FLUIDIC ASSEMBLY OF HIGHLY ORGANIZED SINGLE-WALL CARBON NANOTUBES IN NANO AND MICRO SCALES - CHARACTERIZATION AND INVESTIGATION OF THE ASSEMBLY MECHANISM

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Laila Jaber-Ansari

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# TABLE OF CONTENTS

ABSTRACT .......................................................................................................................... 6

1 INTRODUCTION ........................................................................................................... 8

2 EXPERIMENTAL PROCEDURE ................................................................................. 11

3 MECHANISM OF FLUIDIC ASSEMBLY ................................................................. 19

4 CHARACTERIZATION AND ELECTRICAL MEASUREMENT OF THE SWNT
STRUCTURES .................................................................................................................. 31

5 CONCLUSIONS ........................................................................................................... 41

6 FUTURE WORK OPPORTUNITY .............................................................................. 42

7 REFERENCES .............................................................................................................. 43
LIST OF FIGURES

Figure 1 schematic of the template preparation process and the assembly method. ....... 12

Figure 2. SEM images of the assembled SWNT structures in the 3 inch wafer............ 14

Figure 3. SEM images show diverse organized SWNT architectures fabricated using template guided fluidic assembly process................................................................. 15

Figure 4 Template assisted fluidic assembly of SWNTs in micro- and nanoscale arrangements................................................................. 18

Figure 5 Contact angle analysis for SWNT suspensions on diverse substrates............ 20

Figure 6. Contact angle change vs. time on the same substrates. ............................ 21

Figure 7. Raman shifts of 5 s and 90 s plasma treated Si substrates after 5 min rinse in water......................................................................................................................... 23

Figure 8. Effect of plasma treatment on the surface morphology of Si ..................... 24

Figure 9. Large XPS spectrum of 5 s and 90 s SF₆/Ar/O₂ plasma etched silicon before and after water treatment. ................................................................. 26

Figure 10. Deconvolution of narrow scan XPS spectra of Si 2p peak................. 29
Figure 11. Deconvolution of narrow scan XPS spectra of O 1s peak.............................. 30

Figure 12. I-V curve resulting from the 4-probe measurement. ................................. 32

Figure 13. AFM images of the 3D profile and Raman spectra of the assembled structures in trenches of different widths. ................................................................. 34

Figure 14. I-V measurements for different trench width measured at various locations of the 3 inch wafer................................................................................................................. 35

Figure 15. SEM images of the broken SWNT structure with different width after applying current densities higher than the maximum current capability of the structures .......... 37

Figure 16. Contact resistance of the assembled SWNT structures with different width. 38

Figure 17. Schematic diagram of the fabricated transistors............................................. 39

Figure 18. Typical plot of I_{DS} as a function of V_G for the SWNT structures............... 40
ABSTRACT

I present the liquid-phase fabrication of highly organized single-walled carbon nanotube (SWNT) networks. Using lithographically patterned template assisted dip coating method, SWNTs are directly assembled into pre-designed micro- and nano-scale 1805 and poly methyl methacrylate (PMMA) channels forming densely packed SWNT lateral networks in diverse geometries with pattern width ranging from 150 nm to 10 µm. The nanotubes also become highly aligned as 1805/PMMA template channel width shrinks, leading to a better control of assembled SWNT morphology. Very large scale patterned SWNT networks were also fabricated. Chemical and physical properties of the substrate were characterized using several surface characterization techniques to investigate and control the mechanism of SWNT assembly. We found that 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. Also we found that nanoscale rough surface structures formed during the plasma treatment significantly increased the number of dangling bonds and hydroxide functional groups on the surface. These combined chemical and physical enhancements that attract the SWNT in the aqueous solution enable us to build highly organized and very large scale SWNT network architectures effectively in various dimensions and geometries. Room temperature, two
and four probe I-V characterization of fabricated high coverage SWNT wires shows linear ohmic behavior. This work provides a simple and flexible way of building nanotube-based electronics in a variety of dimensions with high-rate.

**KEYWORDS:** Assembly mechanism, Surface properties, Single-walled carbon nanotubes.
1 INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991, extensive studies have been carried out on their properties and methods to exploit them. SWNTs have specially attracted significant interest due to their one-dimensional nanostructure and unique electrical and mechanical properties. They offer potential to serve as building blocks for future electronic devices such as field emission displays (FEDs), field effect transistors (FETs), sensors and actuators. The most essential prerequisite for realizing this goal is to be able to place nanotubes at desired locations, in predetermined orientations and to form stable interconnections in a large scale. A few approaches have been reported to assemble SWNTs using chemical functionalization, electrophoretic deposition (EPD), or dielectrophoresis (DEP). DEP has the advantage of fabricating highly oriented nanotubes between electrodes, but is only effective within local areas where the electric-field is maximum.

Extensive attempts have been made to make aligned arrays of nanotubes in order to improve their properties. In several applications however, horizontally aligned nanotubes seem to be more pertinent. For example, microelectronic applications often demand to make horizontal interconnections between components or horizontally aligned
CNT field emitters demonstrate higher stability and uniformity than vertically aligned ones\textsuperscript{27}.

It also has been demonstrated that capillary force can be used to produce well-controlled, ordered nanoparticle structures in trenches,\textsuperscript{28,29} but the assembly of SWNTs in relief structures is more difficult due to the high aspect ratio of individual nanotube or bundles. In this work, we present surface controlled microfluidic approach for fabricating highly organized SWNT networks in various dimension and geometries using template assisted dip coating method.

The fluidic assembly of SWNTs could 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 can fulfill their potential applications such as active elements in transistors, horizontal interconnect systems, and sensors. However there has been no clear explanation for the mechanism of this site selective assembly of SWNTs and control for the very large scale assembly. Here we report the results of a study that clearly elucidate the role of chemical and physical surface properties for the assembly of SWNTs and their control toward building highly organized SWNT network architectures on a wafer level.

Our developed SWNT assembly technique has three remarkable features. First, without resorting to complex wet chemical functionalization of the substrate, tailoring the hydrophilic property of a substrate enabling effective SWNT attachment to the predefined locations can be obtained using a simple dry plasma treatment on the photoresist patterned silicon or silicon oxide substrates. This process is important in
achieving a uniform and dense coverage of SWNT films on the desired trench areas. Second, the SWNT distribution within trenches relies on the orientation of trench axis with respect to the liquid-air contact line and the hydrophobic/hydrophilic properties of the patterned substrate. Therefore it is possible to control alignment and orientation of assembled SWNTs effectively. Third, produced micro- and nano-scale SWNT networks can be directly used as interconnect wires, diverse sensing elements, and other active components in electronic devices. In addition, our approach is compatible to current complementary metal oxide semiconductor (CMOS) process and can be easily scale up towards high rate and high volume process.


2 EXPERIMENTAL PROCEDURE

For the assembly of SWNTs into horizontally organized network architectures, we used 0.23 wt% SWNT-deionized (DI) water solution (obtained from Nantero Inc.) with the SWNT’s length of 2-3 µm. The utilized SWNTs were terminated with carboxylic acid groups partially dissociate into H⁺ cations and COO⁻ anions in the aqueous solution leading to the presence of a net negative charge on the surface of SWNTs. In order 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 (20sccm), SF₆ (20 sccm) and Ar (5sccm). Then a photo/e-beam resist film on the Si or SiO₂ substrate was patterned using optical or electron-beam lithography techniques and vertically submerged into the SWNT solution using a dip-coater and then gradually lifted from the solution with a constant pulling speed, 0.1 mm/sec. The schematic diagram of the fabrication process is shown in Figure 1. To characterize physical property of template surface and their role for SWNT assembly, Scanning electron microscopy (SEM), Raman spectroscopy, and Atomic force microscopy (AFM) were used. To investigate chemical properties of template surface and their role for SWNT assembly, a
contact angle measurement system and X-ray photoelectron spectroscopy (XPS) were employed.

**Figure 1** schematic of the template preparation process and the assembly method.

Figure 2 is a representative of optical and SEM images of patterned SWNT network structures fabricated on the 3 inch wafer using the above mentioned template guided fluidic assembly process. It is clearly seen that SWNTs are assembled only on open areas such as Si or SiO₂ (negative patterns of photoresist) and form highly organized arrays precisely occupying predesigned shapes and sizes (1 µm-10 µm). One of the most important features of our developed assembly process is that effective micro- and nanoscale SWNT assembly resulting in very large scale SWNT network architectures is accomplished using a simple dry plasma treatment to change the surface property of patterned silicon or silicon dioxide substrates into hydrophilic without the need to resort to complex wet chemical functionalization processes. Figure 2(c) shows the assembled SWNTs demonstrating a robust network that can be bent or folded without damaging their assembled structures (SWNT networks in this figure were bent and folded by strong blow-drying of nitrogen gas). It also indicates that patterned SWNT networks don’t have
a very strong bonding with the substrate and can be removed easily and therefore shows strong potential to be transferred to other substrates. (Possible future work in this area includes the investigation of the transfer mechanism of these structures and the nature of the broken bonds).

The assembly of SWNTs was also possible in different shapes such as crossbar architectures. Figure 3 shows the SEM images of highly defined microscale crossbar architectures consisting of SWNTs before and after PMMA removal, respectively. The building of such a complex SWNT-based lateral architecture has been achieved simply by making a PMMA pattern and performing site-selective assembly of SWNTs on the opened hydrophilic surface of silicon oxide while leaving few or no nanotubes on hydrophobic PMMA areas.
Figure 2. SEM images of the assembled SWNT structures in the 3 inch wafer with pattern widths of (a) 3 μm, (b) 9 μm and (c) Bent and folded structures of assembled SWNTs showing the robustness of these structures.
Figure 3. SEM images show diverse organized SWNT architectures fabricated using template guided fluidic assembly process. (a) A crossbar network of SWNTs on a PMMA patterned silicon oxide substrate, where few nanotubes are deposited on the PMMA islands (square parts). (b) The same crossbar SWNT networks (Figure 3a) after removing PMMA patterns.

Apart from large scale assembly of SWNTs, assembly in nano scale is also possible using our fluidic method. Figure 4 shows detailed characteristics of SWNT assembly in liquid phase template assisted process. 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 4a). This interesting phenomenon can be explained by studying the three phase liquid-air-solid contact line passing over two different patterned regions as shown in the schematics (Figure 4b). It is well known that when droplets containing particles or carbon nanotubes are dried on a flat substrate, ring-like structures are usually formed due to the migration of nanoelements toward the three phase contact line at the perimeter of liquid dome\textsuperscript{30,31}. Similarly, if the substrate is patterned into areas having different wetting (hydrophilic/hydrophobic) properties, 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. As a thin liquid film attached in the trenches start to evaporate, the contact receding lines in trenches will move downward during the dip-coating process, and SWNTs tend to migrate upward along the trenches towards the three phase contact line. Therefore, the concentration of SWNTs submerged in the lower liquid domain becomes less due to this unidirectional migration, which could result in a depletion of SWNTs in the solution before the liquid is completely dried, thereby leaving the bottom part of the trenches uncovered. 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 4c 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 following the mechanism as mentioned before, while the trench areas that are covered with SWNTs may have less affinity to new nanotubes during the second dip-coating process. Figure 4d shows similar SWNT assembly on silicon oxide substrate. The AFM measurements on both the top and bottom trenches yield no obvious difference in the film thickness, confirming our prior assumption on the SWNT film uniformity. In our experiment, we also note that the SWNT coverage along the trenches parallel to the pulling direction is higher than the perpendicular ones (figure is not shown in here). A previously studied combing mechanism for CNT and DNA\textsuperscript{19,32} shows that the rode-like nanocomponents can be oriented parallel to the flow direction, which will favor the assembly of CNTs in trenches parallel to pulling direction. To improve the assembly of SWNTs in trenches with varied orientations (e.g. crossbar structures), a multiple dip-coating process is preferred with a rotation angle corresponding to the specific trench orientations. The effect of the trench widths on the SWNT alignment is investigated using trenches of a few hundred nanometers wide. Figure 4e-f show well aligned SWNTs inside PMMA trenches of a few hundred nanometers wide. From SEM observation, we find that the degree of SWNT alignment dramatically increases as the size of trenches decreases, especially in submicron scale. We do not yet have a full understanding of the self alignment mechanism of SWNTs in this liquid phase deposition method. However, the SEM results show that nanometer scale trenches combined with strong capillary force and pulling direction, parallel to trench axis, enable highly aligned SWNT assembly along the geometries of patterns.
Figure 4 Template assisted fluidic assembly of SWNTs in micro- and nanoscale arrangements. (a) microscale assembly by vertically dip-coating the PMMA template in SWNT suspension only once. (b) schematic illustration of SWNT migration and assembly in trenches by capillary induced flow. (c) Complete SWNT assembly on silicon substrate showing both ends of PMMA trenches covered with nanotubes by performing dip-coating process twice. (d) SWNT assembly on silicon oxide substrate after PMMA trench templates being removed. (e) and (f) Well oriented SWNTs assembled in submicron PMMA trenches.
3 MECHANISM OF FLUIDIC ASSEMBLY

The effect of plasma treatment on the wetting behavior of SWNT solution on various types of substrate by measuring the contact angle between them was investigated (Figure 5). The contact angles of SWNT droplet on untreated silicon or silicon oxide substrate ranged between 30 ° to ~40 °, and 72 ° on PMMA (Figure 5 (a-1), (b-1) and c). After plasma (SF₆/O₂/Ar) treatment, the change in contact angle on different substrate varies. The contact angle on the oxide surface experienced little change (Figure 5 (a-2)), while that on the silicon surface is reduced by around 42% as shown in Figure 5 (b-2). However, after flushing the silicon or silicon oxide substrate in DI water for a few seconds and have the surface dried, the contact angles on both substrates decreased to nearly zero. Almost complete wetting behavior was observed as shown in Figure 5 (a-3) and (b-3).
Figure 5 Contact angle analysis for SWNT suspensions on diverse substrates. (a-1) SWNT droplet on SiO₂ substrate before (SF₆/O₂/Ar) plasma treatment. (a-2) SWNT droplet on plasma treated SiO₂ surface. (a-3) complete wetting behavior of SWNT droplet on plasma treated water flushed SiO₂ surface. (b) the wetting behavior of SWNT droplets on Si surface under similar conditions as described in (a). (c) The hydrophobic behavior of SWNT droplet on PMMA surface (contact angle =72 º).

As was mentioned before, 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(a) shows the results of the contact angle (Θ) measurement right after dropping the SWNT-DI water solution on silicon substrates treated with different plasma time (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 (0º) 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 gradually changed to 0°. Figure 6(b) 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.

![Figure 6](image)

**Figure 6.** (a) Contact angle (Θ) measurement of Si substrate after 5, 30, 60, and 90 seconds of SF₆/O₂/Ar plasma treatment. (b) Contact angle change vs. time on the same substrates.
To characterize the nature of the Si surface changes further as a result of plasma treatment, we used Raman spectroscopy with 443 nm line of HeNe 20 mW laser for excitation on these plasma treated substrates. Figure 7 shows Raman bands of bare and plasma treated (5 and 90 sec) silicon. The maximum intensity in Silicon Raman spectra was achieved after 5 sec plasma treatment. The enhanced Raman scattering from silicon surface of different structures has been reported in the literature. Baroult et al. performed in situ Raman on silicon substrate subjected to SF$_6$/Ar plasma and they reported enhanced Si Raman peak as the result of roughness due to plasma treatment. The enhancement of Si peak (at 521 cm$^{-1}$) can be explained by electromagnetic cavity resonance as a result of the matching of the frequency of the incident field with that of an electromagnetic eigenmode of the surface particles, leading to an increase in both inelastic and elastic scatterings.
Figure 7. Raman shifts of 5 s and 90 s plasma treated Si substrates after 5 min rinse in water showing the enhanced Raman peaks resulting from plasma treatment; The inlet shows the magnified Raman peak of the untreated silicon substrate.

SEM and AFM results for the 5 sec plasma etched sample [Figure 8 (b1)] shows nano-structures on the surface of silicon were 50 nm wide and 5 nm high but the 90 s plasma etched sample [Figure 8 (c1)] shows surface structures of around 400 nm wide with a height variation of about 5 nm over that area where as 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 8 (b2 and c2)]. These results are in complete agreement with Raman
spectra showing an enormous increase in roughness after 5 sec plasma etching treatment [Figure 8 (b1 and b2)] and then diminishing of the surface roughness with further etching of the substrate [Figure 8 (c1 and c2)].

Figure 8. Effect of plasma treatment on the surface morphology of Si (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.

Although the Raman and 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. To acquire a better understanding of the latter, we performed XPS on the plasma etched silicon surface. The XPS experiments were performed on a KRATOS Analytical
spectrometer using Mg kα (1253.6 eV). Narrow scan spectra of all regions of interest were recorded with 160 eV pass energy in order to identify the elemental bonding states. Figure 9 shows a large XPS spectrum acquired with low resolution of plasma etched and water treated silicon substrate. The XPS analysis shows that the surface layer of samples after exposure to SF6/Ar/O2 plasma consists mainly of silicon, oxygen and fluorine and a small amount of carbon. Analysis of silicon XPS required correction of spectral energy scale due to specimen charging. The binding energy was aligned such that the C 1s line from adventitious carbon contamination is at 284.8 eV. The fluorine amount at the surface after plasma treatment is much larger for the 5 sec plasma treated sample (about 7% of surface atoms) compared with 90 sec plasma treated silicon (less than 1% of surface atoms). The fact that fluorine peaks vanish after rinsing both samples in water shows that the Si-F bonds that formed are easily replaced by Si-OH groups in the presence of water. The F terminated surface is electrically polarized, and the water molecule is also polar. Hence, the interaction of the H-OH with the F-terminated surface results in the formation of a stable adsorption structure due to the Coulomb attraction between the H atom of the water and the F atom on the surface. This leads to the breaking of the Si-F bond and the formation of the Si-O bond. This replacement can be observed in the XPS spectra where the fluorine disappearance is correlated with the increase in the intensity of oxygen peaks in the water treated sample.
Figure 9. Large XPS spectrum of 5 s and 90 s SF$_6$/Ar/O$_2$ plasma etched silicon before and after water treatment. The fluorine peak that is observed after plasma treatment, vanishes with rinsing the sample in water.

Figure 10 represents the narrow scan spectra of silicon 2p after 5 s and 90 s plasma etching. The data processing included a background subtraction by Tougaard method and curve deconvolution using Gaussian-Lorentzian mixture ratio. The peak attribution, binding energy, FWHM and percent of total area (contribution of several bonds to the integrated peak) are listed for each sample. The Si 2p spectrums can be resolved into Si-Si, Si-O/F and SiO$_2$. The silicon peaks at 103.8 and 103.7 eV for 5 s and 90 s plasma etched samples are in Si$^{4+}$ peak range and can result from normal Si-O bond in SiO$_2$ [Figure 10 (a and b)]. The peaks at 102.0 and 101.8 eV for these samples however, mean incomplete oxidation of silicon (Si$^{2+}$ and Si$^{3+}$) and the Si-O bonds contain a small
quantity of Si-F bonds because some fluorine was revealed to bind to silicon in F 1s spectrum. After rinsing the specimens in DI water [Figure 10 (c and d)], the fluorine will be replaced by oxygen and hydrogen atoms. The peaks at 103.2 and 102.9 can belong to Si-OH and SiO (Si\textsuperscript{+}), SiO (Si\textsuperscript{2+}) or Si-O-OH (Si\textsuperscript{3+}). The narrow scan spectra of the Si 2p showed that Si-O, SiO\textsubscript{2} and Si-F bonds exist on the surface of the silicon after plasma treatment. The 90 sec plasma etched sample however has fewer amounts of Si-F bonds since Figure 9 shows a small amount of fluorine existing on its surface.

The O 1s spectrums for these samples after immersing in DI water are represented in Figure 11. The oxygen peak for the 5 s plasma etched specimen can be deconvoluted into three peaks. The peak position of O-Si bonds in SiO\textsubscript{2} for O 1s spectra can vary from 533.0 to 534.3 eV\textsuperscript{37}. Therefore the 533.5 peak for the 5 s plasma etched sample can be an indication of those bonds. The 532.6 peak however, shows the bonding of oxygen with both silicon and hydrogen and therefore hydrophilic hydroxide OH\textsuperscript{-} groups. We observed that such peak doesn’t exist in the specimen after increasing the plasma time to 90 s (Figure 11 b) but the SiO\textsubscript{2} peak, shifts to lower energies that can indicate a small amount of Si-OH bonds. The incomplete bonding between silicon and oxygen shows that a lot of dangling bonds exist on the surface after plasma treatment that can enhance the hydrophilicity of the silicon surface. Due to higher roughness and higher amount of broken bonds, 5 second plasma treatment was chosen to functionalize the surface of silicon and silicon dioxide samples for self assembly of SWNTs.

This shows that a lot of dangling bonds exist on the surface of this substrate along with hydrophilic OH\textsuperscript{-} groups and hence the reason to hydrophilicity of such substrate. Therefore the highly increased surface area of the 5 s plasma treated silicon along with
the large number of hydrophilic groups lead to immediate change of surface to hydrophilic during contact angle measurement (Figure 6); in 90 s plasma treated sample, however, it takes longer for the surface to become hydrophilic due to lower concentration of OH⁻ groups and smaller surface area.
Figure 10. Deconvolution of narrow scan XPS spectra of Si 2p peak for (a) 5 s plasma
(b) 90 s plasma
(c) 5 s plasma + water
(d) 90 s plasma + water
treated (b) 90 s plasma treated (c) 5 s plasma treated and rinsed in DI water (d) 90 s plasma treated and rinsed in DI water silicon.

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Figure 11. Deconvolution of narrow scan XPS spectra of O 1s peak for (a) 5 s plasma treated silicon (b) 90 s plasma treated silicon, both after rinsing in DI water.
4 CHARACTERIZATION AND ELECTRICAL MEASUREMENT OF THE SWNT STRUCTURES

For the characterization of the assembled SWNT structures we performed SEM, AFM and four probe I-V measurements. Figure 12(a) shows 9 µm wide SWNT patterns with gold pads on them for resistivity measurement. AFM showed that these structures have an average height of 25 nm [Figure 12(b)]. This value was used in resistivity calculations. The resistance of the 9 µm wide SWNT bundles was measured with a Keithly current/voltage supply using a four probe setup to eliminate the contact resistance. Figure 12(c) shows that the measured I-V curve has a linear behavior. The resistivity of these structures was found to be $3.7 \times 10^{-6} \, \Omega\cdot m$. 
Figure 12. (a) 9 µm wide assembled SWNT structures with 50 nm gold pads on them for resistivity measurements, (b) Three dimensional AFM image of a 11×11 µm² area and (c) I-V curve resulting from the 4-probe measurement.

AFM and Raman spectroscopy was carried out to determine three dimensional profiles of the SWNT structures, the nature of the SWNTs and the uniformity of assembly over the whole wafer. The results are shown in Figure 13. It is interesting to note that the assembly over the width of the trench is not uniform and that at the edges of the structures the height of the assembled SWNT was more than that in the middle of the structure. The capillary action in the structures and the hydrophilicity of the substrate result in the formation of the concave meniscus driving most of the SWNTS towards the edges. From the AFM images in Figure 13, one can observe that for larger structures the
thickness of the assembled SWNTs is lower than that of narrow structures. This can be correlated to the concentration of the SWNTs in the solution and fact that the diffusion rate is the same for SWNTs assembly in all of these structures.

Raman spectroscopy for the radial breathing mode (RBM), D-band and G-band was carried out on these assembled structures at various locations in the wafer. RBM mode revealed that the SWNTs have diameters from 0.71nm to 1.42nm, while the D band for these was consistent over the whole wafer. The G-band spectrum of these samples revealed that the assembled bundles comprises of both semiconducting and metallic SWNTs.

In spite of these observations, the electrical measurements carried out on these structures showed linear ohmic behavior indicating that the electrical conduction is dominated by the metallic SWNTs. Employing percolation theory it has been shown that if the density of the assembled SWNTs are above a critical threshold, then metallic conduction dominates while below the critical threshold the conduction is mainly semiconducting. In all of our structures the density of the assembled SWNTs remained above the threshold and hence yielding metallic conduction properties. I-V measurements carried out across various locations of the wafer for different widths are shown in figure 4. It is clear that the conduction properties varies by less than 10% of the mean value for the 3µm and 9µm structures while for the 1µm structure this variation is in the order of 30%. The calculated resistivity of the assembled SWNTs structures from electrical measurements were in the orders of 10−6Ω m which is similar to the reported conductivity of SWNT bundles with metallic property.
Figure 13  Shown in figure are the AFM images of the 3D profile and Raman spectra of the assembled structures in trenches of different widths. The RBM mode of the Raman spectra taken at various locations of the 3 inch wafer reveals that the diameter of these SWNTs are between 0.71nm and 1.42nm, while the G and D band shows that they are composed of both semiconducting as well conducting carbon nanotubes. (a) SWNT assembly in a 9μ wide trench. The cross-section morphology of the assembled structure shows that the height of the assembly is ≈ 7nm. b) SWNT assembly in a 3μm wide trench. The cross-section morphology of the assembled structure shows that the height of the assembly is ≈ 16nm and (b) SWNT assembly in a 1μ wide trench. The cross-section morphology of the assembled structure shows that the height of the assembly is ≈ 34nm.
Figure 14 Shown are the I-V measurements for different trench width measured at various locations of the 3 inch wafer. (a) 9µm wide trench, (b) 3µm wide trench and (c) 1µm wide trench. (d) Shown is the plot of resistance and resistivity of these assembled SWNTs as a function of width. The calculated resistivity is in the range of µΩm. (e) The SEM image of the measured devices.
Our first impression, when dealing with the resistivity measurement of these structures, was that the narrower SWNT structures will have higher conductivity due to higher alignment of the carbon nanotubes. In other words, since the charge transport properties are better along the length of each nanotube than between entangled nanotubes, we expected that nano size structures that have higher alignment (Figure 4 e and f) will lead to lower resistivity. Our measurements (Figure 14 d) however showed that the wider structures (9 µm) had lower resistivities than narrower structures (1 µm and less). If the applied voltage is high enough, these assembled structures can break down due to the increase of current density to a value higher than the maximum current density that the device can endure. This maximum current density depends on several factors like defects in the structure or the quality of the assembly (density and alignment of the SWNTs). For our structures the maximum voltage varied between 1 to 5 V at the breaking point. shows the SEM images of these broken structures. As we can see in this figure, in wider patterns (9 µm), the path of the breakage is clearly marked. This means that the current will not pass uniformly through the structure. In other words the current can chose the lowest resistant path and therefore these structures show a lower resistivity. The narrow structures like the 500nm wide structure that is shown in Figure 15 (b) is not wide enough to have a preferable low resistivity path and therefore the current must pass through the whole structure. This can be one reason why the narrower structures show higher resistivities despite their better CNT alignment. Another reason can be defects in the assembled structures. In the dip-coating process, as the width of the channels decrease, the wet ability of the bottom of the trenches become harder and therefore the assembled
structures may result in more defects such as discontinuities or low density areas that obviously have higher resistivities.

Figure 15 SEM images of the broken SWNT structure with different width after applying current densities higher than the maximum current capability of the structures (a) 9 µm wide structures and (b) 500 nm wide structures.
It is necessary to mention that 50 nm of gold was deposited (using an e-beam evaporator) as the metal contacts for electrical measurement of these structures. The contact resistance of these structures varies with the width of the CNT structures. Figure 16 shows the relationship between the contact resistance and the size of these SWNT bundles.

![Graph showing contact resistance vs. structure width]

**Figure 16** Contact resistance of the assembled SWNT structures with different width.

We measured the Field Effect Transistor (FET) properties of the SWNT structures. Figure 17 shows the schematic diagram of these transistors. The gate voltage was applied from -20 V to 20 V to these structures and the $I_{SD}$-$V_{SD}$ curve was plotted. For the wide SWNT structures (more than 1 µm wide), no significant split was observed in the $I_{SD}$-$V_{SD}$ curve with the change of the gate voltage. For trenches narrower than 1 µm however, the structures show some FET properties.
Figure 17 Schematic diagram of the fabricated transistors.

The FET measurements show that the narrower structures show better transistor properties. This can be due to the alignment of the carbon nanotubes or because of the fact that narrower channels result in a less dense structure and therefore the semiconducting properties will be dominant.
Figure 18 Typical plot of $I_{DS}$ as a function of $V_G$ for the SWNT structures with widths of (a) 1µm, (b) 500nm and (c) 200nm.
5 CONCLUSIONS

In conclusion, we have assembled SWNTs into various geometries and sizes using a template assisted liquid phase self-assembly technique. Also by using plasma treatment, further controlled hydrophilic/hydrophobic properties of silicon and silicon oxide substrates are obtained. We found that 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. Also nanoscale rough surface structures formed during the plasma treatment significantly increased the proximity of hydroxyl functional groups on the surface. These combined chemical and physical enhancements that attract the aqueous SWNT solution effectively enable us to build highly organized and very large scale SWNT network architectures in various dimensions and geometries. This method provides simple and effective way to build highly organized SWNT based lateral architectures in a large scale with high-rate. Also these assembled SWNT based networks are stable and metallic in their electrical characteristics due to the high density SWNT assembly. These structure and their properties has immediate and immense implications for the development of carbon nanotube based interconnect systems and diverse electro-mechanical devices.
6 FUTURE WORK OPPORTUNITY

The fabricated devices and structures in this project have many interesting properties. Not all of these properties have been investigated during this project and many opportunities for further research are still available. Some of the titles for further research that I propose are:

- Electrical measurements in different temperature
- Doping of the SWNT structures and improving the FET characteristics
- Transfer of the SWNT structures to flexible plastic substrates such as PMMA and PDMS for application in flexible electronics
- Testing of the mechanical properties of these structures
REFERENCES


40. F. Kreupl, et al., *Microelect Eng.* 64, 399, **2002**.