ENGINEERING HIGHLY ORGANIZED AND ALIGNED SINGLE WALLED CARBON NANOTUBE NETWORKS FOR ELECTRONIC DEVICE APPLICATIONS: INTERCONNECTS, CHEMICAL SENSOR, AND OPTOELECTRONICS

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Young Lae Kim

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ABSTRACT OF DISSERTATION

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Abstract

For 20 years, single walled carbon nanotubes (SWNTs) have been studied actively due to their unique one-dimensional nanostructure and superior electrical, thermal, and mechanical properties. For these reasons, they offer the potential to serve as building blocks for future electronic devices such as field effect transistors (FETs), electromechanical devices, and various sensors. In order to realize these applications, it is crucial to develop a simple, scalable, and reliable nanomanufacturing process that controllably places aligned SWNTs in desired locations, orientations, and dimensions. Also electronic properties (semiconducting/metallic) of SWNTs and their organized networks must be controlled for the desired performance of devices and systems. These fundamental challenges are significantly limiting the use of SWNTs for future electronic device applications. Here, we demonstrate a strategy to fabricate highly controlled micro/nanoscale SWNT network structures and present the related assembly mechanism to engineer the SWNT network topology and its electrical transport properties. A method designed to evaluate the electrical reliability of such nano- and microscale SWNT networks is also presented. Moreover, we develop and investigate a robust SWNT based multifunctional selective chemical sensor and a range of multifunctional optoelectronic switches, photo-transistors, optoelectronic logic gates and complex optoelectronic digital circuits.
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Introduction

Since the discovery of single walled carbon nanotubes (SWNTs) in the early 1990s [1, 2], there has been intense activity exploring the electrical properties of these systems and their potential applications in electronics. SWNT is a graphene roll with a diameter of 0.5 to a few nanometers that can be either metallic or semiconducting depending on its chirality. However, multi walled carbon nanotubes (MWNTs) are concentric graphene tubes that can have diameters typically from 2 nm to 25 nm. The unique properties of carbon nanotubes (CNTs) can be attributed to the one-dimensional nature of nanotubes, the strong $sp^2$ carbon bonds, and the peculiar band-structure of graphene. The $sp^2$ bonding in graphene is even stronger than the $sp^3$ bonding in diamond [3], and therefore CNTs have very high mechanical strengths. The combination of high degree of crystalline order with very less defects, large mechanical strength and the relatively small interaction between electrons and carbon atoms enables CNTs to conduct very large current densities of $10^9$ A·cm$^{-2}$ [4].

In chapter 1, the electronic structure and properties of SWNTs were discussed for understanding basic physics of them. This chapter also discussed a fabrication method and transition for SWNT networks. The many possible symmetries or geometries that can be realized on a cylindrical surface in SWNTs without the introduction of strain are the importance to carbon nanotube physics. For one-dimensional (1D) system on a cylindrical surface, translational symmetry with a screw axis could affect the electronic structure and related properties. With understanding the basic physics of SWNTs, this chapter focuses on the structure, electrical properties, and optical properties of SWNTs. Then, this chapter introduced a fabrication method for micro-to-nano scale patterned SWNT networks using a newly developed template guided fluidic assembly process. A mechanism for SWNT assembly and their control was described
here. To maximize the directed assembly efficiency of SWNTs toward a wafer level SWNT deposition, Si or SiO$_2$ substrate was pretreated with precisely controlled plasma treatment. Chemical and physical properties of the surface were characterized using several surface characterization techniques to investigate and control the mechanism of SWNT assembly. Last, this chapter demonstrated the effectiveness of directed assembly on channels with varying degrees of confinement as a simple tool to tailor the conductance of the otherwise heterogeneous network, opening up the possibility of robust large-scale carbon nanotube networks (CNN)-based devices.

In chapter 2, the fabrication and characterization of nanoscale electrical interconnect test structures constructed from aligned single walled carbon nanotubes using a template-based fluidic assembly process were presented. These structures can withstand current densities $\sim 10^7$ Acm$^{-2}$, comparable or better than copper at similar dimensions. In addition, we present a novel Pt-nanocluster decoration method that drastically decreases the resistivity of the test structures. Ab-initio density functional theory calculations indicate that the increase in conductivity of the nanotubes is caused by an increase in conduction channels close to their Fermi levels due to the platinum nanocluster decoration, with a possible conversion of the semiconducting single walled carbon nanotubes into metallic ones.

In chapter 3, a method is presented for significantly reducing the interfacial contact resistance of SWNT interconnect test-structures. Conventional lithographic cleaning steps are insufficient for complete removal of lithographic residues in SWNT networks, leading to large interfacial contact resistance. Using improved purification procedures and controlled developing time, the interfacial contact resistance between SWNTs and contact electrodes of Ti/Au were found to
reach values below 2% of the overall resistance in two-probe test-structures of SWNTs, demonstrating the importance of cleaning lithographic residues from the surface of SWNTs before the fabrication of metal electrodes.

In chapter 4, the effective detection of hydrogen sulfide gas by a redox reaction based on SWNTs functionalized with TEMPO as a catalyst was introduced and we also discuss the important role of water vapor on the electrical conductivity of SWNTs during the sensing of H$_2$S molecules. To explore the H$_2$S sensing mechanism, we investigate the adsorption properties of H$_2$S on CNTs and the effects of the TEMPO functionalization and we summarize current changes of devices resulting from the redox reactions in the presence of H$_2$S.

Chapter 5 introduced a radically unconventional, voltage-tunable, sharply non-linear and extremely sensitive photo-response in fludically-assembled single walled carbon nanotube/Si heterojunctions, with high photocurrent responsivity, high photovoltage responsivity, high electrical ON/OFF ratios and optical ON/OFF ratios. The large scale optoelectronic sensor was demonstrated by fabricating an array of 250,000 micron-scale photo-active junctions covering a centimeter-scale wafer. We also presented bidirectional phototransistors, and novel logic elements such as a mixed optoelectronic AND gate, a 2-Bit optoelectronic ADDER/OR gate, and a 4-Bit optoelectronic D/A converter.
Chapter 1: Single Walled Carbon Nanotubes

The many possible symmetries or geometries that can be realized on a cylindrical surface in SWNTs without the introduction of strain are the importance to carbon nanotube physics. For one-dimensional (1D) system on a cylindrical surface, translational symmetry with a screw axis could affect the electronic structure and related properties [5]. With understanding the basic physics of SWNTs, this chapter focuses on the structure, electrical properties, and optical properties of SWNTs.

1.1 Structure of Single Walled Carbon Nanotubes

In the theoretical carbon nanotube structure, single walled tubes are focused, cylindrical in shape with caps at each end, such that a fullerene can be formed with the two caps. The cylindrical portions of the tubes consist of a single graphene sheet which is formed the cylinder. With the discovery of SWNTs [6, 7], it is possible to investigate the predictions of the theoretical calculations [5]. It is convenient to specify a general carbon nanotube in terms of the tube diameter d, and the chiral angle θ, which are shown in Figure 1(a). The chiral vector \( C_h \) is defined as

\[
C_h = n\vec{a}_1 + m\vec{a}_2 \equiv (n, m),
\]

which is often described by the pair of indices \((n, m)\) that denoted the number of unit vectors \( n\vec{a}_1 \) and \( m\vec{a}_2 \) in the hexagonal honeycomb lattice contained in the vector \( C_h \) [8]. The vector \( C_h \) connected two crystallographically equivalent sites O and A on a two dimensional graphene sheet where carbon atom is located at each vertex of the honeycomb structure [9]. The chiral
Figure 1. Honeycomb lattice of a nanotube. H. Dai, *Accounts of chemical research*, 2002 [10].

(a) The chiral vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ defined on the honeycomb lattice of carbon atoms by unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ and the chiral angle $\theta$ with respect to the zigzag axis. Along the zigzag axis $\theta = 0^\circ$. Also shown are the lattice vector $\mathbf{T}$ of the 1D nanotube unit cell. The rectangle $OABB$ defines the unit cell for the nanotube. (b) Possible vectors specified by the pairs of integers $(n, m)$ for general carbon nanotubes, including zigzag, armchair and chiral nanotubes. Below each pair of integers $(n, m)$ is listed the number of distinct caps that can be joined continuously to the carbon nanotube denoted by $(n, m)$ [10]. (c) $\theta = 30^\circ$ direction: an armchair $(n, n)$ nanotube. $\theta = 0^\circ$ direction: a zigzag $(n, 0)$ nanotube, a general $\theta$ direction with $0 < \theta < 30^\circ$: a chiral $(n, m)$ nanotube [11].
angle $\theta$ between the $C_h$ direction and the zigzag direction of the honeycomb lattice (n,0) is related to the integers (n, m). We can specify a single walled C$_{60}$-derived carbon nanotube by bisecting a C$_{60}$ molecule at the equator and joining the two resulting hemispheres with a cylindrical tube having the same diameter as the C$_{60}$ molecule, and consisting of the honeycomb structure of a single layer of graphite (a graphene layer).

Figure 1(b) shows the number of distinct caps that can be formed theoretically from pentagons and hexagons, such that each cap fits continuously on to the cylinders of the tube, specified by a given (n, m) pair. Figure 1(b) also shows that the hemispheres of C$_{60}$ are the smallest caps satisfying these requirements, so that the diameter of the smallest carbon nanotube is expected to be 7 Å, in good agreement with experiment [6, 7]. It also shows that the number of possible caps increases rapidly with increasing tube diameter.

If the C$_{60}$ molecule is bisected normal to a five-fold axis, the “armchair” tube shown in Figure 1(c) is formed, and if the C$_{60}$ molecule is bisected normal to a 3-fold axis, the “zigzag” tube in Figure 1(c) is formed [9]. Armchair and zigzag CNTs of larger diameter, and having correspondingly larger caps, can likewise be defined, and these nanotubes have the general appearance of “armchair” and “zigzag” shown in Figs. 1(c). In addition, a large number of chiral carbon nanotubes can be formed for $0 < |\theta| < 30^\circ$, with a screw axis along the axis of the tube, and with a variety of hemispherical caps. A representative chiral nanotube is shown in Figure 1(c). The unit cell of the carbon nanotube is shown in Figure 1(a) as the rectangle bounded by the vectors $C_h$ and $T$, where $T$ is the 1D translation vector of the nanotube. The vector $T$ is normal to $C_h$ and extends from the origin to the first lattice point $B$ in the honeycomb lattice.

The unique electronic properties of SWNTs are caused by the quantum confinement of electrons normal to the nanotube axis. In the radial direction, electrons are confined by the
monolayer thickness of the graphene sheet. Consequently, electrons can propagate only along the nanotube axis, and so to their wave vector points. It is extraordinary that SWNTs can be either metallic or semiconducting depending on the choice of \((m, n)\), although there is no difference in the chemical bonding between the carbon atoms within the nanotube and no doping or impurities are present.

1.2 Electrical Properties of Single Walled Carbon Nanotubes

Each carbon atom in the hexagonal lattice possesses six electrons and carbon has two \(1s\) electrons, three \(2sp^2\) electrons and one \(2p\) electron in the graphite structure. The three \(2sp^2\) electrons form the three bonds in the plane of the graphene sheet, leaving an unsaturated \(\pi\) orbital [3]. This \(\pi\) orbital, which is perpendicular to the graphene sheet and the nanotube surface, forms a delocalized \(\pi\) network across the nanotube, which is responsible for its electronic properties. To obtain the electronic structure of CNTs, we start from the bandstructure of graphene and quantize the wavevector in the circumferential direction,

\[
k \cdot C = k_x C_x + k_y C_y = 2\pi p,
\]

where \(C\) is shown in Figure 1(a) and \(p\) is an integer [12]. This equation provides a relation between \(k_x\) and \(k_y\) defining lines in the \((k_x, k_y)\) plane. Each line gives a one-dimensional energy band by slicing the two-dimensional bandstructure of graphene shown in Figure 2. The particular values of \(C_x, C_y\) and \(p\) determine where the lines intersect the graphene bandstructure, and thus each CNT will have a different electronic structure. Perhaps the most important aspect of this construction is that CNTs can be metallic or semiconducting, depending on whether or not the lines pass through the graphene Fermi points. This concept is illustrated in Figure 3.
Although graphene is a zero-gap semiconductor, SWNTs can have the electrical properties of metals or semiconductors with different sized energy gaps, depending on their diameter and chirality. The salient electronic properties of nanotubes may be understood in terms of a simple tight-binding model [13]. For instance, consider an infinite graphene sheet. Carbon nanotubes are formed when the graphene sheet is rolled up into a cylinder in such a way that the carbon atoms connect seamlessly with each other. This implies that carbon atoms whose relative position vector is Equation (1.1) must overlap, which in turn gives the condition $k.C = q2\pi$, where $q$ is an integer. This relation defines a set of parallel lines with a relative separation $C/2\pi$. Schematically, these lines are represented for three types of nanotubes with helicity indices $(n,m)$ (Figure 3). The $K$ point ($k_K = (a - b)/3$) is the point where the $\pi$ and $\pi^*$ bands of a graphene sheet meet, defining the Fermi energy. Depending on whether a line intercepts or misses the $K$ point, the

The lines $\mathbf{k} \cdot \mathbf{C} = q2\pi$ are drawn for (a) an armchair (3,3), (b) a zigzag (3,0), and (c) a chiral (4,2) nanotube. The $K$ point of the Brillouin zone is the crossing point of the $\pi$ and $\pi^*$ bands. The nanotube will be metallic only if one of the lines intercepts this point. From the drawing, this condition will only be met for certain orientations and spacing ($\sim R^{-\frac{1}{2}}$) of the set of lines. J.

The resulting nanotube will be either metallic or semiconducting. Thus tubes for which $(m - n)$ is divisible by three will have a finite density of states at the Fermi level and will therefore be metallic. In particular, all armchair $n = m$ nanotubes are metallic, whereas only third of the $m = 0$ zigzag nanotubes have metallic characteristics.

Although this model is relatively simple, it works remarkably well. There are, however, limitations that result from a possible mixing between the in-plane $\sigma$ and out-of-plane $\pi$ orbitals. These orbitals are, of course, orthogonal for a simple graphene sheet but may be somewhat mixed for highly curved systems. As a general rule, this mixing can be neglected for nanotubes with radii greater than 10 Å. For nanotubes with radii in the range of 2.5 to 10 Å, a small band gap decreasing with the second power of the radius appears in all but the armchair nanotubes.
For nanotubes with even smaller radii—some of which have been synthesized recently—the simple model presented here is no longer valid, and more fundamental, first-principles calculations are needed to adequately describe the electronic properties of these very-small-diameter nanotube systems [15]. Furthermore, single walled nanotubes usually self-assemble in bundles called ropes owing to van der Waals attraction. The intertube interactions introduce small pseudogaps in ropes of nominally metallic tubes [16, 17].

### 1.3 Optical Properties of Single Walled Carbon Nanotubes

The optoelectronic properties of carbon nanotubes have gained much attention recently, stimulated by their unique electronic structure [18-25]. Reports have revealed intriguing behavior for nanotubes, which show a strong interaction between electrical transport and optical fields. Typical examples include the use of aligned nanotube arrays as microwave amplifiers and radio antennas [24, 25]. The nanotubes, when receiving the incident electromagnetic waves, generate enhanced electrical signal due to their small dimension and sharp tips. The optical absorption and emission from SWNTs cover a spectrum from the visible to the infrared range, which is important for making optoelectronic devices [21-23]. Recently, the photoconductivity of nanotubes has been studied theoretically in a nanotube p–n junction [20], a single SWNT transistor [19], and thin SWNT films [18]. The photocurrent has a resonance-to-photon energy in the range of 0.7 to 1.5 eV with peak positions corresponding to the bandgap of semiconducting SWNTs, promising that nanotubes can act as photosensitive materials [26].

Photo-absorption in SWNTs is directly related to their unique electronic density of states (DoS) which is characterized by a number of van Hove singularities which are symmetrically
Figure 4. DoS and optical excitations of SWNT. H. Kataura et al, Synthetic Metals, 1999.

(a-b) DoS and possible optical excitations in (a) a (8,8) metallic and (b) a (9,7) semiconducting SWNT, both of which have a diameter of about 1.1 nm. (c) Variation of excitation energies with diameter in the SWNT family.

distributed about its Fermi level [27]. As a result, photo-induced excitations in SWNTs occur not only at the band-gap, but also between energy levels corresponding to electron-hole pair (Exciton) formations between its mirror-symmetric van Hove singularities. Figure 4(a) and 4(b) shows the 1D DoS and its corresponding possible optical excitations in a metallic and a semiconducting SWNT [28]. Depending on the chirality (m,n) and diameter, SWNTs can have a whole range of possible optical excitations, as seen in figure 4(c). As an optical material, carbon nanotubes are extremely unique, since nanotubes within a short diameter range can have vastly varying possible optical excitations. In a bundle, rope, films or ribbon configurations, SWNTs hence form a very unique nanoscale semiconductor material with a large number of Excitonic energy levels.
1.4 Fabrication of Highly Organized SWNT Networks

The most essential prerequisite for realizing SWNT based electronic devices is to have an ability to place SWNTs at desired locations, in predetermined orientations and to form stable interconnections at a large scale. A few approaches have been reported the assembly of SWNTs using chemical vapor deposition (CVD) [29, 30], chemical functionalization, electrophoretic deposition (EPD), or dielectrophoresis (DEP) [31, 32]. CVD is an effective method to directly synthesize CNTs at the desired locations on a substrate by patterning catalyst materials. But its high temperature process (500-900°C) and difficulty in controlling the growth direction and the density of CNTs significantly limits its effectiveness, especially for electronic device applications. EPD has an advantage of fabricating highly oriented nanotubes between electrodes, but it is effective only within local areas where the electric-field is at maximum. We have demonstrated recently the liquid-phase fabrication of highly organized SWNT lateral network architectures [33]. In this method using a lithographically patterned template assisted dip-coating, SWNTs were directly assembled on a hydrophilic surface, between pre-designed photoresist channels, forming organized SWNT lateral networks in diverse geometries with feature sizes ranging from 100 nm to 10 µm.

Figure 5 shows detailed characteristics of SWNT assembly in liquid phase template assisted process. Figure 5a schematically explains the basic steps of building organized SWNT lateral architectures. First, a plasma treatment is used to enhance the hydrophilic nature of the SiO₂ surface. Second, a e-beam resist film on SiO₂ substrate are constructed using electron-beam lithography (EBL) to build micro/nano-scale channels which form templates for building the SWNT architectures. Next, these templated substrates are dip-coated in a SWNT-deionized
Figure 5. Template assisted fluidic assembly of SWNTs. X. Xiong, et al., Small, 2007 [33].

(a) Schematic showing template-based fluidic assembly of high density and highly organized SWNT architecture. (b) Microscale assembly by vertically dip-coating the PMMA template in SWNT suspension only once. (c) Schematic illustration of SWNT migration and assembly in trenches by capillary induced flow, where the left vertical arrow denotes the template pulling direction and the two right ones represent the sweeping direction of the liquid-solid contact line in PMMA trenches. (d) Complete SWNT assembly on silicon substrate showing both ends of PMMA trenches covered with nanotubes by performing dip-coating process twice, with a 180 degree rotation of the template for the second time pulling. (e) SWNTs assembled in microscale and (f) well aligned nanoscale SWNTs inside PMMA trenches on silicon oxide substrate. (g) Parallel arrays of aligned nanoscale SWNTs on silicon oxide substrate after removing PMMA template.
(DI) water solution at a constant pulling rate of 0.1 mm·min⁻¹, which in stable and densely aligned SWNT lateral network architectures having well-defined shapes at micro/nano-scale and were defined by the geometry of e-beam resist patterns on the substrate. We used 0.23 wt % SWNT-DI water solution (obtained from Brewer Science Inc.) with the mean length of 610 nm and mean diameter of 1.1 nm. Finally, the photoresist is removed to obtain well organized and aligned SWNTs lateral networks. We observed that in a single dip-coating process, SWNT coverage along the parallel PMMA trench arrays is not complete (leaving the bottom end of trenches open without assembly of SWNTs as shown in Figure 5b. As shown in Figure 5c, SWNT solution will preferentially attach to pre-defined channels with hydrophilic properties while the hydrophobic areas have little or no affinity to the solution or SWNTs. As a result, the previously described migration process will only be confined within the trenches. In order to achieve full assembly, a second dip-coating process can be employed with switching the template orientation by 180°, making the prior bottom part of trenches as a top one, and vice versa. Figure 5d shows the complete coverage of SWNTs in both ends of PMMA patterned trenches on silicon surface after employing a second dip-coating process by rotating the trench template 180°. Such a process is proposed to yield a uniform coverage of SWNTs along the trenches because the uncovered areas will be attached with SWNTs, while the trench areas that are covered with SWNTs may have less affinity to new nanotubes during the second dip-coating process. The effect of the trench widths on the SWNT alignment is investigated using trenches from a few micrometers to hundred nanometers wide. Compared with microscale assembled SWNTs in Figure 5e, Figure 5(f and g) show well aligned SWNTs inside PMMA trenches of a few hundred nanometers wide. From scanning electron microscope (SEM) observation, we find
that the degree of SWNT alignment dramatically increases as the size of trenches decreases, especially in submicron scale.

1.5 Assembly Mechanism of Highly Organized SWNT Networks

This section describes the assembly mechanism of organized SWNT networks developed in our lab [34]. The fluidic assembly of SWNTs can be improved when the substrates are pre-treated with plasma and followed by deionized water flush resulting in enhanced hydrophilic behavior. The level of control provided by this method enable us to construct complex SWNT architectures, which could fulfill their potential electronic applications. To understand a mechanism for SWNT assembly and their control, the first step towards selective assembly of SWNTs is to produce appropriate sites on the substrate that can attract the SWNT solution selectively. Since we used a SWNT-DI water aqueous solution, one of the main issues was the wetting ability of this solution for our particular substrate. The initial contact angle measurement of SWNT-DI water solution on the untreated silicon and silicon dioxide surfaces were 36° and 30° respectively [33]. Our experiment result showed that plasma treatment of the substrate in a mixed gas flow of O₂ (20 sccm), SF₆ (20 sccm) and Ar (5 sccm) can improve interaction between the substrate and the SWNT-DI water solution drastically. Figure 6 shows the results of the contact angle (Θ) measurement right after dropping the SWNT-DI water solution on silicon substrates treated with plasma for times (5, 30, 60, and 90 sec). The lowest contact angle (the best hydrophilic behavior) of SWNT solution was obtained with 5 sec plasma etched silicon substrate (0°) and the contact angle increased as the plasma etching time increased. However, given enough time, the contact angle between all silicon substrates and SWNT solution
Figure 6. Contact angle measurements. L. Jaber-Ansari, et al, *JACS*, 2008 [34].

Contact angle (θ) measurement of Si substrate after 5, 30, 60, and 90 seconds of SF₆/O₂/Ar plasma treatment. Contact angle change vs. time on the same substrates.

gradually changed to 0°. It also shows the change of the contact angle with the time after depositing a droplet of the SWNT solution on these substrates. The result indicates that the 5 sec plasma etched sample changes instantly to a completely hydrophilic surface while it takes more time to produce hydrophilic groups for the longer plasma etched silicon substrates. SEM
Figure 7. Effect of plasma treatment on the surface morphology of Si. L. Jaber-Ansari, et al, *JACS*, 2008 [34].

(a) AFM image of a 1 µm× 1 µm area of bare Si, (b1) AFM image of a 1 µm× 1 µm area of 5 s plasma treated Si, (b2) SEM image of 5 s plasma treated Si, (c1) AFM image of a 1 µm× 1 µm area of 90 s plasma treated Si and (c2) SEM image of 5 s plasma treated Si.

and atomic force microscopy (AFM) results for the 5 and 90 sec plasma treated Si surfaces are shown in Figure 7. The 5 sec plasma etched sample (Figure 7b1) shows nano-structures on the surface of silicon were 50 nm wide and 5 nm high, but the 90 s plasma etched sample (Figure 7c1) shows surface structures around 400 nm wide with a height variation of about 5 nm over that area whereas in bare silicon the surface protuberances are only 100- 200 Å deep. These surface structures can be seen as the grain shaped domains in the SEM images (Figure 7(b2 and c2)). These results show an enormous increase in roughness after 5 sec plasma etching treatment.
(Figure 7(b1 and b2)) and then a diminishing of the surface roughness with further etching of the substrate (Figure 7(c1 and c2)). Although the AFM results show an increase in the physical activity of the plasma treated substrates, such as enhanced roughness, the nature of the chemical functional groups that are produced as the result of plasma treatment remains unclear. This shows that a lot of dangling bonds exist on the surface of this substrate along with hydrophilic OH\(^-\) groups and hence the reason to hydrophilicity of such substrate. Therefore, the highly increased surface area of the 5 sec plasma treated silicon along with the large number of hydrophilic groups leads to the immediate change of surface to hydrophilic during contact angle measurement (Figure 6); in 90 sec plasma treated sample, however, it takes longer for the surface to become hydrophilic due to lower concentration of OH\(^-\) groups and smaller surface area [34].

1.6 Topological Transitions in CNT Networks via Nanoscale Confinement

This section describes the topological transitions in organized SWNT networks modeled by Upmanyu et al. [35]. Precise control over the electron transport in SWNT networks is challenging due to (i) an often uncontrollable interplay between network coverage and its detailed topology and (ii) the inherent electrical heterogeneity of the constituent SWNTs. In this reason, we explored the effect of nanoscale confinement on carbon nanotube networks (CNNs) deposited on patterned channels with varying width. While the resistivity strongly suggests a metallic-to-semiconductor transition with decreasing width (see Figure 10d before Pt decoration), direct confirmation requires detailed field characterization. To bypass the current experimental limitations and to capture the effect of these network features in detail, we turn to systematic model computations of nanotube assembly on experiment-scale channels. SWNTs coarse-grained as rigid rods are employed to
gain sufficient statistics on the interplay between topology and the nature of electrical percolation within the network; the effect of channel width $W_c$ is explored using 2D computations, while multilayer, quasi-2D computations are used to study the effect of channel thickness.

The random stick model that has been employed in earlier studies [36] is clearly inadequate in capturing key phenomena such as SWNT bundling during self-assembly. In order to generate realistic topologies, we further relax the network by allowing the coarse-grained SWNTs to interact. The inter-CNT interactions, localized at the junctions, are obtained by integrating the well-known Lennard-Jones (LJ) based description of the van der Waals between graphene surface elements. As an example, for fully aligned SWNTs, the axially averaged inter-CNT interaction energy per length $U(R, r)$ is again a 6 - 12 LJ-type potential with constants that are scaled by surface integrals which depend entirely on the ratio of the intertube distance to the CNT radius $R/r$ [37, 38]. Note that this intertube interaction is shortranged and negligible for $R \geq \sqrt{3}r$; that is, it is limited to first nearest neighbors. For partially aligned CNTs, the van der Waals potential can again be integrated over the surfaces of the (pair) of CNTs. The resultant effective inter-CNT interactions are angular as they now depend on the degree of misalignment at the CNT - CNT junction $\varphi$, $U \equiv U(R, r, \varphi)$. In the case of fully aligned bundles, this intertube potential accurately describes equilibrium intertube spacing, cohesive energy per atom, and bulk modulus. The interactions serve as inputs for classical dynamical simulations aimed at locally relaxing the random network with respect to both translational and angular degrees of freedom of the individual SWNTs. Sliding between the CNTs at the junctions is ignored. A time step of 1 $\mu$s is employed, and the simulations are performed until the interaction energy associated with the network stabilizes.
Figure 8a shows specific instances of the electrically heterogeneous network topologies obtained in three simulations with varying widths, $W_c = 1 \, \mu \text{m}$, $500 \, \text{nm}$, and $100 \, \text{nm}$. In each case, the SWNT network is confined, $l/W_c > 1$, which forces the topology to become increasingly aligned with decreasing width. While the as-generated random topologies are geometrically aligned along the channel, we find that the SWNT interactions always work toward increasing the degree of alignment. This is not surprising as the orientation dependence of the interaction potential favors a nematic-like phase consisting of fully aligned nanotubes [39]. For each relaxed CNN with a prescribed network density, the electrical transport characteristics are extracted by fixing the overall ratio of semiconducting-to-metallic SWNTs to the theoretical heterogeneous density. To this end, each SWNT is randomly assigned a metallic or semiconducting character and the overall percolation across the CNN is measured. The overall percolation can result in (i) open circuit (OC), (ii) semiconducting, or (iii) metallic conductance across the network. Multiple simulations ($\sim 100$) are performed for each channel geometry and density to determine the form of percolation.

Figure 8(b – d) shows the percolation probability through monolayered CNNs as a function of the network density for the three widths shown in Figure 8a. All CNNs exhibit two transitions as the network density is increased: OC-to-semiconducting at low densities, and a semiconducting-to-metallic at high densities. Qualitatively similar transitions are also observed for unrelaxed networks that are used as input in random stick models (shown as dotted lines), and comparisons with percolation in relaxed structures indicate that the enhanced alignment driven by the SWNT interactions shifts the transitions to higher network densities. The effect is dramatic at
Figure 8. Probabilities of CNNs and their contour plots. Upmanyu, et al., ACS nano, 2010 [35].

(a) CNNs observed in three different 2D simulations with varying channel widths, $W = 1 \mu m$, 500 nm, and 100 nm. In each case, 5 $\mu m$ length of the 20 $\mu m$ long channel is shown. For clarity, detailed view of a 1 $\mu m$ long segment of the $W = 100$ nm channel is also shown. Coloring scheme is based on nature of electrical transport; blue and red indicate metallic and semiconducting nanotubes, respectively. The relative number of metallic and semiconducting nanotubes is fixed at the theoretical ratio, 1:3. (b - d) Plots of the probability of the nature of electrical percolation through the network as a function of network density, $\rho_{NT}$. The solid black, red, and blue curves are probability of open circuit, semiconducting, and metallic conductance across the network, respectively. 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 width ($y$-axis) and density ($x$-axis). The length of the channel is fixed at $L = 20 \mu m$. (f) Same as in (e) but for multilayer, quasi-2D simulations with varying channel thicknesses, $t = 1 - 5$ monolayers. The length and width of the channels are fixed, $L = 5 \mu m$, $W = 200$ nm.
decreasing widths, underscoring the importance of intertube interactions in developing a quantitative understanding of electrical transport across CNNs. The effect of decreasing width is similar as it also enhances the alignment along the channel for a given network density, the networks show a marked reduction in metallic transport as the alignment effectively shields the active components. This interplay between channel width and network density is more clearly seen in Figure 8e, a contour plot of the probability of semiconducting percolation across the channel as a function of these two variables. The network density ranges for semiconduction increases substantially as the width is decreased below $W_c \sim 300$ nm. Note that the probability of an open circuit also increases with decreasing width, but the extent of this effect is smaller than the enhancement in semiconduction.

The thickness of the CNNs permits control over out-of-plane confinement of the SWNTs, and we explore this effect by performing percolation studies on relaxed multilayered networks with fixed width and length. For computational efficiency, we have chosen networks with smaller lengths ($L_c = 5$ µm) and channel width ($W_c = 200$ nm). Note that the network is already confined at this width. Figure 8f shows the contour plot associated with probability of semiconduction along the channel as a function of number of monolayers (ML), $t = 1 - 5$ ML. Our results show that thin CNNs have a higher probability for semiconduction, and the probability decreases (at the expense of metallic behavior) rapidly within the first few monolayers. While we have not studied thicknesses greater than $t = 5$ ML, the contour plot shows that the marginal decrease should be much smaller.
Chapter 2: Metallization of SWNT Network for Interconnect Applications

2.1 Introduction

As elements of integrated circuits downsize towards a few nanometers, existing interconnect technology faces a tremendous bottleneck due to the electromigration failure of Cu lines [40, 41]. In addition, as the lateral dimension of interconnects approaches the mean free path of Cu (~40 nm at room temperature), the impact of grain boundary scattering, surface scattering, and the presence of a high-resistivity material as a diffusive barrier layer causes a rapid increase in their overall resistivity. In this context, CNTs have been envisioned as a possible replacement for Cu electrical interconnects for future gigascale integration considering their immense individual failure current densities (> 10^9 A·cm^2) [42, 43]. Especially at the nanoscale, highly aligned parallel nanotube architectures comprising of all-metallic SWNTs are expected to outperform Cu in terms of failure current density, power dissipation, and on-chip signal transfer delays [44, 45]. However, to fabricate such highly aligned SWNT-based interconnects in an integrated device, a complementary metal-oxide-semiconductor (CMOS)-friendly scalable manufacturing process that can controllably place aligned SWNTs in desired locations, orientations, and dimensions is extremely crucial. In addition, since naturally grown SWNTs comprise of a mixture of metallic and semiconducting nanotubes, there is an imminent need to develop a process that will convert semiconducting nanotubes into metallic ones within such architectures. Therefore, a single-step, simple, and CMOS compatible method that can simultaneously convert semiconducting SWNTs into metallic ones, and also possibly increase the conductance of existing metallic SWNTs, is
highly desirable. Addressing these technological challenges is essential before carbon nanotubes can be realistically implemented as future interconnects.

Recently, we have demonstrated a novel template-based fluidic assembly process for fabricating highly organized SWNT lateral network architectures at wafer scales [33, 34]. We have also shown that the conductance of individual MWNTs can be improved significantly by decorating its surface with Pt nanoclusters [46]. Field theoretical analysis confirm that this is caused by the increase in the number of conductance channels of the nanotubes. *Ab-initio* density functional theory (DFT) calculations indicate that charge transfer from decorated Pt nanoclusters on nanotubes can increase the number of bands near the Fermi level of the nanotubes, and increase their density of states (DoS). DFT calculations also show that Pt-nanoclusters can convert semiconducting SWNTs into metallic ones, and improve the conductance of metallic nanotubes as well.

In this chapter, we combine these ideas to develop highly organized aligned arrays/channels of Pt-decorated SWNT interconnect test structures, with vastly improved performance over pristine SWNT architectures. In general, we find that the nanotube alignment improves noticeably with decreasing lateral channel widths, with the best alignment obtained for widths close to 200 nm. Significantly robust against the lithographic and electrodeposition steps, these interconnect test structures were capable of withstanding current densities up to $\sim 10^7$ A·cm$^{-2}$. Upon Pt decoration, the average electrical resistivity of these SWNT interconnect test structures decreased by 45%, with a 52% drop for the narrowest channels. In more than 25% of the tested structures, the resistance of the Pt-decorated structures fell to 1/3$^{rd}$ of its pristine value, indicating that most of the semiconducting nanotubes between the Ti/Au-contacted SWNT arrays have converted to metallic ones. In a few cases, this value fell below 1/3$^{rd}$, indicating that the
conductance of the metallic nanotubes have gone up as well. These completely CMOS-compatible and scalable process steps together reflect a huge step towards integration of carbon nanotubes into existing interconnect technologies.

2.2 Fabrication of Highly Aligned SWNT Lateral Architectures

Figure 9 shows representative scanning electron microscopy (SEM) images of our aligned SWNT lateral architectures fabricated on SiO$_2$/Si substrates using our template guided fluidic assembly process. Figure 9a schematically explains the basic steps of building organized SWNT lateral architectures described in chapter 1.4. Figure 9b is an SEM image of a typical SWNT lateral structure attached on top with two contact pads of Ti/Au, fabricated using a standard EBL process. Figures 9c – 9e are higher magnification SEM images showing the relative alignments of lateral SWNTs along the channels with approximate widths of 1000 nm, 500 nm, and 200 nm respectively. An important outcome of our SWNT assembly technique is that the degree of alignment of SWNT structures tends to increase with lower channel widths.

2.3 Detailed Study of the Alignment of SWNT Architectures

Polarized Raman spectroscopy has been used in the past to study the symmetry of the vibrational modes of carbon nanotubes [47]. Using this technique, past workers have reported study of SWNT alignment in fibers [48]. In particular, the tangential modes give rise to a number of Raman active peaks at positions between 1550 cm$^{-1}$ – 1610 cm$^{-1}$. By changing the
Figure 9. Schematic and SEM images showing super-aligned SWNT interconnect structures.

a) Schematic showing template-based fluidic assembly of high density and highly aligned SWNT architectures. b) SEM image of typical SWNT lateral structures with two-probe contact pads. Scale bar = 2 μm. c) – e) High magnification SEM images showing the degree of alignment of the SWNTs within channel widths of ~1000 nm, ~500 nm, and ~200 nm respectively. Scale bars = 200 nm.

polarization of the Raman Laser with respect to the alignment direction of our arrays, and noting the relative intensities of the largest tangential peak (with respect to the intensity of the same peak in an unpolarized Raman spectrum), it is possible to quantify the degree of alignment of our SWNT arrays.
Figure 10. Polarized Raman spectra from SWNT arrays.

a) Tangential modes of 1000 nm width SWNTs channel. b) Tangential modes of 500 nm width SWNTs channel. c) Tangential modes of 200 nm width SWNTs channel. As channel width decrease from 1000 nm to 200 nm, the intensities of parallel-polarized tangential modes decrease and that of the perpendicularly polarized tangential modes increase. d) Degree of alignment of the SWNT arrays of different channel widths, relative to the degree of alignment of the 200 nm SWNT array.

Highly organized and aligned SWNTs arrays in the nano structures were confirmed by polarized Raman spectroscopy. Figure 10a, 10b and 10c shows the tangential modes of aligned SWNT recorded using a micro Raman spectrometer with excitation wavelength of 785 nm. Each spectrum represents 60 accumulations each having an exposure time of 2s/spectrum. A 600 gr/mm grating was used, and the confocal hole diameter was set to 200 μm. In the polarized Raman experiments, half-wave plates were inserted allowing the rotation of the incident and scattered polarizations. The tangential modes of highly organized aligned SWNTs arrays were recorded using the VV configuration (same polarization for the incident and scattered light) [47, 48]. The parallel polarized intensities of the SWNTs arrays tangential mode (90° - shown with a
blue line) decreased as the SWNTs channel width decreases from 1000 nm to 200 nm (10a to 10c). On the other hand, it is clearly seen that, as the size of SWNTs array decreases from 1000 nm to 200 nm (10a to 10c), the perpendicular polarized intensities of tangential mode (0°, red line) increase. Figure 10d shows the relative degree of alignment of aligned SWNTs arrays (1000 nm, 500 nm and 200 nm), the degree of alignment calculated by ratio of the relative polarized Raman intensities of SWNT arrays (at 1583 cm$^{-1}$) with respect to that of the 200 nm SWNTs array since G band intensity is closely related with the population of graphitic structure. We find that the degree of alignment increase as the array width decrease from 1000 nm to 200 nm. We believe that the increasing alignment occur during the dip-coating process due to the increasing confinement of the PMMA trench geometry with decreasing channel widths.

2.4 Electrical Properties of SWNT Architectures before Metallization

Two-terminal current-voltage ($I$-$V$) characteristic and resistance $R$ (from the slope of the $I$-$V$ near $V=0$) was measured in all the test structures before decoration with Pt-nanoclusters. A number of test structures (having 25 μm length between two contact pads) of representative channel widths (700 nm, 500 nm and 200 nm) were characterized this way. Figure 11a-c shows the resistance histograms of the test structures of different channel widths. The resistances of the channels were mainly distributed around 4 kΩ, 5 kΩ, and 60 kΩ for channel widths of 700 nm, 500 nm, and 200 nm respectively indicating that as the channel width narrows, its resistance increases. We observed that test structures with width ~200 nm have much higher resistance values compared to the wider channels. Average resistivities calculated for each channel width
Figure 11. Electrical characterization of aligned SWNT interconnect structures.

a) – c) Resistance histograms of pristine devices. The values were distributed mainly around 4 kΩ, 5 kΩ, and 60 kΩ for channel widths of 700 nm, 500 nm, and 200 nm respectively. d) Current-voltage (I-V) curves between different contact pads A, B, and C separated by a distance of 10 μm between them (as shown in the inset schematic) for calculation of contact resistances (see text).

(see figure 14d) show an increasing trend when the channel width is decreased indicating increasing semiconducting behavior as the channel width narrows down. Similar observations have been experimentally reported for random SWNT mats with decreasing height [49]. Since we do not yet have a clear understanding of the self alignment mechanism of SWNTs during the assembly process, especially the degree of alignment with different channel widths, at this stage we cannot explain this related electronic property change. However, based on previous studies of percolation theory of SWNT networks [50, 51], we feel that the alignment of SWNTs in
narrower channels statistically reduces the formation of metallic conduction paths between the two contacts, resulting in a dominant semiconducting property of the arrays.

To estimate the contact resistance for a given test structure, three contact pads (A, B, and C) separated by a distance of 10 μm were fabricated for each representative channel width. \( I-V \) measurements were performed between pairs of contact pads A–B, B–C, and A–C as shown in Figure 11d. The inset shows a schematic of these three contact pads on the test structures. The measured resistance (from the slope of the \( I-V \) curves) between the contact pads A and B can be written as \( R_{AB} = R_{CA} + R_{DAB} + R_{CB} \), where \( R_{CA} \) (or \( R_{CB} \)) = contact resistance at pad A (or B) and \( R_{DAB} \) = device resistance between pads A and B. In this way, the contact resistance at pad B, \( R_{CB} \) can be written in terms of \( R_{AB} \), \( R_{BC} \) and \( R_{CA} \) as:

\[
R_{CB} = \frac{R_{AB} + R_{BC} - R_{AC}}{2}
\] (2.1)

From three different test structures for each channel width, we found that the contact resistance was within 20% of the total resistances of the test-structure. These values did not change appreciably after the Pt-decoration experiments described later.

### 2.5 \textit{ab-initio} Density Functional Theory Calculations

Having characterized the pristine interconnect test structures, we now turn towards maximizing their electrical properties for interconnect applications. As-received SWNTs are a mixture containing approximately \( \frac{2}{3} \)\textsuperscript{rd} semiconducting and \( \frac{1}{3} \)\textsuperscript{rd} metallic carbon nanotubes. In aligned architectures such as ours, due to the high resistance of the semiconducting nanotubes
(almost 2-3 orders of magnitude larger than that of metallic nanotubes) [52], only 1/3rd of the nanotubes actively conduct current, and the rest remain dormant, vastly degrading the potential performance of the interconnect structure. Hence, it is essential to change the electrical property of semiconducting nanotubes into metallic ones for nanoscale interconnect applications. Moreover, we find that our narrower lateral SWNT architectures tend to have higher resistivity, presumably due to decreased number of metallic conduction paths within the nanotube arrays. Our past work has shown that Pt-decoration of carbon nanotubes can be an effective method for increasing the number of conduction channels near the Fermi level [46], which increases the conductance of multi-wall carbon nanotubes. Question arises if similar effects can be used to improve conductance of SWNTs as well. To elucidate the possible underlying effects of Pt-nanocluster decoration on the electronic band structure of metallic and semiconducting SWNTs, we first present *ab-initio* Density functional theory (DFT) calculations on these systems. The calculations are based on a super cell approach with periodic boundary conditions, where Pt-clusters lie at the center of each supercell. Detailed calculations were performed for two semiconducting SWNTs (with chiralities [8,0] and [10,0]) and one metallic ([9,0]) SWNT, for increasing number of Pt atoms (n = 0-13) per cluster. Our calculations show that the introduction of Pt-atoms gives rise to new electronic bands near the Fermi level of all the SWNTs that directly impacts the band gap, which defines the semiconducting or metallic nature of the nanotubes. Figure 12a shows the variation of band gap $\Delta E_G$ in the three SWNTs for different number of Pt-atoms, n, per cluster. We see that with increasing number of Pt atoms per cluster, the band gaps of the semiconducting nanotubes [8,0] and [10,0] rapidly approach $\Delta E_G \approx 0$ by n=3, and then remain close to zero for n>3. For the metallic nanotube [9,0], the gap remains very close to zero for almost all values of n. Further, the proximity of these additional bands to the
Figure 12. Calculations of the effect of Pt-decoration on electronic properties of SWNTs.

a) Band-gap closing in semiconducting [8,0] and [10,0] SWNTs due to Pt-nanocluster decoration. The gaps close within 3-Pt coverage and then remain close to zero. The metallic [9,0] nanotube remains metallic after 3-Pt coverage. b) Effect of Pt-decoration on the zero-bias Landauer conductance at T=300K in a semi-log plot. The conductance of the semiconducting nanotubes [8,0] and [10,0] increases by several orders of magnitude and approach $G=4e^2/h$ within 3-pt decoration, and fluctuate close to this value. The metallic [9,0] nanotube continues to remain metallic without any significant drop in conductance, and in some cases the conductance in both metallic and semiconducting nanotubes, $G$ exceeds $4e^2/h$. The insets represent the optimized structure of representative cluster sizes. The purple atoms are the last ones to be added.
Fermi level enhances their contribution to the total conductance compared to the pristine SWNTs. Figure 12b shows a semi-log plot of the zero-bias Landauer conductance [53, 54] as a function of number of Pt atoms per cluster for all three SWNTs, calculated at T=300K. It is seen that the semiconducting nanotubes undergoes 4-5 orders of magnitude increase in conductance within as low as n=3, approaching the value $G=4e^2/h$. For n>0, G remains orders of magnitude more conducting compared to the pristine systems, and significantly close to $4e^2/h$, which makes them metallic for all practical purposes. The metallic (9,0) nanotube continues to remain metallic. In all cases, the conductance of nanotube exceeded $4e^2/h$ for certain values of n. This indicates that uniform decoration of small (few nanometers) clusters of Pt can potentially convert semiconducting SWNTs into metallic ones, and further enhance the conductance of metallic nanotubes [55].

2.6 Pt Decoration of SWNT Architectures

Hence, we have adopted this procedure of Pt-nanocluster decoration to improve the overall conductivity of our SWNT interconnect arrays. Pt nanoclusters were electrochemically decorated on the SWNT arrays without disturbing their aligned architecture. Figure 13a is a schematic of the Pt decoration process on SWNTs. To decorate Pt nanoclusters on the surface of SWNTs, we immersed the assembled SWNT test structures in a 5 mM chloroplatinic acid solution. A negative potential ($-Ve$) of 50 mV was applied on a contact pad for 2 seconds using a Keithley 2400 sourcemeter, and the other probe was immersed in the same solution without touching any contact pads. When a negative potential is applied to the contact pad of the test structures, Pt ions having positive charges are nucleated selectively on the surface of the contact
Figure 13. Pt-decoration on SWNTs and its characterization.

a) Schematic representation of Pt-decoration of SWNT test structures in a dilute chloroplatinic acid solution. The application of a negative electric potential on one of the contact pads (directly contacted) induces (indirect) negative potentials on the neighboring devices due to the capacitive effect of the oxide-coated silicon wafer. b) Typical SEM image of Pt decoration on the surface of directly contacted SWNT bundles. Scale bar = 200 nm. c) SEM image (left) and its corresponding energy dispersive x-ray spectroscopy (EDS) map (right) of indirect Pt decoration with dashed lines indicating the position of the SWNT test structure. d) EDS spectrum from the same structure in 3c showing that Pt nanoclusters are decorated on the SWNT belt.
pads and the SWNT architectures. At the same time, induced negative potential is created on the neighboring test structures by a capacitive effect of the underlying highly doped Si substrate and its SiO$_2$ insulating layer. This resulted in decoration of smaller Pt nanoclusters (< 5 nm) on the surface of the other assembled SWNT arrays as well. We found that this “indirect” deposition was more effective as it gave clusters of extremely small size, and there were no damages to the arrays due to accidental static discharge when the probes are contacted to the pads. Figure 13b is an SEM image of SWNT arrays on which Pt nanoclusters, decorated directly, are clearly visible. Figure 13c shows an SEM image and energy dispersive x-ray spectroscopy (EDS) maps of an SWNT array indirectly decorated with Pt nanoclusters. In this case, the Pt-clusters were almost indistinguishable in the SEM images, but the EDS map for Pt shows very small amounts of Pt decoration, as confirmed by the EDS spectrum in figure 13d. The EDS map along with the spectral analysis is consistent with the fact that extremely small (~ a few nanometers) Pt nanoclusters are uniformly decorated over the surface of aligned SWNT network structures without forming a continuous Pt film. The small amount of Pt-nanoclusters in the surrounding region of the SWNT array was decorations on the SiO$_2$ surface and did not contribute to the conducting mechanism in any way. This was confirmed by physically breaking some of the test structures after which no current was detected between the contact pads when a voltage was applied.

2.7 Electrical Properties of Highly Aligned SWNT Structures after Pt Decoration

Figures 14a-c shows change in resistance before and after Pt-decoration for samples having widths approximately = 700 nm, 500 nm, and 200 nm (with five test structures for each width),
and a length of 25 μm between two contact pads. The measured resistance includes the contact resistance and the device resistance. Most test structures undergo a large reduction of resistance with Pt decoration, which is consistent with our theoretical results. In the case of a 700 nm channel width, the average total resistance of pristine test structures was about 4.6 kΩ which dropped to 3.1 kΩ after Pt-decoration reducing 33% of its resistance on an average. The drop in average resistance was found to be 64% and 49% in the case of a 500 nm and 200 nm channel widths, respectively. The resistivity of test structures with different channel widths (before and after Pt-decoration) is shown in figure 14d. To calculate the resistivity, the length and width (at 5 positions along the length) of the test structures were obtained from SEM images, and height was averaged from 15 points on the same structure using cross-sectional AFM height measurements. We found that as the channel widths of the SWNT arrays decrease, the values of resistivity increase, indicating a great dominance of semiconducting nanotubes in the narrower structures. The average decrease of resistivity after Pt-decoration is hence also different for different channel widths. In the case of a 200 nm channel width, resistivity is reduced by 52% changing from 7.385 mΩ·cm to 3.534 mΩ·cm. The drop in resistivity was found to be about 48% and 34% for 500 nm and 700 nm channel test structures, respectively, after the Pt-decoration. The obtained resistivities have higher values (~ one order of magnitude) compared to reports by other groups on individual SWNT ropes [56, 57]. This is a direct outcome of the fact that our “electrode on top of sample” configuration allowed the formation of contacts with only the outer nanotubes of the array. Since inter-nanotube conductance is extremely low, most of the currents flowed through only the “contacted” nanotubes, leaving a significant portion of nanotubes dormant in the conduction mechanism (see later), but became included when the nominal resistivity was calculated using the overall geometry of the arrays. At this point, it is not possible
Figure 14. Electrical properties of SWNT structures before and after Pt decoration.

a) – c) Resistance of pristine and Pt-decorated devices with 700 nm, 500 nm, and 200 nm channel widths. Most Pt-decorated structures exhibited dramatically reduced resistance compared to their pristine states. d) Resistivity of structures with different channel widths before and after Pt decoration. e) Failure current density with a guide curve for structures having various channel widths, showing that narrower devices have better current-handling capability.

to determine the exact number of “uncontacted” nanotubes. However, our future research will attempt to overcome this problem by fabricating arrays of extremely small heights (less than a few nanometers).

The larger percentage drop in resistivity for the narrower channels is consistent with the fact that before Pt-decoration, the overall fraction of semiconducting nanotubes between the two contacts was larger for narrower channels, which, when converted to metallic nanotubes, causes a higher percentage change. If every contacted semiconducting nanotube were to be completely
converted to metallic one \textit{in all the test structures}, the final resistivity would be independent of channel size. From figure 14d, (where average values for 5 test structures have been plotted for each channel width) we find that complete “metallization” of all nanotubes in all test structures were not achieved due to variations in experimental conditions, although the slower dependence of resistivity on channel-width, after Pt-decoration, compared to that of the pristine structures is a very encouraging result. We will discuss this metallization issue in greater detail later on.

Another important criterion for interconnect applications is the failure current density. Individual MWNT can withstand current densities of $\sim 10^9$ A·cm$^{-2}$ at 300°C for a short time [42]. Also, MWNT via structures were shown to operate at a current density of $2\times10^6$ A·cm$^{-2}$, comparable to Cu vias [58]. Individual SWNTs can withstand a current density $> 10^9$ A·cm$^{-2}$ [59]. However, it appears that such high current densities in highly organized and aligned lateral SWNT structures have not been reported so far. Failure current density was measured in our structures by increasing an applied voltage in steps of 3 V in a vacuum chamber. Figure 14e shows failure current density (the dashed line is a guide to the eye) for test structures with different channel widths. The averaged value of failure current density was $7.34\times10^6$ A·cm$^{-2}$, while the maximum failure current density was measured up to $9.62\times10^6$ A·cm$^{-2}$ obtained for the narrower channels. Although these values are lower than that of individual metallic CNTs, we note that even for these calculations, we have assumed that all the nanotubes participate in the conduction of charges, whereas in reality only a part that is electrically contacted conducts the charge carriers, hence lowering the calculated current density. In any case, the values are larger than that of MWNT via bundles, and increases for lower channel widths, easily comparable or better than that of Cu at these size-scales.
The apparent lack of any measurable accumulation of damage over time suggests that the strong, covalently bonded carbon atoms in individually wired CNTs may not be subject to electromigration, as further supported by the observed electromigration resistance of CNT–Cu composite interconnects [60, 61]. However, all of these studies were based on single CNT failures without any repeated experiments to confirm the results and gather statistics. Moreover, the long-term performance and reliability of CNT-based devices have been largely neglected, despite their likely exposure to significant current densities and high temperatures that may directly induce thermal failure [62], cause thermal–mechanical fatigue or stimulate de-adhesion and significant interdiffusion at critical interfaces between CNTs, metals, dielectrics and polymers [63, 64]. To test reliability of SWNT networks, super-aligned networks of SWNTs, such as the one shown in Figure 9e, were fabricated for this reliability test. All measurements were obtained by the use of pseudo four-terminal sensing in air at room temperature with a commercial power supply, where both the applied voltage source and current sensing tungsten probes were placed on the same Ti/Au electrode pairs. Thus, the measurement probe resistances were removed from the resistance measurement of the total system, but the contact resistance between the SWNTs and Ti/Au electrode was included. In this work, we report only total line resistance, which includes the resistances of the CNT–electrode interface, the individual SWNTs and the SWNT–SWNT junction resistances. Each networked SWNT line was subjected to a constant DC input voltage $V_{\text{input}}$, which was varied from line to line, while the current ($I_{\text{measure}}$) was collected as a function of time. The input voltage was always ramped from 0 to $V_{\text{input}}$ over the course of several minutes. The magnitude of $V_{\text{input}}$ was chosen differently for each line to explore the effect of the electrical stress magnitude. If the chosen values of $V_{\text{input}}$ were too small (typically <4 V), the lines would last several days with no signs of damage. The SWNT array
lines were placed on a heat-controlled chuck, and the resistance was found to decrease nonlinearly with an increase in temperature, as is typical of other SWNT networks [65, 66]. The current densities in the networked CNT lines were found to be between 0.93 and 9.7MA·cm\(^{-2}\), as calculated by dividing the maximum \(I_{\text{measure}}\) in each line by the cross-sectional area of a ‘typical’ line, assuming full packing density [67]. Actual current densities in individual SWNTs were probably higher, because it was likely that some of the SWNTs in the cross section did not conduct equally or at all, and the SWNT packing density must be <1.

### 2.8 Calculation of Resistance before and after Pt Decoration

If, as our DFT results indicate, the Pt-decoration indeed results in the enhanced metallic behavior of individual nanotubes, it is important to investigate the degree of metallization that the semiconducting nanotubes in the test structures undergo. As discussed earlier, the electrode-on-top configuration does not contact all the nanotubes electrically. Hence, from the resistivity values itself, it is not possible to comment on how many semiconducting nanotubes were converted to metallic ones. However, since the same number of nanotubes remain in contact with the leads before and after the Pt-decoration, we can use the known ratio of semiconducting to metallic nanotubes (2:1) for naturally grown SWNTs, to predict the overall change in resistance if all semiconducting tubes were converted to metallic ones. We assume that this ratio is extendable to the two kinds of nanotube paths (metallic or semiconducting paths) between the two contacts of our aligned array.
Let us assume that, in any test structure, the number of nanotubes is \( X \) and the number of nanotubes electrically contacted is \( N \), where \( N < X \) (e.g. \( N \) could be equal to 30\% of \( X \)). Out of these \( N \) nanotubes, \( N/3 \) are metallic and \( 2N/3 \) are semiconducting ones. In the simplest case, if we assume that the nanotubes are parallel resistors in the device, the total resistance of the pristine array of nanotubes is,

\[
\frac{1}{R_{\text{total}}} = \sum \frac{1}{R_m} + \sum \frac{1}{R_{sc}} \tag{2.2}
\]

where \( R_m \) is the resistance for a metallic SWNT and \( R_{sc} \) is resistance for a semiconducting SWNT.

To simplify calculations, let us assume that all metallic SWNTs have resistance of \( R_m \) and semiconducting SWNTs have resistance of \( R_{sc} \). Then, equation (2) can be written as

\[
\frac{1}{R_{\text{total}}} = \sum_{n=1}^{N/3} \frac{1}{R_m} + \sum_{n=1}^{2N/3} \frac{1}{R_{sc}} \tag{2.3}
\]

Typically, \( R_{sc} \gg R_m \) by about two to three orders of magnitude. In this case, the term \( \sum_{n=1}^{2N/3} \frac{1}{R_{sc}} \approx 0 \) compared to the term, \( \sum_{n=1}^{N/3} \frac{1}{R_m} \). Therefore, resistance of device before Pt decoration can be written as

\[
R_{\text{total}} = \frac{3R_m}{N} \tag{2.4}
\]

After Pt decoration, if all semiconducting SWNTs get converted to metallic ones, then their converted resistance is same as that of the metallic SWNTs (i.e. \( R_m \)). Therefore, the total resistance after Pt-decoration would be given by,
Figure 15. Comparison between predicted and experimentally measured resistance ratio of Pt-decorated and pristine test structures.

\[
\frac{1}{R'_{\text{total}}} = \sum_{n=1}^{N/3} \frac{1}{R_m} + \sum_{n=1}^{2N/3} \frac{1}{R_m} = \frac{N/3}{R_m} + \frac{2N/3}{R_m} = \frac{N}{R_m}. \tag{2.5}
\]

Hence, the resistance of device after Pt decoration can be written as:

\[
R'_{\text{total}} = \frac{R_m}{N}. \tag{2.6}
\]

Hence, the predicted ratio of resistance between the decorated and pristine test structures,

\[
\frac{R'_{\text{total}}}{R_{\text{total}}} = \frac{R_m/N}{3R_m/N} = \frac{1}{3}. \tag{2.7}
\]
which is independent of how many SWNTs are electrically contacted.

Figure 15 shows the comparison between the predicted value and experimental results for the ratio of resistance before and after Pt decoration for all test structures of different channel widths. The test structures have been plotted in increasing order of the ratio values for clarity. We find that more than 25% devices attained the predicted ratio of 0.33 (indicating conversion to “all-metallic” test-structures after Pt-decoration). In case of the other test structures, the process of Pt decoration may have been incomplete due to variabilities associated with our electrodeposition experiments in terms of time, concentration of electrolytes, electric fields, access to all nanotubes etc., and these issues will be addressed in future. In some cases, the ratio was below 0.33, indicating that some of the metallic nanotubes may have undergone conductance enhancement as well, as predicted by density functional theory calculations. Our future research will attempt to fabricate test structures of very low heights such that all the nanotubes can be electrically contacted. This will remove many of the discussed ambiguities that have evolved during this work.

2.9 Conclusions

In conclusion, using a template-guided fluidic assembly process, we have fabricated highly organized, scalable and aligned SWNT array interconnect test structures. The narrowest lateral widths of test structures presented here (~200 nm) are limited by our current lithographic facilities and in principle can be reduced further down to lower sizes. The structures become increasingly aligned with decreasing channel width. We have also demonstrated a Pt nanoclusters
decoration technique to enhance the overall conductive nature of these structures. Due to our top-contacted geometry that did not electrically contact all the nanotubes, accurate estimates of resistivity of the nanotube array was not possible. However, the Pt-decoration leads to significant reduction of the nominal channel resistivity, with evidence of complete conversion of the semiconducting nanotubes into metallic ones in some cases, in agreement with our calculations of band gap and Landauer conductances. These interconnect test structures are able to handle high current densities, approaching nominal values of \(~10^7\) A·cm\(^{-2}\) (comparable to or better than that of Cu). The processes involved in the fabrication and performance enhancement via Pt-decoration are simple to implement, are CMOS compatible, and easily scalable to wafer levels. The fabrication and performance enhancement of these interconnect test structures demonstrate a big step towards integration of carbon nanotubes into microelectronic platforms for future gigascale interconnects.
Chapter 3: Reducing Interfacial Contact Resistance of Organized SWNT Interconnect Structures

3.1 Introduction

The continuous downsizing of active elements such as memories, switches, and transistors in a bid to improve the overall microprocessor performance is beginning to pose severe constraints on the reliability of interconnects, which transfer signal and power to and between these active elements\(^\dagger\). In particular, issues related to electromigration failure and increasing resistivity due to surface and grain boundary scattering in conventional Cu interconnects of widths below its mean free path (~40 nm) lead to critical concerns regarding their increased power dissipation, signal transfer delays, and ultimate reliability. This has generated a strong motivation for seeking alternative materials for future interconnect technologies. In this context, densely aligned, horizontally organized SWNT networks are promising candidates for replacing Cu-based interconnects in future microprocessors\(^\dagger\).

Over the years, CNTs have gained prominence for their enormous potentials for nanoscale electronic [68, 69] and electromechanical devices [70-72] due to their one-dimensional nanostructure, high electron mobility [73], huge failure current density [42], (orders of magnitude higher than that of Cu), and outstanding mechanical stability. In our previous works [74-76] we had demonstrated a unique, CMOS-compatible method for assembling SWNTs in the form of horizontally organized networks with controllable geometries with widths down to 200 nm. These SWNT networks could handle nominal current densities in excess of \(10^7\) A/cm\(^2\). We also demonstrated a method for improving their conductance via a Pt-nanocluster decoration method.

These architectures are attractive for building horizontally organized SWNT interconnects. However, several issues need to be addressed before these can be realistically integrated into existing interconnect device platforms. Among these, one issue of key importance is that of contact resistance at SWNT – metal interfaces.

Due to its unique one-dimensional electronic structure, individual CNTs will always have a minimum quantum contact resistance at the metal-nanotube interface. This quantum contact resistance has been theoretically predicted and experimentally demonstrated [77] to be \( \frac{h}{4e^2} \approx 6.5 \text{ k\Omega} \) due to their four available conduction channels, where \( h \) is Planck’s constant and \( e \) is the charge of electron. In horizontally organized SWNTs, where thousands of nanotubes are expected to conduct in parallel, the effect of quantum contact resistance becomes negligible. However, in addition to this, interfacial contact resistance, which results from the formation of imperfect bonds between metals and SWNTs, or due to the presence of impurities, can additionally cause high contact resistance. For example, Yao et al. [78] reported a metallic SWNT with two-terminal resistances as high as 110 k\Omega at room temperature. In fact, developing metal-SWNT interfaces with low interfacial contact resistance is the one of key challenges in fabricating interconnect structures using CNTs.\(^\dagger\) Researchers have attempted various methods to reduce the contact resistance between CNTs and metals [79-81]. Bachtold et al. [82] showed the decrease of contact resistance of MWNTs deposited on Au contact pads by selectively exposing MWNTs to an electron beam. Dong et al. [83] studied local Joule heating processes that could reduce the contact resistance between individual CNTs and metallic electrical contacts. However, these methods are not easy to implement as a wafer-scale protocol for interfacial contact-resistance-free SWNT networks, which is required in order to implement them as future SWNT interconnects. In this chapter, we report the investigations of a number of extra cleaning steps

during the SWNT-metal interconnect fabrication process that renders lower contact resistances between SWNTs and metal contacts of Ti/Au. Under optimal conditions the average interfacial resistance at a metal-SWNT was found to be 15 Ω, which is less than 1 % of the SWNT network resistance. The significant decrease of contact resistance in our SWNT networks using wafer-scale implementable processes represent a big step towards utilizing SWNTs for future nanoscale electrical interconnects.

3.2 Fabrication of Organized SWNT Interconnect Structures

Highly organized SWNT networks were fabricated using a template-guided fluidic assembly method reported previously [75]. Briefly, this method uses lithographically fabricated linear poly methyl methacrylate (PMMA) patterns on a plasma-treated SiO$_2$/Si substrate as templates (see Figure 5a) that provide channels of well-defined widths described in chapter 1.4. Figure 16 shows scanning electron microscope (SEM) images of aligned SWNT networks with different widths. It is found that the alignment improves significantly with decrease in channel width [75, 80] – a fact that makes them extremely favorable for low dimensional interconnects (sub-100 nm). Figure 16d shows an interconnect test structure device with multiple contacts fabricated using an EBL. The dimension of interfacial area between metallic electrodes and a bundle of SWNTs is 1µm width and 2µm length with metal electrodes on the top of SWNT line structures.

3.3 Measurement of Contact Resistance
Figure 16. SEM images of a highly organized SWNT structure.

(a) SWNT test structure is fabricated on SiO$_2$/Si substrate having the dimension of 1 µm width and 50 µm long. (b) High magnification SEM image shows the highly organized and densely packed SWNTs. (c) Sub-100 nm interconnect structure. (d) Deposition of Ti (5 nm) and Au (150 nm) on the top surface of SWNTs to make the contact pads for electrical measurements, having the distance of 5 µm space between them.

To obtain a reasonable estimate on the contact resistance, three equally spaced identical electrodes, a Ti (5 nm)/Au (150 nm) bi-layer, were fabricated using a magnetron sputter-coater. Figure 17a schematically shows the cross-section of a SWNT network test structure with three
electrical contact pads (A, B, and C) for measuring contact resistance as well as overall resistance of SWNT network. Typical current-voltage (I-V) dependences for the contact resistance measurement are plotted in Figure 17b, showing a linear dependence of current with voltage. The estimation of interfacial contact resistance assumes that the two-terminal resistance (inverse slope, dV/dI) between any two electrodes (e.g. $R_{AB}$ between A and B) is the sum of the device resistance (i.e. quantum contact resistance + resistance due to scattering within the nanotubes) of the SWNT networks and the interfacial contact resistance at each contact. From the two-terminal I-V characteristics, the resistance $R$ was measured in all test structures which have a width of 1 µm. The three contact pads were separated by the distance of 5 µm from each other. I-V measurements were conducted between the pairs of A – C, A – B, and B – 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

$$R_{B}^c = \frac{R_{AB} + R_{BC} - R_{AC}}{2} \quad (3.1)$$

where $R_{AB} = R_A^c + R_{dAB} + R_B^c$, $R_{BC} = R_B^c + R_{dBC} + R_C^c$, and $R_{AC} = R_A^c + R_{dAC} + R_C^c$ [75]. The resistance $R_{dAB}$ is defined as a device resistance between a contact pad A and B. Since the electrodes were identically fabricated, the contact resistance at the center lead B can be assumed to be similar to those of A and C, apart from that arising from a small amount of inhomogeneity of the SWNT alignment at each of these leads. An alternate method for obtaining contact resistance that involves separately measuring the resistances by 2-probe and 4-probe methods and comparing the two, introduces a similar amount of error compared to our proposed method. Hence we chose to use our presented method for estimation of contact resistances, and we present our data in the form of percentage changes. In all devices, this fabrication protocol was kept constant, and contact resistance was measured for the center lead B under different cleaning processes. It turns out that the contact resistance of a SWNT-based interconnect device can be
Figure 17. Measurement of contact resistance in SWNT architectures.

(a) Schematic of a cross-section shows the structure of a substrate, SWNTs, and contact pads. Two-terminal measurements were carried out between the pair of contact pad A – B, B – C, and A – C. (b) *I-V* curves measured of a typical aligned SWNT test structure for the calculation of contact resistance.

minimized using an optimal combination of purification methods. The resistances were estimated using a Keithley 2400 source meter having 0.012 % basic accuracy. Plugging this back into the
above equation (8) gives a total percentage error below 5 %, which is a reasonable value. A small but unavoidable error is introduced in our measurement due to the finite contact areas of the leads.

3.4 Purification Methods for Contact Area between SWNTs and Contact Electrode

Both for SWNT assembly and contact fabrication, we used PMMA, which is a conventional EBL resist, and is a polymerized version of methyl-methacrylate CH2=C(CH3)COOCH3 – a sticky, resin-like material (commonly found in paints etc.). PMMA is extremely useful for a high-resolution EBL, and regular semiconductor fabrication processes have well-developed methodologies for cleaning PMMA, such that the exposed surface for metallization etc. is free of any residual impurities for the formation of robust, low-interfacial-resistance contacts. Over the years, researchers have adopted this methodology to form metal contacts with non-conventional graphitic nanomaterials, such as CNTs and graphene. However, little effort has gone into analyzing whether conventional cleaning procedures are adequate for the complete removal of PMMA from graphitic surfaces.

Recently, Dan et al. [84] showed, through a combination of AFM step height measurement and electrical characterization, that conventionally implemented EBL processes can leave behind a nanometer-thick layer of PMMA on graphene. To circumvent this, the authors reported a very high-temperature cleaning step (flowing Ar/H2 at 400 °C for 1 hr.) that appeared to remove the residual PMMA from graphene. This demonstrates that the monolayer of PMMA can be a reasonably resilient residue which requires proactive cleaning steps on graphene. Structurally, CNTs are not very different from graphene, and it is not hard to see that conventional PMMA-
cleaning protocols could leave behind similar residues on nanotubes. In particular, a nanometer or thicker residue between nanotubes and metal contacts could easily lead to large percentages of interfacial electrical resistance, which is a critical problem in SWNT interconnect fabrication. Hence it is essential to develop a facile, CMOS-compatible process for complete cleaning of residual PMMA on assembled SWNT networks.

Here we demonstrate that a set of extra cleaning steps can remove this residual resist to enable very low interfacial electrical contact resistance in SWNT networks. The process steps that help in decreasing the contact resistance can be categorized into a “pre-cleaning” step, and a “post-cleaning” step. This has been schematically outlined in Figure 18. The pre-cleaning steps were used to remove residual PMMA from the assembled SWNT networks before the contact fabrication steps (i.e. deposition of PMMA) were performed. The normal step [75] and two new pre-cleaning steps have been outlined in Figure 18a. The pre-cleaning steps were found to be extremely important for the formation of robust and low-resistance contacts as we will discuss later on. In the normal process, after the SWNT networks have been assembled, the PMMA templates are dissolved by immersing the wafers in acetone for 90 seconds (we call this the first acetone wash). This is sufficient to dissolve and remove the PMMA template from the SiO2/Si substrate. However, in the process, it also deposits a large quantity of PMMA into the assembled SWNT structures. Figure 19a shows an SEM image of a random network of assembled SWNT structure after the first acetone wash. It is seen that during the washing process, a significant amount of PMMA gets trapped into the SWNT network. To remove this, the substrates are taken out and placed in a second (uncontaminated) acetone bath. In pre-cleaning process 1, this additional pre-cleaning was performed at room temperature for 90 seconds, which we call the second acetone wash. In a second pre-cleaning method (process 2), the first acetone
Figure 18. Purification processes of highly organized SWNTs.

(a) Pre-cleaning steps are used to remove PMMA layer from the assembled SWNT networks before the steps for the contact pads. (b) Post-cleaning steps are performed in the developing solution of the mixture of MIBK and IPA.
wash was performed in warm acetone (at 35°C), and was followed by rinsing in Isopropyl alcohol (IPA) and DI water.

After the assembled structures have been thoroughly cleaned, they were prepared for contact fabrication using standard EBL procedures. Then, the “post-cleaning” steps were performed after the electron beam writing step. Normally, after the writing is performed, the substrates are immersed in developing solution of the mixture of **Methyl isobutyl ketone** (MIBK) and IPA (1:3) for 80 seconds and then rinsed in IPA for 30 seconds (figure 18b). In post-cleaning process 1, the developing time was increased to 90 seconds, whereas in post-cleaning process 2, the developing time was increased to 180 seconds. The rinsing steps were kept the same, and then Ti/Au electrodes were coated to form contacts (as described before). The overall two-terminal resistance in a large number of devices was measured (each type of measurement was done on 5 devices) using the normal and each one of the new cleaning processes. In addition to these process steps, a fifth process was also developed, which was a combination of pre-cleaning process 2 and a post-cleaning with an even longer developing time of 210 seconds. Figure 19b shows an SEM image of the assembled SWNT structures using this last method, where visual inspection shows removal of all contamination of PMMA. Equation 1 was used to estimate the contact resistance of the central electrode in each of the cases. Here we compare the average results of each of the cleaning processes. All other assembly-related parameters were kept constant.

### 3.5 Contact Resistance depending on Purification Methods
The effect of the second acetone wash (pre-cleaning process 1) can be brought out by comparing the resistances of the SWNT networks that have been fabricated with and without the second acetone wash. The overall two-terminal resistances of the SWNT networks which undergo one and two acetone washes, respectively, were 4403 Ω and 3416 Ω on the average, showing a decrease of 22.4 % in overall resistance. For the measured value of contact resistance, this is the contact resistance at one contact, $R_{cB}$. The contact resistances of their structures were 1025 Ω and 313 Ω on the average, respectively, a decrease of 69.5 % in case of the second acetone washed devices. Note that this pre-cleaning is effective even though PMMA is coated once again in both devices for contact fabrication. This clearly brings out that PMMA contamination during the first acetone wash is more severe compared to any surface-adhesion during the spin-coating step of the second PMMA layer. As we will see later, this pre-cleaning step is crucial for obtaining lower contact resistances in these structures.

To compare the effects of post-cleaning, the pre-cleaning acetone wash was fixed at 180 seconds. For 90 seconds and 180 seconds development in the mixture of MIBK and IPA, the overall SWNT network resistances were 1898 Ω and 1530 Ω on the average, respectively, indicating a decrease of 19.4 % in overall resistance. The contact resistances, $R_{cB}$, of their structures were 462 Ω and 259 Ω on the average, respectively, a decrease of 43.9 % in contact resistance with 180 seconds developing treatment. This clearly showed that the post-cleaning step was also very important in removing residual PMMA from the SWNT networks.

In order to optimize the cleaning process, various combinations of pre- and post-cleaning steps were investigated, and the lowest contact resistance was obtained when the pre-cleaning process 2 was combined with a 210 seconds post-cleaning MIBK development time. Under this combination of steps, the average overall resistance and contact resistances ($R_{cB}$) were 1776 Ω.
Figure 19. Electrical properties and SEM images of SWNT structures depending on the treatment of cleaning.

(a) SEM image is for a typical surface of SWNTs after the first acetone wash for 90 seconds, showing the residues of PMMA. (b) Typical SEM image for the surface of SWNTs with warm acetone, IPA, and 210 seconds developing time, showing a clean surface. (c) Overall resistances according to the cleaning methods. (d) Their contact resistance in overall resistance. This is the value at the central lead (B) (see text).

and 15 Ω, reflecting a decrease by 59.7 % and 98.5 %, respectively, compared to the SWNT networks that underwent only the first acetone wash treatment i.e., the contact resistance was enormously reduced using this procedure. Figure 19c and 19d plot the average overall and contact resistances at the central lead (B) for SWNT networks which have undergone different cleaning procedures. Note that compared to the original method, the optimal method has a contact resistance which is very close to zero.
To conclusively establish that the resistance change was occurring only at the interface between the SWNT networks and the metal contact, we also performed a control experiment that studied the effect of acetone treatment on the contact resistance after putting contact leads. It details the overall and contact resistances in SWNT networks that undergo one wash (normal), and compares them to SWNT networks which are washed a second time after the metal electrodes were fabricated (i.e. the contact area was covered with metal), keeping all other steps identical. It was found on an average that the overall resistance varied only within 6.8 %, with no clear decreasing trend. In fact, the contact resistance increased by a few percents in some cases. This result clearly shows that cleaning the contact area before metallization is crucial in lowering both the contact and overall resistance of SWNT network interconnects, and that the decrease of contact resistance is not due to any doping effects from acetone.

We next look at the average percentage contribution of the contact resistance to the average overall two-terminal resistance of our SWNT interconnects at the end of each cleaning process steps. Figure 20 summarizes these data. We note that the percentage of the contact resistance has been calculated taking both contacts into account, assuming that the second contact has an identical contact resistance. We find that in all cases, the contact resistances decrease significantly after second treatment except for the control experiment (cleaning after contact pads were fabricated). In the controlled experiment where the second acetone wash was performed after putting contact metals, the contact resistance did not change much compared to those SWNT networks that were treated with only the first acetone wash, showing a nominal difference of 0.65 % (Group number 1). The percentage of contact resistance corresponding to a developing time of 180 seconds was reduced by 14.82 % (33.86 % compared to the value of 48.68 % for the 90 seconds developing time) (Group number 2). Adding the second acetone
Figure 20. Percentage of contact resistance in overall resistance, showing the contact resistances are decreased according to the different cleaning process.

Group number 1: acetone wash after contact pads, Group number 2: developing time dependence for contact pad fabrication, Group number 3: acetone wash before contact pads, Group 4: warm acetone + IPA + 210 seconds developing (see text). This percentage has been calculated taking BOTH contacts into account, assuming the second contact has an identical contact resistance. A second acetone wash and more developing time to the SWNT device play an important role in reducing its interfacial contact resistance.

Wash before putting contact pads reduced the contact resistance from 46.56 % to 18.33 %, decreasing by 28.23 % (Group number 3). However, the best results were clearly obtained by using a combination of warm acetone (second wash) and IPA and 210 seconds developing time, whereby the average percentage of contact resistance was reduced to 1.69 % of the overall resistance of SWNT networks (Group number 4). We note that in some cases, the contact resistance was found to be below 1% of the overall resistance, which we consider to be below are experimental error limit. Hence, we find that the optimal cleaning procedure described above can
lower the contact resistance to *lower values* compared to the average contact resistance of 48.67 % for in normal SWNT architectures, approaching values which are very low within our experimental accuracy.

### 3.6 Dependence of Contact Resistance on Temperature

Under real operations, interconnects in microprocessors are known to work at elevated temperatures, and hence we also investigated the robustness of the low contact resistance at a higher temperature of 100 °C and 180 °C (under vacuum) as shown in figure 21 for a typical device. The contact resistance of this device remained the same at 100 °C, and increased by 1.76 % at room temperature after one hour annealing at 100 °C. After keeping at 180 °C for one hour, the percentage of contact resistance reduced again by 0.8 % compared to the previous room temperature value. These measurements indicate that the change of contact resistances is within 2 %, demonstrating their robustness against realistic operational temperatures over hours of operation.

### 3.7 Conclusions

In summary, a simple and scalable set of extra cleaning steps has been developed that reduces interfacial contact resistances to values below 2 % of the total SWNT network resistance. The significant decrease due to additional pre-cleaning establishes clearly that surface contamination during the first acetone wash is much more detrimental than that which occurs during the second PMMA spin-coating step, and hence the pre-cleaning process is vital in our method. The post-
The change of percentage of contact resistance in overall resistance depending on temperature shows that the variation is within 1.76%. The contact between highly organized SWNTs and electrical contact electrodes has a stable ohmic contact with maintaining lower contact resistance. Cleaning step of additional developing time was found to be extremely effective in removing any surface contamination during the second PMMA coating step. With optimal cleaning conditions using warm acetone, IPA, and longer developing time, the contact resistance can get as low as 11 Ω which is just 0.74% of the overall resistance in our SWNT network interconnect test structure, and is comparable in value with that of the nanoscale metal electrodes. Moreover, the contact resistance remains in very little change even after hours of heating at temperatures up to 180 °C.
Controlled experiments performed after the metal electrodes were deposited showed very little change in contact resistance, indicating that the entire “decreased” contact resistance pertains to impurity removal at the nanotube-metal interface, and is not any extraneous effects such as doping, *etc.* The enormous decrease of contact resistance in highly organized SWNT networks demonstrates a big step towards their integration into existing CMOS platforms as future interconnects.
Chapter 4: Chemical Sensor Based on Highly Organized SWNT Networks for Hydrogen Sulfide

4.1 Introduction

Recently there has been significant interest in using carbon based nanomaterials as chemical sensors due to several advantages of nanostructured carbon such as light weight, high electrical conductivity, electrochemical surface area and superior sensing performance. Particularly, CNTs are a growing demand due to their high electron mobility and large current capability, which on one hand can potentially help in reducing power consumption of the sensor whereas, on the other hand high temperature stability and chemical inertness of CNTs may provide a stable and robust platform to detect specific gas [85-91].

Since pristine CNTs based chemical sensors utilize their intrinsic electrochemical properties, to overcome their limitations in selectivity and sensitivity the most promising approach is to functionalize CNTs with covalent or non-covalent materials [92, 93]. However owing to their one-dimensional nanostructure CNTs are highly sensitive to environment such as humidity and temperature [94, 95], in practice the effect of the relative humidity (RH) in CNT based chemical sensors must be investigated further because the humidity varies greatly depending on the season, region and weather.

Un-functionalized SWNT based two terminal as well as field effect devices have been proposed and fabricated for sensing gases like alcohols [96], hydrogen sulfide (H₂S) [97], ammonia [98], nitrogen dioxide [99] etc. However, due to different redox properties of these gasses, it is difficult to understand the exact sensing mechanism that leads to changes in conduction characteristics of SWNTs. These un-functionalized SWNT sensors are also not specific. Therefore, for a highly sensitive chemical sensor with very high specificity,
functionalized SWNTs have to be utilized. In order to increase the specificity of SWNTs based chemical sensors, SWNTs decorated or functionalized with different sensory molecules or nanoclusters as sensory elements can be employed. Complex as well as simple molecules can be attached to SWNT surface to alter their properties by the formation of charge transfer complex or by redox reactions occurring in the close proximity of SWNTs.

H₂S is a deadly gas which causes asphyxiation, lung damage, and teratogenic effects when exposed to it [100, 101]. Thus the monitoring and elimination of H₂S is very important for safety because this gas is found widely in industry such as natural gas, petroleum and mines, and is given off as a by-product in the manufacture of rayon, synthetic rubber, dyes and the tanning of leather [102]. So far wide varieties of inorganic and organic materials such as tungsten oxide, tin oxide and carbon have been proposed as electrical sensors that can detect the H₂S gas [103-109]. Although there are several successful devices available commercially, drawbacks of existing H₂S monitors include high power consumption, high operating temperatures, short lifetime, interference from other gases and high cost [110].

4.2 Fabrication of SWNT Networks for Sensors

We developed template-guided directed fluidic assembly process for fabricating high density SWNT highly organized structures and networks [32, 34, 111] described in chapter 1.4. Figure 16 shows typical SWNT lateral structures fabricated by the template-guided fluidic assembly of SWNTs. Figure 16 a and 16b show highly dense and assembled SWNTs line structures in the low and high magnification of a channel of approximately 1µm. Figure 22 shows the SWNT-based sensor devices with wire bonding to reduce the electrical noise from ambient environments
and vibrations. Figure 22a and 22b show SEM images with a wire bonding process in the overall structure and individual test structure, respectively. However, as shown in Figure 22c, the SWNT chemical sensor can be damaged due to the electrostatic discharge (ESD) or thermal oxidation of SWNTs during the wire bonding process. In order to solve this problem, a new design of metal contact pads was implemented in which the contact pads were placed far away from the SWNT sensor as shown in Figure 22d such that ESD or oxidation would not affect SWNT sensing platforms during wire-bonding. With this new design of contact pads, the SWNTs chemical sensors were quite stable in the H₂S gas testing.

4.3 Non-covalent Functionalization of SWNTs

This covalent functionalization can be effectively achieved in two ways. (i) Creating a defect site on SWNTs followed by addition of the desired functional groups at the defect site. (ii) Utilizing carboxylic acid, aldehyde or alcohol functionalities that are already present on the sidewall of SWNTs as a result of oxidation processes used in SWNT purification. However, covalent functionalization of SWNTs not only changes the electronic properties of SWNTs (because of the defects) but also affects chemical, thermal, and mechanical stability of SWNTs and hence not desirable in developing electronic sensor application which should be used in harsh environments. To overcome drawbacks of covalent functionalization, researchers have widely investigated non-covalently functionalized SWNTs. Various species of polymers,
Figure 22. SEM images of SWNT-based devices with wire bonding.

(a) and (b) show typical SEM images with wire bonding process in the low and higher magnification, respectively. (c) Damaged SWNT device during H$_2$S gas test. (d) Modified contact pads design to solve the problem with larger distance between the sites of wire bonding.

Poly nuclear aromatic compounds, surfactants and small molecules and bio-molecules have been explored. Non-covalent functionalization of SWNTs have been implemented to exfoliate bundles and prepare these suspensions of individual SWNTs. Non-covalent functionalization of SWNT is particularly attractive because it presents the possibility of modifying surface chemistry of sidewalls of SWNTs without affecting the electronic properties of SWNT network. Since the surface of SWNTs is chemically equivalent to that of graphite (extremely hydrophobic), with proper design of solute-solvent-substrate interactions, one can selectively functionalize the
sidewalls of SWNTs with a desired molecule. The non-covalent interaction is based on van der Waals forces or p-p stacking, and it can be controlled by thermodynamics.

4.3.1 Functionalization of SWNTs with Nitroxy Radical Based Compounds

In the following sections, the functionalization procedure for attaching the sensory TEMPO molecules to the SWNTs without affecting their sensitivity is presented. Both covalent as well as non-covalent functionalization procedures were evaluated and their advantages and disadvantages are discussed below specifically in the context of SWNTs functionalization with TEMPO. Non-covalent functionalization technique is carried out by drop casting a solution containing the sensor molecule onto assembled SWNTs. The advantage of this process is two folds: (i) functionalization of SWNTs is very easy and fast without disturbing the assembly, (ii) repeated optimization of fluidic assembly conditions for SWNTs functionalized with different sensor molecule is not required. Two different molecules were tested for non-covalent functionalization. The 4-amino TEMPO molecule was used for all the preliminary H₂S detection experiments reported here. The presence of an amino group, however, makes this molecule fairly soluble in water and is not desirable to be used in down-hole environment. Therefore, the TEMPO molecule was adopted for non-covalent functionalization of SWNTs instead of the 4-amino TEMPO molecule. The absence of any hydrophilic amino functionality in the TEMPO molecule makes them easily attachable onto sidewalls of SWNTs as well as helps in understanding the sensing mechanism.

4.4 Hydrogen Sulfide Gas Detection of SWNT Networks
Non-covalently functionalized SWNT devices were exposed to H$_2$S gas under normal atmospheric conditions as well as under controlled environments. The general term “Response Time” used for other similar sensors is used here to define the comparison of detection characteristic of the sensors in various environments. Response time is defined as the time period in which the detector output signal is reduced to 90% of the initial value. Since the SWNT chemical sensor’s current is measured for a constant applied voltage as function of time, the response time in such a case is taken as the time period the sensor takes to drop 10% of the initial current value as shown schematically in the Figure 23. A larger response time indicates that the sensor is not highly sensitive whereas a shorter response time indicates a highly sensitive sensor.

The tests were carried out in a glass chamber designed for these tests as shown in Figure 24. In the following comparisons the response time measured in air was taken as a reference for different concentrations of H$_2$S gas. Also, all of the data shown in the following sections was obtained using SWNT devices functionalized using the TEMPO molecule.

### 4.4.1 Detection of Hydrogen Sulfide in Air

Any sensor usually has an optimal working range for analytic concentrations. This optimal concentration range defined for a given sensor in a given environment allows one to calibrate the sensor and detect unknown concentrations. Thus, in order to investigate the optimal working range for our sensor, we exposed the sensor to different concentrations of H$_2$S gas ranging from 10-1500 ppm. The applied bias voltage was kept constant for every measurement and changes in current were monitored as a function of time for different gas concentrations. The glass chamber was kept closed until the current decreased to 10% of its original value. Once the current
Figure 23. Shown schematically is the definition of the “Response Time” for an electrical sensor.

Figure 24. Glass chamber setup for controlled environment measurements.
Figure 25. Current vs. time plot monitored for different concentrations of H₂S gas. Injection of different concentrations of H₂S gas in the close chamber is indicated by arrows.

decreased more than 10% of the initial value, the glass chamber was opened in order for the sensor to recover. These sensors showed almost 100% recoveries. After the sensor was recovered, glass chamber was closed and the sensor was exposed to a different H₂S gas concentration.

Figure 25 shows current vs. time plot for the functionalized SWNT sensor when exposed to different concentrations of H₂S gases. Sharp decrease in current indicates sensor response to H₂S gas when certain amount of H₂S gas is injected in the close chamber. Rise in current resulted when the glass chamber is opened and the sensor is allowed to recover in open air. For all concentrations shown in Figure 25, response time was calculated. The plot in Figure 26 clearly shows that sensor response is linear for 25-100 ppm concentration of H₂S gas whereas for 200-1500 ppm shows almost a flat line indicating the saturation region for the sensor. This saturation is determined by the loading of the sensor molecule on the SWNTs. Thus the working range of
Figure 26. Shown is a plot of Response time vs Concentration of H$_2$S gas clearly revealing the working range and saturation region for the functionalized SWNT sensor.

the SWNTs can be changed and expanded by altering the loading of the sensor molecule resulting in a versatile fabrication procedure for sensor device.

4.4.2 Detection of Hydrogen Sulfide with Metallic/Semiconducting SWNTs in condition of Water Vapor

In the previous section, we used a mixture of metallic and semiconducting SWNTs for the devices. Here, we report for the first time molecular doping of 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) as a catalyst on the surface of metallic/semiconducting SWNTs and the effective
detection of H$_2$S gas by a redox reaction at room temperature. We will also discuss the important role of water vapor on the electrical conductivity of SWNTs during the sensing of H$_2$S molecules.

Figure 27 depicts a device schematic and the behavior of H$_2$S and H$_2$O molecules on SWNTs functionalized with TEMPO molecules. SWNTs serve as an active channel layer because of their ultra-high surface area to volume ratio and no chemical interaction with H$_2$S or other gases that may interfere. Especially, semiconducting SWNT (s-SWNT) plays a major role in gas detection due to their different redox properties [112, 113]. In order to investigate H$_2$S sensing on SWNTs with different electronic structures (semiconducting and metallic), we performed a controlled experiment where, 99% purity of metallic SWNT (m-SWNT) and s-SWNT solutions (purchased from NanoIntegris Inc.) were drop-casted on each inter-digitated finger electrodes. Then we deposited TEMPO on the SWNT based devices using a vaporization method to achieve uniform and thin coating for the functionalization of SWNTs, which was then carefully outgassed by joule heating under 10$^{-3}$ torr for 1hr followed by injection of dry N$_2$ gas in a sensing chamber. Since TEMPO possesses stable nitroxyl group provided by the adjacent four methyl groups, it has widely been used as a radical trap, as a structural probe for biological systems, as a reagent in organic synthesis, and as a mediator in controlled free radical polymerization [114-116]. Thus it is also capable of oxidizing the gaseous H$_2$S and can be utilized as a sensory molecule for making a chemical sensor to detect H$_2$S. Non-covalently functionalized SWNT devices were exposed to H$_2$S gas under dry N$_2$ or controlled water vapor. Clearly, in all the above-mentioned detections, the sensing materials come in contact with either H$_2$O or H$_2$S or mixtures of these two.
Figure 27. Device schematic and the behavior of H$_2$S and H$_2$O molecules on SWNTs functionalized by TEMPO.

Figure 28 shows sensing of H$_2$S molecules with SWNT devices and the effect of relative humidity. In order to investigate exact sensing mechanism and interactions between SWNT-TEMPO-H$_2$S-H$_2$O, we compared sensor performances under absence or presence of water between s-SWNT and m-SWNT devices which are functionalized by TEMPO or not. First, to understand the effects of H$_2$S gas on a bare SWNT, SWNT-based sensor devices without TEMPO functionalization were exposed to H$_2$S gas of 5, 10, 50, 100, and 200 ppm, respectively in the chamber with dry N$_2$. For each concentration of H$_2$S, we evaluated sensitivity $S$ defined by $S = ((I_i - I_{gas})/I_i) \times 100$, where $I_i$ is the initial current in dry N$_2$ and $I_{gas}$ is the changed current after injection of H$_2$S gas. Figure 28a shows the sensitivity of bare s-SWNT device with H$_2$S concentration in dry N$_2$ (see Appendix A figure S1 for real time current change). Sensitivity at 200 ppm of H$_2$S shows 38 % change. However, bare m-SWNT device shows less than 5 % sensitivity (Appendix A figure S2) on detecting H$_2$S gases. This result is consistent with previous reports [90], indicating more redox properties of the s-SWNTs.
**Figure 28.** Sensitivity and real-time current measurements for detection of H$_2$S gas.

(A) Sensitivity of a bare s-SWNT device as a function of H$_2$S concentration. Real-time current measurement of (B) a bare s-SWNT device and (C) a device functionalized with TEMPO as a function of RH. (D) Sensitivity of B and C. In the range of current reduction of B and C, red and green area mean injection of H$_2$S and H$_2$O molecules respectively, and increase of current indicates recovery into the initial current value of each RH.

To investigate the effect of H$_2$O on sensing of H$_2$S molecules, we used only 100 ppm concentration of H$_2$S since it is known that, above that concentration, the human olfactory nerve can be paralyzed in a few inhalations. Then sensing of H$_2$S gas was performed under different RH. Figure 28b shows the real-time current changes in a bare s-SWNT device when 100 ppm H$_2$S gases were exposed at RH of 0, 20, 40 and 60 % (see Appendix A figure S3 for more details and Appendix A figure S4 for bare m-SWNT device). First, we observed that the current in s-
SWNT device decreased when exposed to water vapor. Then a further substantial reduction in conductance was observed when H$_2$S gas was introduced in the presence of predetermined RH. After each sensing test under a given RH, the chamber was exposed to dry N$_2$ for the sensor recovery for sensing of H$_2$S in increased RH. The real-time current measurements clearly demonstrate that redox properties do change in the presence of H$_2$S and water vapor. The sensitivity of bare s-SWNT devices was increased significantly to 150% at 60% RH (figure 28d).

H$_2$O molecules can be adsorbed on the surface of SWNTs and act as electron donors in a p-type semiconductor reducing the hole density in s-SWNTs resulting in the current decreases [94]. This fact is consistent with the initial current drop observed when only water vapor was introduced as shown in the figure 28b and Appendix A figure S5. To explain the increased H$_2$S sensitivity of s-SWNT, the interaction of H$_2$S and H$_2$O molecules is a possible subset. H$_2$S is slightly soluble in water (its solubility is about 3.8 g per kg in water) and acts as a weak acid. The concentration of 60 % RH at 20 °C is about 38000 ppm, which is enough to dissolve the 100 ppm of H$_2$S. Therefore, the conductance after injection of H$_2$S gas can be changed significantly by hydrosulfuric acid formed by water molecules attached on the surface of s-SWNTs. This fact indicates moisture is one of important factors in practical applications and sensitivity of the chemical sensors.

To maximize sensitivity based on the above facts, TEMPO was used as a homogeneous catalyst for redox reaction of H$_2$S and H$_2$O. As shown in figure 28c and 28d (see Appendix A figure S6 for more details), s-SWNT devices functionalized with TEMPO showed 420 % sensitivity at 60 % RH, which is about 3 times higher than bare s-SWNT sensor at the same RH, and 17 times higher than bare s-SWNT device under dry N$_2$ condition.
Figure 29. Schematic of redox reactions of H$_2$S on p-doped CNT (due to, for example, O$_2$ adsorption) with TEMPO functionalization in the presence of H$_2$O. Here, red dot: oxygen, yellow: sulfur, and white: hydrogen.

To explore the H$_2$S sensing mechanism of TEMPO-functionalized CNT devices, we investigated the adsorption properties of H$_2$S on CNTs and the effects of the TEMPO functionalization. We also considered the humidity (H$_2$O) effect as well. To understand the underlying sensing mechanism, we paid attention to the redox reactions of various molecules existing near active CNT channels, which exhibit the p-type characteristics in the ambient condition. This is attributed to the fact that the CNT is p-doped due to the oxygen adsorption, through which each O$_2$ molecule takes an electron away from, or donates a hole to the CNT. These adsorbed O$_2$ molecules existing in the form of O$_2^-$ will participate in our proposed redox reaction by donating electrons back to the CNTs resulting in less p-doped CNT channels. Figure 29 shows a schematic of a full cycle of the redox reactions that we propose to occur for H$_2$S detection near CNT channel functionalized by TEMPO in the humid condition. At the first stage of the redox reactions, TEMPO is oxidized to be TEMPO$^+$ with powerful positive, which is an important product for H$_2$S dissociation, while H$_2$O molecules with O$_2$ molecules from O$_2^-$ reduce. At the second stage of the redox reactions, the reduction reaction of TEMPO$^+$ to TEMPO-H is
coupled to the dissociation process of $\text{H}_2\text{S}$ to $\text{S} + 2\text{H}^+ + 2e^-$. At the final stage of the redox reactions cycle, the sulfur atoms produced by the latter reaction at the second stage react with oxygen ions ($\text{O}_2^-$) responsible for p-type characteristics of CNT devices and thus form various sulfuric oxides such as $\text{SO}$, $\text{SO}_2$ as the oxidation reaction during which the remaining electrons are back-donated to the CNT channels being less p-type. In the counter reduction reaction, TEMPO-H becomes back to TEMPO in the presence of other TEMPO molecules, and the detached H atoms may be involved in the formation of $\text{H}_2\text{SO}_4$ from the sulfuric oxides. Through such a complete reactions cycle, the TEMPO molecules together with water play a significant catalytic role for $\text{H}_2\text{S}$ detection.

4.5 Conclusions

In summary, we have fabricated micron scale SWNT based chemical for the detection of $\text{H}_2\text{S}$ with detection limit as low as 5 ppms. Several design modifications are implemented to increase the reliability and yield of the sensors. Fabricated two wire sensors (resistance based) had resistance values suitable for detecting $\text{H}_2\text{S}$ in ppm range. Non-covalently functionalized SWNT chemical sensor has been tested for detecting $\text{H}_2\text{S}$ in the environments of Air. Response time was found to be as low as seconds and is a function of environment and concentration of $\text{H}_2\text{S}$. Sensor recovers back to its original conductance when exposed back to the atmosphere. Simple device fabrication and complete recovery of the sensors shows a path to manufacturing low-cost effective SWNTs based sensors. To date, application of this phenomenon according to the relative humidity in gas detection has been less studied. Such a platform can open new possibilities in development of multi-functional gas senor that can truly act as an “electronic nose”
by selectively detecting multiple gaseous species. Our sensors offer promising perspectives for real-time monitoring of H$_2$S gases with highest sensitivity and low power consumption and potentially at a low cost. Small size of the system will also allow future integration with low power microelectronics.
Chapter 5: Optoelectronic Properties of Heterojunction between SWNTs and Silicon

5.1 Introduction

In recent times, there has been a remarkable progress in the development of key photonic circuit components such as on-chip sources, sub-wavelength manipulators, detectors, storage, filtering and multiplexing technologies [117-120] that are architecturally compatible with the conventional Si-based integrated circuit (IC) platform. A successful synergy of the ultra-high-speed, high-bandwidth, low-loss photonics-based data transfer technology with the speed and performance of densely integrated, ultrafast electronic logic and memory elements of conventional integrated circuits [121] could significantly mitigate near- and long-term critical challenges of delay, bandwidth, and quantum-confinement effects associated with the downward scaling of conventional ICs [122].

One component which could significantly benefit the integration of photonic and electronic circuits is a hybrid logic element that can operate with both optical and electronic inputs. Historically, logic operations in purely electronic circuits are achieved through switching of field-effect transistors [123]. In contrast, a variety of methods can achieve switching in purely photonic circuits, ranging from the use of second harmonic generation in non-linear optical materials [124] to the more recent, opto-mechanical resonance techniques [125]. Given the technological dissimilarity between electronic and optical logic elements, hybridizing these two could be quite challenging. One approach would be to develop a new type of device, the logic
output of which depends on the logic state of both optical and electronic inputs. In principle, this could be possible if one could develop a photocurrent-generating device whose output can be also independently controlled by an external voltage. Conventional semiconductor junction diodes are used in a variety of operational configurations (e.g. p-n, p-i-n, or Schottky junctions) for photocurrent generation over a wide spectral range. These junctions are ubiquitously characterized by exponentially growing forward currents and a bias-independent reverse current. Under illumination, the reverse currents, while remaining bias-independent, grow linearly with the incident photon flux. This linearity can last over several decades of incident power, rendering them excellent for optical power meters. However, in the context of a hybrid integrated circuit, the absence of a method for voltage-control of photocurrents prevents photoswitches from being used as logic elements, and remains passive communication-enabling switches. Hence, while voltage-control of electrical currents has existed for decades, the design of a photocurrent-generator (e.g. a photodiode) whose photocurrent can be switched using an electrical voltage, appears to be absent.

In this chapter, we show that heterojunctions of SWNTs form a unique junction with lightly p-doped Si that can very effectively address this issue. Remarkably large switching of photocurrents can be obtained due to their low dark currents, low short-circuit photo-currents and high photocurrent responsivity at low reverse biases. This striking behavior, previously unreported in SWNT/Si junctions, is understood to be an outcome of three key factors: (a) SWNTs have a very low density of states (DoS) near their Fermi level, which restricts the number of carriers that can be injected at this energy level, resulting in the low short-circuit photocurrent irrespective of the input light power; (b) Unless special care is taken, Si can easily form surface states and hence get “pinned” [126] to the charge-neutrality level of these states;
and (c) the closeness of the work function of SWNTs and the electron affinity of Si, which, in a Si-pinned junction, allows the Fermi level of SWNTs to lie very close to the conduction band edge (CBE) of Si, where the photo-excited carriers inject from. These factors, along with the fact that an external voltage, applied directly to the SWNTs, can very effectively modulate its Fermi level into regions of high DoS, enable a unique voltage-controllable injection of photo-excited carriers into SWNTs resulting in the observed voltage-controllable responsivity of these junctions. Further, the entire fabrication process rests on our previously developed “template-assisted fluidic assembly” method – one of the few techniques that can achieve wafer-scale uniform assembly of SWNT mats/belts and other architectures with nanoscale precision [33, 74, 75]. As we show, this enables us to obtain highly reproducible and complex optoelectronic logic elements.

5.2 Literature Review

5.2.1 Conventional Photodetectors

Semiconductor heterojunction photodetectors are extremely popular due to their broad spectral responsivity, excellent linearity, high quantum efficiency, and high dynamic range of operation. In addition, they are highly suitable for scaled-up manufacturing, for example in arrays of pixels for imaging purposes (e.g. in digital cameras). Numerous semiconductors in a variety of operational configuration are commonly used to detect and measure electromagnetic waves over a wide spectral range. For example, GaAs (band gap Eg=1.43 eV), GaN (Eg=3.4 eV), AlGaN (Eg=3.4–6.1 eV) [127], SiC (Eg= 2.36-3.05 eV) and Si (Eg=1.12 eV) etc. are popular UV detectors [128] both in the photoconductive as well as photovoltaic modes. Si and Ge
(Eg=0.67 eV) are compatible with detection in the visible-NIR regions (above these wavelengths, pyroelectric and bolometric measurements are favored). In most cases, these materials function as p-n, p-i-n, or Scottky photodiodes. In a reverse-bias condition, the reverse current saturates and becomes voltage-independent, and is usually linearly related to the incident photon flux. In this mode, the junctions are usually quite linear over a large range of incident optical power, and are excellent for optical power meters.

### 5.2.2 Optoelectronic Photoswitches

Optoelectronic photoswitches are key elements of digital optoelectronic circuits that require high ON/OFF ratios at low optical incident power levels. Devices that can change its current by orders of magnitude at low incident light powers (resulting in high ON/OFF ratios), potentially through sharply non-linear responses, are appropriate for photoswitches. The linear photoresponse in conventional photodiodes and their voltage-independent reverse current results in low ON/OFF ratios. As a result, the use of photodiodes renders a limitation on the optical power requirement in optoelectronic integrated circuits. Avalanche photodiodes can overcome this limitation by operating near breakdown reverse voltages. However, such breakdown voltages are extremely high, often exceeding 10s to 100s of volts, and are problematic for high-speed optoelectronic switches due to their high noise and unstable recovery. In this context, a device which demonstrates a low dark reverse-bias current, and responds with very high reverse photocurrents (equal or more than the forward bias currents) at very low reverse bias values would be a very effective photo-switch.

### 5.2.3 Carbon Nanotubes and CNT-Si Heterojunction based Photo-devices
SWNTs are one-dimensional (1D) rolled up sheets of graphene (carbon in sp2 hybridized sheets) [129]. The chirality [129] of a specific SWNT and its 1D confinement enable a whole family of SWNTs which can be metallic (i.e. with a zero gap at the Fermi level), or semiconducting (i.e. with a finite band gap) with a whole range of gap values. MWNTs are closely related materials with multiple coaxial shells. Over the past years, we have developed a broad variety of carbon nanotubes, and have also demonstrated a number of their important electronic [130], optical [131], and thermal properties [132].

The presence of discrete energy levels with poor intra-tube charge-transfer presents itself as a unique system, especially since it forms a very complex band-alignment when placed in close proximity of a bulk semiconductor such as Si. This is even more so, since nanotube diameters are far smaller than typical junction depletion widths, and hence the nanotubes in direct contact with Si may be almost completely free-carrier depleted. This implies that any photo-excitation could render near-instantaneous carrier separation across the junctions, with very low thermal or recombination loss.

The photoresponse properties of SWNT-Si based heterojunctions has been a topic of enormous interest in recent times due to their potential usefulness in low-cost, intermediate efficiency (4%-13%) solar cells [133-138]. In all these reports, the dark and photo-induced current-voltage (IV) curves are similar to those seen in conventional p-n or Schottky barrier junctions, i.e. a near-exponential forward bias current and a voltage-independent reverse bias current whose magnitude changes linearly with the incident photon flux. Qualitatively, the overall behavior of the photo-response in SWNT-Si heterojunctions, hence, is very similar to that of a Schottky junction as shown in the inset of figure 30c. The dark IVs in SWNT-Si
heterojunctions fabricated via a template-guided fluidic assembly method have a similar diode-like behavior, as seen in the inset of figure 30b.

5.3 Optoelectronic Properties of SWNT-Si Hetrojunction

We has developed a novel template guided fluidic assembly technique for depositing well controlled SWNT architectures onto Si and SiO$_2$ substrates described in chapter 1.4. A very important aspect of this technique is that effective micro- and nanoscale patterned SWNT assembly is accomplished using a simple dry plasma treatment to control the surface property of silicon or silicon oxide substrates without the need to resort to complex wet chemical functionalization processes. Figure 30a and 1b show a schematic and a digital image of a typical test structure prepared to examine the photoresponse in SWNT/Si junctions. For the purpose of characterization, the SWNT belts were extended well into the bare Si area, such that an incident light spot could be selectively positioned only on the junction, to avoid the role of contacts. SWNT belts of various dimensions, with lateral dimensions ranging between millimeters (figure 30b) to sub-micrometer (as shown in the SEM image in figure 30c) were fabricated. The assembly process allows one to obtain highly aligned SWNTs in the belts for belt widths <1 μm [75], whereas progressively more random SWNT networks form for structures of larger size.

In the past, SWNT mats/thin films have been extensively used to develop a wide range of applications including transistors [139-141], flexible electronics [142-144], sensors [86, 145, 146], and transparent conductive films for touch-screen [147-149] and energy [147, 150-154] technologies. More recently, the photo-response properties of SWNT-Si based heterojunctions have generated enormous interest for low-cost, intermediate efficiency (4%-13%) solar cells
Surprisingly, there has been comparatively little attention so far on the development of scalable SWNT-based high-performance photon-sensing and photoswitching architectures that can have a sizable impact on next-generation optoelectronics, with the most promising architecture being an unpinned SWNT/p:Si junction with a responsivity $R \approx 133 \text{ mA/W}$ [155]. In all these architectures, the detailed electronic structure and the effective DoS of SWNT films are usually ignored, and their photoresponse behavior is often modeled in terms of a metal-semiconductor “Schottky-barrier” junction, where the SWNTs are treated as passive, transparent conductive (metallic) electrodes. This is quite consistent with their photocurrent response behavior, which has been inevitably shown to be reverse-bias independent, as expected for both Schottky-junction or p-n junction photodiodes/solar cells. In stark contrast, the photocurrents in our junction depend strongly on the applied reverse bias. Figure 30d shows the dark-and photo-IV curves in our SWNT/Si junctions, where the reverse-bias photocurrent clearly deviates from the conventional behavior, with a near-zero short-circuit current (independent of the incident power, see Appendix B) that sharply rises within a few volts of applied reverse bias. A striking difference is observed between the nature of the photo-IVs of SWNT/Si and that of a conventional metal/Si Schottky junction of comparable dimensions, illuminated with the same light source. The inset of figure 30d shows the photocurrent as a function of reverse bias, as well as a plot of the calculated number of accessible states as a function of the reverse bias (as discussed later).

It is well-known that unless adequate care is exercised, the presence of surface states on Si (arising from dangling bonds or native oxides) can dominate its band-bending process in Si, resulting in a “pinning” of its Fermi level to the surface-charge-neutrality level, typically located
Figure 30. SWNT/Si heterojunction structure and photoresponses.

(a) Schematic and (b) digital photograph of a SWNT/Si heterojunction test-structure (2cm×2cm) with electrical contacts. (c) Pseudo-colored SEM image of a sub-micron-width fluidically assembled SWNT belt. (d) Dark and Photo-IV (117μW broadband visible illumination) curves of a typical SWNT/Si heterojunction. The Photo-IV curve of an Au/Ti/Si junction of similar dimensions and illumination condition is also shown for comparison of their shapes. Inset: Comparison of the photocurrent data with an empirical model as described in (e). (e) Schematic energy-level diagram of Si undergoing photoexcitation, adjacent to the cumulative DoS (CDoS=∑_{m,n} D_{m,n}(ε)) of selected d≈1nm SWNTs (with chirality values (m,n) as shown). The photocurrent due to injected electrons from Si into SWNTs is limited by the number of accessible states in SWNTs, n[ε=V_r]=∫CDoS(ε)dε, integrated between ε=0 and ε=εV_r (V_r = reverse bias), as shown. The dashed line is a schematic trace connecting the quasi-Fermi levels: due to photoexcited electrons in Si, and due to the application of a reverse bias in SWNTs. (f) Broadband responsivity and ON/OFF ratios of the SWNT/Si junction as a function of the reverse bias. (g) Change in open-circuit voltage under 1μW illumination.
about 0.37 eV above its valence band edge. Since SWNT surfaces are chemically inert due to their well-satisfied chemical bonds within the sp$^2$-hybridized C lattice, the Fermi level in Si is very likely going to be “pinned” unless its surface is carefully prepared and passivated [156]. Although such a junction is rectifying, the Schottky barrier height is fixed (about 0.8 eV in n:Si, and ~0.37 eV in p:Si, the so called Bardeen limit [157]). In the absence of any surface/interfacial gap-states, the Fermi level of unpinned Si aligns itself with that of SWNTs under thermal equilibrium, forming a Schottky barrier that depends on the work-function (and hence the position of the Fermi level) of SWNTs. Since the Fermi level of SWNTs (as also in graphene) can be externally tuned (unlike conventional metals), recent works have exploited unpinned SWNT/Si and graphene/Si junctions to obtain variable-Schottky-barrier, high performance solar cells [158], “barristors” [156], and field-effect tunneling transistors [159].

The expected hole Schottky barrier for a completely unpinned SWNT/Si junction is $\phi_{bp} \approx \chi_{Si} + E_g - \phi_{SWNT}$, where $\chi_{Si} = $ electron affinity of Si $\approx$4.05eV, $E_g$ = band gap of Si $\approx$1.12eV, and $\phi_{SWNT}$ is the intrinsic work-function of SWNT mats that ranges between 3.7eV to 4.4eV [158]. Hence, an unpinned SWNT/Si junction can be expected to have a $\phi_{bp} > 0.77$ eV. In contrast, $\phi_{bp}$ of our SWNT/Si junctions is about 0.35 eV, close to the Bardeen limit for Si ($\approx$0.37 eV), which suggests that our SWNT/Si junctions form non-ideal Schottky junctions where the Si energy levels are pinned to its own surface states. This implies that although the SWNT belts lie in physical contact with Si, their effective Fermi level of can remain close to its native (free-state) position, which is close to the conduction band edge (CBE) of Si, since $\chi_{Si} \approx \phi_{SWNT}$. Since SWNTs have extremely low DoS, D(\varepsilon), near their Fermi level (assigned as $\varepsilon=0$), photoexcited electrons near the CBE find very few accessible states, resulting in the near-zero short-circuit photocurrent seen in our devices. Moreover, the application of a reverse-bias allows a direct
lowering of the effective Fermi level resulting in a voltage-tunable quasi-Fermi level that lies below the original Fermi level. Hence, under reverse bias, a number of unoccupied states open up allowing an increased injection of photoexcited electrons to inject in from Si, increasing the photocurrent. Since the photocurrent is limited by the number of accessible states between the position of the CBE of Si (near $\varepsilon=0$) and the quasi-Fermi level (at $\varepsilon=\varepsilon_{tr}$, where $\varepsilon_{tr}$ is the reverse bias) in SWNTs, its voltage dependence can also be expected to follow the dependence of the number of accessible states, $n(\varepsilon=\varepsilon_{tr})$, where $n(\varepsilon=\varepsilon_{tr})$ can be obtained by integrating the SWNT DoS between $\varepsilon=0$ and $\varepsilon=\varepsilon_{tr}$.

To obtain this trend, we employ a toy model to describe the effective electronic structure of the SWNT belts. Since the as-received SWNTs had $d\approx1\,\text{nm}$, we assume that the belts contain an equal distribution of all chiralities $(m,n)$ \cite{8} with $d\approx1\,\text{nm}$. The cumulative DoS (CDoS) of the SWNT belts can be assumed to be proportional to an equally weighted sum of the individual DoS \cite{27} of each chiral type, $\text{CDoS} = \Sigma_{m,n} D_{m,n}(\varepsilon)$. Here, $\varepsilon=0\,\text{eV}$ is the Fermi level, assumed to be the same for all SWNTs for the sake of simplicity. We note that this approach is inadequate for correctly describing the actual CDoS of our SWNT belts. Obtaining a realistic CDoS of the SWNT belts is a considerable computational challenge, and is currently beyond our capabilities. The attempt is to obtain a qualitative understanding of how much the photocurrent could potentially change as a function of the position of the quasi-Fermi level. Figure 30e shows the CDoS of SWNTs (obtained by summing the DoS of 22 different chirality values of SWNTs with $d\approx1\,\text{nm}$ as shown) according to our model, as a function of electronic energy, $\varepsilon$. The CDoS has been placed adjacent to a schematic energy-level diagram of Si near its band gap, with the SWNT Fermi level in the vicinity of the CBE of Si (as discussed before). Under an applied reverse bias, the Fermi level and hence the number of electron-occupied states of the SWNT belt
moves to lower energies, opening up accessible states for photoexcited electrons to inject from Si into the SWNTs. From the CDoS, \( n(V_r) \) is calculated as

\[
    n(eV_r) = \int_{V_r=0}^{eV_r} \sum_{m,n} D_{m,n}(\epsilon) d\epsilon.
\]

\( n=\sum_{m,n} D_{m,n}(\epsilon) d\epsilon \) has been plotted in the same figure, as well as in figure 30d inset for comparison. It can be seen that despite the simple approach of this model, the shape of \( n(n(eV_r)) \) is quite consistent with that of our experimental photocurrent data, suggesting that the SWNT DoS plays a key role in determining the photocurrent response in these devices. We believe that a more accurate description of the CDoS, incorporating the atomistic interaction between SWNT/Si and SWNT/SWNT junctions (sidewall and end-end) can result in more quantitative insight of the behavior of these junctions.

Figure 30f shows the variation of photocurrent responsivity \( R=\frac{\text{photocurrent}(I_{ph})}{\text{incident power}(P)} \), the electrical ON/OFF ratio \( I_{p}(V)/I_{p}(V=0) \) and optical ON/OFF ratio \( =I_{p}(V)/I_{dark}(V) \) of the SWNT/Si junction. Commercial photometers using Si-based photodiodes have responsivities ~ few tens of mA/W in the visible region. In comparison, the maximum responsivity \( R_{max} \) obtained at a low reverse bias (-3V) exceeds 1A/W. Although there are a few reports on higher responsivities obtained in quantum-dot, quantum-well and other novel structures [160-162], the photocurrent responsivity obtained in our devices stands much higher than most past reports on a variety of photodetectors those on SWNT/Si junctions [26, 155]. In addition, the response is completely tunable between 0<R<\( I_{max} \) within using very low voltages, which is extremely useful for brightness adjustable imaging in variable-light conditions. Further, the low dark current and the incident power-independent low short-circuit currents coupled with this high responsivity at \( V=-3V \) results in high electrical ON/OFF ratio exceeding \( 2.5 \times 10^5 \), and optical ON/OFF ratios exceeding \( 10^4 \). Such high current-switching ratios are impossible to conceive in mixed-chirality
SWNT arrays using purely electrostatic (gate-voltage-induced) modulation, primarily due to the roughly 1/3rd number of metallic SWNTs always present in these arrays [163], in addition to screening of inner SWNTs of the array from the gate voltage by the outer ones. We show later that a combination of these factors, along with the robust scalability of our architectures can be utilized to develop a variety of highly reproducible analog and digital optoelectronic devices.

In comparison to photocurrent detection, a more energy-efficient method for photodetection is to measure the photo-induced open-circuit voltage, $V_{oc}$. This approach neither requires an external bias, nor consumes power through Joule-heating. These factors are critical for most scaled-up sensing devices such as a camera, which often operates on batteries or solar cells (as found in terrestrial sensors/cameras). Figure 30g shows the dark and $P=1\mu W$ IV curves in the SWNT/Si device. Under $1\mu W$ incidence, the open-circuit voltage shifts by an amount $\Delta V_{oc} = 113$ mV, which corresponds to a significantly large voltage responsivity of $R_V > 10^5$ V/W. Such a large photovoltaic response is about 4-5 orders of magnitude higher than past reports [164-167] on carbon nanotube and graphene-based photodetectors, making it extremely appealing for designing low-power/portable weak-signal detecting, imaging, and on-chip analytical photochemistry applications.

5.4 A Very-large Scale Sensor Array of SWNT-Si Hetrojunction

The robust structural scalability and functional reproducibility of the TGFA method was demonstrated by fabricating an array of 250,000 sensors on a $12\times12\text{mm}^2$ area $\text{SiO}_2$/Si chip, designed to mimic the front-end of a 0.25 Megapixel focal plane array. Each sensor contains an
Figure 31. Large scale sensor array and photocurrent map.

(a) Digital photograph of a 0.25 Megapixel array of SWNT/Si sensors (array area 12mm×12mm), shown with increasing levels of magnifications in (b) and (c). (d) SEM image of the “core” of the sensor, showing a circular window of Si in a SiO$_2$/Si substrate overlaid with SWNTs. Inset: SEM image of the SWNT packing on Si. (e) Scanning photocurrent map of a 2×2 pixel area of the sensor array, where the pixels were electrically attached to an external lead, while the back surface of Si was used as the second contact.

isolated 15×15 μm$^2$ TGFA-assembled SWNT film conformally overlaid onto a 5-μm-diameter Si window etched out of a 400-nm thick SiO$_2$ layer. Figure 31a-c shows digital photographs of one such sensor array at different magnification levels, highlighting the fault-free large-scale integration achievable using our technique. The dense, uniform coverage of the circular Si window without any stray suspended SWNTs or bubbles as seen in figure 31d is typical for all areas across the chip, and no structurally defective “sensor” could be found under random SEM
inspection of hundreds of sensors over the entire chip. Such a high degree of structural reproducibility is critical for large-area integration of sensors. We also note that such large-area uniform integration of high-density SWNT arrays arranged conformally over patterned, uneven surfaces is quite challenging to implement using conventional SWNT mat-preparation techniques such as spin-coating [168], drop-casting [169], contact transfer [143], ink-jet printing [170] or electrospinning [171]. Figure 31d shows a typical scanning photocurrent map of four pixels. We note that in this case, a background current subtraction was performed. Although each SWNT film was isolated, the underlying Si is continuous, which resulted in small but finite photocurrents in a sensor even when the light spot (d≈2.5μm) was a few tens of microns away. This effect is not expected to appear if the underlying Si is also segmented, as expected in a “real” device.

5.5 Optoelectronic Logic Devices based on SWNT-Si Hetrojunction

The low dark-current, high photocurrent responsivity and switching ratio obtained at low reverse-biases, coupled with the robust scalability and compatibility with conventional semiconductor down-scaling and processing steps of these architectures make these architectures highly appealing for novel on-chip analog and digital optoelectronic circuitry. The unidirectional photocurrent (i.e. only in the reverse-bias condition) is easily overcome by defining “interdigitated” SWNT belts connected to source and drain electrodes as shown in figure 32a. In this manner, two “back-to-back” photodiodes form a bidirectional phototransistor, as seen from the dark and photo-IV curve 3b. In darkness, the device remains switched OFF for applied voltages of either polarity, while under illumination, an ON state can be obtained for both positive and negative voltages. In this configuration, the device is an optoelectronic equivalent of
Figure 32. Phototransistor and AND gate based on SWNT/Si heterojunction.

(a) A bi-directional phototransistor using inter-digitated SWNT fingers attached to source-drain leads. (b) Typical IV curve obtained in such a device under dark and illuminated conditions showing photo-induced ON and OFF states. (c) An AND gate with optical and electrical inputs, and an electrical output. The inset tabulates a typical set of operating conditions determining the “low” and “high” logic states for both input and output conditions, as determined by the dark and photocurrents shown in (d). (e) Output of the AND gate for different input logic states as a function of time.

A symmetric MOSFET, where the gate voltage has been replaced by photons. Further, the applied voltage and incident light form two independent methods for controlling the channel current, both of which must be present to obtain an ON state. This feature allows one to construct a mixed-input optoelectronic AND gate, as described in figure 32c. Here, the light spot incident on the SWNT/Si junction (input 1 measured in μW) and the applied bias (V_{IN}) are the two logic inputs, while the measured current output I_{OUT} is the logic output. The optical and electrical ON
Figure 33. ADDER and 4-BIT optoelectronic D/A converter based on SWNT/Si heterojunction.

(a) Two identically fabricated SWNT/Si structures serving as independent optical inputs for an optoelectronic ADDER element. Two 650nm LASERs were used to independently address these two inputs. \( I_{\text{OUT}} \) is an analog electrical output signal which is proportional to the sum of the two digital inputs. Depending on the required operational condition, this element also doubles as an OR gate (see text). (b) \( I_{\text{OUT}} \) as a function of different input configurations changed as a function of time. The colored circles indicate the states (ON or OFF) of the two optical inputs. The output current shows a striking response-reproducibility for independent illumination of the two structures, as does the current doubling when both inputs are simultaneously illuminated. This response reproducibility is crucial in designing scalable optoelectronic architectures such as the 4-BIT Optoelectronic D/A converter shown schematically in (c). Here, each successive input has twice the number of (identical) SWNT belts (see text), corresponding to successive Bit-significance as shown. (d) Analog current output corresponding to digital optical inputs ranging from binary \( 0000_2 \) \((0_{10}) \) – \( 1111_2 \) \((15_{10}) \).

and OFF states for a typical device can be obtained for the dark and photo-IV curves as shown in figure 32d, and for convenience, has been tabulated in figure 32c. Figure 32e shows a typical
time-trace of the output state $I_{\text{OUT}}$, for different logic states of inputs 1 and 2, confirming its operation as a mixed optoelectronic AND gate.

Due to the highly reproducible responsivity in different junctions fabricated in the same batch, our “optical input – electronic output” devices are capable of operating with multiple optical inputs. Figure 33a shows a 2-Bit, digital-input, analog-output ADDER circuit, where the device performs a dual function of adding two digital input signals and provides an output which is an analog equivalent of the digital sum. Under appropriate logic conditions, this also serves as an OR gate, and these operations can be seen in the output time-trace for different input states in figure 33b. The high-fidelity adding operation can be extended to design more complex input bits by lithographically designing junctions with highly controlled surface areas. Figure 33c demonstrates a 4-Bit optoelectronic Digital to Analog converter. To achieve this conversion, 4 separate SWNT/Si junctions, with their junction area proportional to $2^0, 2^1, 2^2$, and $2^3$ were designed (by fabricating 1,2,4, and 8 parallel identical SWNT belts, respectively) to mimic the significant bits of a 4-Bit optical input, each of which could be independently illuminated (or kept dark), resulting in binary inputs, 0000 – 1111. The corresponding output current is proportional to the analog equivalent of these inputs, as seen in figure 33d. We note that using a circular laser spot on the parallel SWNT “lines” prevented us from exact area-multiplication. Nevertheless, we feel that as a proof-of-principle, the analog reproduction of the binary inputs is quite remarkable.
5.6 Conclusions

In summary, we report that the photoresponse of SWNT-Si heterojunctions fabricated using a template-guided fluidic assembly method shows that a nonlinear reverse bias photocurrent that increases sharply both with increasing photon flux as well as increasing reverse bias. These devices possess a radically unconventional photo-response that enables extremely high photo-induced ON/OFF ratios as high as $10^4$ with responsivity values of $\sim 1$ A/W as low as -3V. Remarkably large switching of photocurrents can be obtained due to their low dark currents, low short-circuit photo-currents and high photocurrent responsivity at low reverse biases. This photo-response allows us to develop a range of multifunctional optoelectronic switches, phototransistors, optoelectronic logic gates and complex optoelectronic digital circuits.
Conclusions

In this dissertation, the engineering highly organized and aligned SWNTs has been demonstrated for electronic devices applications such as interconnects, chemical sensor, and optoelectronic sensors. Those results were composed of a precisely controlled templated fluidic assembly technique and their electrical and optical properties based on the devices of SWNTs. Chapter 1 discussed the electronic structure and properties of SWNTs to understand basic physics. For 1D system on a cylindrical surface, translational symmetry with a screw axis could affect the electronic structure and related properties. A fabrication method for micro-to-nano scale patterned SWNT networks using a newly developed template guided fluidic assembly process was introduced. A mechanism for SWNT assembly and their control was also described. In order to maximize the directed assembly efficiency of SWNTs toward a wafer scale SWNT deposition, SiO$_2$ substrate was treated with controlled plasma treatments. As a result, hydrophilic chemical groups such as hydroxides were created on the silicon or silicon oxide surface through the controlled plasma treatment and fluidic SWNT dip-coating process. Nanoscale roughness of surface structures formed by plasma treatment increased the number of dangling bonds and hydroxide functional groups on the surface. These combinations of chemical and physical enhancements attracted SWNTs in the aqueous SWNTs solution. This technique enables us to make highly organized SWNT networks effectively in various dimensions and geometries. Moreover, we explored the effect of geometric confinement on the network topology fabricated by a template-assisted fluidic assembly of SWNT networks. Heterogeneous SWNT networks became increasingly aligned with decreasing channel width and thickness. Experimental-scale coarse-grained computations of interacting SWNTs showed that the effect is a reflection of a
topology that is no longer dependent on the network density, which emerges as a robust knob that can induce semiconductor-to-metallic transitions in the network response. In chapter 2, the nanoscale electrical interconnect test structures constructed from aligned single wall carbon nanotubes were fabricated and characterized. This process enabled the formation of highly aligned SWNT interconnect structures on SiO$_2$/Si substrates of widths and lengths that are limited only by lithographical limits. These structures had high current densities, which was comparable or better than copper at similar dimensions. The nanotube alignment and failure current density improved with decreasing width of the structure. We also presented a Pt-nanocluster decoration method that significantly decreases the resistivity of the structures with a possible conversion of the semiconducting SWNTs into metallic ones. A method was presented for significantly reducing the interfacial contact resistance of SWNT interconnect test-structures in chapter 3. Conventional lithographic cleaning steps remained to large interfacial contact resistance for the SWNT interconnect structures. With improved cleaning procedures and controlled experimental methods, the interfacial contact resistance between SWNTs and contact electrodes of Ti/Au were found to reach values below 2% of the overall resistance of SWNTs. These results demonstrated the importance of cleaning lithographic residues from the surface of SWNTs before the fabrication of metal electrodes. These low-resistance contacts are also quite stable over a large temperature range. In chapter 4, the effective detection of hydrogen sulfide gas by a redox reaction based on SWNTs functionalized with TEMPO as a catalyst was introduced. We also discussed the important role of water vapor on the electrical conductivity of SWNTs during the sensing of H$_2$S molecules. To explore the H$_2$S sensing mechanism, we investigated the adsorption properties of H$_2$S on CNTs and the effects of the TEMPO functionalization and we summarized current changes of devices resulting from the redox
reactions in the presence of H$_2$S. The semiconducting SWNT device functionalized with TEMPO showed very high sensitivity of 420 % at 60 % humidity, which is 17 times higher than a bare s-SWNT device under dry condition. Promising perspectives for personal safety and real-time monitoring of H$_2$S gases with highest sensitivity and low power consumption and potentially at a low cost were offered. Chapter 5 introduced optoelectronic devices in fludically-assembled single walled carbon nanotube/Si heterojunctions. These results showed an unconventional, voltage-tunable, sharply non-linear and extremely sensitive photo-response in, with photocurrent responsivity $>1$A/W, photovoltage responsivity $>10^5$ V/W, electrical ON/OFF ratios $>2.3 \times 10^5$ and optical ON/OFF ratios $>10^4$. The scalability of our technique was also demonstrated by fabricating an array of 250,000 micron-scale photo-active junctions covering a centimeter-scale wafer. Bidirectional phototransistors, and novel logic elements such as a mixed optoelectronic AND gate, a 2-Bit optoelectronic ADDER/OR gate, and a 4-Bit optoelectronic D/A converter were also presented. These photocurrent-tunable devices are highly attractive for low-cost, high-performance on-chip photodetection/imaging, photo-switching, and analog and digital optoelectronic circuitry.
Appendix A

Standard lab preparation of H$_2$S gas molecules

For generation of H$_2$S gas, ferrous sulfide (FeS, purchased from Sigma-Aldrich) was reacted with sulfuric acid. FeS(s) + H$_2$SO$_4$(aq) → FeSO$_4$(s) + H$_2$S(g). Because H$_2$S gas is denser than air, it is more convenient to collect it in a glass vial by downward delivery. The gas produced in a chemical reaction is passed through a delivery tube into the glass vial, where it sinks and pushes the air out of the top. Calculated volumes of the H$_2$S were then introduced in 1 L of a gas sensing chamber using a microliter syringe.

Gas detection using SWNTs (w/wo TEMPO) devices

10 mL of 99% pure s-SWNT and m-SWNT solutions (purchased from NanoIntegris Inc.) were dropcased on interdigitated finger electrodes. The solution was allowed to dry and was rinsed with water to remove surfactants until maximum current was recorded. After this step, the devices were exposed to TEMPO vapors for 15 min. The devices were then cooled down at room temperature and allowed to equilibrate for additional 30 min. For gas sensing, each device was carefully outgassed by joule heating under 10$^{-3}$ torr for 1hr in a sensing chamber followed by flow of dry N$_2$ gas. Gas chamber was then closed and pre-calculated amount of H$_2$S gas was introduced in it. To understand the effects of concentration of H$_2$S gas, the sensor devices were exposed to H$_2$S gas of 5, 10, 50, 100, and 200 ppm, respectively in the chamber with dry N2. To investigate the effect of H$_2$O on sensing of H$_2$S molecules, 100ppm H$_2$S gas was introduced in the presence of 20, 40 and 60 % RH. Changes in current were observed until it reached saturation. Once the current saturated, the chamber was exposed to dry N$_2$ for the sensor recovery.
Figure 34. Real time current changes of bare s-SWNT device exposed to H$_2$S gas of 5, 10, 50, 100, and 200 ppm in dry N$_2$.

Figure 35. The sensitivity of a bare m-SWNT device as function of the H$_2$S concentrations in dry N$_2$.
Figure 36. Real-time current measurement of a bare s-SWNT device as a function of RH. The current reaches almost its saturation value.
Figure 37. A bare m-SWNT device test with H$_2$O vapor and H$_2$S gas.

(a) Sensing of H$_2$O vapor by a bare m-SWNT device, (b) real-time current changes in a H$_2$S gas detection of bare m-SWNT device under different RH (20, 40 and 60 %). Here in the range of current reduction, red and green area mean injection of H$_2$S and H$_2$O molecules respectively, and increase of current indicates recovery into the initial current value of each RH. (c) Comparison of sensitivity as function of the RH in H$_2$O and H$_2$O+H$_2$S detection.
Figure 38. Real-time current drop of the s-SWNT device without TEMPO. (a) and with TEMPO (b) observed when only water vapor was introduced.

Figure 39. Real-time current measurement of s-SWNT device functionalized with TEMPO as a function of RH. The current reaches almost its saturation value.
Figure 40. A bare m-SWNT functionalized device test with H₂O vapor and H₂S gas.

(a) Sensing of H₂O vapor by a m-SWNT device functionalized with TEMPO, (b) real-time current changes in a H₂S gas detection of the m-SWNT+TEMPO device under different RH (20, 40 and 60 %). Here in the range of current reduction, red and green area mean injection of H₂S and H₂O molecules respectively, and increase of current indicates recovery into the initial current value of each RH. (c) Comparison of sensitivity as function of the RH in H₂O and H₂O+H₂S detection.
Appendix B

Fabrication and optoelectronic properties of SWNT/Si heterojunction

The SWNT solution was obtained from Brewer Science Inc. with the mean length of 610 nm and mean diameter of 1.1 nm. The solution composed of 0.23 wt % SWNT-DI water solution (CNTRENETM C100). A silicon wafer with 400-nm-thick SiO2 layer was obtained from the University Wafer. Half layer of SiO2 was etched by Buffered Oxide Etch (BOE) 10:1 solution for 9 min. to expose Si surface to form heterojunction between SWNTs and Si surface. Then, to improve the contact between the SWNT-deionized water solution and substrate, the substrate was pretreated using an Inductively-Coupled Plasma (ICP) with mixed gas flow of O2 (20 sccm), SF6 (20 sccm), and Ar (5 sccm). The substrate was then spin-coated with a photoresist film and patterned with trenches using an optical lithography. Patterned substrate was vertically submerged into the SWNT-DI water solution using a dip-coater and gradually lifted from the solution with a constant pulling speed of 0.1 mm·min⁻¹. Two dip-coating processes with 180 degree rotation were applied to make a better coverage of SWNTs along with the trenches. After this assembly process, a photoresist film was removed in acetone and rinsed in DI water. Then, the substrate was dried with nitrogen. For electrical characterization, contact pads were fabricated on the surface of SWNTs and oxide substrate using an optical lithography and Ti (5 nm)/Au (150 nm) deposition followed by a lift-off process. To make Ohmic contact between Ti/Au and Si surface in area of NO SWNTs, Si surface was scratched gently right before the deposition of Ti/Au electrodes (see Figure 30(b)). The electrical characterization was conducted using a Janis ST-500 electrical probe station connected to an Agilent 4156C precision semiconductor parameter analyzer.
Figure 41. Optical properties in heterojunction between SWNTs and Si.

(a) Compare to a typical Schottky junction photodiode as seen in Figure 30(a) measured between leads A and C where, the reverse photocurrent remains almost independent of increasing reverse bias, similar to that seen in p-n junction diodes. (b) IV curves measured between leads B and C in Figure 30(a) at different optical powers. (c) Absolute forward and reverse bias current density under the different incident powers. (d) ON/OFF ratios at different optical powers and reverse bias values.
Fabrication of a very-large scale sensor array of SWNT-Si hetrojunction

The 400-nm thick SiO$_2$ substrate was spin-coated with a photoresist film and patterned with dot using an optical lithography. With the first mask process, an array of 250,000 holes (500 by 500) on a 12×12mm$^2$ area SiO$_2$/Si chip was made to open the Si surface window for the assembly of SWNTs. Patterned chip was etched by BOE 10:1 solution for 9 min. to expose Si surface to form heterojunction between SWNTs and Si surface (see Figure 42(a and b)). Then, to improve the quality of assembly of SWNTs, the substrate was pretreated using the same plasma treatment described above. Next, the second mask process was conducted for the SWNTs assembly followed by another optical lithography (see Figure 42(c and d)). Patterned substrate was vertically submerged into the SWNT-DI water solution using a dip-coater and gradually lifted from the solution with a constant pulling speed of 0.1 mm·min$^{-1}$. Four dip-coating processes with 90 degree rotation each time were applied to make a good coverage of SWNTs along with the square patterns (see Figure 42(e and f)). After this assembly process, a photoresist film was removed in acetone and rinsed in DI water. Then, the substrate was dried with nitrogen.

For the metal electrodes, the third mask process was conducted by another optical lithography to open a boundary area between SWNTs and SiO$_2$ surface (see Figure 43(a and b)). Then, contact pads were fabricated on the surface of SWNTs and oxide substrate with Ti (5 nm)/Au (150 nm) deposition followed by a lift-off process (see Figure 43(c and d)). With all mask processes, an array of 250,000 holes on a 12×12mm$^2$ area SiO$_2$/Si chip, designed to mimic the front-end of a 0.25 Megapixel focal plane array was fabricated (see Figure 31(a)). Each sensor contains an isolated 15×15 μm$^2$ assembled SWNT film overlaid onto a 5-μm-diameter Si window etched out of a 400-nm thick SiO$_2$ layer.
Figure 42. Optical and SEM images of a very-large scale sensor array.

(a and b) Optical images of etched Si surface with 5 µm diameter holes (green color: SiO₂, gray color: Si). (c and d) Optical images after the first mask process (green color: photoresist, purple color: SiO₂, orange color: Si surface). (e and f) SEM images after assembly of SWNTs.
Figure 43. Optical images of assembled SWNTs and electrodes.

(a and b) Optical images after the second mask process for electrodes (green color: photoresist, purple color: SiO$_2$, blue color: SWNTs). (c and d) Optical images with electrodes of Ti/Au (yellow color: Au, purple color: SiO$_2$, assembled SWNTs on holes).

Figure 44. Tested sensor array images for a Raman mapping measurement.
Figure 45. G-band intensities using a Raman mapping process corresponding to 2 by 2 sensor array. These Raman mapping processes were matched in Figure 31(c and e).
Bibliography


