbar |\mathbf{p}| \text{ for small } \mathbf{\kappa} = |\mathbf{\kappa}|
\]

where \(\mathbf{p} = \hbar \mathbf{\kappa}\) is the momentum and \(v\) is the velocity of the order \(c / 300\) with \(c\) being the light velocity. Based on the special theory of relativity, the relativistic particle energy is given by

\[
\varepsilon = \sqrt{m^2 c^4 + \mathbf{p}^2} \text{ with } m \text{ being a rest mass.}
\]

The phase of the wave function changes by \(\pm \pi\) when the direction of the motion is rotated by 2\(\pi\), changing its sign. Since the backscattering corresponds to the rotation of the amplitudes for \(\pm \pi\) rotation and the direction by \(\pm \pi\) cancel each other due to the sign difference, there is no backscattering when a particle is scattered by impurities. When the resistance is determined solely, the electron motion along the circumference in CNTs is quantized and becomes one-dimensional. Consequently, the absence of backscattering leads CNTs to be metallic as an ideal conductor with perfect conduction even in the presence of scatters.
Figure 3. Electronic structure and properties of graphene; (a) The energy bands near the Fermi level in graphene. The conduction and valence bands cross each other at the K and K’ point. (b) The conic energy bands in the vicinity of the K and K’ point. (c) The density of states near the Fermi level with Fermi energy $E_F$. Reproduced with permission from ref. 24 (Copyright 2009 Nature Publishing Group).

CNTs are constructed in a way that the hexagon at position of lattice translation vector $L$ is rolled onto the hexagon at the origin. This $L$ becomes a circumference of the CNTs. The CNTs usually have helical structure because the axis is perpendicular to $L$. The quantization of the electron wavevector $\kappa$ in SWNTs is along the circumferential direction due to periodic boundary conditions as follows

$$\kappa \cdot L = 2\pi q$$

where $q$ is an integer.\textsuperscript{23} So, only a particular set of states are allowed which are parallel to the corresponding nanotubes axis with a neighboring spacing $2\pi / L$ as illustrated in Fig. 4. On the
basis of a simple scheme, whenever the allowed wavevector passes through a Fermi $K$ and $K'$ points, there is no gap at the Fermi level and the nanotubes is a metallic with a nonvanishing density of states at the Fermi level, and otherwise it is a semiconducting with different size energy gaps near the Fermi level.\textsuperscript{23} The straight line closest to the $K$ and $K'$ points provide the conduction and valence bands in semiconducting nanotubes. The energy gap is proportional to the inverse of the diameter $d = L / \pi$ because the neighboring spacing between lines is $2\pi / L$ and the energy is a linear function of the wavevector.\textsuperscript{24}

![Figure 4](image.png)

**Figure 4.** Equi-energy lines of the valence band in the wave-vector space; The straight dashed lines show wave vectors allowed when graphene is rolled into a cylinder forming carbon nanotubes. The hexagon denotes the first Brillouin zone, $L$ is the chiral vector, $\eta$ is the chiral angle, and the dashed lines are perpendicular to $L$. (a) The K and K' points lie on the dashed line in metallic carbon nanotubes. (b) They are not on any of the dashed lines in semiconducting nanotubes. Reproduced with permission from ref. 24 (Copyright 2009 Nature Publishing Group).
2.2 Carbon Nanotubes Assembly Techniques

As promising building blocks for nanoelectronics, carbon nanotubes (CNTs) have showed unique nanoscale dimension and remarkable electronic properties depending on size and structures. For various potential applications, lots of techniques have been developed for alignment and / or patterning of CNTs into hierarchical arrays with a controllable orientation, location, shape and density of nanotubes. In this chapter, I will review the development of CNTs synthesis and assembly methods under two categories of direct synthesis assembly and post synthesis assembly of CNTs, with emphasis given to the post-synthetic approach.

2.2.1 Direct Synthesis of Carbon Nanotubes

CNTs have been produced by catalytic synthesis methods such as arc discharge, chemical vapor deposition (CVD), laser ablation, and hydrocarbon flame synthesis. Figure 5 shows a schematic representation of these catalytic synthesis process. The reactor of the synthesis processes consists of three essential components: (1) source of gaseous carbon, (2) source of heat and (3) catalyst particles at appropriate temperature.

In 1991, CNTs were first synthesized using arc discharge method by Iijima. The condensation of carbon atoms are generated from evaporation of a solid carbon source. When high electric current (~ 50 – 120 A) is passed graphite electrodes in the chamber, the materials are sublimated from the cathode and the nanotubes are formed on the anode at very high temperature (~ 3200 K). The arc discharge method is cost and energy intensive process so it is
relatively low yield of CNTs. In the laser ablation method, a high energy laser ablates a carbon target which contains nickel and cobalt in a tube furnace with high temperature (~ 1400 K). The CNTs downstream is carried by a the flow of inert gas to a collector surface through the chamber. CNTs produced by the laser ablation process are of a higher quality than those synthesized by the arc discharge process, however, the production rate is also low because the laser ablation method is both capital and energy intensive.

A well-known direct-synthesis method for CNTs production is CVD process that is an alternative method to arc discharge and laser ablation methods. CNTs are grown using catalyst, which involves a decomposition of a hydrocarbon gas over a transition and saturation of carbon atoms in the catalyst metal nanoparticles. The formation of CNTs is caused by the precipitation of carbon from the saturated metal particles. The CVD method can produce high-quality of CNTs and better yield so it is scalable manufacturing process. Hydrocarbon flames method utilizes a combination of the chemical and catalytic factors. A diverse source of gaseous carbon is presented from gases (CO, CH₄, C₂H₂, C₂H₄, and C₂H₆) in the post flame environment. The endothermic carbon deposition reactions occur by the chemical energy released in the form of heat in the flame. The structural properties of CNTs are determined by the geometry and characteristics of the catalysts.
Figure 5. Schematic representation of methods used for carbon nanotubes synthesis; (a) Arc discharge, (b) Chemical vapor deposition, (c) Laser ablation, and (d) Hydrocarbon flames. Reproduced from ref. 26 (Copyright 2011 Intech Open Science).

Figure 6 demonstrates mechanism of CNTs formation in a catalytic synthesis process. Baker et al.\textsuperscript{27} proposed dissolution-diffusion-precipitation mechanism. Spherical catalytic nanoparticles from transitional metal / metal alloys (e.g. Co, Fe, and Ni) are floating on a substrate. The catalytic carbon precursor molecules (e.g. CO, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, and C\textsubscript{2}H\textsubscript{6}) are decomposed on one half of the nanoparticle surfaces. The carbon atoms released by chemical energy diffuse into the nanoparticles until super-saturation of carbon.\textsuperscript{28} After super-saturation of the catalyst particle, the precipitated carbon atoms form on the opposite half of the catalyst particle.\textsuperscript{26} The specific physical structures (e.g. single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs), and amorphous carbon) of the precipitated solid carbon are
determined by catalyst particle size and precipitation rate. Graphitic layers are formed when the carbon diffusion rate is in equilibrium with or larger than the precipitation rate. CNTs growth can occur when the carbon diffusion rate is less than the precipitation rate. For the catalytic nanoparticles smaller than 20 nm, carbon atom cannot precipitate from the vertex of the hemisphere but a circular ring around the spherical nanoparticle. Therefore, CNTs grow upward from the nanoparticles (Fig. 6(a)) or lift the catalyst nanoparticles (Fig. 6(b)). SWNTs are predominantly formed from the nanoparticles of the order of 1 nm diameter. Catalyst nanoparticles of the diameters in the range of 10 ~ 50 nm form MWNTs. When large nanoparticles larger than 50 nm are covered with amorphous graphitic sheet, nano-onion structure is formed (Fig. 6(c)).

Figure 6. Mechanism for carbon nanotubes growth; (a) Base growth, (b) Tip growth, and (c) Structural dependence on catalyst particle size. Reproduced from ref. 26 (Copyright 2011 Intech Open Science).
2.2.2 Post Synthesis Carbon Nanotubes Assembly

Significant research efforts have been contributed to the realization of the large-scale direct synthesis CNTs methods for high-density horizontally aligned SWNTs. Furthermore, transfer techniques have been developed to transfer SWNTs on various types of rigid and flexible substrate, enabling the demonstrate high-performance SWNTs electronic device.\(^2^9\) Even though the growth methods allow it to produce high-purity CNTs on desired locations, it is somewhat problematic to mass-produce to commercial manufacturing. Alternative to vapor-phase growth synthesis methods is the solution-phase post-synthesis, which has various advantages such as rather low temperature process, relatively inexpensive instruments, and convenient in compound alteration.\(^3^0\) The post synthesis methods have different synthetic frameworks based on controlled precipitation from nanotubes-suspended homogeneous solutions using external guiding forces or internal interactions. The direct assembly techniques using guiding forces have been developed to build highly organized CNTs arrays.

Krupke et al.\(^3^1\) used dielectrophoresis (DEP) method to assemble CNTs by applying an electric field between a pair of electrodes. The DEP assembly method utilizes electric field to polarize CNTs. A schematic diagram of DEP assembly of CNTs is shown in Fig. 7.\(^3^2\) CNTs are polarized by induced large dipole moments in an alternating current (AC) electric field and then large aligning torques force CNTs to move towards the electrode gap along the electric field orientation. Kamat et al.\(^3^3\) utilized an electrophoretic deposition (EPD) technique for the alignment of SWNTs by applying a direct current (DC) electric field. The SWNTs bundles suspended in tetrahydrofuran (THF) solution were stretched out when a higher DC electric field
was applied and aligned perpendicular to the electrode surface.\textsuperscript{34}

Huang et al.\textsuperscript{35} developed directed assembly of one-dimensional nanostructures such as nanowires and nanotubes into functional networks using physical fluidic-flow. Nanowires were assembled through well-defined fluidic channel between PDMS structure and flat substrate with control of the separation and by combining fluidic alignment (Fig. 8(a)).\textsuperscript{35} Langmuir-Blodgett (LB) technique has introduced for the assembly of anisotropic building blocks such as nanowires and nanotubes.\textsuperscript{36,37} The nanotubes are functionalized with macromolecules to solubilize in an organic solvent and the nanotubes suspension is spread on the water surface. The floating nanotubes surface layer are then compressed slowly with trough barriers to closely pack in confined surface area. At proper stages of compression, the aligned nanotubes monolayer at the water-air interface is then transferred onto desired substrates for hierarchically aligned SWNTs structures (Fig. 8(b)).\textsuperscript{30,34}
Figure 7. Dielectrophoretic (DEP) assembly of carbon nanotubes (CNTs); (a) Illustration of CNTs assembly on microelectrodes by using AC DEP. (b) SEM image of the assembled SWNTs between the electrodes. (c) Schematic of DEP assembly of CNTs onto an electrode gap. Reproduced with permission from ref. 32 (Copyright 2007 American Chemical Society and 2013 Elsevier B. V.).
A novel evaporation-based self-assembly method has been used to obtain alignment of nanotubes strips from solution. A planar substrate with micron-wide strips is immersed vertically in the nanotubes-suspended solution. As the solvent evaporates, capillary force arises at the solid-liquid-vapor interface (contact line) and meniscus is formed. The convective transport makes the nanotubes to be aligned along the contact line and be assembled on the substrate.\textsuperscript{38} Figure 9\textsuperscript{38} demonstrates the evaporation self-assembly process. The contact line is generated due to the forces of a friction force ($f$) on the surface and the liquid surface tension ($\gamma_f$). When the solution evaporates, the capillary force ($\gamma_L$) arises at the interface and pulls the solution inward so that allow nanotubes to be aligned along the contact line.\textsuperscript{39}
Figure 9. Evaporation-based self-assembly method; (a) Schematic illustrating the assembly mechanism responsible for self-assembly of the single-walled carbon nanotubes. (b) and (c) SEM micrograph of the nanotubes within a strip. Reproduced with permission from ref. 38 (Copyright 2008 American Chemical Society).

At the same time with the directed assembly using the external forces, internal molecular forces have been employed for self-assembly of CNTs in post synthesis directed-assembly. Surface of the substrate is selectively modified with self-assembled monolayers (SAMs) molecule using photolithography,\textsuperscript{40} dip-pen lithography (DPN)\textsuperscript{41} and microcontact printing (MCP).\textsuperscript{42} SWNTs are selectively assembled on the chemically functionalized patterns on a substrate using internal interaction. SAMs layer is patterned selectively to place nanotubes on a solid substrate by adsorption of nanotubes with high precision in the suspensions. Rao et al.\textsuperscript{43}
utilized organic molecule marks chemically to functionalize patterns on the surface using DPN or MCP. The distinct surface patterns are divided by either polar chemical groups with amino (-NH$_2$ / -NH$_3^+$) or carboxyl (-COOH / -COO$^-$) or nonpolar chemical groups with methyl (-CH$_3$). Individual SWNTs in a suspension are attracted towards the polar chemical groups and self-assembled along pre-determined patterns as shown in Fig. 10.

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**Figure 10.** Atomic-force micrographs showing large-scale self-assembly of single-walled carbon nanotubes (SWNTs).\(^{43}\) (a) Image showing the topography of SWNTs. (b) Topography of an array of individual SWNTs. (c) Topography of an array of junctions. Reproduced with permission from ref. 43 (Copyright 2003 Nature Publishing Group).

Park et al.\(^{44}\) have developed a selective placement of solution-based nanotubes method on a specific substrate by chemical functionalization. The surfactant-wrapped CNTs interact with the functional surface monolayer based on ion exchange. The strong internal electrostatic interaction between the nanotubes and surface molecules leads to the self-assembly of individual nanotubes on the functionalized patterned surface as shown in Fig. 11. The surface monolayer
contains hydroxamic acid end group was formed from 1-(N-hydroxycarbonxamido)-1-methylpyridinium iodide (NMPI) on HfO$_2$ regions of a patterned SiO$_2$/HfO$_2$ substrate. The nanotubes were solubilized in aqueous solution by wrapping using an anionic surfactant (sodium dodecyl sulfate, SDS). The strong coulombic attraction between the positively charged anion of NMPI monolayer and the negatively charged anionic surfactant led a high density of CNTs assembly.

![Diagram](image)

**Figure 11.** Selective placement of carbon nanotubes by an ion-exchange process$^{44}$ (a) Schematic of nanotube placement on the surface monolayer. (b) SEM image of nanotubes deposited on an open HfO$_2$ area. (c) SEM image and (d) AFM (phase) image of the nanotubes selectively deposited on an array of 200-nm-width HfO$_2$ trenches. Reproduced with permission from ref. 44 (Copyright 2012 Nature Publishing Group).
2.3 Aligned Single-Walled Carbon Nanotubes for SWNTs Thin Film Electronics

Since single-walled carbon nanotubes (SWNTs) are electronically heterogeneous, the large number of SWNTs thin film provides high current output and good device-to-device uniformity in properties. Therefore, SWNTs are needed to be efficiently aligned to ensure optimal and reproducible electronic properties.\(^{45}\) For electronic device applications, SWNTs have been used as an active layer in SWNTs network for transistors, sensors, optoelectronics, and transparent conductors with high performance alternative to amorphous-Si technology. Even though individual SWNTs have excellent mobility (\(\mu\)),\(^{46}\) the SWNTs-based thin-film transistors have suffered from low drive current (\(I_D\)) and difficulties in precise control of orientation and placement of individual nanotubes.\(^{47}\) Compare to the random SWNTs networks, the aligned SWNTs thin film enables to avoid percolation transport pathways, tube-to-tube junction resistances, unusual scaling of device properties, and other undesirable features.\(^{45}\) In this chapter, I will demonstrate the effects of aligned SWNTs on thin film electronics performance and assembly techniques for aligned SWNTs networks.

2.3.1 Percolation Transport of Aligned SWNTs Networks

SWNTs have been emerged due to the most intriguing electronic property of high room-temperature mobility for thin film electronic applications where larger currents have to be switched or detected such as field-effect transistors, flexible electronics, or sensors. SWNTs have served as a high-mobility transport channel for SWNTs-based thin film transistors.\(^{48}\) Current
flows through the conduction path of the SWNTs networks. The geometry of a percolating network strongly influences the electrical characteristics and device properties.\textsuperscript{49} A parallel alignment of a large number of SWNTs is required in order to avoid conductance drop at nanotubes junctions and surpass the current drive of the device because the maximum current carrying capacity per individual SWNTs is limited to about 25 $\mu$A.\textsuperscript{50}

Stadermann et al.\textsuperscript{51} showed conduction behavior through nanotubes random networks in Fig. 12. The conductance drops sharply at crossed metallic and semiconducting nanotubes junctions because the nanotubes junction is a Schottky barrier, which has a higher resistance.\textsuperscript{51} Figure 13 demonstrates the crossed SWNTs junctions between metallic (M) and semiconducting (S) nanotubes. While MM and SS junctions have high conductance, MS junction forms a rectifying Schottky barrier because the semiconducting nanotubes are depleted at the junction by the metallic nanotubes.\textsuperscript{52} Local conductance depends on the number of conduction paths. The multiple conduction paths reduce resistance and increase the probability of a chain of nanotubes stretching to the electrode.
Figure 12. Nanoscale study of conduction through carbon nanotube networks; (a) Topography image of a nanotube network with low interconnectivity. The network contains bundles as well as individual tubes. These tubes were deposited from suspension and form clusters. (b) Conductance image of the same network taken simultaneously. (c) Conductance decreases coincide with nanotube junctions. Reproduced from ref. 51 (Copyright 2004 American Physical Society).

Figure 13. Crossed nanotube junctions; (a) AFM image of a crossed SWNTs device. (b) and (c) The structures used to calculate the conductance of the junction between two metallic SWNTs. (d) I-V characteristics of several SWNTs junctions. Band structures near junctions for (e) MM and (f) SS junctions. (g) In the MS junction, a Schottky barrier of height $E_{barrier}$ forms in the semiconducting SWNTs because of charge transfer from the metallic SWNTs. Reproduced with permission from ref. 52 (Copyright 2000 American Association for the Advancement of Science).
Kumar et al.\textsuperscript{53} showed 2D percolating random network to account for conductance transport properties of the nanotubes networks as a function of nanotubes densities and channel lengths. Figure 14(a) and (b) shows schematic of 2D percolating random network. For a transport in the diffusive limit, when the channel length ($L_c$) is longer than the mean free path and the nanotubes density is below the percolation threshold ($\rho < \rho_{th} \sim 1 / L_s^2$), the diffusive transport passes through the nanotubes because of low probability of nanotube-to-nanotube interaction. The network current transport is proportional to the number of nanotubes (indicating directly bridging source and drain) but inversely proportional to the channel length.\textsuperscript{53} When the channel length is long and the nanotubes density is higher than the percolation threshold, the nanotube-to-nanotube contact and conduction path are significant and current can flow through the electrical path of the network from source and drain.\textsuperscript{53} Figure 14(c) and (d) shows diffuse-limit conductance and conductance exponent as a function of $L_c / L_s$ for several nanotubes densities above the percolation threshold. The nonlinear behavior for low density is that because it is close to the percolation threshold.\textsuperscript{53}
Figure 14. Percolation conduction in finite nanotubes networks; (a) A thin film network transistor. (b) Nomenclature for bridging nanotubes calculation. (c) Conductance dependence on channel length for different densities. (d) Dependence of the conductance exponent (n) on channel length for different densities. Reproduced from ref. 53 (Copyright 2005 American Physical Society).

The contact barriers at nanotube-to-nanotube junctions can impede effective electron transport in SWNTs thin film. Well-aligned SWNTs networks can have excellent intrinsic
electrical properties of SWNTs thin film. Moreover, aligned SWNTs array can improve device mobility in thin film transistors because of the long, straight geometries of the nanotubes and the absence of nanotube-to-nanotube junctions.\textsuperscript{54} Therefore, control of alignment of the SWNTs is important because the percolation conductivity of SWNTs networks depends on alignment as well as device dimensions.\textsuperscript{55} The resistivity of the SWNTs thin film significantly depends on the percolative conduction through the nanotubes alignment of the film\textsuperscript{48} and exhibits an inverse power law dependence on device dimensions near the percolation threshold.\textsuperscript{56} Behnam et al.\textsuperscript{57} showed the effects of nanotube alignment on the resistivity in SWNTs thin film by randomly generating the nanotubes using Monte Carlo simulations. Figure 15(a) and (b) shows an atomic force microscope (AFM) image of randomly oriented nanotubes film in the plane of the substrate and a 2D nanotubes film using the simulation code between the source and drain.\textsuperscript{57} The nanotube alignment angle ($\Theta_a$) is a measure of the degree of nanotube alignment in the film. The measurement direction angle ($\Theta_m$) is the channel direction between the source and drain electrodes.

Figure 16(a) shows the graph of normalized resistivity according to nanotube alignment angle.\textsuperscript{57} When channel length is larger than nanotube length ($L_c > L_s$), the resistivity decreases as $\Theta_a$ is reduced and the minimum resistivity occurs at $\Theta_a = \sim 45^\circ$ for $\Theta_m = 0^\circ$. This is interpreted that as the nanotubes are getting aligned, the nanotubes form conduction paths with fewer tube-tube junctions and shorter lengths between the source and drain.\textsuperscript{57} As the nanotubes are more aligned perfectly parallel to the channel direction, however, the resistivity increased significantly. This is because that the number of conduction paths starts to decrease significantly with very few
junctions. While the decrease in the junction numbers and conduction path lengths decreases the resistivity, the decrease in the conduction path numbers increases the resistivity. Consequently, the minimum resistivity is obtained for a partially aligned rather than a perfectly aligned nanotube film. In a case the nanotube length is longer than the channel length ($L_c < L_s$), perfect alignment of nanotubes would reduce the resistivity because single nanotubes connect the source and drain. As the channel length decreased below nanotube length, the ratio of drain current of aligned ($I_{||}$) and random ($I_{random}$) networks increased as shown in Fig 16(b). High current gain can be obtained with perfectly aligned networks for short channel transistors.

Figure 15. Randomly oriented nanotubes film; (a) AFM image of a nanotube film with an approximate thickness of $t = 15$ nm where nanotubes are randomly distributed. (b) A 2D nanotube network generated using a Monte Carlo process for a device with device length $L = 4 \mu m$, device width $W = 4 \mu m$, $l_{CNT} = 2 \mu m$, $n = 2 \mu m^2$, and $t = 15$ nm. In this case, the nanotube alignment angle $\theta_a = 27^\circ$ and the measurement direction angle $\theta_m = 45^\circ$, where the definition of the two angles is illustrated in the inset. Reproduced with permission from ref. 57 (Copyright 2007 AIP Publishing LLC).
Figure 16. Effects of nanotubes alignment on percolation resistivity; (a) Log-plot of normalized resistivity vs. nanotube alignment angle for three measurement direction angles. The inset shows the percolation probability vs. nanotube alignment angle. (b) Theoretical (line) and experimental (symbol) results for $I_{iel} / I_{random}$ as a function of $L_c / L_s$. Reproduced with permission from ref. 47 and 57 (Copyright 2007 IEEE and 2007 AIP Publishing LLC).
2.3.2. Assembly Techniques for Aligned SWNTs Networks

Precisely placement of SWNTs is beyond the capability of current growth and assembly techniques and presents a major technical hurdle for SWNTs-based electronic applications. The current process on the production of aligned SWNTs can be divided into two categories: the in-situ growth and the post synthesis assembly approaches.

Vertically aligned carbon nanotubes (CNTs) can be synthesized by the direct in-situ growth method using chemical vapor deposition (CVD) synthesis process. Dai and co-workers produced directed aligned SWNTs by applying an external electric field during the CVD synthetic process. The van der Waals interactions with nearby surfaces allowed the SWNTs which are suspended in an air to be aligned across over the trenches between the electrodes during the growth process. Liu and co-workers prepared long aligned SWNTs by fast heating CVD technique using Fe-Mo nanoparticles as catalysts and CO as feeding gas flow. The fast heating leads that the SWNTs grow quickly and slide along the substrate surface without surface interaction. The grown-SWNTs are aligned along the direction of the flowing feeding gas (Fig. 17(a) and (b)). Figure 17(c) shows a kite mechanism of the fast heating CVD process for the growth of aligned SWNTs. The fast heating causes a temperature difference between solid sample and the surrounding gas, which generate a convection flow so that the gas flow lifts nanotubes up with the catalysts on their tips. Therefore, the laminar flow dominates the nanotubes growth orientation during the growth stage (Fig. 17(d)).
Figure 17. Direct in-situ growth of aligned SWNTs using gas-flow-directed CVD growth; (a) SEM image of SWNTs prepared using fast heating processes. (b) SEM image of directly grown 2D network of SWNTs by a two-step growth process. (c) Schematic of the kite mechanism. (d) SEM image of a high-density aligned array of SWNTs grown on a silicon wafer using copper catalysts. Reproduced with permission from ref. 34 (Copyright 2011 Elsevier B. V.).

Alignment techniques of post synthesis assembly approach involve dispersion of SWNTs in aqueous solutions and aligning them by external forces using spin-coating, electric and magnetic field, mechanical shearing, or blown bubble film techniques. A one-dimensional nanostructure with high aspect ratio can be extended straight and aligned with shear force orientation. Figure 18(a) demonstrate mechanical shearing for aligning lyotropic nematic phases of SWNTs in aqueous suspension. Homma and co-workers employed contact printing process to transfer randomly grown SWNTs thin films from SiO$_2$ onto another surface. During the transfer process, the random SWNTs thin film was aligned with high density when the SiO$_2$ substrate was slid over the receiver substrate (Fig. 18(d)).
Ko and Tsukruk\textsuperscript{62} used fluidic flow directed alignment method by dropping SWNT solution on the tilted substrate which is coated with NH$_2$-terminated self-assembled monolayers (SAMs). SWNTs are assembled on the hydrophilic microchannels along the confined hydrophobic micropatterned geometry (Fig. 19(a)).\textsuperscript{34} The tilted substrate produces unidirectional microfluidic flow to align SWNTs (Fig. 19(b)). As a droplet of SWNTs suspensions evaporates, the drying droplet is pinned along the contact line of solid-liquid-vapor. An internal flow is generated toward the contact line from the interior and carries the suspended SWNTs toward the edges of the droplet.\textsuperscript{63} Figure 19(c) and (d) shows the alignment of SWNTs on patterned stripes and in the edge of a polar region by the hydrodynamic flow.\textsuperscript{34}
Figure 19. Fluidic flow directed alignment method; (a) Schematic for the tilted-drop fabrication of a thin film on an amine-terminated SAM surface micropatterned with photoresist polymer stripes. (b) AFM topographical image of carbon nanotubes film showing uniaxially oriented, densely packed CNTs bundles. (c) Hydrodynamics in a cylindrical drop to align and place anisotropic nanoparticles. (d) AFM topographic image showing alignment and placement of individual SWNTs along the edges of the polar SAM. Reproduced with permission from ref. 34 (Copyright 2011 Elsevier B. V.).

An electric field is applied to provide large aligning torques on CNTs along the electric field orientation by introducing large dipole moments because the static polarizability tensor $\alpha$ of CNTs is highly anisotropic. $^{64}$ Chen et al. $^{65}$ used alternating current (AC) electric field with frequency of 5 MHz and magnitude of 10 V peak to peak to align SWNTs in a 25 $\mu$m gap between gold interdigitated electrodes (Fig. 20(a)). Figure 20(b) shows that the SWNTs were highly aligned along the direction of the applied AC electric flux and linked up to the electrodes. The orientation of the nanotubes is significantly dependent on the frequency and magnitude of the electric field. $^{65}$ Kamat et al. $^{33}$ investigated the alignment of SWNTs using electrophoretic
deposition method in direct current (DC) electric field. Quaternary ammonium ion-capped SWNTs with tetraoctylammonium bromide (TOAB) were suspended in tetrahydrofuran (THF) organic solvent to polarize them asymmetrically in a DC electric field (Fig. 20(c)). Under the influence of a DC electric field, the SWNTs bundles are stretched out into the solution and anchored on the positive electrode. At higher applied voltages (> 100 V), the TOAB-capped SWNTs suspensions in THF become charged symmetrically under the applied dc electric field and are aligned themselves perpendicular to the electrode surface (Fig. 20(d)).\textsuperscript{33} The alignment of the SWNTs bundles is due to the strong dipole moments along the longitudinal axis. This is because that the polarizability along the nanotubes is much higher than that perpendicular to the nanotubes axis.\textsuperscript{34}
Figure 20. Electric field directed alignment methods; (a) Schematic diagram of aligning single-walled carbon nanotubes with an alternating-current electric field. (b) SEM image of the SWNTs sample aligned with and AC electric field. (c) Charge stabilization in CNTs by the tetraoctylammonium and bromide ions following the application of the direct-current electric field. (d) Schematic illustration of the linear alignment of SWNTs in the DC electric field. Reproduced with permission from ref. 33 and 65 (Copyright 2014 American Chemical Society and 2001 AIP Publishing LLC).
2.4 Single-Walled Carbon Nanotubes-based Functional Device Applications

2.4.1 SWNTs-based Thin Film Transistor

The commercial applications of carbon nanotubes (CNTs) began to grow substantially due to their exceptional electrical, mechanical, chemical, and thermal properties associated with their unique quasi one-dimensional structure, nanometer geometry, and atomically monolayered surface.\textsuperscript{66,67,68} Especially, the potentially most lucrative application for nanotubes is to replace the role of silicon in transistors. Single-walled carbon nanotubes (SWNTs) thin films are one of the most promising materials to replace poly-silicon or amorphous-silicon in high performance thin-film transistors owing to its quasi-ballistic transport, intrinsic ultra-thin body, and nearly transparent electrical contacts to metal electrodes and bring added values including high mobility, optical transparency, and compatibility with low-temperature processing.\textsuperscript{69}

First SWNTs tunneling field effect transistor (FET) showed a subthreshold swing of < 60 mV decade\textsuperscript{1} in 2004 and SWNT FETs with sub-10 nm channel lengths showed a normalized current density (2.41 mA $\mu$m\textsuperscript{-1} at 0.5V), which is greater than those obtained for silicon devices in 2012.\textsuperscript{70} The transistors using horizontally aligned CNTs arrays achieved mobilities of 80 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}, subthreshold slopes of 140 mV decade\textsuperscript{-1}, and on / off ratios as high as $10^5$.\textsuperscript{70,71} Recently, high-performance thin-film transistors and integrated circuits were fabricated on flexible and transparent substrates with mobility of 35 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} and an on / off ratio of $6 \times 10^6$.\textsuperscript{72,73} Despite the promising performance of individual SWNTs devices, manufacturing technique to control of nanotube diameter, chirality, density, and placement still have remained insufficient for SWNTs-based electronic production, especially over a large area.\textsuperscript{70} Therefore,
precisely controllable SWNTs assembly method which is compatible with current CMOS technologies and understanding of SWNTs electrical characteristics are desirable for high performance SWNTs transistors.

Kocabas et al. explained the percolation transport behavior of large-scale and partially aligned arrays of SWNTs thin film transistor. A stick-percolation-based transport model was employed to interpret the electrical performance of partially aligned heterogeneous SWNTs thin film according to channel lengths and orientations. Figure 21 illustrates SWNTs transistor performance with which correlated levels of coverage and alignment. The configuration with low coverage and high degrees of alignments leads to large drain current \( I_D \) because of many bridging nanotubes and few nanotube-to-nanotube junctions (Fig. 21(b) and (e)). As the coverage is increased, the alignment becomes poor and it forms percolation transport pathways. But this configuration provides high \( I_{on} / I_{off} \) ratio due to the low probabilities of bridging nanotubes or metallic current pathways (Fig. 21(a) and (e)). In terms of alignment, perpendicular orientation nanotubes show lower drain current \( I_D \) and higher \( I_{on} / I_{off} \) ratio compared to the parallel orientation (Fig. 21(c), (d) and (f)). Figure 21(g) shows a current anisotropy \( A = I_\parallel / I_\perp \) in the parallel and perpendicular direction. The aligned SWNTs networks have high anisotropy. The anisotropy decreased as the coverage and channel length increased due to the percolation transport pathways.

In this dissertation, I have fabricated SWNTs-based thin film transistor using developed assembly techniques for highly dense and aligned thin film transistors. The transistors were characterized according to the alignment to verify the percolation transport behavior.
Figure 21. Study of transport behavior through large-scale, partially aligned arrays of single-walled carbon nanotubes thin film; SEM images of transistors with channel lengths of 50 μm (a and b) and 25 μm (c and d) with different orientations and degrees of alignment and coverage. (e) Transfer curves of two devices with different nanotubes coverage. (f) Transfer curves of devices with oriented parallel (\(\parallel\), black) and perpendicular (\(\perp\), red). (g) Channel length dependence of ON current anisotropy (\(I_\parallel / I_\perp\)) for aligned (green), dense partially aligned (red), and random networks (blue). Reproduced with permission from ref. 74 (Copyright 2007 American Chemical Society).
2.4.2 SWNTs-based Antenna for Energy Harvest Application

SWNTs-based electronics have attracted intensive research interest due to its excellent electrical and mechanical properties such as high electron mobility, large current carrying capability, and unique one-dimensional nanostructure.\textsuperscript{75,76} SWNTs-based antennas that can operate over a wide range of frequencies are emerging as promising devices for energy harvesting techniques.\textsuperscript{77,78,79} A π-electronic conjugation in cylindrical or spherical structures, especially, has paved new ways to design energy conversion architectures.\textsuperscript{80,81,82} Full spectrum electromagnetic (EM) radiation originating from the sun gives a constant energy source to the earth.\textsuperscript{83} Currently, solar energy converting technologies are under-utilized to harvest the energy reaching the earth from the sun in both the visible and IR regions and the reradiated IR energy.\textsuperscript{83} Photovoltaic cells are invented to convert solar energy to electricity. Rectenna is a combination of the receiving antenna and a rectifier to capture electromagnetic energy and convert it to direct current (DC) power.

Robert Bailey\textsuperscript{84} proposed in 1975 the use of antennas to convert solar energy to electricity. Periodic arrays of simple dipole antenna with length half the wavelength of the incident EM waves were used to collecting the energy and rectified to a DC output as demonstrated in Fig. 22.\textsuperscript{85} The incoming electromagnetic waves from solar radiation are received by antenna, which convert it to alternating current (AC). The converted current passes through a diode, which converts the AC to DC, and generates usable power.\textsuperscript{85} This idea was extended and exhibited by Brown\textsuperscript{86,87} for absorbing energy from transmitted microwaves. He showed that capturing incident electromagnetic energy and converting it to electrical energy with efficiencies as high as
84% can be achieved.\textsuperscript{88} To extend this to the solar energy spectrum, two main obstacles remained; fabricating features in nanometer-scale and rectifying diodes operating in THz range. Due to recent advancements made in nanotechnology and nanomanufacturing, efforts to harvest energy from the incident solar radiation started during the last decade. Kempa et al.\textsuperscript{89} proposed using multi-walled carbon nanotubes (MWNTs) perpendicular to the substrate as antennas for absorbing incident solar radiation in the visible spectrum. Initial theoretical modeling showed that they had very good resonances and had minimal variation with respect to an incident polarization. Novack et al.\textsuperscript{90} proposed to use a gold nanowire dipole antenna in a coiled fashion as antennas. The antennas were fabricated utilizing nanoimprint lithography. Emission properties of this antenna were studied by heating up the substrates to 200 °C and FTIR conformed with HFSS software. Even though there has been remarkable progress made in the development of antenna arrays by various researchers, the lack of diodes operating in the Terra Hertz range impeded them from obtaining any actual power output from these rectenna arrays in the visible spectrum. For the microwave regime in the 2.3 GHz - 12.6 GHz range, there have been several successful efforts carried out by researchers in NASA, NERL, universities in Taiwan,\textsuperscript{91} Japan resulting in operational power harvesting devices from ambient microwaves in the environment.

In this research, I have developed large-scale SWNTs assembly techniques using template-guided fluidic assembly and proposed SWNTs-based rectenna by incorporating MIM (metal – insulator – metal) diodes to harvest energies in a microwave regime.
Figure 22. Schematic of the rectenna solar cell; The antenna converts incoming solar radiation to a petahertz alternating current through the dipole, which rectifies it. The resulting direct-current (DC) power is available at the output leads. Reproduced from ref. 85 (Copyright 2011 SPIE).
2.4.3 SWNTs Thin-Film Chemical Sensors for Ultrasensitive Gas Detection

Gas sensors are required for leakage detections of explosive gases and real-time detections of toxic or pathogenic gases with high sensitivity and selectivity. Since the most common gas sensing principle is the electrical conductivity changes through the charge transfer of gas molecules by adsorption and desorption of gas molecules on sensing materials, it is understandable that by increasing the contact interfaces between the analytes and sensing materials, the sensitivity can be significantly enhanced. The unique one-dimensional nanostructures which have extremely high surface-to-volume ratio and hollow structure are ideal sensing materials for gas molecules adsorption and storage. Therefore, gas sensors based on nanomaterials, such as CNTs, nanowires, nanofibers, and nanoparticles, have been investigated widely. CNTs have some advantages: small size with a larger surface, high sensitivity, fast response and good reversibility at room temperature and enhanced electron transfer. Upon exposure to certain gases, the change in the properties of CNTs or CNTs-based composites can be detected by various methods. As a result, CNTs-based gas sensing systems and the theoretical analyses of gas adsorption and collision effects on the nanotubes have been the subjects of intense research.

Several methods have been reported to integrate CNTs for gas sensor. Figure 23 shows a gas sensor fabricated by growing a SWNTs thin-film directly on an Al₂O₃ substrate for NO₂ and Cl₂ gas detection. Li et al. developed a resistive gas sensor by simple casting SWNTs on interdigitated electrodes (IDEs). Screen-printing of MWNTs onto patterned electrodes was reported by Lee et al. for NO₂ detection. Another dielectrophoresis (DEP) method (Fig. 24(a))
was utilized with AC voltage to suspend MWNTs between microelectrodes to detect various vapors such as NH$_3$, NO$_2$, SO$_2$ and HF.$^{97}$ Well aligned CNTs are required for better sensor behavior. So vertically aligned CNTs were directly grown on the sensor substrates by thermal CVD to fabricate a three terminal N$_2$ gas sensor as shown in Fig. 24(b).$^{98}$ To avoid direct growth method with high temperature, post-synthesis of CNTs assembly techniques are emerged by harvest CNTs from thermally grown CNTs separately. Hence, a significantly progressive assembly technique is destined simultaneously to meet all the integration requirements of precise control of the desired location, density, large area and alignment.

In this thesis, I have developed high-rate SWNTs assembly method using electric-assisted template-guided fluidic assembly to enhance electron transport behavior for highly ultrasensitive gas detection.
Figure 23. Single-walled carbon nanotubes thin-film sensor for ultrasensitive gas detection; (a) Schematic view and (b) photograph of SWNTs thin-film gas sensor. SEM images of as-grown SWNTs on (c) Al₂O₃ substrate and (d) at boundary between Al₂O₃ layer and Pt electrode. Sensor response of SWNTs thin-film to (e) NO₂ and (f) Cl₂ at different concentrations. Reproduced from ref. 95 (Copyright 2005 JSAP).

Figure 24. Fabrication of carbon nanotubes gas sensors: (a) SEM image of single-walled carbon nanotubes across two gold electrodes by dielectrophoresis assembly. (b) Cross-sectional SEM image of the vertically aligned CNTs mat using CVD growth. Reproduced from ref. 92 (Copyright 2009 Hindawi Publishing Corporation).
2.4.4 SWNTs Biosensors for In-vivo D-glucose Detection

Recently, nanowires, nanotubes, and nanosphere, as donors of electrical response, have been studied for the minimized nanostructures in a field of biosensors. Nanoscale of biosensor device can support in-vivo application, high sensitivity, and low limit concentration of detection.\textsuperscript{99} In addition, researches of nanoscale biosensors try to obtain the ease detections, such as label-free, rapid, low-cost, multiplexed analysis.

SWNTs are attractive materials for their use in nanoelectronics.\textsuperscript{19,100,101} Specifically, the electrical properties of SWNTs are good for use in advanced biological electronics and biosensors. SWNTs and gold assembly onto silicon wafer enables to affect the electrical response for a high sensitivity biosensor. Electrostatic or capillary are usually utilized for SWNTs assemblies onto silicon wafer. The detection of these analyses using SWNT-based chemiresistive / field-effect transistor (FET) sensors is familiar to apply medical sensors in-vitro system as shown in Fig. 25.\textsuperscript{102,103,104,105} However, FET device requiring three electrodes (working, reference and counter) and a large size is hard to apply in-vivo medical detection system though it can obtain more high detected response of target materials.

Miniaturized biosensors should detect and quantify small molecules with high sensitivity and selectivity. A variety of electrode modification techniques have been utilized for the immobilization of biomolecules onto SWNTs with covalent or noncovalent bonding methods. The covalent bonding method onto SWNTs using SWNT modification with chemical functional groups severe problems concerned with electrical properties of SWNTs because there are probabilities that the method can change.\textsuperscript{106,107} On the contrary, non-covalent bonding method
using π-π stacking does not enable to transfer chemical characteristics because it only utilizes physical forces to immobilize materials onto SWNTs. Enzyme immobilization is also one of the important processes for increasing the sensitivity and stability of biosensor. The low activity of immobilized enzyme is due to different local pH or electrostatic interactions at the matrix-enzyme interface, covalent linking to enzyme changing overall enzyme structure, and matrix induced confinement decreasing enzyme mobility for conformation changes during substrate catalysis.108,109,110

In this study, a novel D-glucose biosensor with high sensitivity was developed utilizing resistance response with the immobilized glucose oxidase (GOD) immobilized SWNTs bundle with a simple device manipulation.
Figure 25. Glucose biosensor based on boronic acid functionalized carbon nanotubes transistors;\textsuperscript{105} (a) Schematic of the experimental geometry. (b) Illustration of glucose binding to a nanotube functionalized with pyrene-1-boronic acid. (c) Bound glucose forms a boronate anion complex that has electrostatic effects on the nanotube field-effect transistor. Reproduced from ref. 105 (Copyright 2013 AIP Publishing LLC).
CHAPTER 3: LARGE-SCALE SINGLE-WALLED CARBON NANOTUBES ASSEMBLY USING TEMPLATE-GUIDED FLUIDIC ASSEMBLY

3.1 Template-guided Fluidic Assembly for Large-scale Single-Walled Carbon Nanotubes Assembly on Flexible Substrate

3.1.1 Background

It is crucial to incorporate individual carbon nanotubes (CNTs) onto devices that present a major technical barrier preventing proliferation of CNTs-based functional device applications. Several approaches have been reported for incorporating parallel arrays of CNTs and can be grouped into two main categories: 1) the in-situ synthesis approach by direct growth chemical vapor deposition (CVD)\textsuperscript{111} and 2) the post synthesis assembly approaches, which involve harvesting nanotubes from CNTs-suspended solution.\textsuperscript{34}

Although the in-situ CVD growth method can directly synthesize CNTs at the desired locations on a substrate by patterning catalyst materials, the high temperature process (500 – 900 °C) and difficulty in controlling the growth direction and density of CNTs significantly restrict its compatibility, especially for flexible electronic device applications.\textsuperscript{111} The post-synthesis assembly techniques such as electrophoretic deposition (EPD)\textsuperscript{112} or dielectrophoresis (DEP)\textsuperscript{113} can effectively fabricate highly oriented nanotubes between electrodes using an electric field. However, it is effective only within the where the electric-field is at maximum so that it is not compatible with large-scale CNTs assembly.\textsuperscript{114}

A template-guided fluidic assembly method has been developed to harvest nanotubes from
nanotubes-suspended solution and assemble them at the desired location by Prof. Busnaina and Prof. Jung’s groups.\textsuperscript{114,115,116,117,118,119} Compare to other assembly techniques, the template-guided fluidic assembly is relatively directed, robust, and precisely controllable at room-temperature. The lithographically patterned templates guide the nanotubes along the micro- or nanotrenches for highly organized SWNTs lateral network architectures.

In this dissertation, the template-guided fluidic assembly process has been employed to integrate single-walled carbon nanotubes (SWNTs) on a flexible substrate over large-area. The template-guided fluidic assembly technique is a surface-controlled microfluidic approach so that it features; (a) micro- and nanoscale SWNTs assembly can be accomplished by surface property treatment, (b) SWNTs alignment can be controlled with respect to the liquid-air contact line at nanoscale, and (c) it can be applied to diverse substrate materials at room temperature. Figure 26 shows the schematic diagram of the template-guided fluidic assembly process. Fluidic assembly uses capillary effect of water to assist the assembly of SWNTs into lithographically patterned structures. The lithographically patterned template was immersed in the SWNTs-based solution to selectively assemble SWNTs networks. While pulling the template up vertically, the capillary action forces the water to reach and spread across the hydrophilic substrates along the pulling direction, creating a hydrostatic dilation stress. The presence of the hydrostatic dilation stress causes the SWNTs to be assembled in the trench structures allowing the SWNTs to become tightly packed with higher density. In addition, aligned SWNTs bundles were obtained along the vertical pulling direction because the SWNTs-solution spreads because the surface tension force straightens the SWNTs by hydrodynamic flow.
Figure 26. Template-guided fluidic assembly process; (a) Schematic diagram of template-guided fluidic assembly. Hydrophobic photoresist is patterned to guide SWNTs being assembled into the trench. The SWNTs are assembled on the hydrophilic substrate by capillary force at the interface of the solution and the substrate. (b) Optical and SEM images of assembled SWNTs. Reproduced with permission from Ref. 114. (Copyright 2009 American Chemical Society).
3.1.2 Experimental Procedure

The template-guided fluidic assembly process has been used to integrate SWNTs. Fluidic assembly employs capillary effect of water to assist the assembly of SWNTs into desired structures. The capillary force causes the SWNTs to be assembled in the structures allowing the SWNTs to become tightly packed with higher density. A 3-inch Si wafer was used as a substrate (Fig. 27(a)). A 500 nm thick thermal oxide was deposited on the Si wafer. A conventional piranha cleaning process which is a mixture of sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂) was used not only to clean organic residues off substrates but also to hydroxylate surfaces making hydrophilic. The SiO₂ substrate were functionalized by plasma treatment using inductively-coupled plasma (ICP) etch system (Unaxis 790, Plasma-Therm Inc., USA) to terminate the surface with hydroxides chemical groups (-OH) (Fig. 27(b)). Figure 28 shows surface treatment results using simple chemical cleaning process and dry plasma treatment to control the surface property of the silicon oxide substrate. After preparation of the substrate, a 600 nm thick layer of polymethylmethacrylate (PMMA) resist (950 PMMA A, Micro Chem., USA) was spin-coated. PMMA is an electron beam sensitive polymer so that when the PMMA is irradiated, the polymer-electron interaction causes the polymeric chain to break, leading to shorter chains (lower molecular weight). The exposed resist can be dissolved in a solvent that is a mixture of isopropanol (IPA) and methyl isobutyl ketone (MIBK). Templates that have trenches (3 x 50 μm) for SWNTs assembly were formed directly through electron-beam lithography process using the used field emission scanning electron microscope (FE-SEM, Supra 25, Carl Zeiss Inc. USA) (Fig. 27(c)). The SWNTs have been assembled on the template-guided
substrate using fluidic assembly method by dip coater (KSV Dip Coater, KSV Instruments Ltd., Finland). The templates were dipped in a DI water-based SWNTs solution which concentration is 0.046 wt% (Brewer science, USA) and then it were pulled up with pulling speed of 0.05 mm/min (Fig. 27(d)). Since the assembly of the SWNTs on the desired position, the guided template, PMMA, was removed by dissolving in acetone solution (Fig. 27(e)). Finally, the titanium (5 nm thick) and gold (150 nm thick) metals were deposited on the assembled SWNTs bundles using electron-beam evaporation (MDC E-beam Deposition System, MDC Vacuum Products LLC., USA) after electron-beam lithography process. Then the metal electrodes were formed by lift-off process (Fig. 27(f)). The effects of surface energy and relative humidity on SWNTs assembly efficiency were investigated by contact angle goniometry (Pheonix 300, SEO, Korea). The surface energy was calculated by Owens-Wendt geometric mean method using polar and non-polar liquids. The morphology and thickness of the assembled SWNTs were analyzed by atomic force microscopy (AFM) (NX-10, Park System, Korea), and filed emission scanning electron microscopy (FE-SEM) (Supra 25, Carl Zeiss Inc., USA). The electrical properties of the assembled SWNTs were characterized using semiconductor parameter analyzer (HP 4156C, Agilent Technologies, USA) with micromanipulator.
Figure 27. SWNTs device fabrication procedure using template-guided fluidic assembly: (a) Si wafer as used as a substrate. (b) SiO₂ were deposited on the substrate and O₂ plasma treatment was carried out for hydrophilic surface. (c) Microtrenches were formed through the photolithography process. (d) SWNTs were assembled onto the hydrophilic surface using template-guided fluidic assembly process. (e) Photoresist was removed by dipping in the acetone solution. (f) Metal contact pads were fabricated by metal deposition and lift-off process.

Figure 28. Contact angle measurement results for surface property control process; (a) SiO₂ substrate before cleaning, (b) after piranha cleaning process, and (c) after dry O₂ plasma treatment.
3.2 Results and Discussion

3.2.1 Surface Energy Effects on SWNTs Assembly Efficiency

The interaction of SWNTs with a substrate surface at the air-water-solid interface is important in SWNTs assembly field. Therefore, the water capillary force which occurs between two contact surfaces inevitably presents and plays an important role. The capillary force between tow contacting surfaces of sphere-on-plane geometry in a vapor environment is given as

\[ F_C = 4\pi\gamma R \cos \theta \]  \hspace{1cm} (1)

where \( \gamma \) is the surface tension of the liquid and \( \theta \) is the contact angle, and \( R \) is the radius of the sphere.

Since the capillary force arises at the interface of the substrate surface and solution, the surface energy is crucial for an eventual accurate alignment and assembly efficiency. The study of the surface energy effects on SWNTs assembly efficiency is shown in Fig. 29(a). The assembly efficiencies are strongly affected by the surface energies. The surface energies of the surface-water interface are calculated by contact angle measurements using Owens-Wendt geometric mean method. When the solution spreads in the narrow trenches, high surface energy attracts the SWNTs-solution so that leads high SWNTs assembly efficiency over a large area. Moreover, humidity of the environment during an assembly process plays a key role on the assembly of SWNTs. To the best of our knowledge it has not been investigated in great detail. The effect of environmental humidity on template guided fluidic assembly of SWNTs during the process was also investigated.
Figure 29. Investigation of the effect of surface energy and relative humidity on SWNTs assembly efficiency; (a) the graph shows the SWNTs assembly efficiency increases as an increase of the surface energy (inset shows SEM images of the assembled SWNTs according to the relative humidity). The surface energy is calculated by contact angle measurement. Graph (b) shows the effects of relative humidity on SWNTs assembly efficiency. The efficiency decreases as an increase of the relative humidity (inset shows SEM images of the assembled SWNTs according to the relative humidity).

Under the above equation (1), the capillary force is humidity independent because it holds for most macroscopic measurements. For microscopic objects, the capillary force is strongly humidity dependence so that it is strongly reduced at low humidity. This is because of the multiasperity nature of the contact. At low humidity, the effective radius of the asperities much smaller that the sphere radius \( R \) so the capillary force formed around these small asperities. In contrast, the capillary force formed around the large sphere at high humidity. Consequently, SWNTs assembly using fluidic assembly is strongly dependent on humidity due to the small radius.

The influence of the water vapor in the environment during the fluidic assembly process
on the SWNTs assembly is shown in Fig. 29(b). These experiments were performed using microstructure templates (3 μm of width and 50 μm of length) by varying the relative humidity from 30 to 90 %. The assembly efficiency reduces drastically when the relative humidity is above 40 %. The fluidic assembly takes advantage of the capillary force of water. High relatively humidity prevents the ability of water to rise along the guided template structures during the assembly process thus preventing full SWNTs coverage in the trenches. Therefore, high SWNTs assembly efficiency system was set up by surface energy control process and humidity control system for large area SWNTs assembly.
3.2.2 Surface Energy Control Process for Highly Dense SWNTs Networks

The SWNTs are assembled on the hydrophilic surfaces by the meniscus inducement into the template confinement that leads to the formation of ordered continuous structures. In addition, the more hydrophobic surfaces of the guided template can increase the condensation force exerted by the meniscus that is parallel to the template structures and become sufficiently strong to enhance SWNTs density on the hydrophilic surface.\textsuperscript{121}

Surface energy control process is illustrated in Fig. 30(a). A piranha cleaning process which is a mixture of sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) was used to hydroxylate silicon dioxide (SiO\textsubscript{2}) surfaces making hydrophilic substrate. For high surface energy surface, the hydrophilic SiO\textsubscript{2} surface with hydroxides chemical groups were achieved through oxygen plasma treatment, which enhances wetting of the surfaces in addition to enabling the SWNTs to be assembled directly during the fluidic assembly process. The SiO\textsubscript{2} substrate were functionalized by plasma treatment using inductively-coupled plasma (ICP) etch system (Unaxis 790, Plasma-Therm Inc., USA) to terminate the surface with hydroxides chemical groups (-OH) on the hydrophilic surface. Then, photoresist was coated to guide SWNTs being assembled on the hydrophilic surface. Two different types of photoresists, microposit S1805 and S1813 which thicknesses are 500 nm and 1.5 µm, respectively, were purchased from MicroChem Corp., USA, to control the assembled SWNTs density. I have developed super hydrophobic template guided fluidic assembly to enhance the SWNTs assembly density. Trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane (FOTS) for super hydrophobic layer coating was commercially obtained from Sigma Aldrich, USA, and used as received. The FOTS SAMs (Self-assembled
monolayers) layer was grown on the photoresist using a vapor phase coating process to decrease the photoresist template surface energy. The chemical structure of the FOTS is demonstrated in the inset of the Fig. 30(a). Next, optical photolithography process is carried out to create trenches as templates for SWNTs assembly. Finally, the SWNTs were assembled on the hydrophilic substrate using template-guided fluidic assembly method followed by photoresist removal.

The surface energy changes were monitored by contact angle measurements as shown in Fig. 30(b). The plasma-treated substrate has high surface energy showing low contact angle. The fluorocarbon-based FOTS SAMs layer can significantly reduce the surface energy showing high contact angle.122 Indeed, high surface energy potential between a surface and guided template can increase the assembled SWNTs density. Typical current-voltage (I-V) curves of assembled SWNTs were plotted in Fig. 30(c), showing a linear dependence of current with voltage. Moreover, the measured resistance and the increased SWNTs thicknesses by surface energy control process were shown in Fig. 30(d). Two 1813 and 1805 photoresists, which thicknesses are 1.5 μm and 500 nm, respectively, were used as a template and FOTS-coated samples were used for highly dense SWNTs assembly. The templates with thick photoresists have high assembled SWNTs thickness and the FOTS-coated samples showed highly packed assembly results.
Figure 30. Surface energy control processes. (a) Surface energy control process procedure. (b) Surface energy modification using contact angle measurements. (c) I-V curves of the assembled SWNTs assembly samples. (d) The measured resistance and thickness of the samples; the thickness can be controlled according to the photoresist thickness and the samples which are coated with FOTS-SAMs layer enable to enhance the density of the SWNTs assembly due to the high surface energy contrast.
3.2.3 Highly Organized SWNTs Networks for Large-scale Assembly

Highly organized SWNTs networks over a large area have been achieved using the developed template-guided fluidic assembly process based on surface energy control processes to assemble SWNTs at desired location with controlled orientation. The SWNTs have been assembled on the substrate using dip coater (KSV Dip Coater, KSV Instruments Ltd., Finland). The templates were dipped in a DI water-based SWNTs solution which concentration is 0.046 wt% (Brewer science, USA) and then it was pulled up with pulling speed of 0.05 mm/min under 30% of humidity. During an assembly process, impact of various parameters needed to be studied in order to assembly SWNTs over length mm. scales. I found that an organic residue on the substrate is one of the major inhibitors towards achieving consistent and continuous assembly. I overcome this by baking the substrate at 150 °C for 5 minutes before spinning the photoresist as shown in Fig. 31.
Figure 31. Prebaking substrate to remove organic contamination. Shown are top viewed SEM micrographs (a) Without prebaking of substrates and (b) with prebaking of substrates.

When I assembled SWNTs over a large area, there was discontinuous area due to low diffusion rate of SWNTs in the solution as shown in Fig. 32. I employed multiple times the fluidic assembly process to ensure that SWNTs are assembled throughout the trench structures without any discontinuity, which is shown in Fig. 33. The resulting large-scale SWNTs assembly structures had a total length and width of 21 mm and 3 μm respectively.
Figure 32. Discontinuous SWNTs assembly over a large area using one-step fluidic assembly process. Shown in SEM images (a) - (c) are top viewed SEM micrographs of discontinuous SWNTs networks. (d) The electrical signal of the discontinuous SWNTs networks.
Figure 33. Continuous SWNTs assembly over a large area by employing two-step fluidic assembly process. Shown in SEM images (a) and (b) are top viewed SEM micrographs of large-scale SWNTs networks and (c) is lateral connection networks and metallization. (d) The electrical signal of the continuous large-scale SWNTs networks.
3.2.4 Electrical Characterizations of Highly Organized SWNTs Networks

Highly organized SWNTs bundles were assembled using template guided fluidic assembly to characterize the electrical properties of the SWNTs. Two-terminal current-voltage (I-V) characteristic method is employed to measure the resistance (R) and conductance (G) which is obtained from a slope of the I - V curve. The ratio (V / I) is referred to as a static resistance, as it corresponds to the inverse slope of a chord between the origin and an I-V curve. For a wide variety of materials, V and I are directly proportional to each other, and, therefore, R and G are constant. The test structure of the SWNTs devices has two metal electrodes with 2 μm of channel length between two contact pads. Two groups of SWNTs structures that channel widths are 1 μm and 3 μm were characterized. Figure 34 shows the resistance histogram of the SWNTs structures of different channel widths of 1 μm (Fig. 34(a)) and 3 μm (Fig. 34(b)). The mean resistances of the SWNTs structures were mainly distributed around 3 kΩ and 850 Ω for channel widths of 1 μm and 3 μm respectively. The electrical resistance of SWNTs is the opposition of the passage of an electric current through the nanotubes; the electrical conductance, the ease at which electric current passes, can be calculated using the channel dimensions. The uniform cross section of SWNTs bundles has a resistance proportional to its resistivity and length and inversely proportional to its cross-sectional area. The 1 μm channel width SWNTs structure has a higher resistance than 3 μm channel width SWNTs structure indicating that the resistance increases as the channel width narrows. The calculated resistance and normal distribution data for each channel width are illustrated in Table 1 and 2 respectively.
Figure 34. Electrical characterization of assembled SWNTs bundles. Resistance histogram of (a) 1 μm and (b) 3 μm width of SWNTs devices. The channel length is 2 μm for test structures. The mean resistances were distributed around 3 kΩ and 800 Ω for channel widths of 1 μm and 3 μm, respectively.

Table 1. The calculated resistance results of SWNTs test structures

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<tr>
<th>Width</th>
<th>1 μm</th>
<th>3 μm</th>
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<tbody>
<tr>
<td>Mean</td>
<td>3.15 k-Ω</td>
<td>844.16 Ω</td>
</tr>
<tr>
<td>STD</td>
<td>1.72 k-Ω</td>
<td>350.05 Ω</td>
</tr>
<tr>
<td>Min</td>
<td>723.52 Ω</td>
<td>335.33 Ω</td>
</tr>
<tr>
<td>Max</td>
<td>8.38 k-Ω</td>
<td>1.52 k-Ω</td>
</tr>
<tr>
<td>σ</td>
<td>1.69 k-Ω</td>
<td>338.94 Ω</td>
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Table 2. The normal distribution results of SWNTs test structures

<table>
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<tr>
<th>Width</th>
<th>1 µm</th>
<th>3 µm</th>
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<tr>
<td></td>
<td>σ</td>
<td># of Chips</td>
</tr>
<tr>
<td>1σ</td>
<td>31</td>
<td>77.5%</td>
</tr>
<tr>
<td>2σ</td>
<td>6</td>
<td>15%</td>
</tr>
<tr>
<td>3σ</td>
<td>3</td>
<td>7.5%</td>
</tr>
</tbody>
</table>

I investigated the resistance changes at the cross junction of the assembled SWNTs networks. The junction resistance is measured and it is found to be of the order of 10 kΩ (ΔR = 16.34%). Shown in Fig. 35 are SEM images and the corresponding linear, junction resistance and their statistical deviations for the devices that were fabricated. The resistivity of the assembled SWNTs is of the order of ~10⁻⁴ Ω·cm, which is one of the lowest values reported in a literature. The statistical deviation of these values is very low and they showed consistent values for different experimental runs.
Figure 35. Investigation of cross junction resistance of SWNTs bundles. (a) A schematic of the positions of the test electrodes. (b) The SEM images of the assembled SWNTs networks (inset shows high magnification image of the cross junction of SWNTs bundles). The corresponding measured resistances for the (c) linear as well as the (d) junctions.

Large-scale SWNTs structures were accomplished over mm-scale. To measure large-scale SWNTs uniformity, metal electrodes were placed on every 250 μm pitches along the SWNTs structures as shown in Fig. 36(a) and (b). Several measurements were made at various sections of the 2 mm length to ensure uniformity and consistency in the assembly. Figure 36(c) shows the I-V characteristics according to the channel length showing linear and symmetric ohmic contact properties. The resistance measurements of large-scale SWNTs structures show that a linear increase of resistance according to the channel length indicating that uniform SWNTs bundles assembly as shown in Fig. 36(d).
Figure 36. SEM images showing large scale SWNTs structure with metal electrodes; (a) Overall image of the 2 mm length of SWNTs structures and (b) high magnification images with metal contact. Electrical characterizations of the large scale SWNTs structures; (c) I-V curves of the 2mm length of SWNTs structure showing ohmic contact behavior and (d) resistance measurements according to the increase of the distance showing uniform SWNTs structure.
3.2.5 Sub-100nm Assembly for Highly-aligned Nanoscale SWNTs Networks

It has been a challenge to harness the highly efficient electronic transport in CNTs because of difficulties in manipulating individual CNTs from a mixture of metallic and semiconducting nanotubes separately. S. Somu et al.\textsuperscript{123} showed that intrinsic electrical heterogeneity of the constituent SWNTs can be obtained via topological transition in CNTs networks by nanoscale confinement. The topological confinement effects have been investigated to see electrical percolation behavior of the nanoscale SWNTs networks from a 2D ultrathin CNTs networks modeling by Prof. Upmanyu.\textsuperscript{123} Figure 37 shows the simulation results\textsuperscript{123} of electrically heterogeneous network topologies via nanoscale confinement with various channel widths conducted by Prof. Upmanyu. The CNTs networks become geometrically aligned along the channel as decreasing topological channel width. In addition, the alignment of CNTs driven by nanoscale confinement shifts the transitions to higher networks densities and shows marked a reduction in metallic transport. Therefore, the nanoscale geometries can effectively shield the effect of active components inherent in heterogeneous SWNTs solution and the challenge of the inherent electrical heterogeneity of the constituent SWNTs for large-scale SWNTs-based electronic devices.
Figure 37. Topological transition of nanoscale SWNTs structure; (a) 2D simulation results of CNTs assembly with varying channel widths. (b) – (d) Plots of the probability of the nature of electrical percolation through the network as a function of network density. The dotted lines correspond to simple stick percolation models for randomly assembled networks. (e) Contour plot of the probability of semiconducting behavior across the 2D network (shaded red) as a function of a width (y-axis) and density (x-axis). (f) Same as in (e) but for multilayer, quasi-2D simulations with varying channel thickness. Reproduced with permission from Ref. 118 (Copyright 2010 American Chemical Society).
The fluidic assembly can manipulate individual SWNTs precisely. Y. L. Kim et al. have investigated the effect of geometric confinement on the nanoscale SWNTs network topology down to 200 nm of channel width.\textsuperscript{123} I achieved SWNTs assembly down to 50 nm of channel width to see the electrical transition in nanoscale SWNTs networks. Heterogeneous SWNTs networks were assembled onto submicrometer wide channels (~3 μm, ~1 μm, ~500 nm, ~100 nm, and ~50 nm) with significantly large channel length (~ 50 μm) as shown in Fig. 38(a). I conducted the electrical characterization of the assembled SWNTs networks. Figure 38(b) shows the variation in the resistivity for the five channel widths corresponding to Fig. 38(a). The electrical resistivity (\(\rho = R_c W_c t / L_c\)) was calculated from the resistance (\(R_c\)), channel length (\(L_c\)) and width (\(W_c\)), and SWNTs thickness (\(t\)). The SWNTs thickness abruptly increased as the channel width approached nanoscale confinement. It shows an increasing trend in resistivity when the channel width is decreased indicating semiconductor behavior as the channel width narrows. There are lots of metallic conduction paths in microscale networks due to the large number of percolation junctions. The number of conduction paths is reduced as the nanotubes are highly aligned parallel to the channel direction by nanoscale confinement method. Figure 38(c) shows the orientations of the assembled SWNTs. The SWNTs networks have become increasingly aligned with decreasing channel width due to confinement. When the channel width is larger than nanotubes length, nanotubes are aligned along the contact line of the solution perpendicular to channel direction. When the channel width decreases less than nanotubes length, meanwhile, the nanotubes are highly aligned along the channel direction. Therefore, the aligned topology can effectively shield the metallic SWNTs within the heterogeneous network, resulting in transport that becomes increasingly controlled by nanotubes junction characteristics.\textsuperscript{123}
Figure 38. Investigation of the effect of nanoscale confinement on SWNTs assembly on submicrometer channel widths; (a) High magnification SEM images of SWNTs assembly showing the degree of alignment of the SWNTs within channel widths of ~3 μm, ~1 μm, ~500 nm, ~100 nm, and ~50 nm. (b) Electrical characterization of aligned SWNTs networks structure; I-V curves, conductivity and thickness of SWNTs channel widths of ~3 μm, ~1 μm, ~500 nm, ~100 nm, and ~50 nm. (c) Schematic and orientations of the assembled SWNTs.
3.2.6 SWNTs Thin Film for Transparent and Flexible Electronics

A two-dimensional thin film network of CNTs has been regarded as a promising transparent electronic material with excellent electrical, mechanical and optical properties. As a candidate material for flexible electronics, the CNTs thin film should display high carrier mobility, high conductivity and optical transparency, in addition to robustness, flexibility and environmental resistance.\textsuperscript{124} For those plastic SWNTs-based electronic, manufacturability and system integration on a plastic substrate at room temperature is required for the exploitation of the attributes of SWNTs thin film. The template-guided fluidic assembly technique is utilized because it is a relatively simple, cost-effective method and can be performed at large-scale at a room temperature.

The highly organized SWNT thin film is achieved on a polymeric substrate by performing site-selective template-guided fluidic assembly. A polyethylene naphthalate (PEN) (Teonex Q65, DuPont Teijin) polymer is used as a flexible substrate. The surface property of the presented PEN plastic substrate is readily modified from hydrophobic to hydrophilic utilizing a short O\textsubscript{2} plasma treatment. High density SWNTs networks were assembled on a micropatterned substrate using dip coating process. I have obtained micropattern arrays and mm-scale of SWNTs structures on the PEN substrate by template-guided fluidic assembly process. Figure 39 shows optical and SEM images of fully assembled microscale SWNTs network structure on a PEN substrate. The assembled micropattern arrays (Fig. 39(a)) and mm-scale SWNTs networks (Fig. 39(b)) retain their original shape after the removal of the photoresist. The SWNTs arrays are 3 μm of width and 50 μm of length and the large-scale SWNTs network is 100 μm wide over 4x4
mm area. The assembled SWNT structures are dense and show complete coverage on the PEN surface. These results indicate that the template-guided fluidic assembly technique can be utilized to fabricate high density microscale SNWTs networks on a flexible substrate.

Figure 39. Optical and SEM images of the assembled SWNTs networks on PEN substrate; (a) Microscale SWNTs network arrays which dimension is 3 μm of width and 50 μm of length. (b) Macroscale SWNTs network which dimension is 100 μm wide over 4x4 mm area.
The large-scale assembly of SWNTs on PEN substrate offers several advantages for flexible electronic applications. These features derived from the architecture itself, excellent electrical, optical, and mechanical properties of the constituent SWNTs, the ease of manufacturing, and compatibility with various substrate materials. In Figure 40, mesh structures of SWNTs thin film have been fabricated on PEN substrate and electrical and optical properties were characterized for transparent plastic electronics. The two-dimensional architecture of the SWNTs thin film with components that are a mixture of metallic and semiconducting nanotubes is illustrated in Fig. 40(a) and (b). The dimensions of SWNT mesh structure are 10 µm line and 10 µm spacing (sample name is 10 / 10) and 5 µm line and 50 µm spacing (sample name is 5 / 50). To fabricate this SWNT mesh structure, the PEN substrate was treated with O₂ plasma and optical lithography method was applied to make the mesh structure; and then the fluidic assembly technique described above was used with hydrophilic and hydrophobic properties of PEN substrate and photoresist, respectively. This assembly technique for making mesh structures SWNTs thin film can be expanded for a large-scale fabrication such as 3-inch wafer assembly and even larger. Therefore, it opens up the possibility of robust large-scale SWNTs thin film networks-based flexible electronic devices.

Networks of different densities lead to different sheet resistances, and optical transmittance. The sheet resistance per square is given, for a film of thickness \( t \), by \( R / \text{sq} = \rho / t \), where \( \rho \) is the resistivity of the film. The sheet conductance, \( S / \text{sq} \), is the inverse of the sheet resistance. Electrical property, sheet resistance, of the SWNTs thin films is measured using four-point-probe (4PP) (Fig. 40(c)). These values of propositions assume that the conductivity of
the SWNTs thin films is large; the larger the SWNTs conductivity, the better the SWNTs network conductance. Due to the one-dimensional nature of the SWNTs, the network is also highly transparent in the infrared and visible spectral ranges. For the transparent and flexible substrate, PEN is a good candidate for this purpose of the project. The transmittance of SWNTs thin film architecture on PEN substrate was conducted using UV-vis measurements from the wavelength of 200 nm to 400 nm. The transparency for SWNTs-PEN is ranging from 70% to 90% depending on the scanned wavelength, indicating a good optical property and excellent candidate for transparent plastic electronic applications (Fig. 40(d)). First, the reference PEN substrate without SWNTs thin film was scanned through the UV-vis scanner and then SWNTs-PEN device was scanned at the same conditions of measurements. By modifying the dimensions of mesh structures, this transparency can be tuned for the specific requirements such as a wavelength band range.
Figure 40. Transparent and flexible SWNTs thin film on PEN substrate for plastic electronic application. SEM images of assembled SWNTs mesh structure architectures of (a) 10 µm line and 10 µm spacing (sample name is 10/10) and (b) 5 µm line and 50 µm spacing (sample name is 5/50). (c) Sheet resistance of SWNTs thin films with different dimensions. (d) Wavelength dependence of the transmittance in the UV-vis spectral range for SWNTs thin film.
3.3 Summary

In this chapter, I demonstrated large-scale SWNTs assembly on a flexible substrate using the template-guided fluidic assembly method. I have employed fluidic assembly process to assemble and integrate SWNTs on lithographically patterned plastic template. Template-guided fluidic assembly method is a relatively simple process compared to transfer printing process because it can be applied to a wide range of substrates. PEN (Polyethylene naphthalate) plastic films feature low coefficient of thermal expansion, high resistance to most solvents, and heat stabilized material so that it is compatible with conventional CMOS process. For the highly dense SWNTs assembly, the influence of humidity and surface energy on template-guided fluidic assembly of horizontally aligned SWNTs has been studied and surface modification processes are developed. Surface energy control process is developed to enhance the density of the SWNTs structure through surface treatment processes. Super hydrophobic layer which has low surface energy is coated using FOTS self-assembled monolayer. Large-scale SWNTs networks are achieved on a flexible substrate using the developed fluidic assembly process from micro to mm scale area with high density.

I also have achieved nanoscale SWNTs structures down to 50 nm of channel width for intrinsic electrical heterogeneity of the constituent SWNTs. The SWNTs networks become geometrically aligned along the channel as decreasing topological channel width. In addition, the alignment of SWNTs driven by nanoscale confinement shifted the electrical transitions from metallic to semiconducting behavior due to a reduction in metallic transport. Therefore, the nanoscale geometries can effectively shield the effect of active components inherent in
heterogeneous SWNTs solution and the challenge of the inherent electrical heterogeneity of the constituent SWNTs for large-scale SWNTs-based electronic devices.
CHAPTER 4: HIGH-RATE SINGLE-WALLED CARBON NANOTUBES ASSEMBLY
USING ELECTRIC-ASSISTSED TEMPLATE-GUIDED FLUIDIC ASSEMBLY

4.1 Electric-assisted Template-guided Fluidic Assembly for Highly Aligned SWNTs

4.1.1 Background

The utilization of carbon nanotubes (CNTs) has been widely developed into a potential building block for future nanoscale electronic devices owing to the unique mechanical and electrical properties\(^8,\)\(^125\) such as interconnects,\(^126,\)\(^127\) field-effect transistors (FETs),\(^128,\)\(^129\) and nano-electrical-mechanical-system (NEMS).\(^130\) Single-walled carbon nanotubes (SWNTs) in particular are the focus of interest in chemical, optical and biological sensing applications because they are capable of transporting high current densities\(^131,\)\(^132\) and have a unique geometry featuring of being all surface reaction and large surface area.\(^133,\)\(^134\) One of the central challenges for building nanomaterial devices is the problem of the controlled organization of individual nanomaterials in defined nanometric surface areas. Therefore, it is critical to assemble SWNTs into underlying circuitry over a large area with precision control of the location, density, and alignment.\(^135\)

As I demonstrated in Chapter 3, a number of attempts have been reported in incorporating nanotubes into nanometric devices on the level of individual nanotubes. The nanotubes assembly methods have been classified into two main areas: synthetic and post-synthetic approaches. There was success in a synthesis of CNTs on the large areas to growth aligned CNTs via thermal decomposition of acetylene gas in nitrogen gas at high temperature for synthesizing CNTs.\(^136\)
Nevertheless, these direct growth methods with high temperature (typically > 800 °C) are incompatible with current CMOS technology. Alternative various techniques to the direct growth method have been developed to avoid high temperature process by harvesting CNTs from thermally grown CNTs separately and assemble them onto the substrate. The direct assembly techniques of post-synthetic regime using electric-field such as electrophoresis and dielectrophoresis are not suitable for large-scale assembly because it is only effective at local areas where the electric-field is at maximum. Other techniques, spin-coating and drop casting of CNTs-dispersed solvent methods, results in random orientation assembly of CNTs disorderly with low densities. Randomly dispersed SWNTs cause anomalous electron-transport behavior due to kinks and bends of CNTs that can prevent ultrafast transient and transporting excited charges. The template-guided fluidic assembly method has been utilized to assemble CNTs on desired location over a large area with high density. Since the fluidic assembly uses capillary force at the interface of the surface, however, it is a diffusion-limited process; the CNTs are slowly attached on the surface while the solution is evaporated. Hence, a significantly progressive assembly technique is destined simultaneously to meet all the integration requirements of precise control of the desired location, density, large area and alignment with high assembly speed.

Herein, I demonstrate a high-rate SWNTs assembly technique using electric-fluidic assembly method to accurately assemble highly aligned SWNTs arrays with high density. It utilized directed assembly strategies by integration of electrophoresis and fluidic assembly methods to enhance the assembly efficiency and orientation. The applied electric-field not only
increases partial concentration of the individual nanotubes suspended in solution, but also enables orientation of the electrically-driven SWNTs on the electrode surface in a desired direction to align along the assembly direction; the fluidic assembly process speed has been improved by 1000 times.
4.1.2 Experimental Procedure

The fabrication process of microtemplate for the electric-assisted template-guided fluidic assembly process is depicted in Fig. 41. Microtemplates were fabricated through conventional microfabrication processes. To fabricate the template for electric-fluidic assembly, a thermally oxidized SiO₂ (500nm) / Si wafer was used as a substrate (Fig. 41(a)). Piranha cleaning was carried out for substrate preparation. A 500 nm thick photoresist layer (S1805, Microchem Corp., USA) was spin coated on the substrate (Fig. 41(b)). Micropatterns were transferred from photomask using a photolithography process (NXQ-4000, Neutroniz-Quintel, USA) for metal electrodes (Fig. 41(c)). 5 nm of Ti and 150 nm of Au were deposited on the patterned substrate using e-beam evaporation method (Fig. 41(d)). Top and bottom electrodes were created after lift-off process to apply electric-field on the top electrode (Fig. 41(e)). The fabricated 3-inch microtemplate is shown in Fig. 41(f).

The integration procedure for the SWNTs assembly on the microtemplate using electric-fluidic assembly process is depicted in Fig. 42. Two metal electrodes (5nm of Ti and 150 nm of Au) were created on a SiO₂ / Si substrate (Fig. 42(a)). Top electrode is used as a working electrode to apply electric voltage and bottom electrode is used as a metal pad to measure electrical properties of the assembled SWNTs. A poly methyl methacrylate (PMMA) film (950 PMMA, MicroChem Corp., USA) was spin-coated on the patterned electrodes (Fig. 42(b)). Microtrenches that provide channels of well-defined width were transferred to the PMMA resist between two electrodes by e-beam lithography process (Supra 25, Carl Zeiss, USA) (Fig. 42(c)). The hydrophobic microtrenches act as a guided template that allows a hydrophilic surface onto
which SWNTs could be assembled. Then, highly aligned SWNTs networks were assembled using the electric-fluidic assembly. The template with such lithographically patterned channels on the metal electrodes and counter electrodes were dipped into SWNTs-dispersed DI-water solution (0.046 wt%, pH = 6.0). Direct current (DC) electric voltage was applied to the top electrode for 20 seconds and then pulled out to assemble SWNTs networks (Fig. 42(d)). The previously reported assembly pulling speed for template-guided fluidic assembly\textsuperscript{115,116} is less than 0.5 mm/min and the electric-assisted fluidic assembly method can increase the assembly pulling speed up to 50 mm/min. The suspended SWNTs were attracted by the electric-field and placed, aligned, and trapped into the trenched by the hydrodynamic force. The guided PMMA resist was removed by dissolving in acetone (Fig. 42(e)). The organized SWNTs structures were analyzed by field emission scanning electron microscopy (FE-SEM) (Supra 25, Carl Zeiss, USA) (Fig. 42(f)) and atomic force microscopy (AFM) (NX-10, Park System, Korea). The electrical properties of the SWNTs networks can be characterized right after assembly process by two terminal, top and bottom, electrodes using semiconductor parameter analyzer (HP 4156C, Agilent Technologies, USA) with micromanipulator.
**Figure 41.** Integration procedure for fabricating microtemplate; (a) A 500 nm of SiO$_2$ is deposited on a Si substrate. (b) Photoresist layer is spin-coated on the substrate. (c) Micropatterns are transferred by photolithography process. (d) Ti/Au thin film is deposited by electron-beam evaporation. (e) Top and bottom electrodes are created after lift-off process. (f) Microtemplate is fabricated on the 3-inch SiO$_2$/Si substrate.

**Figure 42.** Integration procedure for fabricating highly aligned SWNTs network structure; (a) A microtemplate which has top and bottom electrodes on a SiO$_2$/Si substrate is fabricated through microfabrication processes. (b) A 500 nm of PMMA layer is coated on the electrode. (c) Building a template of micro channels done by e-beam lithography process. (d) SWNTs are assembled into the trench by electric-assisted fluidic assembly. (e) The highly aligned SWNTs structures are obtained after removing PMMA resist. (f) SEM image of the organized SWNTs assembly.
4.2 Results and Discussion

4.2.1 Electric-Fluidic Assembly of Polarized SWNTs

The template-guided fluidic assembly process has been employed to integrate SWNTs at desired location for nanotubes manufacturing process. However, the slow process of the fluidic assembly remained one of the main insuperable obstacles blocking in future electronic device applications because the fluidic assembly uses capillary effect of water to assist the assembly of nanotubes into lithographically patterned structures. Therefore, I integrated the electrophoresis and fluidic assembly techniques to enhance the assembly speed.

Figure 43 demonstrates the electrically-driven SWNTs assembly process. The microtemplate is fabricated using the conventional microfabrication processes. Next, microtreches are formed on the microtemplate using the e-beam lithography process. The lithographically patterned template is submersed in the SWNTs-based solution to selectively assemble SWNTs networks (Fig. 43(a)). The SWNTs are dispersed as a random mat network in the DI-water solution (Fig. 43(b)). The DC electric voltage is applied on the top electrode to induce the electric-field on the suspended SWNTs in the solution to accelerate the electrically-driven SWNTs diffusion. The applied electric-field induces electric dipoles in the SWNTs in the suspension. The polarized SWNTs are stretched out and attracted to the top electrode and anchored by strong electrostatic force (Fig. 43(c)). Then, the template is pulled up with constant speed and the anchored SWNTs on the top electrode are assembled along the water-air-substrate interface on the hydrophilic surface by hydrodynamic flow. As the water gradually move down, the capillary action forces the water to reach and spread across the hydrophilic
substrates and continuous SWNTs films are formed (Fig. 43(d)). The presence of the hydrostatic dilatation stress causes the SWNTs to be assembled in the trench structures allowing the SWNTs to become tightly packed with higher density.\textsuperscript{142} In addition, highly aligned SWNTs are obtained onto the wide trenches which dimension is much large than nanotube length along the microtrench parallel to the assembly direction.
Figure 43. Electric-assisted template guided fluidic assembly process: (a) Schematic of the assembly technique and demonstration of the assembly process. (b) SWNTs are dispersed as a random network in solution with no electric-field. (c) SWNTs are polarized by applied electric-field and driven to the top electrode. (d) SWNTs are assembled into the guided trench by capillary force of the fluidic assembly.
My colleague, Asli Sirman, modeled the electric field simulation to analyze the electric field magnitude effects on SWNTs assembly efficiency. We used Flow-3D simulation program to simulate electric field magnitude for different applied voltage values and microtrench structures as shown in Fig. 44. The dimension of the test structure is that 150 µm x 150 µm of top and bottom electrodes on microtemplate and distance between the electrodes is 20 µm. And distance between microtemplate and counter electrode is 5 mm. The electric potential on the gold electrode is higher than on the PMMA and SiO₂ regions that are adjacent to the gold due to the effects of the nearby components and material properties. The electric field magnitude at the top electrode is high and decreases as it moves away from the gold. So, SWNTs are attached on the top electrode where the electric field is high then gradually assembled into the microtrench along the pulling direction (Fig. 44(a)). Electric field magnitude figure shows results simulated for four different voltage values ($V_{dc} = 1 \text{ V} \sim 2.5 \text{ V}$) and different thicknesses of PMMA ($t_{\text{PMMA}} = 100 \text{ nm}$ (Fig. 44(b)), $t_{\text{PMMA}} = 500 \text{ nm}$ (Fig. 44(c)), and $t_{\text{PMMA}} = 1 \text{ µm}$ (Fig. 44(d))) with 3 µm of channel width. The electric field contours in a right indicates the electric field magnitude strength. Higher electric field magnitudes focused on the near gold electrode and decreased along the x and y direction. The electric field magnitude increases as an increase of the applied voltage due to the high electric potential. So, there is a slight increase in the electric field near PMMA surface due to edge effect creating higher electric fields so that the electric magnitude increases as decrease of PMMA thickness.
Figure 44. Simulation illustrating electric field magnitude along the microtrench according to an electric field and different PMMA thicknesses; (a) Schematic of microtrench on microtemplate for electric field magnitude simulation. Electric field magnitude simulation results of the microtemplate structure according to the applied voltages along the x-axis for (b) 100 nm, (c) 500 nm, (d) 1 µm of PMMA thicknesses with 3 µm of channel width. Simulation results indicating the electric field is high near the top electrode and decreases along the x-axis. The electric field magnitude changes according to the structure geometries. The electric field magnitude increases as decrease of PMMA thicknesses.

The electric field polarizes the nanotubes in the solution and the electrically polarized nanotubes are driven toward to the top electrode. Therefore, high electric field will lead high assembly efficiency. Figure 45 shows electric field magnitude at 20 µm of x distance away from the top electrode for different PMMA thicknesses. Electric fields near gold for an applied
voltage of 2 V_{dc} give field magnitude as 2.11 \times 10^3 \text{ V/m}, 1.7 \times 10^3 \text{ V/m}, and 1.49 \times 10^3 \text{ V/m} for 100 \text{ nm}, 500 \text{ nm}, and 1 \mu \text{m} of PMMA thickness, respectively. To see the electric field magnitude effects on assembly efficiency, I found DC voltage conditions of 100 \text{ nm} (1.85 \text{ V}_{dc}), 500 \text{ nm} (2 \text{ V}_{dc}) and 1 \mu \text{m} (2.06 \text{ V}_{dc}) of PMMA thicknesses for 1.7 \times 10^3 \text{ V/m} of electric field magnitude. Figure 46 demonstrates the electric field magnitude effects on the SWNTs assembly efficiency. When dc voltages are applied on the top electrode for 100 \text{ nm} and 500 \text{ nm} of PMMA thickness structures and pulled up the template with high pulling speed of 5 mm/min. The assembly efficiency of the SWNTs was strongly affected by the applied voltage. Below 1.7 \times 10^3 \text{ V/m} of electric field magnitude, few SWNTs are assembled from the suspension in the trench. At higher electric field magnitude (> 3.74 \times 10^3 \text{ V/m}), lots of SWNTs were over-assembled. I found the optimized DC electric voltage condition of 1.85 and 2.0 \text{ V}_{dc} for 100 \text{ nm} and 500 \text{ nm} of PMMA thicknesses, respectively, to be present for high assembly efficiency for 1.7 \times 10^3 \text{ V/m} of electric field magnitude.
Figure 45. Electric field magnitude at 20 um of x distance from gold electrode for 100 nm, 500 nm and 1 µm of PMMA thicknesses. DC voltage conditions of 100 nm, 500 nm and 1 µm of PMMA thicknesses for $1.7 \times 10^3$ V/m of electric field magnitude are 1.85 V$_{dc}$, 2 V$_{dc}$ and 2.06 V$_{dc}$, respectively. Above $3.74 \times 10^3$ V/m of electric field magnitude, lots of SWNTs were over-assembled. Below $1.7 \times 10^3$ V/m, few SWNTs are assembled. The optimized assembly condition for high assembly efficiency is between $1.7 \times 10^3$ V/m and $3.74 \times 10^3$ V/m.
Figure 46. SEM images of the assembled SWNTs bundle under different biasing conditions for (a) 100 nm and (b) 500 nm of PMMA thickness. Various dc electric voltages are applied on the top electrode and assembled SWNTs with 5 mm/min of pulling speed. Few SWNTs are assembled below $1.7 \times 10^3$ V/m of electric field magnitude by applying a dc voltage of 1.5 V. Optimized electric-fluidic assembly condition is between $1.7 \times 10^3$ V/m and $3.74 \times 10^3$ V/m of electric field magnitude. Over assembly is observed by applying a dc voltage of 2.5 V above $3.74 \times 10^3$ V/m of electric field magnitude.
Since the electric field magnitude decreases along the y-axis as well, the concentration of the SWNTs near top electrode in the solution also decreases along the assembly direction. I measured the thickness of the assembled SWNTs networks according to the pulling speed using AFM as shown in Fig. 47. The thickness is decreased along the assembly direction due to the decrease of the electric field magnitude. The developed electric-assisted template-guided fluidic assembly can not only improve the assembly speed up to 50 mm/min but also control the SWNTs thickness from 5 nm to 25 nm by controlling the pulling speed.

**Figure 47.** Highly-aligned SWNTs network using electric-assisted template-guided fluidic assembly; (a) AFM image of the SWNTs structure which width is 3 μm and length is 20 μm. (b) The thickness of the assembled SWNTs structure along the pulling direction with various assembly speeds.
4.2.2 Aligning SWNTs Networks by External Guiding Forces

I have assembled SWNTs using the presented electric-assisted template-guided fluidic assembly methods and compared with template-guided fluidic assembly method. The SWNTs have to be assembled in a particular direction to build functional electronic nanodevices.\(^\text{141}\) The high aspect ratio objects such as nanotubes, nanowires, and conducting polymer chains should have high alignment of conducting phase to increase the percolation conductivity.\(^\text{55,143,144}\) Previously reported papers\(^\text{114,115,116,117,118,119}\) by Prof. Busnaina and Prof. Jung’s groups showed that SWNTs can be assembled into uniform and ordered form into patterned and periodic structures by dip coating process. In terms of alignment of SWNTs, the SWNTs bundles are aligned in-plane along the water-air-substrate interface into the lithographically patterned trenches when the water is evaporated.\(^\text{142}\) When the channel width is larger than nanotubes length, for the template-guided fluidic assembly method, the SWNTs bundles are oriented along the water that spreads perpendicular to the assembly direction at the interface between the patterned hydrophobic and hydrophilic region as shown in Fig. 48.\(^\text{142}\) To obtain highly aligned SWNTs networks, therefore, channel width should be shorter than nanotubes length. As I demonstrated in Chapter 3.2.5, highly aligned SWNTs are assembled in nanoscale trenches by topological geometry confinement method using the template-guided fluidic assembly. However, highly aligned SWNTs networks over large area are required for large-scale SWNTs electronic device applications.
Electrophoresis deposition technique has been developed for manipulating nanoparticles on an electrode.\textsuperscript{145} When an electric field is applied, the charged particles are forced to move toward an electrode and deposited via particle coagulation. The motion of the charged particles \((q)\) under the applied electric field is governed by the zeta potential on the particles as follow\textsuperscript{146}

\[
q = 4\pi R \varepsilon_r \varepsilon_0 (1 + \kappa R) \zeta
\]

where \(R\) is the radius of a colloidal particle, \(\varepsilon_r\) is a permittivity of suspension, \(\varepsilon_0\) is a permittivity of free space, \(\kappa\) is inverse debye length, and \(\zeta\) is the zeta potential on the particle. The terminal velocity \((v)\) of the charged particle can be determined from Stoke’s law as follow\textsuperscript{146}

\[
v = \frac{qE}{6\pi \mu R}
\]
where $E$ is the electric field and $\mu$ is the dynamic viscosity of the suspension solution.

This method can be applied to one-dimensional nanostructures dispersed in a suitable solution. So, I applied electric force during the fluidic assembly process to increase the diffusion velocity of the electrically-driven SWNTs in the solution as I presented in Chapter 4.2.1. Moreover, a conducting or dielectric particles develop a dipole moment $P$ by an external electric field $E$ resulting in a large form-anisotropy.\textsuperscript{147} Torque on the polarized particles aligns the objects along the electric field direction. I assumed that nanotubes are conducting and polarized under the electric field. Therefore, the large induced dipole moments will lead to large aligning torques, which force the nanotubes to be aligned along the electric field direction for highly aligned SWNTs assembly.\textsuperscript{148} Consequently, SWNTs arrays with densely packed and aligned SWNTs bundles over a large area have been fabricated using the electric-fluidic assembly technique.

Figure 49 illustrates the rationalized SWNTs alignment by the electric field. Dipole moment $P = a \cdot E = a_{||}E \cos \theta$ is induced on SWNTs. The nanotube is aligned along the electric field direction due to the highly anisotropic polarizability tensor $a$. The nanotube is oriented at an angle $\theta$ with respect to $E$ because the polarizability along the tube axis $a_{||}$ is much higher than that perpendicular to the tube axis $a_{\perp}$.\textsuperscript{148} The torque $\tau = |P \times E| = a_{||}E^2 \sin \theta \cos \theta$ on the dipole moment forces nanotube to rotate along the electric field direction with a rotation force $F_R = a_{||}E^2 \sin \theta \cos \theta / \ell$.\textsuperscript{148}
Kamat et al.\textsuperscript{33} investigated the alignment of SWNTs using electrophoretic deposition method in direct current (DC) electric field. An electric field is applied to provide large aligning torques on CNTs along the electric field orientation by introducing large dipole moments because the static polarizability tensor $\alpha$ of CNTs is highly anisotropic.\textsuperscript{64} Under the influence of a DC electric field, the SWNTs bundles are stretched out into the solution and anchored on the positive electrode as shown in Fig. 50. The alignment of the SWNTs bundles is due to the strong dipole moments along the longitudinal axis. This is because that the polarizability along the nanotubes is much higher than that perpendicular to the nanotubes axis.\textsuperscript{34}
We have modeled the electric field simulation to analyze the motion of CNTs in the solution as I demonstrated in Chapter 4.2.1. The external electric field is critical to explain the nanotubes alignment mechanism. When nanotubes are placed in a uniform external electric field, it will experience no force, but torque. Therefore, the polarized nanotubes will be driven toward the top electrode by net force under inhomogeneous electric field. And the orientation of nanotubes will be determined by the magnitude of the torque with respect to the net force of the electric field as follow

\[ F_{NET} = P \frac{dE}{dx} . \]

Figure 51 shows the electric field distribution between microtemplate and counter electrode. Simulation about the electric field magnification changes according to the structures is carried out to verify the electric field gradient near the top electrode. The thickness of the PMMA
is increased from 0 to 1 μm with 3 μm of channel width. When 2 $V_{dc}$ of an electric field is applied on bare gold that dimension is 150 μm × 150 μm, electric field magnitude is uniform so that the orientation of the assembled is random networks. When microtrenches are formed on the top electrode with 3 μm of channel width, meanwhile, there are electric field gradient near the top electrode. Therefore, the guided template can lead highly aligned SWNTs assembly by inducing electric field gradient.

![Electric field distribution between microtemplate and counter electrode as a function of PMMA thicknesses.](image)

**Figure 51.** Electric field distribution between microtemplate and counter electrode as a function of PMMA thicknesses. 2 $V_{dc}$ of an electric field is applied on top electrode. The electric field distribution of the bare gold electrode is uniform. When the 3μm of microtrenches formed on the top electrode, there are electric field gradient according to the PMMA thicknesses.
We investigated the effects of electric field gradient on alignment of SWNTs assembly. To compare electric field magnitude gradients, different geometries ($t_{\text{PMMA}} = 100 \text{ nm and } V_{\text{dc}} = 1.85 \text{ V}$, $t_{\text{PMMA}} = 500 \text{ nm and } V_{\text{dc}} = 2 \text{ V}$, and $t_{\text{PMMA}} = 1 \mu\text{m and } V_{\text{dc}} = 2.06 \text{ V}$) of the structures are considered with same electric field magnitude base line ($1.7 \times 10^3 \text{ V/m}$) at 20 $\mu$m of x-axis from Fig. 45. Figure 52(a) shows the electric field magnitude gradient according to the structural geometries. The test structures have different gradient and same electric field magnitude baseline at 20 $\mu$m of distance. The electric field magnitude gradient is increased as increase of the applied voltages and PMMA thicknesses. I speculated that the nanotubes are polarized under the applied electric field and aligned along the electric field direction. Therefore, the high electric field gradient can attract the nanotubes and lead highly aligned SWNTs assembly. Figure 52(b) and (c) shows the experimental results of SWNTs assembly according to the electric field gradients. SWNTs are assembled on the microtemplates that have 3 $\mu$m of channel widths with 100 nm and 500 nm of PMMA thicknesses, and 1.85 V and 2 V of an electric field are applied, respectively. The assembled SWNTs with the higher electric field magnitude gradient shows highly aligned nanotubes networks than the lower gradient assembly conditions. This is because that the high electric field gradient has the high net force in the solution. The polarized nanotubes are rotated along the electric field direction by torque and driven toward to the top electrode by net force under inhomogeneous electric field. Consequently, highly aligned nanotubes networks can be obtained by the high electric field magnitude gradient.
Figure 52. Electric field magnitude gradients according to the structural geometries. (a) Simulation results for different geometries ($t_{\text{PMMA}} = 100 \text{ nm}$ and $V_{dc} = 1.85 \text{ V}$, $t_{\text{PMMA}} = 500 \text{ nm}$ and $V_{dc} = 2 \text{ V}$, and $t_{\text{PMMA}} = 1 \mu \text{m}$ and $V_{dc} = 2.06 \text{ V}$) with same electric field magnitude base line ($1.7 \times 10^3 \text{ V/m}$) at 20 µm of x-axis. SEM images of aligned SWNTs assembly according to (b) low gradient and (c) high gradient of electric field magnitudes.
We investigated the electric field effects on nanotubes alignment as a function of applied voltages. The electric field magnitudes and gradients are simulated for 100 nm of PMMA thickness. Different voltages of an electric field are applied from 1.85 V to 2.5 V on 3 µm of channel width to see the gradient change. Figure 53(a) shows that the electric field magnitudes and gradients increase as increase of the applied voltages. Alignment angles ($\theta_a$) of the assembled SWNTs networks are measured as a function of the applied voltages. The electric field magnitude gradient is increased by increase of the applied voltages, and that allowed highly aligned nanotubes networks along the assembly direction (Fig. 53(b)). Experimental results show that nanotubes are getting aligned with an increase of the applied voltages of 1.85 V (Fig. 53(c)), 2 V (Fig. 53(d)) and 2.5 V (Fig. 53(e)).
Figure 53. Electric field effects on the electric field magnitude and gradient as a function of applied voltages. Different voltages of an electric field are applied on microtrenches with 100 nm of PMMA thickness; (a) Electric field magnitude and gradients according to the applied voltages. (b) Measured alignment angles of the assembled SWNTs assembly as a function of applied voltages. SEM images for different electric field magnitude gradients by applying (c) 1.85 V, (d) 2 V, and (e) 2.5 V of electric field.

Since the electric-fluidic assembly method uses an electric field and assembles SWNTs with high assembly speed, the orientation is not affected by the surface capillary forces at the interface and aligned along the channel direction. The orientation of SWNTs is improved with an electric field due to alternating force exerted rapidly on the field-induced SWNTs and the SWNTs align nearly at right angle to the metal electrode as shown in Fig. 54.\textsuperscript{141}
Figure 54. Measurements of the SWNTs assembly alignment using electric-assisted template-guided fluidic assembly; The angular alignment (Θ) is calculated from the equation of $\Theta = 90 - \Theta'$ ($\Theta'$ is measured as an angle from SEM images). The angular alignment is defined as 0° is perfect alignment and plots of angular alignment of the assembled SWNTs by fluidic and electric-fluidic assembly methods. SEM images of SWNTs bundles selectively placed in the trench that the channel width is 3 μm.
The topological geometries of the two assembled nanotubes structures are demonstrated using AFM measurement in Fig. 55. The highly aligned SWNTs assembled by the electric-fluidic assembly method show uniform and organized nanotubes networks. However, there are high heights at edges of the SWNTs structure assembled by the fluidic assembly method. When the solution is evaporated, because, the nanotubes are assembled along the sidewall of the trenches as well due to the slow assembly speed.

Figure 55. AFM images of SWNTS using (a) electric-fluidic assembly and (b) fluidic assembly which thicknesses of the SWNTs are 15 nm and 25 nm, respectively. Electric-fluidic SWNTs has highly aligned orientation.
The schematic of the angular alignment ($\Theta$) which is defined as 0° is perfect alignment parallel to the pulling direction and plots of angular alignment and plots of angular alignment of the assembled SWNTs bundles are depicted in Fig. 56(a). The orientation of the electric-fluidic assembled SWNTs is improved compared to the fluidic assembly method for wide channel width (3 $\mu$m) and short nanotubes length (1 – 2 $\mu$m). The angular variation of the SWNTs relative to the fluidic assembly is reduced to less than ± 25°. The orientation of the assembled SWNTs using fluidic assembly changed from parallel to perpendicular to the assembly directions (Fig. 56(b)), while, the SWNTs assembled by electric-fluidic assembly were aligned parallel to the assembly direction with high orientation (Fig. 56(c)). Consequently, the developed electric-fluidic assembly method not only can improve the assembly speed, but also can achieve highly aligned SWNTs assembly networks.
Figure 56. Investigation of the SWNTs assembly alignment; (a) Schematic of the angular alignment ($\Theta$) which is defined as $0^\circ$ is perfect alignment and plots of angular alignment of the assembled SWNTs by fluidic and electric-fluidic assembly methods. SEM images of SWNTs bundles selectively placed in the trench that a channel width is 3 $\mu$m. The orientations of the (b) fluidic and (c) electric-fluidic assembly methods are perpendicular and parallel to the assembly direction, respectively.
4.2.3 Mechanical Characterizations of Highly Aligned SWNTs Networks

Conductive films on transparent polymer substrate have been essential components of flexible electronic and optoelectronic devices. Films of carbon nanotubes and graphene have been a promising candidate for such conductive films due to high transmittance and low sheet resistance properties. These availabilities of CNTs thin films could lead to the development of strain or pressure sensor, mechanically robust displays, and skin-like sensors that can wrap or bend around non-planar surfaces.\textsuperscript{149} I will report SWNTs thin film which is assembled on transparent polymer substrate, and characterize the electromechanical properties by applying strain along assembly direction.

The developed electric-fluidic assembly method can be applied to a wide range of substrates, especially to the plastic substrate. The flexible microtemplate for electric-fluidic assembly was fabricated on a PEN (Polyethylene naphthalate) (Teonex, Teijin DuPont Films, Japan) plastic film by utilizing conventional semiconductor processes. The PEN films have superior properties such as strength, heat resistance, anti-hydrolysis, dimensional stability, low oligomer extraction, resistance to organic solvents and chemicals and high durability. Metal electrodes (5nm of Ti and 150 nm of Au) were created on the PEN film through photolithography, metal deposition and lift-off processes. Figure 57 shows the fabricated flexible microtemplate.
Figure 57. Flexible microtemplate is fabricated on the PEN film for SWNTs assembly for flexible device fabrication.

SWNTs networks were assembled on the flexible microtemplate using electric-assisted template-guided fluidic method. SWNTs networks were created on the flexible microtemplate and electromechanical stabilities are characterized by compressing two electrode ends as illustrated in Fig. 58. To test the electromechanical stabilities of the assembled SWNTs structures, the structure was bended to apply mechanical force along the axis of the assembly direction and electrical properties were characterized according to the applied strain. The test structures were wrapped up around bottles with various radiiuses to measure the resistance change as shown in Fig. 59. To hence stress within the SWNTs film, axial strains are estimated as shown in Fig. 58(a). The thickness of the PEN substrate is 100 μm (r = 50 μm) and it is being bent according to a radius of curvature (R). The surface strain (ε = r / R) is calculated from the changed angle (Θ ~
\[ \tan \theta \approx \frac{1}{R} \] after bending. This strain is tensile on the outside of the surface. Figure 58(b) shows the changes in resistance as a function of surface strains. The SWNTs structures (3 μm of width and 40 μm of length) assembled by electric-fluidic method with the parallel align direction show increase of resistance changes as an increase of applied strain. The resistance change can be accommodated strain by means of structural fracture or buckling. Figure 60 shows morphology changes of the SWNTs networks with applying strains. The SWNTs thin film assembled by electric-fluidic assembly method exhibits highly aligned networks with parallel orientation (Fig. 60(a)). When the mechanical strain is applied along the assembly direction, the structural fracture is observed under 5% of strain (Fig. 60(b)). The SWNTs bundles are buckled with high strain (Fig. 60(c)). The buckled nanotube films show high resistance change (26 %). Since I applied mechanical force along the assembly direction by compressing the electrodes, the buckled nanotubes bundles are oriented with the axis of strain exerted by tensile stress. The buckled SWNTs thin film can be used for stretchable electrodes. D. J. Lipomi et al.\textsuperscript{149} reported reversible spring-like SWNTs thin film that accommodates strains of up to 150% in the stretched states using spray coating process. We will carry out the stretching test with wafer-scale aligned SWNTs thin films. These results are fairly promising and indicate the potential capability of the highly aligned SWNTs networks as flexible electronic device applications.
Figure 58. Electromechanical characterization of the assembled SWNTs structures; (a) Schematic diagram showing the strain induced SWNTs on the flat and bent PEN substrates. (b) Resistance changes of the aligned SWNTs (3 μm width and 40 μm length) assembled by electric-fluidic methods.
Table 3. Measured resistances according to the surface strain as a function of curvature radius R.

<table>
<thead>
<tr>
<th>Curvature (R) [cm]</th>
<th>Strain (ε) [%]</th>
<th>Resistance [KΩ]</th>
<th>ΔR/R₀ [%]</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>11.33</td>
<td></td>
</tr>
<tr>
<td>1.255</td>
<td>0.4</td>
<td>11.48</td>
<td>1.56</td>
</tr>
<tr>
<td>0.755</td>
<td>0.67</td>
<td>11.84</td>
<td>3.15</td>
</tr>
<tr>
<td>0.505</td>
<td>1</td>
<td>12.24</td>
<td>3.43</td>
</tr>
<tr>
<td>0.255</td>
<td>2</td>
<td>12.93</td>
<td>5.63</td>
</tr>
<tr>
<td>0.105</td>
<td>4.8</td>
<td>14.33</td>
<td>10.78</td>
</tr>
<tr>
<td>0.055</td>
<td>9.1</td>
<td>18.15</td>
<td>26.63</td>
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Figure 59. Electromechanical Tests of Flexible SWNTs Device: The resistance was measured with increase of bending radius. The flexible SWNTs device is wrapped up around bottles with various radiiuses to measure the resistance change. (a) Flat PEN, (b) Vial (R = 1.25 cm), (c) Cylinder (R = 0.75 cm), (d) Pen (R = 0.5 cm), (e) Syringe (R = 0.25 cm), and (f) Iron rod (R = 0.1 cm).
Figure 60. SEM images of SWNTs networks morphologies with applied strains. (a) SWNTs networks on flat PEN substrate (0% of strain). (b) Structural fracture under 5% of strain. (c) Buckled nanotubes bundles under 10% of strain.
4.2.4 Electrical Characterizations of Highly Aligned SWNTs Networks

The SWTNs networks should be given good metal contacts to electrically transport electrons for nanoscale device applications. The electrical properties of the CNTs device have been characterized using two-terminal measurement to measure the overall resistance, which is sum of the device resistance and the interfacial contact resistance. The device resistance is determined by the quantum contact resistance and scattering of the CNTs. When density of the nanotubes networks is near or below percolation threshold, the device resistance is determined by the number of percolation junctions. Prof. Moneesh\textsuperscript{123} showed that electrical percolation is determined by the number of metallic conduction paths. When nanotubes are highly aligned in nanoscale networks, therefore, the resistivity of the nanotubes networks is increased. Otherwise, when the nanotubes networks are multilayer and density is above percolation threshold, most of nanotubes are connected so that the length of the metallic conduction path is dominant. Electrons in the nanotubes networks will go through the metallic conduction path along the aligned nanotubes orientation. Moreover, it has been a challenging task to significantly reduce interfacial contact resistance of SWNTs interconnects. The interfacial contact resistance results from the formation of imperfect bonds between metals and CNTs caused high contact resistance due to the presence of impurities such as organic and metallic contaminants during the metal contact formation process.\textsuperscript{150} In this chapter, I will characterize electrical properties of the SWNTs networks by calculating the device resistance and contact resistance.

After SWNTs assembly by the fluidic method, the guided photoresists should be removed by organic solvent to form metal electrodes. Lithographic organic residues in SWNTs networks
caused high interfacial contact resistance due to the insufficient lithographic cleaning steps. Kim et al.\textsuperscript{150} reported improved purification procedures to remove lithographic residues through pre and post-cleaning processes. In a case of the electric-fluidic assembly method, it directly assembles SWNTs on the metal electrodes so that does not require post metallization processes. Hence, the developed assembly technique can prevent interfacial contact resistance from lithographic organic residues.

SWNTs devices are fabricated by fluidic and electric-fluidic assembly methods. The overall resistances of the devices are measured by two-terminal method with dimensions of 3 $\mu$m of channel width and 5$\mu$m of channel length. Kim et al.\textsuperscript{150} illustrated the contact resistance characterization using the three electrode measurements. Figure 61 demonstrates the electrical validations of two assembly techniques. The schematic and SEM images of the SWNTs interconnects test structures with three electrical contact pads (A, B, and C) for fluidic and electric-fluidic assembly are illustrated in Fig. 61(a). To measure reasonable estimate on the contact resistance, three identical metal electrodes, 5 nm of Ti and 150 nm of Au, were deposited on the SWNTs bundles assembled by fluidic assembly; SWNTs were assembled on the metal electrodes by electric-fluidic assembly to compare the contact resistance. Figure 61(b) shows the contact resistance which is obtained from three terminal measurements from contact pads of A-B, B-C, and A-C. The contact resistance at contact pad B, $R_B^c$, can be written in term of $R_{AB}$, $R_{BC}$, and $R_{AC}$ as \textsuperscript{150}

$$R_B^c = \frac{R_{AB} + R_{BC} - R_{AC}}{2}$$
where $R_{AB} = R_A^c + R_{dAB} + R_B^c$, $R_{BC} = R_B^c + R_{dBC} + R_C^c$, $R_{AC} = R_A^c + R_{dAC} + R_C^c$. The resistance $R_{dAB}$ is defined as the device resistance between the contact pad A and B. The contact resistances of the fluidic and electric-fluidic assembly are 899 Ω and 107 Ω on the average, respectively, indicating 88% of a decrease in contact resistance. Moreover, the highly aligned SWNTs device assembled by the electric-fluidic method shows low device resistance than fluidic method due to the short conduction path length and low nanotubes junctions. As A. Behnam et al.\textsuperscript{57} reported, the percolation resistivity in SWNTs films decreases as the nanotubes are aligned along the channel direction. This is because that the nanotubes form conduction path with fewer nanotube-nanotube junctions and the conduction path length is reduced as the nanotubes are aligned. When density of the nanotubes is above percolation threshold, therefore, most of nanotubes are connected and electrons go through the metallic conduction paths. Consequently, the resistance of the network is determined by the number of nanotubes junctions and length of the conduction path. The long mean-free path of electrons in the aligned SWNTs networks can produce high percolation conductivity in SWNTs thin film.
Figure 61. Electrical characterizations of highly organized SWNTs networks by fluidic and electric-fluidic assembly methods; (a) Schematic and SEM images of SWNTs networks test structures (b) Contact resistance comparison on the test structures. Two-terminal measurements were carried out between the pair of two contact pads.

Table 4. Measured and calculated resistances of the test structures.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Fluidic</td>
<td>$R_{AB}$ 7.245, $R_{BC}$ 6.557, $R_{AC}$ 12.004</td>
<td>$R_{dAB}$ 5.447, $R_{dBC}$ 4.759, $R_{dAC}$ 10.206</td>
<td>AVG 899, STD 95.7</td>
</tr>
<tr>
<td>Electric-Fluidic</td>
<td>$R_{AB}$ 1.04, $R_{BC}$ 1.592, $R_{AC}$ 2.419</td>
<td>$R_{dAB}$ 0.827, $R_{dBC}$ 1.379, $R_{dAC}$ 2.206</td>
<td>AVG 106.5, STD 153</td>
</tr>
</tbody>
</table>
4.2.5 Controllable and Scalable SWNTs Assembly

The electric-assisted template-guided fluidic assembly technique is developed not only to improve assembly speed but also to control the scalability and density of the SWNTs assembly through the pulling speed control process. One of the main stumbling blocks in the SWNTs assembly area is facile formation of large scale SWNTs networks and its difficulties in thickness control. Figure 62 gives evidence of density control and scalability through film thickness and resistance measurement. The assembled SWNTs thicknesses were determined by AFM according to the pulling speed when 2.0 V_{dc} of electric-field is applied. SWNTs bundles with 3 μm of width and 20 μm of length were characterized for the validation of increased SWNTs thickness according to the pulling speed as illustrated in Fig. 62(a). Since the concentration of the SWNTs is locally much higher at the electric voltage-applied top electrode, the highest thickness of the assembled SWNTs is located near the top electrode and the thickness of the SWNTs linearly decreased according to the increase of the distance away from the top electrode. It was found that SWNTs bundle thicknesses were increased as decrease of the pulling speed with SWNTs-solution concentration of 0.04 wt% due to high hydrostatic dilatation stress on SWNTs bundles. At high assembly speed (50 mm/min), low density of SWNTs was assembled lower than 5 nm of thickness. These assembled SWNTs bundles with assembly speed of 1, 5, 10, 20, 30, 40, and 50 mm/min were characterized through resistance measurement as depicted in Fig. 62(b). As bundles thickness increased, the resistance of the SWNTs assembly decreased indicating high density of SWNTs assembly can directly bridge the source and drain electrodes and thus enhance the current carrying capability. Otherwise, the lowest thickness of SWNTs with high pulling
speed of 50 mm/min shows high resistivity of 234.4 μΩ·m; indicating that the electrical properties can be controlled by controllable electric-fluidic assembly technique. Consequently, this controllable assembly technique can be applied to a wide range of electric device applications such as transistor that requires individual semiconductor behavior nanotubes.

Figure 62. Controllable and scalable SWNTs assembly using electric-assisted template-guided fluidic assembly process; (a) SWNTs density validation using thickness measurement according to the pulling speed. (b) Calculation of conductivity of the assembled SWNTs networks from resistance and thickness measurements. (c) Scale up of channel length of SWNTs networks from pulling speed control process. (d) Electrical resistance measurements on devices with a channel width of 3 μm and channel length ranging from 20 μm to 80 μm. The resistance measurements were made at a voltage of 100 mV.
The electric-fluidic assembly can controllably and simultaneously scale up the SWNTs networks through control of the pulling speed. Figure 62(c) represents the scalability of the electric-assisted fluidic assembly for large-scale SWNTs assembly. The SWNTs assembly scale was increased as decrease of the pulling speed with the source-drain channel length ranging from 20 to 200 µm. The geometric scaling of the device resistance is shown in Fig. 62(d) which plots the source to drain resistance versus channel length. The resistance for the 3 µm channel width of SWNTs networks increased linearly for the 60 µm of channel length but rapidly increased after 80 µm of channel length. This nonlinear scaling is an indication that the SWNTs assembly network is approaching the percolation threshold where the channel length is under 80 µm. These electrical resistance measurement results establish that the SWNTs assembly forms an electrically continuous interconnected network. Figure 63 presents the SEM images of large scale SWNTs assembly for wide channel width and length of 100 µm.
Figure 6.3. SEM images of large scale SWNTs assembly width and length ranging from 200 nm to 100 µm and 10 µm to 100 µm, respectively.
4.3 Summary

In this chapter, I have presented a simple, reliable, and efficient SWNTs assembly method to enhance the fluidic assembly efficiency. Since the fluidic assembly uses capillary force at the interface of the surface, it is a diffusion-limited process; the SWNTs are slowly attached on the surface while the solution is evaporated. Hence, a significantly progressive assembly technique is destined simultaneously to meet all the integration requirements of precise control of the desired location, density, large area and alignment. The developed electric-fluidic assembly can control the location, density, orientation, and scalability of the SWNTs with nanoscale precision. It utilized directed assembly strategies by integration of electrophoresis and fluidic assembly. The applied electric-field not only increases partial concentration of the individual nanotubes suspended in solution, but also enable orientation of the electrically-driven SWNTs on the electrode surface in a desired direction to align along the assembly direction. The developed assembly method improved assembly speed by 1000 times compared to the fluidic assembly process.

Highly dense and aligned SWNTs devices are fabricated on flexible PEN substrate with high electrical conductivity and low contact resistance. The assembly technique is fully compatible with silicon-based semiconductor fabrication technologies and can be applied to flexible electronics applications. The ability to accurately assemble SWNTs from nanoscale to microscale with high precision enable to meet various applications criteria and pave the way for exploring a broad field of CNTs-based devices.
CHAPTER 5: NANOLITHOGRAPHY USING DOUBLE OXIDE DEPOSITION AND ETCHING PROCESS FOR NANOTEMPLATE FABRICATION

5.1 DODE (Double Oxide Deposition and Etching) Nanolithography

5.1.1 Background

I have demonstrated SWNTs assembly techniques using template-guided fluidic assembly and electric-assisted template-guided fluidic assembly. To precisely control the SWNTs assembly at desired location, the guided template is an important part in my dissertation. Microtemplates have been fabricated for microscale SWNTs networks using conventional microfabrication processes. However, nanoscale template has emerged for nanoscale SWNTs electronic devices. In this chapter, I will illustrate nanolithography techniques for nanotemplate manufacturing.

Nanolithography is an emerging technology with a wide range of nanodevice applications that require feature sizes down to the nanometer scale.\textsuperscript{151,152,153,154} High resolution nanopatterning processes are essential for miniaturizing feature sizes into the nanoscale regime in highly integrated nano-CMOS devices.\textsuperscript{155,156,157} In addition, the fabrication of nanotemplate with high aspect-ratio nanostructures has received significant attention for use in biological and chemical nanosensors and energy storage and conversion devices.\textsuperscript{158,159,160,161,162} Thus, considerable interest has been shown in the use of advanced lithography techniques for meeting the strict requirements of high resolution, high aspect-ratio,\textsuperscript{163} large-scale fabrication,\textsuperscript{164} and high throughput (HTP) capability.\textsuperscript{165} The growing demand for sub-100 nm lithography has fostered the development of alternative and complementary nanolithography technologies, such as
Advanced optical lithography, direct writing, and the replication of patterning methods. Advanced optical lithography has evolved from contact printing to projection printing, reduction systems, and step-and-scan systems for leading-edge nanolithography to keep pace with trends in IC (integrated circuit) feature sizes. Figure 64 shows the wavelength down road map towards 10 nm resolutions for memory logic devices.

**Figure 64.** Road map of wavelength down of optical lithography towards to 10 nm resolution.

Currently, lithography performed with a 193 nm wavelength of ArF excimer laser has been reported to reduce a resolution down to 130 nm lines and spaces. Direct writing techniques, such as scanning probe lithography (SPL), dip-pen lithography (DPN), focused ion beams (FIB), and electron-beam lithography (EBL), can produce high spatial resolution.
patterns from 0.1 nm to the micrometer scale with high flexibility. Non-radiation-based replication of patterning methods, such as soft lithography, microcontact printing (μCP), and nanoimprinting lithography (NIL), can achieve high resolution patterning with large-area nanometer-scale patterning up to the wafer level without light diffraction or electron beam scattering in photoresist. Table 5 summarizes the specifications (i.e., minimum feature size and throughput) and applications of the major lithography techniques.

<table>
<thead>
<tr>
<th>Lithography Technique</th>
<th>Minimum Feature Size</th>
<th>Throughput</th>
<th>Applications</th>
</tr>
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<tbody>
<tr>
<td>Photolithography (contact &amp; proximity printings)</td>
<td>2-3 µm</td>
<td>Very high</td>
<td>Typical patterning in laboratory level and production of various MEMS devices</td>
</tr>
<tr>
<td>Photolithography (projection printing)</td>
<td>A few tens of nanometers (37 nm)</td>
<td>High-very high (60-80 wafers/hr)</td>
<td>Commercial products and advanced electronics including advanced ICs, CPU chips</td>
</tr>
<tr>
<td>Electron beam</td>
<td>&lt; 5 nm</td>
<td>Very low (8</td>
<td>Masks and ICs production,</td>
</tr>
</tbody>
</table>
Focused ion beam lithography

- Pattern generation: ~ 20 nm with a minimal lateral dimension of 5 nm
- Resolution: Very low
- Examples: hole arrays, bull’s eye structure, plasmonic lens
- Applications: Patterning in R&D including photonic crystals, channels for nanofluidics

Soft lithography

- Pattern generation: A few tens of nanometers to micrometers (30 nm)
- Resolution: High
- Applications: LOCs for various applications

Nanoimprint lithography

- Pattern generation: 6-40 nm
- Resolution: High (> 5 wafers/hr)
- Applications: Bio-sensors, bio-electronics, LOCs: nano channels, nano wires

Dip-pen lithography

- Pattern generation: A few tens of nanometers
- Resolution: Very low – low
- Applications: Bio-electronics, bio-sensors, gas sensors

However, the optical lithography is limited by the Rayleigh diffraction ratio\textsuperscript{170,171}, which makes it difficult to meet the high resolution requirements of advanced IC manufacturing below the minimum wavelength (193 nm) of an ArF excimer laser\textsuperscript{169,170,171} and presents challenges for
a further wavelength reduction to 157 nm of a F\textsubscript{2} laser and extreme ultraviolet lithography (EUV).\textsuperscript{181,182} Direct writing lithography methods are complicated, difficult-to-control, low-speed processes that are incompatible with large-scale manufacturing. The replication of nanopatterning methods are susceptible to mechanical defects, nanoscale alignment, and nanovoids and require a high-cost nanolithography process for nanomold manufacturing.\textsuperscript{183,184,185} The organic polymers used in nanopatterning resist are ultra-thin layers because of the limitations of light diffraction or electron beam scattering on lithography resolution and consequently exhibit weak plasma-etching resistance.\textsuperscript{186,187,188} Therefore, the nanopatterning with polymer resist is not compatible with plasma etching process for high aspect-ratio nanostructure fabrication. Consequently, a new nanolithography technology is destined to overcome the shortcomings of wavelength diffraction limits, low-speed processes, a polymer resin-based masking layer, and contact-printing-defect issues.

In this chapter, I will present the new double oxide deposition and etching (DODE) lithography method – an integration of thin film deposition and etching process – has been developed as a novel nanolithography technique for overcoming the limitations of optical and alternative lithography methods. I have achieved 50 nm linewidth of wafer-scale grooved nanostructures without the use of direct writing, or replication-of-nanopatterning techniques. The principle of DODE lithography is the fabrication of nanoscale patterns by isotropic oxide deposition and anisotropic oxide etching processes. Our previous research shows that the sidewall thickness can be controlled by changing the thin film deposition time.\textsuperscript{189} The nanopatterns, in this study, were obtained by integrating CVD (chemical vapor deposition)
attributes with a dry etching process on a microstructure. Moreover, the nanostructures fabricated by the DODE lithography method do not use a polymeric resin as a masking layer for high aspect-ratio nanostructure manufacturing. Thus, I could produce periodic arrays of nanostructures over a large area with high resolution by the DODE method with an aspect-ratio that is greater than 20:1.
5.1.2 Experimental Procedure

A schematic of the nanostructure fabrication process procedure for nanostructure manufacturing using DODE lithography method is shown in Fig. 65. First, the microstructures for nanoscale patterning were fabricated via conventional microfabrication processes. A 3-inch Si wafer ((100)-orientation, 0.1-0.5 Ω·cm, p-type) was used as a substrate. The substrate was first prepared using a RCA cleaning process to remove the organic contaminants, thin oxide layer and ionic contamination prior to the high-temperature processing steps. A 3-inch silicon wafer was used as a substrate (Fig. 65(a)) and a 500-nm-thick initial SiO$_2$ layer was deposited on the substrate via thermal oxidation (Bruce Furnace 7355B, Bruce Technology, USA) (Fig. 65(b)). After substrate preparation, a 500-nm-thick of photo-sensitive photoresist layer (S1805, MicroChem, USA) was spin-coated onto the substrate, and the substrate was subsequently baked on a hotplate to form the microstructures (Fig. 65(c)). Micropatterns with 1.5-μm of a linewidth were transferred from the photomask onto the wafer using a photolithography process (Fig. 65(d)). The photoresist was exposed to UV light for 4.5 sec with a 350-450 nm wavelength (NXQ-4000, Neutoniz-Quintel, USA), which enabled the removal of the chemical transfer of the photoresist by agitation in a developer solution (MF-319, MicroChem, USA) for 30 sec. The photolithographically patterned uppermost area of the substrate was etched with a mixture of SF$_6$ (6sccm) and Ar (4 sccm) gases, 5 mTorr of pressure, and RF1 (350W) and RF2 (350W) power using ICP (Plasma Therm 790, Unaxis ICP Etch, USA) dry etching process (Fig. 65(e)). After the dry-etching of the first SiO$_2$ layer, the photoresist was removed from the substrate by sonication in an acetone solution for 3 min (Fig. 65(f)). These microstructures served as a nanotemplate to
define the nanostructures. Next, a second SiO$_2$ layer was conformally deposited on the surface of the microstructures (Fig. 65(g)) for nanoscale patterning using PECVD (STS PECVD, STS, USA). The SiO$_2$ was deposited using SiH$_4$ (10 sccm) / N$_2$O (1420 sccm) / N$_2$ (392 sccm) gas mixtures along the topographical surface features of the microstructures. The deposition pressure was held constant at 900 mTorr, and the RF power was held constant at 30 W. The pattern size of the micropatterns decreased as the thickness of the second SiO$_2$ layer was increased. The linewidths were reduced to nanoscale dimensions through isotropic deposition of the second SiO$_2$ layer onto the micropatterned substrate (right-hand side of Fig. 65(g)). The top layer of the second SiO$_2$ layer over the microstructures and the residual SiO$_2$ layer beneath the nanopatterns were then selectively removed using an anisotropic dry etching process (Fig. 65(h)). The top and bottom layers, but not the sidewall layer, of the deposited SiO$_2$ were etched by ICP (Plasma Therm 790, Unaxis ICP Etch., USA) using a mixture of SF$_6$ and Ar gases to etch the thin film anisotropically. Argon gas enabled physical etching via bombardment of the nanopatterns by heavy ions, whereas SF$_6$ gas enabled reactive chemical etching of SiO$_2$. The ICP system uses a combination of a parallel plate and inductively coupled plasma reactive-ion etching (RIE). A high-density source of ions can be produced by controlling the RIE radio frequency bias, which can increase the etch rate. A separate RF bias can be applied to the substrate plate to create directional electric fields near the substrate to improve the anisotropic etch profile. The main power of the ICP was fixed at 350 W with a mixture of SF$_6$ (6 sccm) and Ar (4 sccm) gas flow rates while the pressure of 5 mTorr was maintained; the effect of the platen power was investigated through the application of different power values to the SiO$_2$ target. Consequently, the nanopatterns were successfully formed on the microstructures via the isotropic deposition
and anisotropic dry etching processes of the DODE lithography method (right-hand side of Fig. 65(h)).

![Figure 65. Schematic diagram of nanomanufacturing process by a double oxide deposition and etching (DODE) lithography process; (a) Si substrate, (b) deposition of the first SiO₂ layer by thermal oxidation, (c) spin-coating of the photoresist, (d) photolithography process, (e) dry etching of first SiO₂ layer by ICP, (f) removal of the photoresist (high magnification image in a right-hand side of Fig. 65(f)), (g) deposition of a second SiO₂ layer using PECVD (high magnification image in a right-hand side of Fig. 65(g)), and (h) dry etching of the residual second SiO₂ layer for nanopatterning (high magnification image in a right-hand side of Fig. 65(h)).]
5.2 Results and Discussion

5.2.1 DODE Nanolithography Process

The DODE lithography process for high aspect-ratio nanostructure manufacturing with sub-50 nm of linewidth is demonstrated in Fig. 66. The cross sectional FE-SEM (field-emission scanning electron microscopy) images in Fig. 66(a) show the 50 nm linewidth of grooved nanostructures fabricated using the DODE lithography process. I have obtained the 50 nm of nanopattern after deposition of the second SiO₂ layer on the microstructures by a conformal oxide deposition process using plasma enhanced chemical vapor deposition (PECVD). The microstructures have the 1.5 µm of micropatterns and the 500 nm of height, and then 1.5 µm of 2nd SiO₂ layer was deposited subsequently to obtain nanopatterns. Although the PECVD could uniformly deposit SiO₂ along with the microstructures, there is an inherent difference in the deposited thickness between in the trench and top of the structures due to the low bottom step coverage in the high aspect-ratio nanotrench.¹⁹⁰,¹⁹¹

The total height of the nanostructures and the residue layer were 2 µm and the 1 µm respectively. The residue oxide deposited beneath the nanopatterns was then removed to expose the substrate surface by an oxide etching process. The optimized plasma conditions with high mean-free-path result in the plasma radicals impacting the substrate almost perpendicularly, so that chemical-reactive etching does not occur on the lateral sidewall layer. Because the lateral sidewalls are not etched, no abrasion occurs, and the nanopatterns obtained by second SiO₂ deposition remain the same size after dry etching.
Figure 66. The DODE nanolithography process is demonstrated. Cross-sectional SEM images of a 50 nm of grooved nanostructure prepared via the DODE lithography process; (a) a nanopattern on a residual SiO$_2$ layer after isotropic deposition of a second SiO$_2$ layer (inset shows high magnification image of the nanopattern) and (b) SiO$_2$-based grooved nanostructure on a Si substrate after anisotropic dry etching of a second SiO$_2$ layer (inset shows high magnification image of the nanostructure). The nanopattern was obtained through 2$^{nd}$ SiO$_2$ deposition process using PECVD on lithographically patterned microstructure. Then, the residual layer under nanopattern was removed using ICP etching process to define high aspect-ratio nanostructure.
5.2.2 Isotropic Oxide Deposition for Nanopatterning

The linewidth of micropatterns was decreased as a function of the thickness of the second SiO$_2$ layer as shown in Fig. 67. The SiO$_2$-based microstructures on a Si substrate with a 1.5 μm micropattern dramatically decreased to sub-50 nm nanopatterns following the second SiO$_2$ deposition accordingly with high step coverage. The oxide layer was deposited onto the microstructure along the surface morphology. Thus, an increase in the sidewall thickness of microstructures caused a decrease in micropatterns producing the nanopatterns.

**Figure 67.** Linewidth in microstructure is reduced according to the increased thickness of the second SiO$_2$ layer by isotropic thin film deposition process (inset shows the SEM images of the 2$^{nd}$ SiO$_2$ deposited nanopatterns). The linewidth of micropatterns was gradually decreased as an increase of 2$^{nd}$ SiO$_2$ thickness up to 50 nm of nanopatterns.
5.2.3 Anisotropic Oxide Etching for Nanostructure Manufacturing

Anisotropic plasma etching is investigated for nanoscale trench plasma etching process. The anisotropy etching can be modulated through adjustment of the parameters of the plasma to deliver the plasma radicals vertically onto the surface. The plasma etching conditions can modify the mean free path of the plasma radicals. A low mean free path produces an isotropic etching profile with a lateral etch rate that is approximately equal to the downward etch rate. Therefore, optimized etching conditions are an important factor in obtaining high-mean-free-path plasma radicals for high aspect-ratio nanotrench. I investigated the relationship between the nanosize of the pattern and the plasma etching conditions by varying the pressure, gas flow rate, and RF power. I defined the anisotropy by following formula to quantify side etch rate:

\[ A = 1 - \frac{R_L}{R_V} \]

where, A is anisotropy, \( R_L \) is lateral etch rate, and \( R_V \) is vertical etch rate. For ideal anisotropic etch profile, the anisotropy, A, should be close to 1 meaning that the lateral sidewalls are not etched but vertically etched.

The mean free path depends on the pressure. The collision probability is proportional to the pressure, so that the radicals collide with the sidewalls at high pressures. Thus, a low-pressure plasma is suited to vertical anisotropic etching. A SF6-based gas mixture is typically used to etch SiO2, where sidewall etching is prevented by the deposition of a fluorocarbon polymer on the sidewall. The effect of pressure is illustrated in Fig. 68. The anisotropy and etch rate decreased as the process pressure was increased (Fig. 68(a)). The other
plasma etching conditions were held constant as follows: platen power (250 W), coil power (350 W), O₂ gas flow rate (0 sccm), SF₆ gas flow rate (6 sccm), Ar gas flow rate (4 sccm), and 5 min of etching time. The process was studied at pressures of 5 mTorr (Fig. 68(b)), 10 mTorr (Fig. 68(c)), and 15 mTorr (Fig. 68(d)). It is verified that the pressure is an important factor in determining the direction of motion of the plasma radicals.¹⁹⁵

Figure 68. (a) Effect of pressure on plasma anisotropic etching: (b) 5 mTorr, (c) 10 mTorr, and (d) 15 mTorr.
The effect of oxygen gas was investigated, as shown in Fig. 69. The nanoscale SiO$_2$ trench was etched using SF$_6$/Ar/O$_2$ gas mixtures in an ICP system. The aspect ratio and etch rate decreased as the oxygen gas was increased (Fig. 69(a)). The effect of the O$_2$ gas flow rate was studied using different flow rates of 0 sccm (Fig. 69(b)), 2 sccm (Fig. 69(c)), and 4 sccm (Fig. 69(d)) with a fixed SF$_6$ (6 sccm) + Ar (4 sccm) flow rate. The increase in the O$_2$ gas flow rate decreased the SiO$_2$ etch rate and the anisotropy. A SF$_6$-based gas mixture is typically used to etch SiO$_2$, where sidewall etching is prevented by the deposition of a fluorocarbon polymer on the sidewall. The O$_2$ gas plays role to decompose the deposition of the fluorocarbon polymer, which decreases the anisotropy.$^{196}$ Thus, oxygen gas is not needed for an anisotropic etch profile in nanotrench.
Figure 69. (a) Effect of O$_2$ gas flow rate on plasma anisotropic etching: (b) 0 sccm, (c) 2 sccm, and (d) 4 sccm.
Our ICP (inductively coupled plasma) system consists of platen power bias (RF1) which is applied to parallel plate and coil power bias (RF2) for a high-density plasma source of ions. A vertical etching profile is related to the direction of motion of incident radicals, which can be implemented by the anisotropic motion of ions. The platen power was applied to the substrate plate to create directional electric fields near the substrate to heighten the anisotropy of the etching profile. The anisotropic etching profile was obtained when the incident ions were delivered over a small angle into the nanotrench through an increase in the platen power. The main coil power of the ICP was fixed at 350 W with a mixture of SF₆ (6 sccm) and Ar (4 sccm) gas flow rates while the pressure of 5 mTorr was maintained; the effect of the plasma etching conditions were investigated through the application of different power values to the SiO₂ target, pressure and gas for high aspect-ratio etching profile (Fig. 70). An increase in the platen power increased both the SiO₂ etch rate and the anisotropy linearly (Fig. 70(a)). The platen power tests corresponded to 150 W (Fig. 70(b)), 250 W (Fig. 70(c)), and 350 W (Fig. 70(d)). A vertical etching profile is related to the direction of motion of incident radicals, which can be implemented by the anisotropic motion of ions.¹⁹⁷ The platen power was applied to the substrate plate to create directional electric fields near the substrate to heighten the anisotropy of the etching profile. The anisotropic etching profile was obtained when the incident ions were delivered over a small angle into the nanotrench through an increase in the platen power.
A previously reported LPNE (lithographically patterned nanowire electrodeposition) technique by Menke et al.\textsuperscript{198} can also fabricate metal nanowires using photolithography and wet etching processes without the use of nanolithography methods; instead, an electrochemical deposition technique is used on the photolithographically patterned nickel nanoband electrode. However, the electrochemical plating process is difficult to control and is incompatible with eco-friendly manufacturing. The DODE lithography technique can simply fabricate the nanostructure without wasting chemical solutions; it also allows the assembly nanoelements in the nanostructures, such as metal particles, CNTs, and organic particles, for future nanowire fabrication.
5.2.4 Large-scale Nanostructure Manufacturing

In terms of large-scale lithography, the nanoimprint lithography process is affected by the mold feature density, complexity and distribution of feature sizes. The resist build-up problems around large feature sizes were reported by Wagner et al. When complex patterns combining large and small feature sizes are imprinted, the polymer is hard to be evenly distributed over the entire surface of the substrate because the polymer chains are very long and entangled. Since the DODE process does not apply pressure on a polymer to form nanopatterns, meanwhile, it can be applied in the various patterned lithography for wafer-scale nanolithography and various nanopatterns can be obtained from various shapes of micropatterns with deposition of the second SiO$_2$ layer. Figure 71 shows various nanopatterning results after of 2$^{\text{nd}}$ SiO$_2$ deposition on various microstructures. Micropatterns of various sizes and shapes were used in the DODE lithography process for nanopatterning. I fabricated various micropattern shapes, including circles, trenches, rings and squares, with micron pattern sizes. The linewidth and diameter of the micropatterns were reduced through variation of the thickness of the deposited SiO$_2$ layer.
Figure 71. Microstructures with various patterns were simply fabricated through microfabrication processes of oxide deposition, photolithography, and oxide etching processes. Next, nanostructures with various shapes were created from micropatterns by deposition of 2\textsuperscript{nd} SiO\textsubscript{2} layer: (a) squares, (b) circles, and (c) rings.

Figures 72(a) and (b) are SEM images of nanotrench and nanowell array patterns, respectively, on wafer-scale nanostructures. A field-emission scanning electron microscope (Supra 25, Carl Zeiss, USA) was used for imaging. The DODE lithography method can be used to fabricate large-scale nanostructures up to the wafer-scale because the microstructures were manufactured on a wafer through microfabrication processes. The minimum patterning sizes of a
50 nm linewidth for a nanotrench and a 400 nm diameter for a nanowell array were obtained using the developed DODE lithography method. In addition, I can manufacture uniform nanostructures with high aspect-ratio by adjusting the thicknesses of the first and second SiO$_2$ layers. In this study, a 1.5-μm-thick second SiO$_2$ layer was deposited onto the microstructure of the 500-nm-thick first SiO$_2$ layer to obtain sub-100 nm nanopatterns and structures with high aspect-ratio. After removal of 1-μm-thick residue SiO$_2$ layer using dry etching process, 1 μm height of SiO$_2$ nanostructure was remained with 50 nm of nanopattern. The nanostructure surface morphologies for the 50 nm nanotrench patterns and the 400 nm nanowell array patterns were analyzed using atomic force microscopy (AFM), as shown in Fig. 72(c) and (d), respectively. The etching profiles of the various nanopattern structures with high aspect ratios were analyzed using an atomic force microscope (NX-10, Park System, Korea). The high aspect ratio of the 7:1 cantilever probe (AR5T-NCHR, Park System, Korea) was used to measure the deep nanostructure morphology. The line profile of a 1-μm-deep nanowell with a 50 nm linewidth was measured (Fig. 72(e)). However, the depth value could not be reliably determined from the AFM images of the height profile because the aspect ratio of the AFM tip (7:1) was difficult to compare with the aspect ratio of the nanotrenches (20:1). However, the line profile of the nanowell array, which had an aspect-ratio of 2.5:1, was accurately measured (Fig. 72(f)). Therefore, the novel DODE nanolithography method paved way to fabricate sub-100 nm nanostructures with high aspect-ratio over large-scale areas using conventional microfabrication processes.
Figure 72. SEM images of large-area of (a) nanotrench and (b) nanowell array and AFM images of (c) nanotrench and (d) nanowell arrays after the DODE lithography process; the inset shows high-magnification images of nanopatterns; and line profiles of each (e) nanotrench and (f) nanowell patterns measured from AFM images; high aspect ratios greater than 20:1 were obtained.
High aspect-ratio nanostructure fabrication techniques have been developed by Morton et al.\textsuperscript{164} using nanoimprint and DRIE (deep reactive ion etching) and by Szeghalmi et al.\textsuperscript{200} using polymer replication process. However, those methods involve nanomold imprinting to transfer patterns on a substrate, sacrificial layers deposition for bulk silicon substrate etching and polymer replication processes, which cause the nanostructure manufacturing process being difficult, time-consuming, and expensive. Meanwhile, the DODE technique can simply fabricate wafer-scale high aspect-ratio nanostructures with nanoscale patterns by isotropic oxide deposition and anisotropic oxide etching processes without e-beam lithography or nanoimprint lithography processes. In addition, the DODE method does not use polymer resin as a masking layer in the dry etching process so the nanostructures fabricated using the DODE process can be used as a polymer-free nanotemplate for various nanoelectronic applications, such as electrochemical, biological, or chemical sensors. In electrochemical applications, the nanotemplates patterned by a polymer resin are mostly used in a DI-water-based solution, which is incompatible with organic solvents such as DMF (dimethylformamide), NMP (1-methyl-2-lyrroloid), DMSO (dimethyl sulfoxide), methylene chloride, and chloroform. The SiO\textsubscript{2}-based nanostructure is a non-polymer-based nanotemplate fabricated via the DODE lithography method and can be used in organic-solvent-based electrochemical applications.
5.3 Summary

In summary, wafer-scale nanopatterning was simply fabricated by the DODE lithography technique, which is developed for nanomanufacturing with linewidths less than 100 nm with high aspect-ratio that were greater than 20:1. The presented technique overcomes the limitations of high-resolution lithography techniques and high aspect-ratio nanostructure manufacturing processes. A nanotrench with a 50 nm linewidth was obtained via isotropic oxide deposition using PECVD, and a 1 μm-deep SiO$_2$-based grooved nanostructure was formed using an anisotropic dry etching process using ICP. The DODE lithography can be used to create well-ordered arrays of nanostructures over large areas. In addition, it is expected to stimulate avenues in high aspect-ratio nanoscale nanomanufacturing, where high resolution is required, using conventional microfabrication technologies. A better understanding of the basic processes of microfabrication and the limits of lithography processes has allowed to develop a simple nanopatterning method and has paved the way for improved nanolithography performance. A strong advantage of this technology is the simplification in nanopatterning of numerous nanostructures on substrates.
CHAPTER 6: SWNTs-BASED FUNCTIONAL DEVICE APPLICATIONS

6.1 SWNTs Thin Film Transistor

Single-walled carbon nanotubes (SWNTs) have been considered to be a promising building block for field effect transistors due to their unique electronic properties such as high mobility and ballistic conductance.\textsuperscript{201} Even though individual nanotubes have shown high mobility of $10^5 \, \text{cm}^2/\text{Vs}$ and high ON / OFF ratios around $10^5$, it has poor device-to-device uniformity due to the electrical inhomogeneity and low drain current. Therefore, SWNTs array thin film has contributed charge transport and increased current outputs. Moreover, the degree of orientation and the density of SWNTs thin film have a great influence on thin film transistor performance.\textsuperscript{202} I demonstrated assembly of SWNTs with high density via fluidic and electro-fluidic assembly processes and investigated detailed electronic transport properties of the aligned SWNTs networks.

Figure 73 shows transfer and output characteristics of the SWNTs-based thin film transistor performance which is fabricated using the template-guided fluidic assembly process. The SWNTs were assembled from a 95% of semiconducting nanotubes aqueous solution (Brewer science, USA) on microtrench with 3 µm width and 20 µm length. The diameter and length of the nanotubes varied from 0.5 to 3.9 nm and 0.7 to 3 µm, respectively. Figure 73(a) demonstrates a schematic of the SWNTs thin film transistor. Highly doped Si wafer is used as a back-gate and 300 nm of SiO$_2$ is deposited as a dielectric layer. Photolithography process is carried out on the substrate to fabricate micropatterns. SWNTs are assembled into the microtrench using the template-guided fluidic assembly process with pulling speed of 0.05
mm/min. Metal electrodes of Ti (5 nm) / Au (150 nm) are deposited on the SWNTs thin film for source and drain electrodes. The operation is largely unipolar p-channel semiconducting behavior. Figure 73(b) present transfer characteristics (plots of drain current ($I_d$) versus gate voltage ($V_g$)) according to the drain voltage of 0 $V_{ds}$, 100 mV$_{ds}$, 1 $V_{ds}$, 3 $V_{ds}$, and 5 $V_{ds}$) indicating the feasibility of the template-guided fluidic assembly process. Figure 73(c) shows the output characteristics ($I_d - V_{ds}$) of the SWNTs thin film networks as a function of the gate voltage.

Figure 73. SWNTs-based thin film transistor fabricated using template-guided fluidic assembly; (a) Schematic of SWNTs thin film transistor. (b) Typical data collected from the represented device of transport and (c) output characteristics for 20 µm channel length.
I fabricated the highly dense SWNTs thin film transistors with channel lengths of $L_c = 5, 10, 15,$ and $20 \ \mu m$ all with widths of $L_w = 3 \ \mu m$. For each device, electrical characteristic of the SWNTs thin film transistors by sweeping the drain voltage between -10 V and 10 V is shown in Fig. 74(a) showing semiconducting non-linear behavior of the SWNTs. For each device, currents between source and drain were measured at a drain bias of 100 mV$_{ds}$ while sweeping the drain voltage between -40 V and 40 V (Fig. 74(b)). To analyze the transport characteristics of the SWNTs thin film transistors, I measured the scaling behavior of On ($I_{on}$) and Off ($I_{off}$) current, as a function of channel lengths ($L_c$) as shown in Fig. 74(c). The On current is measured at $V_{ds} = 100 \ \text{mV}$ and $V_g = -40 \ \text{V}$. The Off current corresponds to the minimum current observed for the range of gate voltages between -40 V and 40 V at $V_{ds} = 100 \ \text{mV}$. The detailed values of the data are displayed in the Fig. 74(d). The typical response of the On and Off currents are channel length dependence. It is simultaneously decreased as an increase of the channel length. However, the On / Off ratio rapidly increased as increase of the channel length. This is because of the existence of the metallic nanotubes between source and drain in short channel transistor. Therefore, the configuration of the long channel transistors leads to percolation transport pathways and high On / Off ratios because of the low probability of the bridging nanotubes or metallic current pathways.
Figure 74. Electrical properties of the SWNTs-based transistor as a function of transistor channel length, $L_c$ of 5 µm, 10 µm, 15 µm, and 20 µm; (a) Output characteristics of the devices display p-type behavior. (b) Transfer characteristics of the device that display a maximum On / Off ratio of $10^3$. (c) and (d) ON current ($I_{on}$), OFF current ($I_{off}$), and On / Off ratio for densely assembled SWNTs thin film transistor.

I have studied effects of the orientation of the aligned SWNTs networks on transistor performance as illustrated in Fig. 75. The different channel orientation leads to different behavior of the thin film transistor. Orientation of the SWNTs alignment can be controlled by external guiding forces. I have obtained perpendicular (Fig. 75(a)) and parallel (Fig. 75(b)) orientation to the channel direction using the fluidic flow and electric-field, respectively. Two different configurations of the devices have same nanotubes coverage and channel dimensions but
different channel orientations. Lower On current and higher On / Off ratio are obtained for perpendicular orientation fabricated by fluidic assembly method (Fig. 75(c)) compared to the parallel orientation fabricated by electric-fluidic assembly method (Fig. 75(d)). The parallel orientation of the SWNTs networks leads to many tubes that bridge the source and drain electrodes with low nanotubes-nanotubes junctions. This configuration provides high On current, but also large Off current because of the presence of the metallic nanotubes.

Figure 75. SWNTs-based thin film transistor performance depending on the orientation of the nanotubes alignments; SEM images of transistors with different channel orientations and degrees of alignment of (a) perpendicular and (b) parallel to the channel direction. Transfer characteristics of the SWNTs thin film transistors fabricated by (c) fluidic and (d) electric-fluidic assembly methods.
6.2 SWNTs-based Antenna Fabrication for Energy Harvest Application

A highly-dense single-walled nanotubes (SWNTs) assembly technique using template-guided fluidic assembly was utilized for large-scale SWNTs-based antenna fabrication. Figure 76(a) shows SWNTs antenna fabrication processes sequence. A highly polished silicon wafer with 1µ thick thermal oxide was used as a substrate. Piranha cleaning is used to remove organic residues from the substrate. After the piranha cleaning, the substrate is blow-dried with a stream of N$_2$ gas. For a dehydration drying process, the substrate was baked in an oven after piranha cleaning followed by oxygen plasma treatment. Subsequently a layer of photoresist is spin-coated on the substrate followed by FOTS SAMs layer coating through vapor-SAMs process for super hydrophobic templates. Then, desired trench features on these SiO$_2$ substrates were created employing conventional microfabrication process. The desired regions on the photoresist were exposed directly by optical photolithography process followed by development. I utilized the surface energy controlled template-guided fluidic assembly process to assemble SWNTs at desired location for highly dense SWNTs over a large area. The SWNTs were selectively assembled on the exposed hydrophilic surface in the microtrenches. After the assembly of the SWNTs on the desired position, the guided template was removed by dissolving in acetone solution. Finally, titanium and gold metals were deposited on the assembled SWNTs bundles after photolithography process and a lift-off process using electron-beam evaporation.

I have designed, fabricated and tested the two different configurations of SWNTs-based rectenna for harvesting energy in both the infrared and the microwave regime. The energy harvested in the IR and the microwave regime with a single rectenna was in the order of a few
nanowatts corresponding to energy densities, which are an order of magnitude greater than those harvested by conventional piezoelectrics and thermoelectrics. It is projected that SWNTs-based rectenna arrays will harvest energy in the infrared and microwave spectrum from including any heat source and to produce a projected 63 W/m² from sun irradiation (1.5AM) and about 5 W/m² from body heat competing with conventional photovoltaics. Energy harvesting can be extended to the near IR spectrum provided that diodes operating in THz range are available. Two types of large-scale closed loop SWNTs antenna and simple dipole SWNTs antenna were fabricated as shown in Fig. 76(b) and (c), respectively.
Figure 76. (a) Shown in figures are the steps involved in the antenna fabrication process. Substrate preparation plays an important role in determining the nature of SWNT assembly. The surface energy control process allowed to manufacture large-scale SWNTs assembly. The FE-SEM images show two different designs of SWNTs-based antenna; (b) closed loop and (c) simple half wavelength dipole.

The MIM diodes and capacitors were wire bonded using the wire bonder with minimal stretch of wires between the SWNTs antenna and the diodes such that the resonance frequency of the antenna is not greatly altered for the half wave and full wave rectifiers. The capacitors are
chosen to be operating in the rectification region of the considered spectrum bandwidth. I expected the presented SWNTs-based rectenna arrays to harvest energy in the infrared and microwave spectrum. These calculations are based on the assumption that the incident powers are 370 W/m$^2$sr, 160 W/m$^2$sr and 80 W/m$^2$sr in the IR-A, IR-B and IR-C spectrums respectively. Table 6 shows the international classification for the IR spectrum. In all the cases, normal incidence is assumed. In these calculations, SWNTs antenna gain for IR-A and IR-B spectrums is considered to be $G = -5$ dB (0.32 in amplitude) while for IR-C it is considered to be $G = -10$ dB (0.1 in amplitude), the rectifier efficiency is assumed to be $\eta_{\text{rectifier}} = 80\%$ while the assumption for the percentage of the antenna array’s area in the substrate $A = 60\%$. A layer structure for harvesting energy from the IR part of the incident solar spectrum is also assumed. The transparency between layers is also assumed to 85%. I characterized the optical properties of SWNT-based IR detector with an IF lamp mounted on the probe station used to measure its electrical properties. Testing was carried out in two different environments; the single loop antenna was tested with an infrared lamp (250 W and 120 V) as being the source and simple dipole antenna was tested with a 9.4 GHz oscillator bridge radiating microwaves through a wave guide as the sources with a -10 dB input power. In both cases, the rectenna is placed at a distance of 10 mm from the source. Different loads were attached to the rectenna and the corresponding operating circuit voltage and the current were determined. The power output is then obtained then determined from these values for the given corresponding load. The resulting I-V characteristics for various loads are shown in Fig. 77. It is clear from the figure that they generate nanowatts of power. The appropriate operating load for the dipole antenna is much higher than that of a single loop antenna. The experimental data are shown in Table 7 and 8.
Figure 77. Shown in (a) is a design consideration for a loop antenna design while in (b) is that for a simple dipole antenna. The corresponding resonance and gain are displayed below the structures and are simulated using HFSS software. The electrical circuit diagram of half (c) and full wave rectifiers for the loop and dipole antenna, respectively. Shown in (e) is the I-V characteristic for a single loop antenna tested with an IR source while (f) is that for a simple dipole antenna tested with a microwave source.
Table 6. Shown in table is the ICI classification scheme for the infrared spectrum, the corresponding frequency ranges and needed element to harvest energy.

<table>
<thead>
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<th>Classificaiton</th>
<th>Wavelength</th>
<th>Frequency</th>
<th>Needed</th>
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<tr>
<td>IR-A</td>
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<td>240 – 430 THz</td>
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<tr>
<td>IR-B</td>
<td>1.25 – 2.5 μm</td>
<td>120 – 240 THz</td>
<td>Rectifying Diodes</td>
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<tr>
<td>IR-C</td>
<td>3 – 1000 μm</td>
<td>300 GHz – 120 THz</td>
<td>Rectifying Diodes</td>
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Table 7. Experimental data of harvested energy of loop antenna device.

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<th>Voltage (mV)</th>
<th>Power (nW)</th>
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Table 8. Experimental data of harvested energy of a simple dipole antenna device.

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<th>Voltage (mV)</th>
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6.3 Chemical Gas Sensor for NO₂ Gas Detection

Gas sensors are required for leakage detections of explosive gases and real-time detections of toxic or pathogenic gases with high sensitivity and selectivity. Since the most common gas sensing principle is the electrical conductivity changes through the charge transfer of gas molecules by adsorption and desorption of gas molecules on sensing materials, it is understandable that by increasing the contact interfaces between the analytes and sensing materials, the sensitivity can be significantly enhanced. \(^92,^93\) Well aligned SWNTs are required to increase the percolation conductivity for better sensor behavior.

I have fabricated densely packed and aligned SWNTs bundles using the electric-assisted fluidic assembly for gas sensing applications which require improved charge transport and enhanced conductivity of SWNTs. NO₂ gas sensing results using the SWNTs gas sensor are demonstrated in Fig. 78. Prof. Haler conducted the gas sensing test. The assembled SWNTs were exposed to NO₂ at different concentrations to demonstrate sensor performance. Figure 78(a) shows the I-V characteristic of SWNTs gas sensor. The electrical properties of SWNTs were strongly dependent on pulling speed, which corresponds to decreasing SWNTs thickness. The SWNTs were assembly using 5 mm/min of pulling speed at 2.0 V\(_{dc}\). After annealing in N₂, the resistance was reduced, which indicates that annealing improves the contact between SWNTs and the metal electrodes. Figure 78(b) shows that the SWNTs sensor gives strong responses to different concentration of NO₂, starting from an initial baseline resistance of approximately 1.95 KΩ. After exposure to NO₂, the resistance of the sensor dramatically decreased depending on the gas concentrations. The detection limit was 200 ppb at room temperature. The sensitivity of the
SWNTs gas sensor was demonstrated in Fig. 78(c). The sensitivity is defined as the relative resistance change for a given NO$_2$ concentration, $\Delta R/R_0 = (R_{eq} - R_0)/R_0$, where $R_{eq}$ is the steady-state resistance after exposure to NO$_2$ and $R_0$ is the initial resistance before exposure to NO$_2$. The SWNTs sensor exhibited a linear response of 2.35 % per ppb NO$_2$ for concentrations ranging from 200 ppb to 1 ppm. These results clearly demonstrate the enhanced sensitivity of the highly-aligned SWNTs gas sensors.
Figure 78. SWNTs gas sensor for NO₂ gas detection: (a) Current-voltage (I-V) curve of the SWNTs gas sensor. After annealing in N₂, the resistance is reduced. (b) NO₂ gas sensing using highly-aligned SWNTs. The arrows show the injected gas concentration. The resistance change is monitored using two-electrode configuration at 100 mV. (c) NO₂ sensitivity of highly-aligned SWNTs to NO₂ concentration.
6.4 Flexible SWNTs Biosensor for In-vivo D-Glucose Detection

I have developed a site-selective fluidic assembly technique for controlled assembly of SWNTs with high density network architectures on flexible polymer substrate. The microscale patterns of SWNTs networks were created on a PEN (Polyethylene naphthalate) plastic substrate by utilizing the surface energy differential between a plasma-treated (hydrophilic) substrate and a FOTS-coated photoresist (hydrophobic) surface. Large scale nanotubes networks with 3 µm width and 50 µm length of micro-array patterns were fabricated on the plastic substrate for flexible biosensor applications. Next, metal pads are formed on the SWNTs structures for electrical measurements.

Prof. Lee conducted the glucose detection test. Figure 79(a) shows the schematic of D-glucose detection using GOD-based SWNTs flexible biosensor. The GOD was immobilized on the SWNTs using non-covalent bonding as shown in Fig. 79(b). The biosensor was characterized by electrical measurements. Increasing glucose concentrations monitored the electrical responses. Fig. 79(c) and (d) shows the developed flexible biosensor can detect D-glucose in the range between 0 ~ 40 mM. Therefore, the GOD modified SWNTs-based flexible biosensor can be suggested for in-vivo glucose detection in a medical system due to the high electrochemical sensitivity.
Figure 79. D-glucose detection using SWNTs-based flexible biosensor: (a) Schematic diagram of GOD-immobilized SWNTs using non-covalent bonding. (b) SEM image of the GOD-immobilized SWNTs. (C) The electrical response by following D-glucose concentration. (d) Real time detection in the range between 0 ~ 40 mM.
CHAPTER 7: SUMMARY

7.1 Conclusion

I have focused on CNTs assembly techniques and nanotemplate manufacturing for single-walled carbon nanotubes (SWNTs)-based functional device applications. A template-guided fluidic assembly method has been utilized for large-scale SWNTs assembly on a flexible substrate because it is directed, robust, and precisely controllable over other assembly methods. For the highly dense SWNTs assembly, the influence of humidity and surface energy on the fluidic assembly efficiency has been studied and surface modification processes are developed for highly organized SWNTs networks. Surface energy control process is developed to enhance the density of the SWNTs structure through surface treatment processes. Super hydrophobic layer which has low surface energy is coated using FOTS self-assembled monolayer coating process. Large-scale SWNTs networks are achieved on flexible substrate using the developed fluidic assembly process from micro – to mm scale area with high density.

Since the fluidic assembly uses capillary force at the interface of the surface, however, it is a diffusion-limited process; the SWNTs are slowly attached on the surface while the solution is evaporated. Hence, a significantly progressive assembly technique is destined simultaneously to meet all the integration requirements of precise control of the desired location, density, large area and alignment with high-rate assembly speed. I have presented a simple, reliable, and efficient SWNTs assembly method using electric-fluidic assembly process to enhance the fluidic assembly efficiency. The developed electric-assisted fluidic assembly can control the location, density, orientation, and scalability of the SWNTs with nanoscale precision. It utilized directed
assembly strategies by integration of electrophoresis and fluidic assembly. The applied electric-field not only increases partial concentration of the individual nanotubes suspended in solution, but also enable orientation of the electrically-driven SWNTs on the electrode surface in a desired direction to align along the assembly direction. The developed assembly method improved assembly speed by 1000 times compared to the fluidic assembly process and can control scale and density of the aligned SWNTs structures.

For nanoscale device fabrication, I developed a new nanolithography technique for the nanotemplate manufacturing using DODE (double oxide deposition and etching) process. A wafer-scale nanopatterning was simply fabricated by the DODE lithography technique, which is developed for nanomanufacturing with linewidths less than 100 nm with high aspect-ratio that were greater than 20:1. The presented technique overcomes the limitations of high-resolution lithography techniques and high aspect-ratio nanostructure manufacturing processes. A nanotrench with a 50 nm linewidth was obtained via isotropic oxide deposition using PECVD, and a 1 μm-deep SiO$_2$-based grooved nanostructure was formed using an anisotropic dry etching process using ICP. The DODE lithography can be used to create well-ordered arrays of nanostructures over large areas. In addition, it is expected to stimulate avenues in high aspect-ratio nanoscale nanomanufacturing, where high resolution is required, using conventional microfabrication technologies. A better understanding of the basic processes of microfabrication and the limits of lithography processes has allowed to develop a simple nanopatterning method and has paved the way for improved nanolithography performance. A strong advantage of this technology is the simplification in nanopatterning of numerous nanostructures on substrates.
Finally, SWNTs-based functional devices were fabricated using the developed assembly methods for electrical, chemical, and biological applications. SWNTs thin film transistor is fabricated using the developed assembly techniques. The percolation transport properties are investigated according to the channel lengths and alignments. Large-scale SWNTs-based antenna is developed using the template-guided fluidic assembly for energy harvesting application. I have fabricated densely packed and aligned SWNTs bundles using the electric-assisted fluidic assembly for gas sensing applications which require improved charge transport and enhanced conductivity of SWNTs. The assembled SWNTs were exposed to NO₂ at different concentrations to demonstrate sensor performance. The site-selective fluidic assembly technique is used for controlled assembly of SWNTs with high density network architectures for in-vivo D-glucose biosensor application. The GOD modified SWNTs-based flexible biosensor can be suggested for in-vivo glucose detection in a medical system due to the high electrochemical sensitivity.
7.2 Future Works

According to presented research works, I have developed single-walled carbon nanotubes (SWNTs) assembly techniques for large-scale SWNTs networks. Highly dense and aligned SWNTs thin film networks are achieved for future electronic device applications. Electrical current flows through the conduction pathways of the networks and percolation pathways affect the device performance. Electrical properties of the SWNTs transistors are characterized according to the orientation of the aligned SWNTs thin film. Highly dense SWNTs thin film is desired for high current output of the devices. I have achieved highly aligned SWNTs networks which orientation is parallel to the channel direction. Even though the aligned SWNTs thin film transistors have high output current, the on / off ratio is low compared to the device that orientation is perpendicular to the channel direction. This is because the small conduction paths and nanotube-nanotube junctions of the networks. Therefore, highly aligned SWNTs networks with low density are destined for high performance thin film transistor. To control the configuration of the SWNTs networks, the external guiding forces such as capillary force and electric-field have to be utilized. Therefore, I need to develop a process for formation of optimized SWNTs networks for high transfer and output currents and on / off ratio performance of the thin film transistor.

The nanoscale SWNTs electronics have been considered as promising building blocks for high performance electronics. I have developed a new nanolithography technique of DODE (double oxide deposition and etching) lithography by utilizing isotropic thin film deposition and anisotropic plasma etching processes. This developed lithography paved way to enable wafer-
scale nanopatterning process without advanced nanolithography methods such as e-beam lithography, nanoimprint lithography, and EUV lithography. I have fabricated large-scale nanotrenches with 50 nm of linewidth using the DODE lithography. SWNTs can be assembled into the lithographically patterned nanotrenches using the developed assembly techniques. The nanoscale SWNTs not only can prohibit the electrical heterogeneity of the SWNTs networks but also enhance orientation of the aligned SWNTs. Consequently, I will keep researching nanoscale SWTNs assembly on nanotrench for high performance nanoscale SWNTs-based functional device applications.
7.3 References


