HIGHLY ORGANIZED SINGLE-WALLED CARBON NANOTUBE–POLYMER HYBRID ARCHITECTURES

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Abstract:

Single-walled carbon nanotubes (SWCNTs) are the ideal building blocks for the functional unit in next generation flexible and transparent electronics due to the combination of superior electronic transport and mechanical properties. Even though remarkable progresses have been made towards the assembly and transfer technologies of SWCNTs, highly controllable and affordable SWCNT-polymer hybrid system is still largely exclusive, due to the difficulties in achieving two most important requirements: i) miniaturized functional unit with deliberately controlled properties and ii) high-rate and large scale integration technologies to construct the functional unit into or onto flexible, transparent and insulating polymeric substrates at desired location with prescribed orientation. In this study, highly organized two-dimensional (2D) to three-dimensional (3D) SWCNT-polymer hybrid systems have been demonstrated with an unprecedented control over growth, assembly and transfer process of SWCNTs.

First, a novel strategy has been developed to control direction transport properties of SWCNT network by creating the heterogeneity within network. 3D heterogeneous film with alternating thin (≤10 nm) and thick strips (~50 nm) has been achieved through a template guided fluidic assembly process with the guidance from alternating hydrophobic and hydrophilic patterns on the template. Higher electrical and thermal conductance can be obtained along the strip alignment direction than those in the transverse direction.

Second, a highly effective and CMOS friendly transfer method, wet-contact printing, has been developed to achieve large scale suspended SWCNT architectures over flexible polymeric substrates with micro to nanoscale precision. The fundamental mechanism involving micro to nanoscale interactions among structures of polymeric substrate, the solid-liquid-vapor interface and the status of SWCNTs (suspended or collapsed) has been systematically studied. The results
reveal that the formation of suspended SWCNT is directly related to superhydrophobicity of the receiving polymeric substrate. The large-scale suspended micro/nanoscale SWCNTs networks on polymer substrates can be used as platforms for building various flexible and transparent MEMS/NEMS devices.

Finally, various mechanically and electrically robust 2D and 3D organized and well-aligned SWCNT networks–polymer hybrid architectures have been demonstrated with the combination of different SWCNT architectures and different transfer technologies.
# Table of Contents

Acknowledgements .......................................................................................................................... 1

List of Figures ................................................................................................................................... 3

List of Tables ...................................................................................................................................... 6

Chapter 1. Introduction ....................................................................................................................... 7

1.1 Motivation of this work ................................................................................................................. 7

1.2 Single-walled carbon nanotube ..................................................................................................... 11

1.2.1 The structure and electrical properties of SWCNT .................................................................. 11

1.2.2 The mechanical properties of SWCNT .................................................................................. 14

1.2.3 The thermal conductivity of SWCNT ....................................................................................... 18

1.2.4 Sorting SWCNT ....................................................................................................................... 21

1.2.5 SWCNT network ....................................................................................................................... 26

1.3 Early methods to integrate carbon nanotube with polymeric substrate ................................. 28

Chapter 2. Smart Assembly of Carbon Nanotube Architectures with Anisotropic Properties .......... 31

2.1 Introduction .................................................................................................................................... 31

2.2 Experimental .................................................................................................................................. 35

2.3 Morphology of 3D SWCNT film .................................................................................................... 37

2.4 Electrical and thermal anisotropy of 3D SWCNT film ................................................................. 39

2.5 Mechanism of the formation of 3D SWCNT film ......................................................................... 42

2.5.1 The cross-talk mechanism ......................................................................................................... 42

2.5.2 The influence of different surfaces ............................................................................................. 48

2.5.3 The influence of solution aging .................................................................................................. 49

2.6 Assembly 3D SWCNT film on different substrates ....................................................................... 51

2.7 Summary ....................................................................................................................................... 52

Chapter 3. Suspended SWCNT–Polymer Architectures and Wet-Contact Printing Method .......... 53

3.1 Introduction ..................................................................................................................................... 53
3.1.1 Methods to suspend SWCNT architectures ................................................................. 55
3.1.2 Superhydrophobic surface and Lotus effect................................................................. 58
3.2 Experimental .................................................................................................................... 62
3.3 Mechanism ...................................................................................................................... 70
  3.3.1 Heterogeneous and homogeneous interface .............................................................. 70
  3.3.2 Potential energy analysis ............................................................................................ 76
  3.3.2 Interfacial energy analysis .......................................................................................... 80
3.4 Results and Discussions .................................................................................................. 83
  3.4.1 Influence of center distance, y .................................................................................... 83
  3.4.2 Influence of different polymeric materials and its fabrication technologies .............. 87
  3.4.3 Influence of height, z .................................................................................................. 90
  3.4.4 Transferring on substrates with micro-posts .............................................................. 96
  3.4.5 Transferring on flexible substrate with pre-strain .................................................... 98
  3.4.6 Transferring at arbitrary angle .................................................................................. 101
  3.4.7 Transferring 100-µm-wide SWCNT micro-lines ....................................................... 102
  3.4.8 Transferring on substrate with metallic surface ....................................................... 104
  3.4.9 Multiple transfers ..................................................................................................... 106
  3.4.10 Transferring SWCNT to nanoscale patterned polymeric substrate ....................... 107
  3.4.11 Transferring graphene ............................................................................................. 109
  3.4.12 Wetting of solution on anisotropic surface ............................................................. 110
  3.4.13 Deformation and folding of suspended SWCNT network ....................................... 113
3.5 Summary ......................................................................................................................... 116

Chapter 4. Highly Organized 2D and 3D SWCNTs-Polymer Architectures ........................................ 119
  4.1 Introduction ................................................................................................................... 119
  4.2 Highly organized 2D SWCNTs-polymer architectures .................................................. 120
  4.3 Highly organized 3D SWCNTs-polymer architectures .................................................. 122
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List of Figures

Figure 1. Flexible devices built on polymeric substrates.......................................................... 8
Figure 2. The structure of carbon nanotube originated from a graphene sheet............................ 12
Figure 3. Molecular models of SWCNTs exhibiting different chiralities.................................... 14
Figure 4. Mechanical properties measurement on SWCNT..................................................... 16
Figure 5. Mechanical properties of SWCNT film..................................................................... 18
Figure 6. Thermal conductivity as a function of temperature.................................................... 20
Figure 7. Strategies of sorting SWCNTs. .................................................................................. 22
Figure 8. The structure of SWCNT network............................................................................. 27
Figure 9. The schematic of transfer printing\(^4\) (a), solution cast-etching transfer\(^24\) (b), direct transfer\(^94\) (c). ......................................................................................................................... 28
Figure 10. Guided assembly of carbon nanotube.................................................................... 31
Figure 11. Templated guided fluidic assembly...................................................................... 34
Figure 12. Morphology of 3D SWCNT film........................................................................ 37
Figure 13. The dependence of \(H_{\text{SWCNT}/\text{SiO}_2}\) (square line), \(H_{\text{SWCNT}/\text{PR}}\) (dot line) on \(H_{\text{PR}}\). ........................................................................................................ 38
Figure 14. Electrical and thermal anisotropy of 3D SWCNT film.............................................. 39
Figure 15. Mechanism of the formation of 3D SWCNT film..................................................... 43
Figure 16. SEM images of SWCNT films formed on PR (a) and on plasma treated SiO\(_2\) surface (b)..... 48
Figure 17. 3D SWCNT film on different substrates................................................................. 51
Figure 18. Methods to suspended carbon nanotube architectures in microscale..................... 55
Figure 19. The interactions among target materials, solution and superhydrophobic substrate and the interface between solution and patterned substrate.................................................. 61
Figure 20. Wet-contact printing method and suspended SWCNTs-polymer hybrid structures in Route 1\(^{162}\). .................................................................................................................................. 63
Figure 21. Wet-contact printing method and suspended SWCNTs-polymer hybrid structures in Route 2.65
Figure 22. The microscale interface for wet-contact printing method (left route) and convention MEMS/NEMS method (right route)........................................................................ 70
Figure 23. The contact angle measurement of water on polymeric substrates (PDMS and SU-8) with constant $x$ and $z$ ($x = z = 6 \, \mu m$) but changing $y$ from 9 to 120 $\mu m$.

Figure 24. Direct evidence for heterogeneous interface and the influence of HF acid solution on surface roughness.

Figure 25. Potential energy schematic of homogeneous (Wenzel’s theory) and heterogeneous interface (Cassie-Baxter’s theory).

Figure 26. Interfacial energy analysis of wet-contact printing method. Left, state before etching, and right, state after etching. The wavy curves indicate the diluted HF acid solution.

Figure 27. Suspended SWCNT architectures on an integrated PDMS substrate ($x = z = 6$ and $y = 9$ to 120 $\mu m$) at right angle.

Figure 28. Suspended SWCNT architectures on an integrated PDMS substrate ($x = 20, z = 6$ and $y = 30$ to 120 $\mu m$) at right angle.

Figure 29. Suspended SWCNT architectures on an integrated SU-8 substrate at right angle to the supporting strips.

Figure 30. Influence of sharp edge on suspended SWCNT micro-line.

Figure 31. Suspended SWCNT architectures on an integrated PDMS substrate with high $z$ ($z = 65, x = 20$, and $y = 30$ to 120 $\mu m$) at right angle.

Figure 32. Influence of height of supporting pattern ($z$) on the yield of suspended SWCNT architectures over the PDMS substrate with same $x$ (20 $\mu m$) and $y$ (60 $\mu m$) but different $z$: $z = 65$ $\mu m$ (a) and $z = 6$ $\mu m$ (b).

Figure 33. Models of heterogeneous interface.

Figure 34. Suspended SWCNT architectures on an integrated PDMS substrate patterned with circular posts.

Figure 35. Miss-alignment of suspended SWCNT micro-lines during transferring to micro-posts.

Figure 36. Arrays of SWCNT micro-arches on pre-stretched PDMS substrates.

Figure 37. Other forms of deformation of SWCNT architectures after releasing the pre-stretched substrate.

Figure 38. Suspended SWCNT architectures on PDMS substrate at the angle of 138 °.

Figure 39. 100-$\mu m$-wide suspended SWCNT architectures on PDMS substrate: (a) $x = 7.5$ $\mu m$ and $y = 15$ $\mu m$, and (b) $x = 20$ $\mu m$ and $y = 40$ to 120 $\mu m$.

Figure 40. Transferring of SWCNT micro-lines to substrate fully or partly covered with metallic surfaces.
Figure 41. Hierarchy SWCNT architectures obtained through repeated wet-contact printing processes. 106
Figure 42. Suspended SWCNT film on nano-patterned PMMA substrates. (a) AFM image of the topology and (b) line profile along red line in (a). ................................................................. 107
Figure 43. Suspended graphene on various substrates with micro- to nanoscale patterns................. 109
Figure 44. Contact angle measurement with data from both front view and side view...................... 111
Figure 45. Deformation of suspended SWCNT network during the transferring process............... 114
Figure 46. Embedded 2D SWCNTs-polymer hybrid structures.................................................. 120
Figure 47. Embedded 3D SWCNTs sandwiched between two polymers (PR and PMMA)............. 122
Figure 48. Embedded 3D SWCNT-PMMA film without PR...................................................... 124
Figure 49. A combined lateral SWCNTs micro-lines and vertically aligned SWCNTs arrays inside of PDMS substrates................................................................. 126
Figure 50. I-V measurement of the combined three dimensional SWCNT device....................... 128
Figure 51. Linear fit of I-V measurement of R_{AB}...................................................................... 130
Figure 52. The circuit model between the horizontally aligned SWCNTs and vertically aligned SWCNTs from C–c, C–D, c–d, and D–d. ................................................................. 132
Figure 53. Set-up of mechanical and electromechanical measurement on suspended SWCNT........ 136
Figure 54. Mechanical property measurement of suspended SWCNT micro-lines....................... 138
Figure 55. Electromechanical test for 10-μm-wide suspended SWCNT film over 20-μm-wide trench... 141
Figure 56. Electromechanical test for 5-μm-wide suspended SWCNT film over 20-μm-wide trench.... 142
Figure 57. Change of current (ΔI) with respect to elongation of the film (Δl) for both b=10- and 5-μm-wide suspended SWCNT film over 20-μm-wide trench............................................. 143
Figure 58. An ethanol sensor based on suspended SWCNTs...................................................... 147
Figure 59. Comparison between suspended and confined SWCNTs micro-lines on ethanol sensing..... 149
Figure 60. Comparison of resistance response between suspended and confined SWCNTs micro-lines on ethanol sensing at low concentration 70 ppm and 30 ppm. ................................. 150
Figure 61. The changing of relative sensitivity (Sensitivity_{suspended}/Sensitivity_{confined}) with respect to ethanol concentration................................................................. 151
Figure 62. Schematic of wet-contact printing method without (left and middle) and with (right) the assistance from external field................................................................. 158
List of Tables

Table 1. Theoretical estimates for drying lengths and film thickness for evaporation-controlled self-assembly. The results in the top and bottom row are for SiO$_2$ and PR lines, respectively. .......................... 46

Table 2. Summary of surface energy of water, carbon nanotube, PDMS and epoxy resins. ....................... 81

Table 3. Calculated interfacial energy. ............................................................................................................ 82

Table 4. Sample code for micro-strip patterned polymeric substrate. In sample code, the word “Line” indicates the substrate is patterned with micro-strips. The first number denotes the value of $x$ and the second number denotes the value of $y$. There is no information about $z$ in the code, because it is a constant ($z = 6$) in all the designs unless mentioned otherwise.................................................................................. 83

Table 5. Resistance between all the existing pairs of contact pads calculated from the $I$-$V$ Measurement in Figure 50. .................................................................................................................................. 130

Table 6. Resistance estimation for the combined SWCNTs structure from $A-a$, $A-B$, $a-b$, and $B-b$. .... 131

Table 7. Resistance estimation for the combined SWCNTs structure from $C-c$, $C-D$, $c-d$, and $D-d$ where $R_c = R_{c1} + R_p + R_{c2}$. ................................................................................................................................ 132
Chapter 1. Introduction

1.1 Motivation of this work

Transparent and flexible electronics with miniaturized size and weight is the direction for next generation electronics\(^1\)\(^-\)\(^{27}\). Figure 1 demonstrates some of the pioneer flexible micro-devices such as transistor (a)\(^{13}\), camera (b)\(^{18}\), light-emitting diodes\(^{23}\) (c) and solar cells\(^{19}\) (d) with deliberately controlled positioning and flexibility by Prof. John Rogers’s group in UIUC\(^{13,18,19,23}\). The basic components for flexible device are the circuit (functional unit) and flexible substrate. The key issue for a successful device is how to integrate large scale electronic circuit onto or into flexible substrate in a highly controlled manner\(^{13,21}\). To solve this problem, the choice of materials for both circuit (functional unit) and substrate and the method of integration are of equally importance. For the choice of materials, single-walled carbon nanotube (SWCNT), seen as a seamless tube formed by welding a single layer of graphene, is a potential candidate for the functional unit of flexible electronics due to its high electrical and thermal conductivity, extremely high mechanical strength, and good chemical stability\(^{5,8,28-30}\). On the other hand, polymer is the most popular material for substrates due to its flexible and transparent nature and relative low price. Insulating polymers are usually applied and the choice of polymer is related to the application and the interaction with functional unit. For example, thermoset elastomer such as Polydimethylsiloxane (PDMS) can be used for highly deformable devices\(^{4,5,7,15-19,23}\).
Two main aspects of integration have to be addressed: i) SWCNTs have to be integrated with desired structure and properties as the functional unit in the device and ii) the SWCNTs functional units have to be integrated with polymeric substrates at desired locations with prescribe orientations and hierarchy architectures. The structures of SWCNTs network (such as alignment, density, number of layers, junctions, and etc.) dictate the properties SWCNTs unit in the device\textsuperscript{9,21}. The structure is mainly controlled during the assembly process with the guidance of catalyst, chemicals, and the external force such as electrical field, magmatic field and even fluidic field\textsuperscript{9,31-37}. Note that the growth method is classified as an assembly process since it can be visualized as the process to assemble carbon atoms with the guidance of catalyst. However, the carbon nanotube architectures with deliberately controlled properties are usually assembled on the rigid substrates, \textit{e.g.}, metal, Si, SiO\textsubscript{2} and \textit{etc.}, which are not favorable substrates for flexible applications\textsuperscript{9,31-37}. Ultimately, to realize the flexible device of SWCNTs, SWCNTs have
to be integrated into or onto the flexible substrate with desired structure and location\textsuperscript{9,13}. Therefore, the second aspect is to address the transferring techniques to integrate highly organized SWCNTs architectures from the original substrate to flexible polymeric substrate with high yield, good efficiency and in a well-controlled manner.

However, despite the remarkable progresses in carbon nanotube technologies and polymer processing technologies, the fabrication of scalable and tightly controlled integrated microscale functional flexible system with highly organized 2-dimensional (2D) and 3-dimensional (3D) SWCNTs architectures remain largely exclusive. On one hand, the strategy for the engineering the properties of SWCNT network is limited, \textit{e.g.}, alignment control assisted by external fields is the only principle for tailoring the directional properties. More strategies are desirable to achieve better property control. On the other hand, the integration process of SWCNT and polymeric substrate is subjected to the challenges such as poor understanding at micro- to nano-scale interface between SWCNT and substrate, difficulties in handling nanostructures and \textit{etc.} At micro- to nano-scale, long range forces such as Van Der Waal forces, electrostatic interaction and \textit{etc} and interfacial forces such as meniscus force (capillary force) and viscous force become dominant\textsuperscript{38-40}. Moreover, these forces are sensitive to environmental parameters such as solution, heating, chemical interaction and \textit{etc.} making the problem even more complicated. Therefore, remarkable efforts have to be made to build a comprehensive understanding at the micro- to nano-scale interface from the assembly to transferring technologies.

The objective of my research is to address several important issues of highly organized SWCNTs-polymer hybrid systems utilizing a bottom-up strategy: i) develop new principle for the directional property control of SWCNT network to build anisotropic functional unit and understand the fundamental controlling mechanism; ii) develop highly effective transfer
technologies to integrate the highly organized SWCNTs into or onto polymeric substrate and investigate the fundamental transfer mechanism addressing the interaction at the micro- to nano-scale interface; and iii) investigate the intrinsic properties of SWCNT network in flexible condition and develop potential applications.

In chapter 1, the structures and properties of SWCNT and early method to build SWCNT-polymer hybrid architectures were summarized. In chapter 2, smart assembly of SWCNT over micro-patterned heterogeneous substrate with alternating hydrophobic and hydrophilic substrate was investigated. A novel strategy of heterogeneous SWCNT film with controlled local thickness has been brought out to realize in-plane electrical and thermal anisotropy of the SWCNT film. In chapter 3, a CMOS compatible and high effective wet-contact printing method has been developed to construct large scale suspended SWCNT architectures over micro- to nano-patterned polymeric substrate. The fundamental mechanism as well as the controlling parameters was identified and discussed. In chapter 4, 2D to 3D SWCNT-polymer hybrid architectures have been demonstrated combining the multi-dimensional SWCNT architecture and various transferring technologies. A robust electrical contact can be built between two types of SWCNT architectures transferred by different methods. In chapter 5, intrinsic mechanical and electromechanical properties of suspended SWCNT network during deformation have been investigated and chemical sensor based on suspended SWCNT-polymer hybrid architectures was demonstrated.
1.2 Single-walled carbon nanotube

1.2.1 The structure and electrical properties of SWCNT.

Carbon nanotubes (CNTs), one important form of carbon, can be visualized as rolled hexagonal carbon networks that are capped by pentagonal carbon rings with the diameter of several to tens of nanometers and the length of many micrometers and even tens of centimeters\(^4^1\). It was first observed by Endo (1975)\(^4^2\), and then clearly demonstrated by Iijima using transmittance electronic microscope (1991)\(^4^3\). CNT can be synthesized by the method of arc-discharge, laser vaporization on graphite targets, electrolysis, Chemical vapor deposition (CVD) and solar production\(^4^1\).

The wall of CNT is only one atomic layer thick and depending on the number of wall, the CNT can be classified as single-walled carbon nanotube (SWCNT or SWNT) with only one wall and multi-walled carbon nanotube (MWCNT or MWNT) with more than one wall. The carbon atoms within the graphene sheet exhibit \(sp^2\) hybridization and the strong C-C \(sp^2\) bond within the \(xy\) plane and the weak bond in the \(z\) axis endorse extraordinary mechanical and electrical properties to CNT. For example, the current density can reach more than \(10^9\) A/cm\(^2\) for an individual MWCNT\(^4^4\). Compared with MWCNT, the property of SWCNT is more sensitive to the environment since all the atoms of SWCNT are on the surface\(^4^5\). Therefore, SWCNT was chosen as the target material in my research and the following discussions will mainly focus on the properties of SWCNT.
Figure 2. The structure of carbon nanotube originated from a graphene sheet.

(a) Schematic showing parameters defining SWCNT from the 2D graphene: chiral vector, \( \mathbf{C_h} \), unit vectors \( \mathbf{a_1} \) and \( \mathbf{a_2} \) and inclination angle \( \theta \). (b) Graphene sheet with chirality mapping of carbon nanotubes\(^{46} \).

A SWCNT is just a rolled up graphene sheet at specific direction and length as shown in Figure 2\(^{46} \). The chiral vector, \( \mathbf{C_h} \), can be denoted as \( \mathbf{C_h} = n\mathbf{a_1} + m\mathbf{a_2} \), where \( \mathbf{a_1} \) and \( \mathbf{a_2} \) denote the unit vector of the hexagonal honeycomb lattice and \( n \) and \( m \) are integers. The geometry of the SWCNT can be specified by \((n, m)\) and the diameter of the SWCNT, \( d \), can be expressed as:

\[
d = \frac{\alpha\sqrt{m^2 + nm + n^2}}{\pi},
\]

(1.1)
where $a = 1.42 \times \sqrt{3} \text{ Å}$ correspond to lattice constant in graphene sheet. Also, the inclination angle $\theta$ can be defined as the angle between $C_h$ and zigzag direction as shown in Figure 2a. By rolling the same graphene sheet with different chiral vectors, the chirality of SWCNT can be changed leading to SWCNT with different structure (armchair, zigzag and chiral) and thereby different electrical properties (semi-conductive and metallic)\textsuperscript{41,46}. The structure of SWCNT is related to the inclination angle, $\theta$: $\theta = 0, (m,n) = (p,0)$, where $p$ is integer (zigzag) and $\theta = \pm 30^\circ, (m,n) = (2p,-p)$ or $(p,p)$ (armchair).

The electronic type of SWCNT is strongly related to its chirality structure. The map in Figure 2b shows the pairs of semi-conductive and metallic SWCNT. Figure 3 shows the typical configuration of armchair, zigzag and chiral SWCNT (Figure 3a to 3c) and corresponding electronic density of state (d)\textsuperscript{47}. Theoretical studies indicate that if $\frac{(2m+n)}{3} = integer$, the SWCNT is metallic. Therefore, $(n, n)$ tubes (armchair) are metals as shown in Figure 3d (lower panel). $(n, m)$ tubes with $\frac{(n-m)}{3} = integer$ ($n$ must not equal to $m$) are very tiny-gap semi-conductors (Figure 3d, mid panel) and all others are large-gap semi-conductors (Figure 3d, upper panel)\textsuperscript{47,48}.
Figure 3. Molecular models of SWCNTs exhibiting different chiralities.

(a) armchair configuration, (b) zig-zag arrangement, and (c) chiral conformation41. (d) Electronic densities of states for the (5, 5), (7, 1) and (8, 0) tubes showing singularities characteristic of 1D systems. The (5, 5) armchair nanotube is metallic for symmetry reasons. The (7, 1) chiral tube displays a tiny gap due to curvature effects, but will display a metallic behaviour at room temperature. The (8, 0) zigzag tube is a large-gap semiconductor47.

1.2.2 The mechanical properties of SWCNT

The C-C bond in graphene layer is among the strongest chemical bonds in nature. Therefore, CNT is expected to have the exceptional mechanical properties. However, due to the difficulties in handling the nanoscale objects, the direct measurement of individual CNT is very challenging48. Treacy et al., investigated the Young's modulus of MWCNT by observing the thermal oscillation amplitude of the free ends of anchored nanotubes with respect to temperature49. The average Young's modulus is calculated to be 1.8 TPa with wide distribution
of individual measurements from 0.4 to 4.15 TPa. The Young's modulus of SWCNT were measured by the same group using the same experimental set-up and a mean value of 1.25 TPa was obtained\textsuperscript{50}. A direct experimental study was performed by Salvetat \textit{et al}\textsuperscript{51}. As shown in Figure 4a, by applying load using atomic force microscope (AFM) tip on suspended SWCNTs fabricated by an ultra-filtration method and observing the force and deflection of SWCNT, an average value of $0.8 \pm 0.4$ TPa was obtained. The first tensile test on SWCNT was performed by Yu \textit{et al}\textsuperscript{52}. The two terminals of individual SWCNT were attached to two opposing AFM tips and then SWCNT was pulled beyond the elastic limit. The Young's modulus of individual SWCNT was between 0.32 and 1.47 TPa with a mean value of 1.002 TPa and the tensile strength was between 13 and 52 GPa with a mean value of 30 GPa. The large variation indicates the presence of defects and their enormous influence on mechanical properties of SWCNT\textsuperscript{48}.
Figure 4. Mechanical properties measurement on SWCNT.

(a) Indentation test on suspended SWCNT rope using AFM tip\textsuperscript{51} and (b) direct tensile test using AFM tip\textsuperscript{52}.

The mechanical properties of SWCNT network are much lower than those of individual SWCNTs and individual SWCNTs bundle and are strongly influenced by interaction among SWCNT and topology of network. For example, Mamedov et al., found that the Young’s modulus of SWCNT composite film obtained by layer-by-layer (LBL) assembly reaches as high as 35 GPa, much lower than the value for individual SWCNT (1TPa) as shown in Figure 5a\textsuperscript{53}. Similar result on LBL SWCNT film was obtained by Xue et al., through the method of nanoindentation and Young’s modulus of 17 GPa was measured at the 30 nm displacement (10% of SWCNT film thickness)\textsuperscript{54}. However, this is rather a composite film with enhance intra-tube
interaction. As shown in Figure 5b, if preferential alignment of SWCNT can be achieved, the Young’s modulus can be improved to 350 to 830 GPa according to Lu et al.\textsuperscript{55}. In the case of buckypaper, the Young’s modulus is much lower than individual CNT even with perfect aligned and densely packed network. Di et al., report an ultra-strong CNT film fabricated by solid-state LBL assembly of aligned few-walled CNT film exhibiting tensile strengths up to 2 GPa and a Young's modulus up to 90 GPa\textsuperscript{56}. Zhang et al., tested the buckypaper with well aligned and densely packed MWCNT and found that the Young’s modulus was in the range of 280–2200 MPa, as a function of the density (from 0.43 to 1.29 g·cm\textsuperscript{−3})\textsuperscript{57}. In addition, the interaction among SWCNT within the bundle is also important. Kis et al., found that by introducing moderate electron-beam irradiation, stable link can be produced between neighboring carbon nanotubes within bundles leading to 30 folds increase of bending modulus (Figure 5c)\textsuperscript{58}. 
Figure 5. Mechanical properties of SWCNT film.

(a) random aligned SWCNT composite film fabricated by layer-by-layer assembly\textsuperscript{53}, and (b) aligned SWCNT film fabricated by dielectrophoresis assembly\textsuperscript{55}. (c) SWCNT bundle with enhanced interaction by creating chemical link through the method of moderate electron-beam irradiation\textsuperscript{58}.

1.2.3 The thermal conductivity of SWCNT

Like graphite, the thermal conductivity of SWCNT is generally dominated by phonons transportation. Due to the long-range crystallinity of nanotubes and long phonon mean free path of SWCNT, the longitudinal thermal conductivity of nanotubes may exceed the in-plane thermal conductivity of graphite which has the highest 3D thermal conductivity\textsuperscript{48}. To study the intrinsic thermal properties of SWCNT, the suspended and isolated individual SWCNT is required to prevent the heat transfer from nanotube to substrate.
The first effort on the measurement of individual SWCNT bundle has been performed by Li, in which suspended SWCNT bundles with the diameters ranging from 10 to 100 nm bridging two heating pads were measured\textsuperscript{59}. The thermal conductance measured between 14.5 K and 320 K reaches the peak of 20 nW/K at 310 K as shown in Figure 6a. However, the thermal conductivity cannot be estimated due to the uncertainty of number of SWCNT. Isolated individual SWCNT was first measured by Yu et al, in the temperature range of 110 to 300 K\textsuperscript{60}. As shown in Figure 6b, an individual SWCNT was directly grown between two platinum electrodes through CVD method with the diameter, $d$, in the range of 1 to 2 nm for most of the tubes. The thermal conductance increases from 0.7 nW/K at 110 K to 3.8 nW/K at 300 K and the calculated thermal conductivity ranges from 2000 W/m·K ($d = 1$ nm) to 10000 W/m·K ($d = 3$ nm) depending the diameter used in calculation (Figure 6b, right panel). Pop et al., measured the thermal conductivity of individual SWCNT at elevated temperature from 300 K to 800 K\textsuperscript{61}. For an individual SWCNT of length 2.6 µm and diameter 1.7 nm, the thermal conductance and thermal conductivity are measured to be 2.4 nW/K and 3500 W/m·K at room temperature, respectively as shown in Figure 6c.
Figure 6. Thermal conductivity as a function of temperature.

(a) SWCNT bundle in the temperature range of 14.5 K and 320 K, (b) individual SWCNT in the temperature range of 110 to 300 K and (c) individual SWCNT in the temperature range of 300 to 800 K.
The thermal conductivity of SWCNT network is expected to be different from that of individual SWCNT due to the existence of inter-tube junctions. Hone et al., performed the measurement on both random aligned SWCNT network and preferential aligned network. At room temperature, the thermal conductivity for random SWCNT network is ~35 W/m·K while that for aligned SWCNT network is above 200 W/m·K. It is evident that the thermal conductivity of SWCNT network is much lower than that of individual SWCNT. The phonon transfer through tube-tube junctions is not as effective as that along the longitudinal direction of the tube. Therefore, in the case of SWCNT network, the heat transfer through the junctions will dominate the final performance of device. Also, the structure of SWCNT network such as alignment can strongly influence the thermal properties.

1.2.4 Sorting SWCNT

The properties of SWCNT such as electronic type and optical properties are strongly related to its chirality, diameter and even length. For example, SWCNT can be either metallic or semi-conductive by simply choosing a different chiral vector as discussed above. Unfortunately, the current synthesis technologies have little control over electronic type, chirality and diameter and mostly SWCNT powder is composed of 67% metallic and 33% semi-conductive SWCNTs with a wide distribution of chirality and diameter.

To achieve the conceivable application of SWCNT, stable and repeatable performance is necessary leading to the strong requirement for sorting monodispersed SWCNT. Prof. Mark Hersam from Northwestern University has summarized the strategies to sort SWCNT with respect to electronic type, diameter and even chirality and classified them into five categories: selective chemistry, selective destruction, electrophoretic separation,
ultracentrifugation\textsuperscript{63,71,72} and chromatography\textsuperscript{73-78}. Additionally, direct spinning on chemically patterned substrate is another recently developed strategy to separate metallic and semi-conductive SWCNT in a fast manner\textsuperscript{14}.

\textbf{Figure 7.} Strategies of sorting SWCNTs.

(a) selective chemistry\textsuperscript{64}, (b) selective destruction\textsuperscript{68}, (c) electrophoretic separation\textsuperscript{36}, (d) ultracentrifugation\textsuperscript{71}, (e) spinning\textsuperscript{14} and (f) chromatography\textsuperscript{78}.  

22
Selective chemistry is normally combined with other technology such as ultracentrifugation, electrophoretic and/or chromatography to sort SWCNT\textsuperscript{63}. Chemistry on SWCNTs can be classified as: A) covalent sidewall chemistry; B) covalent chemistry at defect sites or open ends; C) non-covalent surfactant encapsulation; D) non-covalent polymer wrapping; E) molecular insertion into SWCNT interior as shown in Figure 7a\textsuperscript{64}. Among these chemical methods, chemistry on the exterior sidewalls has the best selectivity\textsuperscript{63}. Covalent sidewall chemistry has selectivity over electronic type and diameter\textsuperscript{63,65}. For example, selective functionalization of metallic SWCNT can be achieved with diazonium salts in aqueous solution\textsuperscript{66,67}.

The strategy of selective destruction is to selectively remove unwanted SWCNT species through solution-phase etching\textsuperscript{79}, gas-phase etching\textsuperscript{80,81}, current flow\textsuperscript{82} and optical irradiation\textsuperscript{83,84}. An example for gas-phase etching is using methane plasma at 400°C, followed by 600°C annealing in vacuum to selectively remove metallic SWCNT as shown in Figure 7b. Even though plasma can kill certain amount of semi-conductive SWCNT by mistake, almost all of metallic SWCNTs can be clearly removed leaving pure semi-conductive device\textsuperscript{68}.

Electrophoretic separation is to sort SWCNTs by physical and electronic properties\textsuperscript{36,69,70}. Depending on the applied electrical field, two different methods can be applied: electrophoresis using direct current and dielectrophoresis using alternating current\textsuperscript{36,69,70,36,69,70}. Electrophoresis sorts SWCNTs according to their mobility difference in gel, capillary or solution under direct current and since the mobility is related to length, this method is mainly length sorting\textsuperscript{48,49}, though some sorting under solution can show electronic type selectivity\textsuperscript{85}. Dielectrophoresis can be used to separate metallic and semi-conductive SWCNT owning to their different dielectric
constant in the presence of an alternating current electric field as shown in Figure 7c\textsuperscript{36}. By increasing the electrical field, the selectivity as well as the alignment of SWCNT can be improved\textsuperscript{86,87}.

Ultracentrifugation can sort SWCNT according to sedimentation coefficient, density and electronic type. Since conventional ultracentrifugation methods suffers from the convolution among multiple structures, Hersam’s group has developed density gradient ultracentrifugation (DGU) allowing SWCNT to be sorted exclusively by their buoyant density\textsuperscript{63,71,72}. This method was first applied to DNA-encapsulated SWCNT and then surfactant-encapsulated SWCNTs\textsuperscript{71,88}. By applying one surfactant, sodium cholate, clear diameter sorting is evident by the visibly distinguishable colored bands shown in Figure 7d, left. By applying co-surfactant mixtures of sodium cholate and sodium dodecyl sulphate, electronic-type sorting can be achieved as shown in Figure 7d, right. This method can achieve 99% purity for electronic-type sorting.

Spinning SWCNT solution on chemically functionalized surface is a facile method developed by Bao’s group in Stanford University to sort SWCNT by electronic type as shown in Figure 7e. Simultaneously, the alignment of SWCNT as well as the network density can be controlled. Amine- and phenyl-terminated silanes were used to functionalize the SiO\textsubscript{2} surface separately. Since amine-group has selective absorption towards semi-conductive SWCNT, while phenyl-terminated silanes selectively interact with metallic SWCNT, a clear enrichment of preferred SWCNT species can be achieved evidenced by the thin-film transistors performance with average on/off ratios of >100,000 for semiconducting SWCNTs and less than 2 for metallic SWCNTs\textsuperscript{14}.
Chromatography including ion exchange chromatography (IEX)\textsuperscript{75,76}, size-exclusion chromatography (SEC)\textsuperscript{73} and gel permeation chromatography (GPC)\textsuperscript{74,78} is another effective method for sorting SWCNT with small diameter (<1.2 nm)\textsuperscript{63}. The first experiment was performed on DNA-encapsulated SWCNT using IEX and separation by electronic type and diameter has been observed\textsuperscript{76}. However, IEX has poor selectivity in SWCNT length. SEC and GPC have been demonstrated for SWCNT length separation\textsuperscript{73,74}. Therefore, a repeated process with alternating SCE and IEX has been proposed and demonstrated with narrow diameter, length and chiral angle distributions\textsuperscript{77}. A recent breakthrough has been made by Kataura’s group in AIST, Japan, simply using gel chromatography as shown in Figure 7f\textsuperscript{78}. Large-scale chirality separation of SWCNTs can be achieved using a single-surfactant multicolumn gel chromatography and 13 different \((n, m)\) species can be collected and metallic SWCNT were collected finally as unbound nanotubes. This is a big step towards the ultimate goal of achieving monodispersed chirality separation. However, the purity as well as the yield was not optimized. The highest purity was 94\% for \((8, 6)\) SWCNTs, while the highest yield was 71\% for \((6, 4)\) SWCNTs.

In summary, significant efforts have been made towards the ultimate goal of large-scale, monodispersed SWCNTs; however, the progress is far from satisfied. The ultracentrifugation method can achieve 99\% separation of metallic and semi-conductive SWCNT\textsuperscript{71}. However, little control has been achieved on chirality. While gel chromatography can achieve monodispersed chirality for 13 species, the purity and the yield is not good enough\textsuperscript{78}. Therefore, further efforts are highly desirable in SWCNT sorting and controlled growth to provide narrow distributed SWCNTs.
1.2.5 SWCNT network

The electronic device fabricated from individual SWCNT suffers from poor stability and reproducibility due to the difficulty to obtain monodispersed SWCNT$^{21,63}$. Moreover, for large scale application, it is very difficult to align large amount of individual SWCNTs into the desired locations and it is not affordable to place the tube one by one using nanoscale handling tools. Considering the scalability, compatibility with industrial process, repeatability as well as the price, using SWCNT network instead of individual SWCNT is more conceivable for real application as demonstrated by many researchers$^{2,6,9,13,21,24,89}$. Also, the technologies in sorting the SWCNT can be easily integrated into SWCNT network fabrication, leading to better performance$^{14,21,36,68}$.

In my research, SWCNT network will be used for device fabrication. On the other hand, the SWCNT network composing both metallic and semi-conducting SWCNT can be regarded as a novel material because the network can show a semiconductor–metal transition as the film thickness increases leading to a variety of different applications$^{30,90}$. For example, the near-percolation networks showing semiconductor behavior can be used as the active layer in thin film transistors and sensors. The 10-100 nm thick networks showing high optical transparency and electrical conductivity can be used as a replacement for indium tin-oxide (ITO) electrodes. Micrometer-thick networks having nanoporous can be used as electrodes for supercapacitors, fuel cells, and battery applications$^{30}$. 


Figure 8. The structure of SWCNT network.

(a) SEM images of SWCNT network obtained by different methods\textsuperscript{21} and (b) X and Y junctions in SWCNT network\textsuperscript{24}.

SWCNT network can be obtained through a wide range of technologies such as growth, solution-phase assembly, deposition and etc\textsuperscript{21,30}. The detailed methods will be discussed in chapter 2. Figure 8a summarized 9 different SWCNT networks obtained by different synthesis method\textsuperscript{21}. Many processes can be scaled from nanoscale to wafer scale. However, despite the apparent advantages in manufacturing, stability and repeatability, the performance of SWCNT network is greatly attenuated compared to individual SWCNT (or individual SWCNT bundle) device due to the existence of large amount of junctions and intertwined architectures\textsuperscript{53,55,58,62}. There are mainly two types of junctions as shown in Figure 8b, “X” junction and “Y” junction\textsuperscript{24}. The formation of junctions and intertwined architectures of SWCNT network is originated from the long-aspect-ratio nature of SWCNT and the strong interaction among SWCNTs. The interaction among SWCNTs and the topology of SWCNT network, \textit{e.g.}, alignment and type of
junction, can greatly influence the performance of SWCNT network such as mechanical, electrical and thermal properties as well\textsuperscript{55,58,62}.

1.3 Early methods to integrate carbon nanotube with polymeric substrate

As we know the guided assembly has limitation on the choice of target substrate, \textit{i.e.}, flexible polymeric substrates are not preferred for high temperature growth\textsuperscript{91}. It is necessary to develop methods to transfer carbon nanotube from unsatisfied substrate to the target substrate with the help of transfer media. The transferring process has to deal with the interaction among nanotube, transfer media, both donor substrate and receiver substrate, and solution if involved\textsuperscript{3,5,6,9,22,92,93}. Here, three types of representative transferring methods are summarized: transfer printing, solution cast-etching transfer and direct transfer.

![Figure 9](image.png)

Figure 9. The schematic of transfer printing\textsuperscript{4} (a), solution cast-etching transfer\textsuperscript{24} (b), direct transfer\textsuperscript{94} (c).

Transfer printing, first described by Kumar and Whitesides\textsuperscript{95-97} and well developed by Rogers’s group at UIUC, was a very powerful technique in transferring the microelement
regardless of chemical composition and surface energy of the substrate\textsuperscript{3-6,9}. An elastic stamp (for example, PDMS rubber) was used as transfer media. The adhesion between microelement (SWCNTs, photoresist pattern, nano wires, nano particle and so on) and stamp is kinetically controllable owning to the viscoelastic nature of the elastomer\textsuperscript{4}. The process was shown in Figure 9a. First, contact the stamp against the donor substrate with microelement and form conformal contact\textsuperscript{5}. Then peel back the stamp with high speed such that the adhesion between microelement and stamp is strong enough to adhere preferentially microelement to the stamp. Third, bring the inked stamp into contact with the receiver substrate and peel back the stamp with sufficient low speed (∼1 mm·s\textsuperscript{-1} or slower). The adhesion between microelement and receiver substrate becomes stronger and microelements were released to receiver substrate\textsuperscript{4}.

Transfer printing is very powerful in constructing well-defined multilayer circuit with different micro-elements and repeated transfer can be processed on the same receiving substrate. Moreover, since it is a dry process, in which no solution is involved, very clean micro-element and substrate can be obtained after transferring. Further, by controlling the morphology of substrate, 2D to 3D architectures can be easily achieved. However, there are two limitations. First, it is not compatible with existing CMOS process where the repeated solution processes are involved. Second, the interaction between micro-elements and donor substrate should be reasonably small such that transfer media can easily remove it from donor substrate. Therefore, in cases where the interaction between donor substrate and microelement is very strong, this method is not applicable.

A transfer method combining solution cast and etching the sacrificial layer on the donor substrate can be used to transfer micro-element regardless of the interaction between micro-element and sacrificial layer\textsuperscript{22,92,98}. As shown in Figure 9b, first, a layer of polymer was cast on
the microelement/donor substrate and cured. So the polymer can form formal contact with microelement and hold it. Then the sacrificial layer under the micro-element was etched to release the microelement. Third, the polymer layer holding the microelement was transferred to the target substrate and dried. Finally, the polymer was stripped off using specific solvent\textsuperscript{92}. This method is widely used in fabrication of 1D to 2D nanomaterials such as carbon nanotube and graphene\textsuperscript{22,92,98}. However, it is hard to build 3D architectures due to the existence of solutions.

In certain cases, the transfer media is not necessary and the direct transfer can be realized by enhancing the affinity between microelement and receiver substrate\textsuperscript{94}. As shown in Figure 9c, the top of vertically aligned carbon nanotube grown on Si wafer was brought in contact with aluminum oxide substrate covered with uncured polymer layer\textsuperscript{94}. After curing the polymer, the carbon nanotube was hold tightly by the receiver substrate. Then, the donor substrate (Si wafer) can be peeled off leaving nanotube to the receiver substrate.

In summary, the transfer techniques have to be designed according to specific substrate, microscale element being transferred and hierarchy structures of the device application. For this reason, to achieve highly organized 2D to 3D SWCNT-polymer architectures, new transfer techniques as well as the combination of existing methods are necessary for the fabrication of various SWCNT-polymer architectures.
Chapter 2. Smart Assembly of Carbon Nanotube Architectures with Anisotropic Properties

2.1 Introduction

The guided assembly is a straightforward method to control the morphology, location and further the properties of SWCNT architectures\(^9,31-35,99,100\). The assembly of SWCNT can be triggered by catalyst deposition\(^9,31,32\), surface chemistry\(^33-35\), external force such as electrical\(^36,37\), fluidic field\(^99,100\) and/or the combination of a few. Therefore, based on the driven force of assembly, the assembly method can be classified as three categories: growth, chemically guided assembly and external force guided assembly.

Figure 10. Guided assembly of carbon nanotube.
(a) vertically aligned carbon nanotube grown by CVD method\(^32\), (b) horizontally aligned carbon nanotube grown by CVD method\(^9\), (c) nanoscale chemical guided assembly\(^34\), and (d) electrical field guided assembly\(^36\).
First, carbon nanotube can be in-situ grown on the target location with preferential alignment using chemical vapor deposition (CVD)\textsuperscript{9,31,32}. A good example is given by Figure 10a, in which the carbon nanotube can be grown perpendicular to the exposed SiO\textsubscript{2} surface using CVD grown forming carbon nanotube flowers on selected sites\textsuperscript{32}. In this case, carbon nanotube was grown perpendicular to the target substrate. The idea to grow well controlled nanotube parallel to the target substrate was realized by Kang et al\textsuperscript{9}. As shown in Figure 10b, perfect aligned SWCNTs was grown parallel to the substrate. To achieve this, the Fe catalyst was patterned lithographically to the quartz wafer and annealed to make isolated catalyst particles. And the growth of nanotube was guided by the crystal steps on the substrate leading to perfectly aligned SWCNTs. Even though, the CVD method can precisely control the location of carbon nanotube, there are several drawbacks. First, the target substrates are limited. For example, in Wei’s work, the CNT can be only grown on SiO\textsubscript{2} surface\textsuperscript{32}. Also, the substrates utilized are rigid which limited the flexible applications. Moreover, the process temperature of CVD is usually very high which greatly limit compatibility with other materials, \textit{i.e.}, polymer material can hardly be integrated into such device before CVD processing\textsuperscript{91}.

Chemically guided assembly is a widely used method\textsuperscript{33-35}. By chemically decorating the target substrate or carbon nanotube, the enhancing the affinity between target site and carbon nanotube can guild assembly of carbon nanotube onto preferred site. As shown in Figure 10c, the chemically functionalize pattern was created on the substrate with functional groups such as amino (–NH\textsubscript{2}/–NH\textsubscript{3}\textsuperscript{+}) or carboxyl (–COOH/–COO\textsuperscript{−}) or non-polar groups (such as methyl (–CH\textsubscript{3})), and the nanotube was confined into the polar region functionalized by cysteamine\textsuperscript{34}. This
method is easy to scale up, but the controllability of individual nanotube is limited, \textit{i.e.} the alignment of carbon nanotube is hard to control\textsuperscript{33}.

External force guided assembly can be classified by the applied force such as electrical\textsuperscript{36}, magnetic\textsuperscript{101}, fluidic force\textsuperscript{102-104} and \textit{etc.} For example, the SWCNTs can develop an induced dipole moment when subjected to an electric field. This induced dipole moment allows one to align and move suspended tubes to the selected site by designing an appropriate inhomogeneity of the electrical field\textsuperscript{36}. Figure 10d shows an example of deposition of aligned carbon nanotubes on a lithographically patterned electrode through alternating current (ac) dielectrophoresis\textsuperscript{36}. Perfect alignment and good site-selectivity can be achieved using external force guided assembly. However, external force guided assembly usually involves in multiple step such as patterning the electrode, applying field and remove the solution. These complex processes hinder the continuity of the manufacturing. Also, the small electrodes have to be patterned using expensive lithography process which further increases the cost of this technique.

Our group has developed the template guided fluidic assembly technique which can synthesis patterned SWCNT film from macro-scale to nanoscale with controlled alignment and electrical properties\textsuperscript{102-105}. The assembly process was summarized in Figure 11a: i) the SiO\textsubscript{2} substrate was pretreated in Plasma-Them 7900 using mixed gas flow of O\textsubscript{2} (20 sccm), SF\textsubscript{6} (20 sccm) and Ar (5 sccm) for 5 seconds to enhance the affinity between SWCNT-deionized (DI) water solution and the assembled surface; ii) photoresist (PR) was patterned on the SiO\textsubscript{2} substrate using optical lithography techniques; iii) the patterned substrate was vertically submerged into the SWCNTs-DI water solution and gradually lifted from the solution with a constant pulling speed; and iv) PR was stripped off using desired solvent. The channel width of resultant SWCNTs pattern can easily go down to several micrometers and further down to hundreds of nanometers\textsuperscript{102,104}. Figure
11b and 11e show the examples of SWCNTs pattern with channel width of 1 µm down to 200 nm, respectively. Good alignment of SWCNTs was achieved when the channel width is less than 1 µm. The interplay between the intrinsic electrical heterogeneity and the nanoscale structure of the assembled SWCNT networks can result in drastically different transport characteristics. Further, this technique has good scalability. Continuous SWCNTs pattern with different channel width can be scale up to 3 inch wafer as shown in Figure 11f.

Figure 11. Templated guided fluidic assembly.
(a) Schematic of fluidic guided assembly, (b) to (e) SEM images of assembled SWCNTs pattern with channel width of 1 µm (b) down to 200 nm (e), and (f) optical image of 3-inch wafer scale assembly of SWCNTs and insets: SEM images of continuous SWCNTs micro-patterns with different widths.

In spite of the remarkable progresses in assembly methods, directional property control at the micro/nanoscale remains a challenge primarily due to issues pertaining to control over the underlying anisotropy and scalability to macroscopic scales. We have developed a facile and
novel approach based on template guided fluidic assembly of high mobility building blocks - SWCNTs - to fabricate ultra-thin and anisotropic SWCNT films. A major advancement is the complete control over the anisotropy in the assembled nanostructure, realized by three-dimensional engineering of the dip-coated SWCNTs ultra-thin film into alternating hydrophilic and hydrophobic micro-line patterns with prescribed intra/inter-line widths and line thicknesses. Variations in the contact line profile results in an evaporation-controlled assembly mechanism that results in alternating, and more importantly, contiguous SWCNTs networks. Evidently, the nanoscopic thickness modulations are direct reflections of the substrate geometry and chemistry. The nanostructured film exhibits significant anisotropy in the electrical and thermal transport properties as well as optically transparent nature as revealed by characterization studies. The direct interplay between the anisotropy and the 3D micro-line patterns of the substrate combined with the wafer-level scalability of the fluidic assembly allows us to tune the transport properties for a host of nanoelectronic applications.

2.2 Experimental

Assembly of SWCNT film. SWCNT-DI water solution was exposed to air for 5 hours at room temperature to age the solution. The SiO$_2$ substrate was pretreated in Plasma-Them 7900 using mixed gas flow of O$_2$ (20sccm), SF$_6$ (20 sccm) and Ar (5sccm) for 5 seconds to enhance the affinity between SWCNT-DI water solution (0.23wt%, Brewer Science Corp.), and the assembled surface. Photoresist (S1805, Shipley Company) was spin coated on the SiO$_2$ substrate at different spinning speeds (2000, 4000 and 5000 rpm) for 45 s with maximum acceleration. Exposure was performed using Quintel 4000 Mask Aligner for 3.5 s and then the exposed substrate was developed in developer (MF-319, Shipley Company) for 20 s. Finally, the
patterned substrate was vertically submerged into the SWCNTs/DI water solution and gradually lifted from the solution with a constant pulling speed, 0.1 mm/sec.

*Measuring the thickness of 3D SWCNT films.* Atomic force microscopy (PSIA XE-150, Park Systems Inc.) was employed to measure the thickness of 3D SWCNT films. First, the profile of photoresist (PR) patterns on SiO$_2$ substrate was demonstrated and the height of photoresist (H$_{PR}$) was obtained prior to the fabrication of SWCNT films. After depositing the 3D SWCNT film, the part of SWCNT film was carefully removed by a tungsten probe to expose SiO$_2$ substrate without any damage on the substrate. The exposed SiO$_2$ surface was used as the reference plane. Then, a large area scanning (30 µm x 15 µm) was performed to determine the thickness of SWCNT film on SiO$_2$ surface (H$_{SWCNTs/SiO2}$) as well as the height of the PR with coated SWCNT film (H$_{PR+SWCNTs/PR}$). Finally, the thickness of SWCNT film on PR (H$_{SWCNTs/PR}$) could be obtained by subtracting H$_{PR}$ from the H$_{PR+SWCNTs/PR}$.

*Thermal conductive measurement.* Heat transport equation can be expressed in terms of the third harmonic voltage signal $V_{3\omega}$ induced by an AC current of the form $I_0 \sin \omega t$ passing through the sample at low frequencies. The AC current with frequency $\omega$ creates a temperature fluctuation at $2\omega$, which further causes a third harmonic voltage signal. The $3\omega$ signals can be used for measuring thermal conductivity of anisotropic SWCNT film. A lock-in amplifier (Stanford Research System SR850) was used for obtaining $3\omega$ signals by amplifying the small voltage and removing the noise. An AC current source (Keithley 6221) was used to provide a stable current supply. All the measurements including resistance, temperature, and $3\omega$ signals were done under high vacuum (P<10$^{-5}$ Torr) in a Janis Research ST-500 cryogenic probe station to reduce radial heat losses through gas convection.
2.3 Morphology of 3D SWCNT film

(a) A tilted SEM of assembled SWCNT film formed on photoresist (PR) micro-lines/SiO$_2$ substrate. A scale bar is 5 μm. The thickness of PR is 360 nm. (b) An enlarged SEM image showing quasi-wavy 3D morphology of ultra-thin SWCNT film. A scale bar is 5 μm. (c) Schematic illustrating anisotropic structures of SWCNT film. (d) Optical microscopy image of the SWCNT film formed on PR/SiO$_2$ substrate. Note that the background colors can be observed directly (pink and blue colors representing the PR and SiO$_2$ strips, respectively) due to the transparent nature of the developed SWCNT film. A scale bar is 10 μm.

Figure 12 shows representative SEM, schematics and optical images of 3D SWCNT films. For this, the underlying SiO$_2$ are first subjected to the plasma treatment to improve their affinity to SWCNT-deionized (DI) water solution$^{102-104}$. Then, chemical heterogeneity is introduced through the fabrication of hydrophobic PR micro-line structures (6 μm in width and 9 μm in space between the nearby strips) with controlled PR thicknesses ($H_{PR}=323$, 360, and 480 nm) using photolithography processes, resulting in a 3D hydrophobic-hydrophilic surface architecture. Finally, the fluidic assembly of SWCNTs is realized by vertically dip-coating the substrate into 0.23 wt% SWCNTs-DI water solution and gradually lifting at a controlled pulling velocity $V=0.1$ mm/min. SEM images (Figure 12a and 2b) clearly show that the assembled SWCNTs network
forms a continuous thin film which inherits the 3D morphology of hydrophobic and hydrophilic micro-lines on the substrate, i.e., the film morphology is quasi-wavy as illustrated schematically in Figure 12c. This assembled SWCNT film is transparent as well, evident from the optical microscope image shown in Figure 12d showing the background color of photoresist and SiO$_2$.

![Figure 13. The dependence of $H_{\text{SWCNTs/SiO}_2}$ (square line), $H_{\text{SWCNTs/PR}}$ (dot line) on $H_{\text{PR}}$.](image)

$H_{\text{SWCNTs/PR}}$ decreased with increasing $H_{\text{PR}}$, while $H_{\text{SWCNTs/SiO}_2}$ is constant. Inset: schematic of the cross section of 3D SWCNT film with continuous but alternating arrangement of thin and thick SWCNTs micro-strips.

Another notable aspect, revealed by atomic force microscopy characterization in Figure 13, is that the local thickness of these assembled SWCNT films differs dramatically between the PR and SiO$_2$ micro-lines, resulting in alternating thin and thick SWCNTs strips. The inset schematic of Figure 13 shows the cross sectional view of the 3D SWCNT films on the patterned substrate. A key aspect that allows us to engineer the SWCNT film morphology is that the SWCNT film
thickness, the thickness of SWCNT film on photoresist ($H_{\text{SWCNTs/PR}}$) is strongly influenced by $H_{\text{PR}}$. For lower $H_{\text{PR}}$ (323 nm), higher $H_{\text{SWCNTs/PR}}$ (40 nm) was observed. Conversely for higher $H_{\text{PR}}$ (480 nm), the film thickness decreases to a few nanometers, $H_{\text{SWCNTs/PR}}=5.5$ nm, while the thickness of SWCNT film on SiO$_2$ ($H_{\text{SWCNTs/SiO2}}$) is relative inert to $H_{\text{PR}}$.

2.4 Electrical and thermal anisotropy of 3D SWCNT film

![Diagram](image)

**Figure 14.** Electrical and thermal anisotropy of 3D SWCNT film.

(a) The dependence of $R_{\text{horizontal}}$ (square line), $R_{\text{vertical}}$ (triangle line), and the electrical anisotropy ($R_{\text{vertical}}/R_{\text{horizontal}}$) on the thickness ratio of SWCNT film ($H_{\text{SWCNTs/SiO2}}/H_{\text{SWCNTs/PR}}$). Inset: SEM image of 3D SWCNT film patterned with the 100×100 μm$^2$ square gold contact pads. (b) Temperature coefficient measurement in vertical and horizontal directions of the anisotropic SWCNT film at $T=21$~$25$ °C. The electrical resistance linearly increases as the temperature rises. The calculated temperature coefficients for vertical and horizontal direction are 31 Ω/°C and 25 Ω/°C, respectively. (c) 3ω amplitude as a function of input current. The measurement was achieved at a working frequency of 1000 Hz.
Controlled modulations in the local thickness of the assembled SWCNT films can be exploited to tailor the directionality of the electrical transport through SWCNT film. To this end, the 100×100 μm$^2$ square gold contact pads were patterned on the SWCNT film with 100 μm space, as shown in Figure 14a (inset). The electrical resistances were measured in the vertical V-V’ direction ($R_{\text{vertical}}$) and in the horizontal H-H’ direction ($R_{\text{horizontal}}$) by two-point probe method. The dependences of electrical resistance ($R_{\text{vertical}}$, red line and $R_{\text{horizontal}}$, green line) as well as the electrical anisotropy ($H_{\text{SWCNTs}/\text{SiO2}}/H_{\text{SWCNTs}/\text{PR}}$, blue line) on thickness ratio of SWCNT film ($H_{\text{SWCNTs}/\text{SiO2}}/H_{\text{SWCNTs}/\text{PR}}$) is shown in Figure 14a. For all samples, $R_{\text{horizontal}}$ are higher than $R_{\text{vertical}}$, showing the strong indication of in-plane electrical anisotropy in these 3D SWCNT films. Furthermore, the electrical resistance in both directions increases with the increase in the ratio $H_{\text{SWCNTs}/\text{SiO2}}/H_{\text{SWCNTs}/\text{PR}}$ or the increase in the thickness of PR. However, $R_{\text{horizontal}}$ increases more rapidly such that the electrical anisotropy expressed by $R_{\text{horizontal}}/R_{\text{vertical}}$ also increases with the increase of $H_{\text{SWCNTs}/\text{SiO2}}/H_{\text{SWCNTs}/\text{PR}}$. This demonstrates that the electrical anisotropy can be controlled by changing the thickness of photoresist, $H_{\text{PR}}$. Decreasing the thickness of film leads to a non-linear decrease of possible conductive path, and thus a non-linear increase of resistance. The effect is a reflection of the reduction in effective conduction pathway of metallic SWCNTs in assembled SWCNT films$^{105}$. It follows then that in the 3D anisotropic system with variations in film thickness, the electrons pass the thin and thick SWCNT strips in parallel along the vertical direction and the thicker films dominate the electron transportation. However, in the horizontal direction, the electrons pass alternating thin and thick strips in series such that thinner SWCNT strips determine the overall electrical transport property of these SWCNT films. In each case, the vertical direction (V-V’) has enhanced conduction pathways relative to the horizontal direction (H-H’), resulting in the electrical anisotropy.
We also investigated thermal transport properties of the assembled SWCNT film having the thickness ratio ($H_{SWCNTx}/SiO2/H_{SWCNTx}/PR$) of 1.44. The measurement of thermal conductivity of the anisotropic SWCNT film was performed by utilizing a self-heating 3ω technique (see Figure 14b and 14c). The 3ω signal correlates with thermal conductivity through Eq. 2.1,

$$V_{3\omega, rms} = \frac{4I^3RR'L}{\pi^4kS},$$

where $L$, $R$, and $S$ are the distance between contacts, electrical resistance, and cross sectional area of the sample, respectively. $R'=(\delta R/\delta T)$ is the temperature gradient of the resistance at the chosen temperature and $k$ is the thermal conductivity. The 3ω method was utilized by the four-point-probe third harmonic characterization to eliminate the contact resistance and to avoid related spurious signals. For this purpose, the resistance of the assembled SWCNT film and its temperature dependency in two directions that are vertical and horizontal was measured at the small temperature ranges of 21 ~ 25 °C, which is close to the measurement temperature of the 3ω signal. The measured resistance and the temperature coefficient are 422 Ω and 31 Ω/°C for the vertical direction (V-V’), and 469 Ω and 25 Ω/°C for the horizontal direction (H-H’) (Figure 14b). The lower temperature coefficient in horizontal direction results from the reduction in effective conduction pathway of metallic SWCNTs. The third-harmonic voltage measured at the frequency of 1000 Hz is shown in Figure 14c. The thermal conductivities calculated with Eq. 2.1 were 22 W/mK and 4 W/mK for vertical and horizontal direction, respectively. We assume that decrease of the effective thermal conductivity in anisotropic SWCNT film of horizontal direction comes from reduced conduction pathways relative to the vertical direction, and additional phonon scattering provided between alternating thin and thick film.
2.5 Mechanism of the formation of 3D SWCNT film

2.5.1 The cross-talk mechanism

To elucidate the formation mechanism of anisotropic 3D SWCNT films, we have first quantified the chemical heterogeneity of the substrate with respect to the SWCNTs-DI solution via microscale static contact angle measurements. Our results reveal (Figure 15a) that the PR is significantly hydrophobic ($\theta = 60^\circ$ for PR-solution) compared to the plasma treated SiO$_2$ ($\theta<5^\circ$). In our experiments, the SWCNTs deposit along the receding liquid-air contact line. Then, the interplay between the chemistry and morphology of the substrate and the microfluidics of the receding contact line becomes important$^{108,109}$, evident from the snapshot of the assembly during the dip-coating shown in Figure 15b. The SEM image above the reservoir is along the film normal while that below is a schematic illustration. The wavy contact line, consisting of liquid bridges across the PR lines that are curved along the dip-coating direction, is a result of a solution that wets into the PR, strongly suggestive of “cross-talk” between the micro-lines, i.e., modification of the contact line dynamics due to chemical heterogeneity of the abutting lines. While its origin follows from the simple fact that the width of the hydrophobic PR pattern lines ($\sim$6 $\mu$m) is much smaller than the capillary length of the SWCNT solution, the effect on the final SWCNT film thickness on both PR and SiO$_2$ micro-lines requires an understanding of the microfluidics during the dip-coating.
Figure 15. Mechanism of the formation of 3D SWCNT film.

(a) Contact angle measurements of SWCNTs/DI water solution on PR (left) and plasma treated SiO\textsubscript{2} surface (right). (b) Schematic showing the fluidic assembly of SWCNTs through a dip coating process. SEM image above the horizontal of the SWCNTs reservoir solution was taken from the top edge of SWCNT film illustrating the initial point when the continuous SWCNT film was formed. A scale bar is 2 μm. (c) The schematic of the liquid-solid contact line formed on low H\textsubscript{PR} (left) and high H\textsubscript{PR} (right). A Cartesian coordinate system is defined: x denotes the direction of plane withdrawal; y denotes the in-plane direction perpendicular to the x direction and z denotes the direction normal to the plane.

The cross-talk in our chemically heterogeneous, 3D patterned substrate is due to the simple fact that the width of the hydrophobic PR pattern lines employed (~6 μm) is much smaller than the capillary length of the SWCNT solution \( l_c = (\gamma/\rho g)^{1/2} \), where \( \gamma \) is the surface tension of the solution, \( \rho \) is the density of solution and \( g \) is the acceleration of gravity. For pure water, typically
this is of the order of a few mm. In this limit, the hydrophilic SiO$_2$ patterns influence the contact line profile in the adjoining hydrophobic pattern and therefore should affect the height of the entrained liquid ribbon as the substrate is removed from the solution reservoir. More specifically, consider the variation in the flow profile as the substrate is retracted at a constant velocity, $V$. Well above the reservoir, the height profile is almost constant (ignoring the weak variation as the profile begins to change its contact angle at the SiO$_2$-PR interface along the streamwise direction) and is determined by viscous forces. On the other hand, near the reservoir the viscous forces are negligible and the profile is now set by the balance between capillary and hydrostatic pressures. In between these two regions, referred to as the dynamic meniscus or the transition zone, the balance between viscous and capillary forces determines the height profile.

The chief reason for the cross-talk is the balance between the capillary and hydrostatic pressures close to the reservoir. The large excess pressure due to the small widths allows the lines to interact with each other and has a significant effect on the resultant profile. As the width is reduced, the large capillary pressures are required to balance the excess pressure, which in turn entail considerable transverse gradients between the transition zone and the reservoir. We should note that the length of the transition zone in the streamwise direction is also affected. Darhuber et al. have shown that it scales with the channel width in this limit, which additionally contributes to liquid pick-up into the PR lines$^{108}$. Overall, the cross-talk between the flow profiles results in a wave-like variation in the receding contact line profile with significantly enhanced wettability of the PR lines, as seen in Figure 15b, and more importantly leads to a continuous liquid height profile.

To illustrate the salient effects, consider a cartesian coordinate system with its $x$-$y$ plane along the substrate (Figure 15c): $x$ denotes the direction of plane withdrawal (streamwise
direction) and $z$ is the direction normal to the plane. The large curvature transverse to the pattern lines and the change in contact angle ($\sim 5^\circ$ to $60^\circ$) at the chemically heterogeneous interface between the patterns modify the excess pressure at the liquid-air interface and therefore the shape of the meniscus $h(x, y)$ associated with the entrained liquid. The excess pressure is central to the extent of the cross-talk between the patterns and for small slopes it can be approximated as $\delta p = \gamma(h_{xx} + h_{yy})$. Near the reservoir, the much larger $h_{xx}$ is controlled by the width of the hydrophobic pattern lines $W$ and scales as $h_{xx} \sim \delta/W^2$ at the center of PR pattern, where $\delta$ is a length scale along the streamwise direction. Evidently, large capillary pressures are required to balance the excess pressure and drive the enhanced liquid pick-up into the PR micro-lines forming a wetting layer well above the horizontal of the reservoir (Figure 15b and 15c).

The above analysis elucidates the basis for the formation of continuous SWCNT thin films, yet the fluidics that controls the local thickness of the film is slightly different in that, i) for the set of deposition variables employed in this study the film thickness is evaporation-controlled, and ii) the variation in the PR step thickness (Figure 15c) introduces an additional transverse curvature $h_{zz}$ due to the out-of-plane variation in the thickness profile, $h = h(y, z)$. In the absence of cross-talk, the film thickness following evaporation is $H \equiv \Phi \theta l_d$, where $\Phi$ is strength of the solution and $l_d$ is the drying length, the length along the streamwise direction at which the SWCNT flux due to motion of the contact line is exactly balanced by the evaporation flux. Following Berteloot, a one-dimensional flux balance yields $l_d = (J_0/V \theta)^2$, where $J_0$ is evaporation constant for the solvent (approximately that of water) which depends on ambient conditions such as vapor saturation concentration, diffusion constant, mass density, and etc. Under standard conditions, $J_0 = 10^{-9}$ m$^{3/2}$s$^{-1}$ for a millimeter sized water droplet. For the dip-coating parameters in our experiments, this yields a drying length of $l_d \sim 4.7 \mu$m and $l_d \sim 0.3 \mu$m for the SiO$_2$ and PR
surfaces, respectively; the corresponding film thicknesses on SiO$_2$ and PR are $\sim 9.5$ nm and $\sim 0.8$ nm as shown in Table 1.

**Table 1.** Theoretical estimates for drying lengths and film thickness for evaporation-controlled self-assembly. The results in the top and bottom row are for SiO$_2$ and PR lines, respectively.

<table>
<thead>
<tr>
<th>Thickness of film H (m)</th>
<th>Drying length $l_d (J_0/V \theta)^{1/2}$ (m)</th>
<th>$J_0$ (m$^{3/2}$ s$^{-1}$)</th>
<th>$V$ (mm min$^{-1}$)</th>
<th>$\theta$ (°)</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.9E-10</td>
<td>3.3E-07</td>
<td>1.00E-09</td>
<td>0.1</td>
<td>60</td>
<td>0.0023</td>
</tr>
<tr>
<td>9.5E-09</td>
<td>4.7E-05</td>
<td>1.00E-09</td>
<td>0.1</td>
<td>5</td>
<td>0.0023</td>
</tr>
</tbody>
</table>

The theoretical film heights due to evaporation-controlled self-assembly are significantly smaller than those we report in this article. In addition to cross-talk across lines, there are several other factors for this disconnect. We have ignored changes in the evaporation constant due to the presence of SWCNTs, and more importantly, the microscale pattern widths. The latter results in significant contact line curvature which further increases $J_0$ ($\sim \kappa$, where $\kappa$ is the mean curvature of the tip of the receding contact line) and thus the thickness of the film. Furthermore, the expression for drying length is at best an estimate as it based on an assumed for the for the flux divergence at the contact line, $J(x) \approx J_0/\sqrt{x}$.$^{109}$ One also needs to factor in the effects of nucleation-controlled SWCNT deposition in solution, which will always serve to increase the film height. Finally, of course, if the film does not have time to dry after film formation, especially on the PR surface, we cannot rule out a transition from evaporation-controlled regime to that where the film thickness is dictated by the height of the wetting layer, as predicted by the well-known Landau-Levich-Derjaguin theory. In this limit, the film thickness increases with dip-coating velocity.

The estimates for film thicknesses represent lower bounds as they correspond to infinite, homogeneous surfaces. The larger thicknesses reported in Figure 15c, especially on PR lines, are in part an indicator of the cross-talk which leads to continuous thin film formation. The traverse
flow decreases the effective velocity of the receding contact line on the PR lines, thereby increasing the drying length and the evaporation-controlled film thickness ($\propto 1/V^2$). The change in the thickness of the SiO$_2$ lines is minimal as the contact line profile lags away from the reservoir such that the transverse flow away from the line occurs at a region where viscous forces become important. The observed trends in the film thickness are due to an out-of-plane curvature that increases with PR step height and works against the in-plane transverse curvature, therefore opposing the liquid pick-up from the SiO$_2$ lines onto the PR surface (see Figure 15c). In the evaporation-controlled limit, this leads to a reduction in the mean local velocity of the entrained liquid relative to the PR surface. As discussed before, we expect minimal changes in the thickness deposited on SiO$_2$ lines, consistent with our data. In summary, the thickness of the PR region, $H_{\text{PR}}$, emerges as a robust knob that offers complete control over the SWCNT film thickness, and the form and extent of the heterogeneity in film morphology.
2.5.2 The influence of different surfaces

Figure 16. SEM images of SWCNT films formed on PR (a) and on plasma treated SiO$_2$ surface (b).

The self-assembly onto the hydrophobic PR surface also can be triggered by static self-assembly of SWCNTs from the solution during the dip-coating, well before the evaporation of the receding contact line during the removal of the solvent. Both inter-SWCNTs and SWCNTs-PR interactions can drive this self-assembly via a heterogeneous nucleation process that depends...
on both deposition and material variables such as SWCNT concentration, diffusivity, surface energies (SWCNT and target surface) and surface roughness. To confirm this, we have performed controlled experiments in which unpatterned substrates, one with plasma treated SiO$_2$ and another fully covered with PR layer, were dip-coated. The pulling speed was deliberately reduced ($v^\prime=0.05\text{mm/min}$) to facilitate the fluidic assembly of SWCNTs. Assembled SWCNT films were observed on both substrates, as seen in Figure 16. Even though, SWCNT can deposit on both substrate, due to different surface condition, such as surface energy, surface morphology and functional group, the ability to deposit nanotube is also different. It is clear that SiO$_2$ is a preferred target substrate. This can further explain the reason of much thinner film on PR in the 3D SWCNT film.

2.5.3 The influence of solution aging

Using the aged SWCNT solution is also a key in obtaining well-defined 3D SWCNT film. As discussed before, it is possible to assemble SWCNT on both PR surface and SiO$_2$ surface. However, the ability to nucleate and forming the film is different depending on the surface condition and the solution condition as well. For fresh solution, after stripping off the photoresist, separated patterns such as arrays of isolated SWCNT micro-lines can be obtained. However, if the solution is repeatedly used for more than three dip coating cycles (each cycle takes about 1.5 hours), 3D SWCNT film began to form. Therefore, to make stable SWCNT film, a five-hour aging of new solution was performed at room temperature. The possible influences from aging in air are solution evaporation and interaction between molecules in air such as O$_2$ and the functional group on the surface of SWCNT. The solution evaporation will cause a slight increase of SWCNT concentration. The interaction between O$_2$ and the functional group on the surface SWCNT can also lead to larger agglomerate of SWCNT and change the interfacial energy.
between SWCNT and the surface of substrate. Unfortunately, we do not have information on the surface functional group due to commercial secret protection. However, it is evident that the interaction between SWCNT and PR surface can be greatly enhanced by this aging process. Considering possible influences, we believe physically increased concentration of SWCNT solution together with the chemically enhanced interfacial interaction between SWCNT and substrate account for better assembly on PR surface.

In summary, as the result of balance between the capillary and hydrostatic pressures close to the reservoir on the surface of heterogeneous patterned substrate, cross-talk between the flow profiles results in a wave-like variation in the receding contact line profile with significantly enhanced wettability of the PR lines, and thereby continuous but heterogeneous SWCNT film deposited.
2.6 Assembly 3D SWCNT film on different substrates

Assembly of SWCNT film on heterogeneous PR/Au/SiO₂ substrate (a) and (b), on PR strips patterned quartz chip, (c), (d) and (e) and PR dots patterned SiO₂ substrate(f). (c) An optical picture of SWCNT film assembled on the quartz substrate after removing the PR.

Figure 17. 3D SWCNT film on different substrates.

To prove the scalability of our technique, SWCNT film can be assembled on different substrates with different patterns. For example, a more complicated substrate can be prepared as follows. First, Au contact pad (50 nm thick) was deposited on the SiO₂ substrate and then PR was patterned using photolithography into strips (6 μm in width and 9 μm in space). As shown in Figure 17a and 17b, SWCNT film was assembly on the heterogeneous substrate and even across the boundary between Au and SiO₂. It is also possible to assembly the SWCNT film on other substrate such as quartz with the same PR pattern size as Figure 17a, as shown in Figure 17c, 17d and 17e. The optical image in Figure 17c, indicates the transparent nature of the 3D SWCNT film. Further, SWCNT film can be assembly on SiO₂ substrate with different PR patterns. As
shown in Figure 17f, PR was patterned in to dot shape (7.5 μm in width and 7.5 μm in space) and SWCNT film was assembly on the lower half of the substrate showing as bright contrast.

2.7 Summary

In this chapter, a facile method to tailor the electrical and thermal properties of ultra-thin SWCNT film has been developed. A micro-patterned heterogeneous substrate with alternating hydrophobic and hydrophilic strips was fabricated as the target substrate for the assembly of SWCNT and SWCNT can selectively assemble on the heterogeneous strips with thinner film formed on hydrophobic regions. The resultant film has higher electrical and thermal conductivity in the direction parallel to the strips than that in the perpendicular direction. The film thickness as well as the anisotropy can be controlled by changing the height of hydrophobic photoresists according to the cross-talk mechanism. Other than conventional methods controlling the alignment of SWCNT network with the help of external field, this method provides a new strategy using the combination of surface chemistry and morphology to control the structure and anisotropic properties of resultant SWCNT film. Since the surface treatment can be processed in large scale and no external field is required during the assembly, our method is more effective and energy saving compared to the conventional methods.
Chapter 3. Suspended SWCNT–Polymer Architectures and Wet-Contact Printing Method

3.1 Introduction

Three-dimensional (3D) hierarchy electronic structure with high input/output (I/O) density is the direction for driving future electronics, especially for micro-electro-mechanical system (MEMS) or nano-electro-mechanical system (NEMS), leading to extensive requirement of miniaturized sensing and driving units. SWCNTs are graphene sheets rolled up into the cylindrical shape with diameters as small as one nanometer. It is an ideal material for MEMS and NEMS devices and systems due to their unique one dimensional nanostructure and extraordinary electrical, mechanical, and thermal properties\textsuperscript{44,48,52,60}. Also SWCNT films are optically transparent but electrically conductive. Therefore, a wide range of applications based on suspended nanotube MEMS/NEMS devices with outstanding properties have been demonstrated, e.g. hysteresis free transistor\textsuperscript{110}, resonators with frequency up to gigahertz\textsuperscript{111,112}, sensor\textsuperscript{113}, actuator such as artificial muscle\textsuperscript{114}, atomic lever balance\textsuperscript{115,116}, switch for memory system\textsuperscript{117}, bolometer\textsuperscript{118} and illuminator\textsuperscript{114}. Note that, as the driving and sensing unit, the suspended SWCNT architectures are desirable, since the properties of SWCNTs with all of carbon atoms are located on the surface are strongly influenced by the surrounding environment\textsuperscript{28,119}. For example, in a thermal fluidic sensor with carbon nanotube on the substrate, the thermal energy generated on carbon nanotube partly dissipated into the substrate other than fully dissipated to the flow leading to a compromised precision and sensitivity\textsuperscript{120,121}. Another example is that photoluminescence can be only found on suspended SWCNTs\textsuperscript{45,122}.

However, in the MEMS and NEMS systems where many suspended and moving units are closed packed, the microscale interactions such as meniscus force, electrostatic force and etc.,
will greatly influence the fabrication process as well as the device performance once the package is becoming smaller and smaller\textsuperscript{38,40,123,124}. Therefore, the fabrication and operating processes have to be taken with extreme care to eliminate the possible microscale interactions and under certain circumstances, special treatments have to be processed which will greatly diminish the producing efficiency. For example, after the wet-etching, supercritical drying has to be processed to remove the residue water or solution preventing the merging or collapse of suspended units\textsuperscript{125}. However, this supercritical drying has to be processed in an isolated chamber and it is impossible to process the whole manufacturing in a continuous manner. Therefore, new techniques to suspend SWCNT with good scalability and efficiency are desirable.

For the future vision of flexible application, it is necessary to integrate suspended SWCNT with flexible substrate. However, it is not applicable to directly grow suspended SWCNT on the polymeric substrate because the high temperature process can easily damage the substrate\textsuperscript{46}. Moreover, the methods of etching polymeric substrate under the SWCNT are subjected to the issues such as poor shape accuracy, degradation of substrate, difficulty to process and low efficiency\textsuperscript{126}. Therefore, transfer methods become the most applicable strategies. But, the scalable integration of SWCNTs into organized and suspended micro/nanostructures on a flexible polymer substrate that harnesses CMOS friendly low-temperature assembly and transfer processes remains extremely challenging by limited fundamental understanding of the interplay at interfaces between SWCNTs, polymer surface and solution.

In this chapter, I have combined the state-of-the art assembly process and novel transfer paradigm, wet-contact printing method, inspired by superhydrophobic Lotus surface to achieve very large-scale suspended nano/microscale SWCNTs networks on patterned polymer substrates which can be used as platforms for building various flexible and transparent MEMS devices. The
interactions among micro-patterned polymer surface, water based solution and their solid-liquid-vapor interfacial behaviors during the transfer process, the influence of chemical nature of the substrate (surface energy), different surface structure as well as dimension of polymer patterns will be systematically investigated to obtain experimental and theoretical guidance for developing fully scalable transfer technology.

3.1.1 Methods to suspend SWCNT architectures

![Figure 18. Methods to suspended carbon nanotube architectures in microscale.](image)

(a) Transmission electron microscopy (TEM) image of suspended carbon nanotube grown on the micropillar\textsuperscript{127}, (b) Scanning electron microscope (SEM) image of the suspended carbon nanotube fabricated by the ac electrophoresis\textsuperscript{126}, (c) schematic of deliberately controlled transfer of suspended carbon nanotube\textsuperscript{93}, (d) schematic of etching method to make suspended carbon nanotube\textsuperscript{125} and (e) schematic of the method of transferring and etching from SWCNT wafer and SEM images of suspended SWCNT film, cantilever and multitier interconnects over Si supports such as pillars and beams\textsuperscript{128}.

Macro-sized thick and strong suspended (free-stand) SWCNT film (sheet or buckypaper) can be obtained by different methods such as filtration method\textsuperscript{129,130}, and drawing from sidewall of as-grown nanotube forests\textsuperscript{2,57,114}. However, in this study, due to the size limitation of
MEMS/NEMS device, microscale SWCNT network is the main target. The methods to achieve microscale suspended carbon nanotube can be divided into five categories: i) directed growth\textsuperscript{110,131-133}, ii) electrophoretic method\textsuperscript{55,126,134}, iii) direct transfer\textsuperscript{93}, iv) backside etching\textsuperscript{111,125,135} and v) transferring and etching\textsuperscript{128}.

The suspended carbon nanotube can be in-situ grown on the isolated islands\textsuperscript{133} or micropillar deposit with catalyst\textsuperscript{45,127,136}. Figure 18a shows the suspended SWCNTs grown on Si pillar\textsuperscript{127}. Ultraclean SWCNTs with well-defined diameters can be obtained\textsuperscript{133}.

In the electrophoretic method, SWCNTs can be suspended between two electrodes by the combination of ac-electrophoresis and lithography. At first, the gap between two electrode was filled with poly(methyl methacrylate) (PMMA) using lithography process, and then SWCNTs were assembled by the method of ac-electrophoresis. Finally, the PMMA under the SWCNTs was lift off leaving suspended SWCNTs as shown in Figure 18b\textsuperscript{126}. Also, SWCNTs can be directly assembled on 3D patterned substrate with electrodes through dielectrophoresis forming 3D SWCNT interconnect architectures\textsuperscript{134}.

In the direct transferring method, individual suspended SWCNT can be mounted on the desired location using the contact stamping transferred method\textsuperscript{93}. A schematic is shown in Figure 18c, in which a SWCNT grown on a quartz substrate is mounted upside-down on a blank mask and transferred to a device substrate with electrodes. SWCNT is cut off at the contact point and the suspended part is released across the electrodes.

Backside etching is widely used in MEMS and NEMS technology and is also a straightforward method to fabricate suspended carbon nanotube as shown in Figure 18d\textsuperscript{125}. First, carbon nanotube was grown on the SiO\textsubscript{2}/Si substrate, and then the surface was pattern using lithograph
to expose the nanotube partly. Using Buffered HF, the SiO$_2$ underneath the exposed carbon nanotube was removed leaving suspended carbon nanotube. Suspended SWCNT architecture can be obtained by evaporating the solution using supercritical drying.

Recently, Hayamizu et al., combined the transferring and etching technology and fabricated large arrays of suspended SWCNT architecture over rigid substrate patterned with Si pillars$^{128}$. The idea of this method is to first transfer SWCNT wafer (a form of nanotube film) to the micropatterned Si substrate and then use photolithography to selectively protect the surface of SWCNT wafer followed by reactive ion etching to form various SWCNT patterns. Finally, after striping the protective photoresist, a variety of suspended SWCNT architectures (film, cross, cantilever and multitier interconnect) can be obtained.

Though remarkable efforts have been made towards highly organized and large scale suspended SWCNT architecture, few methods were compatible with flexible substrate. For example, the direct growth methods involve high temperature processes, which will damage the polymeric substrate. Also, the growth method has poor control over the number, morphology (alignment, junctions) and the properties of SWCNT. The electrophoretic and backside etching methods are originated from conventional MEMS and NEMS technology and therefore are more compatible with current industrial processes. However, since the interactions in micro- to nano-scale are complicated, the controllability as well as the efficiency of process is very low and the processes are expensive. Electron beam (E-beam) lithography, a very expensive and time consuming process, has to be applied to fabricate micro- to nano-scale contact pads. Repeated etching and deposition processes are also required for substrate fabrication. Finally, to avoid meniscus force during drying, supercritical drying is applied which greatly hinder the continuity of the device fabrication. These difficulties make it hard to fabricate large scale SWCNT devices
at one time. Direct transferring method is most straightforward. However, this method requires extreme controllability in alignment and handling which greatly limit the efficiency and thereby the scalability of this method. Moreover, this method is a dry method which is not compatible with current CMOS technologies where repeated solution processes and high temperature processes are usually involved. Finally, the transfer and etching method has been demonstrated on the rigid substrate (Si). However, if applied to flexible polymeric substrates, the interface between nanotube and polymeric substrate needs to be reconsidered because the following etching and lift-off process can easily disturb the suspended architecture.

In summary, the current technologies cannot fulfill the requirement for large scale suspended SWCNT especially in flexible MEMS and NEMS systems due to the nature of nanotube (small size) and polymeric substrate. On one hand, fundamental understanding of the micro- and nano-scale interactions among SWCNT, substrate and environment has to be developed at the interface between SWCNT and substrate. On the other hand, new technologies are highly desirable in the fabrication of organized flexible SWCNT MEMS and NEMS systems in a controllable and scalable manner. Technology that compatible with commercialized MEMS and NEMS fabrications is most valuable because it can be integrate with industrialized process easily. However, since many wet processes (repeated etching and development) are involved, it is of great challenge to maintain the suspended architectures during these processes. Therefore, a smart design is required for flexible polymeric substrate, which will be discussed in the following section.

3.1.2 Superhydrophobic surface and Lotus effect

To develop transferring technology under wet condition, understanding and utilization of solid-liquid-vapor (SLV) interface at microscale are important. Nature has developed a variety of
strategies to manipulate the SLV interface through the creation of micro- to nano-structures on the surface which is of crucial importance for many biological processes\textsuperscript{137}. For example, insects in the dessert can capture water using superhydrophilic surface and Lotus leaves can clean the surface with its self-cleaning function originated from its superhydrophobic surface\textsuperscript{138-142}. Our inspiration for creating suspended architectures is directly coming from the superhydrophobic surface.

A surface is superhydrophobic (or ultrahydrophobic, ultrophobic) if drops move easily on it without pinning, irrespective of the value of their contact angle\textsuperscript{143}. In another definition, a superhydrophobic surface is defined as a surface with water contact angle larger than 150 ° and to the opposite, a superhydrophilic (or ultrahydrophilic, ultraphilic) surface is the surface with contact angle close to zero\textsuperscript{144,145}. In recent years, surfaces with these extreme wettability (both natural and artificial) have been extensively investigated and created\textsuperscript{137,139-142,145-152}. The most important function of a superhydrophobic surface is the so-called Lotus effect (or self-cleaning effect), where the micro- and nano-patterned Lotus leaf surface is strongly repelling the water and the droplets flowing across the Lotus leaves can removed the contaminates such as dirt and pathogens along\textsuperscript{139-141}. By mimicking the microstructures of Lotus leaf surface and other natural superhydrophobic bio-interfaces using artificial structures such as polymer and micro- and nano-particles, researchers can create artificial superhydrophobic surfaces\textsuperscript{145,153,154}. In industry, superhydrophobic surface having self-cleaning function can be designed to stop clotting in artificial blood vessels, to prevent the adhesion of snow to antennas and windows, to fabricate the self-cleaning traffic indicators, to reduce frictional drag on ship hulls, to refine metal, to form stain-resistant textiles and even to separate oil and water\textsuperscript{151,155,156}. 
The superhydrophobic surface is termed as Cassie-Baxter regime (or Cassie regime) where air is trapped under the liquid and a heterogeneous SLV interface composing both solid-liquid and vapor-liquid interface is formed between droplet and supporting substrate\textsuperscript{152}. The schematic of heterogeneous interface can be found in Figure\textsuperscript{19c}, upper panel. A superhydrophobic surface is naturally a self-cleaning surface which has been proven by many researchers\textsuperscript{140,141,151,152}. However, it is interesting to think in a reversed manner, whether it is possible to utilize the hydrophobic properties for sorting or catching the target materials. As shown in Figure \textsuperscript{19a}, for the self-cleaning process, the interaction between target material and substrate is minimized because of the minimized the contact area, and usually the target materials in the nature are more readily wetted by water compared to hydrophobic substrate\textsuperscript{140}. Therefore, as droplet pass through the surface, the target materials go along. Note that, it does not necessarily mean that $\gamma_{\text{target materials-substrate}}$ is larger than $\gamma_{\text{target materials-solution}}$, considering the limited contact between target materials and substrates. In a printing process, as shown in Figure \textsuperscript{19b}, by choosing the combination materials, lower $\gamma_{\text{target materials-substrate}}$ and higher $\gamma_{\text{target materials-solution}}$ lead to a stronger interaction between target material and substrate than that between target material with solution such that target materials can be printed to the substrate and cannot be easily removed by the solution. A conformal contact between target materials and substrate during the transferring process will be helpful to maximize the contact area leading to stable printed structures. At the same time, the solution having high $\gamma_{\text{solution-substrate}}$ can be removed easily similar to the self-cleaning process. Therefore, by simply tailoring the interfacial energy among the target materials, solution and substrate, different function can be realized (self-cleaning or printing).
**Figure 19.** The interactions among target materials, solution and superhydrophobic substrate and the interface between solution and patterned substrate.

Interactions for a self-cleaning process (a) and a printing process (b). (Figure a, Left panel, courtesy from William Thielicke.) The relative strength of the interaction between two contacting materials is proportional to the width of the red arrows. Both interfacial energy $\gamma$ and contact area have to be considered to judge the strength of interactions. (c) The solid-liquid-vapor interface between solution and micropatterned substrate: heterogeneous interface with both solid-liquid and solid vapor interface (superhydrophobic surface) and homogeneous interface with only solid-liquid interface.

As we have discussed, the micro-patterned substrate does not always show superhydrophobic properties. For some designs, the droplet can wet all the protruding features forming homogenous interface (only solid-liquid interface), as shown in Figure 19c, lower panel. The contact angle of water on a micro-patterned substrate can be predicted by Wenzel Equation (homogeneous interface) and Cassie-Baxter Equation (heterogeneous interface)$^{157,158}$. Wenzel deducted the first theoretical analysis of homogeneous interface with the thermodynamic arguments modified Young’s equation and built the relation among surface roughness factor ($r$)
and the apparent contact angle on patterned substrate ($\theta_i$) and true contact angle on flat surface ($\theta_{i,0}$),

$$\cos \theta_i = r \cos \theta_{i,0},$$

(3.1)

where $r$ is the ratio of actual surface area ($A$) and the projected area ($A_0$)\textsuperscript{157}. Alternatively, for heterogeneous interface, the relation between apparent ($\theta_i$) and true ($\theta_{i,0}$) contact angle is given by Cassie and Baxter,

$$\cos \theta_i = \varphi (\cos \theta_{i,0} + 1) - 1,$$

(3.2)

where $\varphi$ is the area fraction of solid that in contact with the solution\textsuperscript{158}. Please note that, the two wetting modes are transformable. One is local energy minimums and the other one is global minimum depending on the structure and material of substrate\textsuperscript{159,160}.

### 3.2 Experimental

The wet-contact printing method can be realized through two different routes. Route 1 is schematically shown in Figure 20a. First, arrays of SWCNTs micro-lines (black strips, step 1) were created on the SiO$_2$ (shown in blue) substrate by using the above mentioned fluidic assembly of SWCNTs\textsuperscript{102-105,161}. The key is the SWCNT structures have to be deposited on the surface of SiO$_2$ layer which will act as a sacrificial layer in the following etching step. Then the substrate was dipped into the diluted HF acid solution to remove a SiO$_2$ sacrificial layer and taken out without drying the surface, followed by an immediate stamping with a pre-patterned PDMS substrate (illustrated as the transparent blue substrate, step 2). This wet-etching process greatly attenuates the adhesion between SWCNTs patterns and the underlying substrate, and when the PDMS stamp is peeled off (step 3), it allows an extremely fast transfer of the
horizontally aligned SWCNTs micro-lines onto the patterned PDMS surface. Figure 20b shows arrays of centimeters long and aligned SWCNTs micro-lines (9 µm in width and 10-20 nm in thickness) suspended orthogonally across PDMS micro-trenches (6 µm in width, 3 µm in depth and 9 µm in space between the nearby trenches). Note that the self-adhesion between the nanotubes is robust and hence it allows a perfect transfer even in the trench regions, where the mechanical support of PDMS is absent.

**Figure 20.** Wet-contact printing method and suspended SWCNTs-polymer hybrid structures in Route 1162.

(a) The schematic of Route 1. Step 1: SWCNTs were assembled into aligned micro-lines structure (black lines) on a Si substrate (yellow layer) with a SiO₂ sacrificial layer on the top (blue layer). Step 2: the SiO₂ was etched using diluted HF acid solution and then a PDMS stamp (blue and transparent) patterned with micro-trenches on the bottom was brought in contact with the SWCNTs/Si substrate at a right angle with respect to the arrays of SWCNTs micro-lines.
Step 3: the PDMS stamp inked with suspended SWCNTs micro-lines was peeled off, put upside down and dried in ambient condition. (b) Highly ordered arrays of one centimeter long SWCNTs micro-lines (9 μm in width) suspended across PDMS micro-trenches (6 μm in width, 3 μm in depth and the distance between nearby trenches is 9 μm). (c) Larger SWCNTs micro-lines (100 μm in width) suspended on similar PDMS micro-trenches but larger depth (6 μm). Scalar bars are 10 μm for both (b) and (c).

Route 2 schematically shown in Figure 21a is slightly different: i) SWCNT micro-lines were patterned on SiO$_2$/Si substrate; ii) a polymeric substrate patterned with micro-strips was brought in contact with SWCNT micro-lines; iii) the combined substrate was brought upside down and then etched by diluted HF acid solution (16 wt%). The SWCNT architectures can be released to polymeric substrate after SiO$_2$ sacrificial layer was etched away and donor Si substrate was removed. iv) The residue HF acid solution was removed by simply tilting the substrate and sample can be dried in atmosphere to get rid of any possible residue solution. In both schematics, we choose micro-lines for SWCNT and micro-strips for polymeric substrate. However, in the real case, various suspended architectures, from individual SWCNT to macro-scale SWCNT film and other nanomaterial such as graphene as well, can be transferred by this method. The choices of micro-morphology and the material of receiving polymeric substrate are wide. Arrays of microscale strips (Figure 21b) or pillars (Figure 21c) with different spacing can be used to support the suspended architectures. Also, we have demonstrated this method with different polymeric substrates: soft PDMS substrate which is a typical elastomer widely used in flexible electronics (Figure 21b and 21c), rigid SU-8 substrate which belongs to the epoxy resin family (Figure 21d) and nanoscale patterned PMMA substrate. Even more interestingly, the suspended SWCNT can be formed on a gold-coated surface (Figure 21e), indicating the possibility of directly building the device on a flexible substrate with pre-deposited metal contact pad.
Figure 21. Wet-contact printing method and suspended SWCNTs-polymer hybrid structures in Route 2.

(a) The schematic of Route 2. (b) Tilted SEM image of 6-μm-wide SWCNT micro-lines transferred to PDMS substrate with different trench widths from 0 to 6 μm. (c) Tilted SEM image of 6-μm-wide SWCNT micro-lines transferred to PDMS substrate with micro-posts with 6 μm in diameter and 12 μm in spacing. The height of the micro-patterns is 6 μm. (d) Tilted SEM image of 6-μm-wide SWCNT micro-lines transferred to SU 8 substrate (e) Tilted SEM image of
6-μm-wide SWCNT micro-lines on Au (150 nm) coated SU 8 substrate. The scalar bars are (b) 10 μm (2 μm for inset), (c) 10 μm (2 μm for inset), (d) 10 μm and (e) 10 μm (1 μm for inset). For SEM imaging, all the samples were coated with a very thin layer (several-nanometer thick) of Au/Pd to eliminate the charging of polymer except (e) where Au layer was deposited under the SWCNT before transferring.

It is clear that both routes can achieve the suspended SWCNT architectures. The difference between two routes is whether to etch the sacrificial SiO\(_2\) layer before contact with receiving polymeric substrate. The advantage of route 1 is that HF can etch the SiO\(_2\) from three directions (top and two sides) leading to a fast etching and thereby fast transferring process. However, if the SiO\(_2\) layer under the SWCNT is completely removed, the alignment of SWCNT architectures can be hardly maintained and the worst case is the complete detachment from the substrate leaving no feature to transfer. So the etching period has to be very short, usually in the order of several seconds, and then the donor substrate has to be lifted from solution and brought into contact with receiving substrate immediately. The operation window between the lift and contact print should be in the order of several seconds to avoid over etching since the acid solution is still reacting with the sacrificial layer. Therefore, even though the process of route 1 is extremely fast, the short working window makes it very challenging to control. That is the reason that we further developed route 2 to achieve better controllability. The advantage of route 2 is evident: the alignment of SWCNT on original substrate can be beautifully maintained because SWCNT architectures are already in contact with receiving substrate before the etching process. The adhesion between SWCNT and substrate can hold SWCNT exactly at the position that in contact substrate. The only drawback is that the HF acid solution has to etch the SiO\(_2\) layer from the side leading to a longer etching period (1 to 2 min depending on the size of the donor substrate). For a 500 μm penetrating distance, one min is good enough to etch through the SiO\(_2\) layer. So for route 2, better controllability is achieved at the cost of increased etching time. But compared to other
methods, one or two minutes is still a very short processing period. Due to the enhanced stability and controllability, I will mainly focus on route 2 in the following discussions.

The receiving substrates were fabricated by different methods due to the nature of materials. Micro-patterned PDMS substrates were obtained by molding from a bas-relief master mode. The master molds are made of SU-8 (2007) photoresist on SiO\textsubscript{2}/Si substrate by optical lithography. The SU-8 (2007) photoresist was spin coated (Laurel Spinner) on SiO\textsubscript{2}/Si substrate at 500 rpm for 20 s with acceleration of 100 rpm/s and then ramp up to 6000 rpm for 60 s with acceleration of 330 rpm/s. The pre-bake was processed at 65 °C for 1 min and then 95 °C for 2 min. Exposure was performed using Quintel 4000 Mask Aligner with polarized filter for 60 s. The post-bake was processed at 65 °C for 1 min and then 95 °C for 2 min. The mold was developed in SU-8 developer for 1 to 2 min followed by rinsing in fresh isopropyl alcohol. The thickness of SU-8 structure for the current receipt is 6 µm. Higher structures can be fabricated by simply lowering down the spinning speed or using SU-8 with higher series number, e.g., SU-8 2025. PDMS (Sygard 184, Dow Corning Corp.) was fabricated by mixing the monomer with curing agent at the ratio of 10:1 and then casting uncured PDMS into a stainless steel mode. The baking temperature was 115 °C and the baking time varied from 1 to 8 min depending on the thickness of the PDMS substrate (from 500 µm to 5 mm). The hardness can be tailored by increasing the ratio of curing agent to 10:3. However, unless mentioned otherwise, 10:1 will be the standard ratio for the PDMS appeared in the following discussions.

Unlike the free stand PDMS substrate, SU-8 substrates were prepared on a supporting substrate (Si, SiO\textsubscript{2}, or glass) due to its thin film structure. To prevent any possible damage from the etching solution, a protective layer SU-8 2007 was spin coated on the surface of supporting substrate following the same procedure as we mentioned before for the mold except that no mask
was applied during the exposure and there was no developing process. For the second layer of SU-8, exact the same procedures were followed as described in the master mold fabrication.

PMMA (Nano\textsuperscript{TM} PMMA, 950,000 molecular weight, Series A7, MicroChem, Corp.) substrate with nanoscale patterns was fabricated using electron beam lithography (Zeiss Surpa 25, SEM with J.C. Nabity ver. 9- lithography and pattern generation system) The PMMA solution was first mixed with thinner to make 250 nm thick layer. The diluted solution was spin coated on Si substrate at the speed of 5000 rpm for 60 s with maximum acceleration followed by baking at 160 °C for 90 s. The PMMA film was further exposed using electron beam lithography and developed in MIBK/IPA (1:3) solution.

Note that SWCNT architectures are not limited to micro-lines in the schematic. Individual SWCNT to macro-scale SWCNT film and other nanomaterials such as graphene can be transferred by this method. Also, there is no specific requirement for fabricating technologies of SWCNT. For example, SWCNT architectures can be achieved through template guided fluidic assembly\textsuperscript{34}, etching large film using plasma\textsuperscript{6}, spinning\textsuperscript{14} and etc. Most of SWCNT micro-line structures in this chapter were obtained through the method of template guided fluidic assembly as described in chapter 2. The width of micro-line is determined by the width of lithographically opened hydrophilic SiO\textsubscript{2} surface treated by plasma. The dip coating speeds were 0.1 mm/min for micro-lines with width less than 10 μm and 0.05 mm/min for 100 μm wide micro-lines or larger film and the concentration of SWCNT/DI water solution was 0.23wt%. Fresh solution was used to make sure well-separated SWCNT micro-lines. Unless mentioned otherwise, the SWCNT micro-line is 6 μm in width. The assembled sample has the drawback of non-uniform cross section, because thicker edges of the SWCNT film are formed at the corner between photoresist and SiO\textsubscript{2} surface. Therefore, for some of the applications (e.g., electro-mechanical test in
Chapter 5), we can first assemble a SWCNT film on bare SiO$_2$/Si substrate. And then spin coat a layer of optical photoresist (S1818) on the top of SWCNT film followed by standard lithography to expose the area for the next O$_2$ plasma etching process. O$_2$ plasma etching (power = 64 W, flow rate =16 sccm) was processed for 4 min to fully remove the exposed SWCNT. Finally, the protective photoresist was stripped off by acetone, rinsed in fresh isopropyl alcohol and dried using N$_2$. By this method, SWCNT film can be fabricated in an arbitrary size with a uniform thickness depending on the dip-coating speed. Individual nanotube can be simply deposited on SiO$_2$/Si substrate by spinning method. SWCNT/DI water solution (0.23 wt%) was dropped on SiO$_2$/Si substrate and spun with initial spinning speed of 200 rpm for 20s and then ramped up to 2000 rpm for 60s. The sample was further dried at 115 °C for 1 min.

For SEM imaging, all the suspended SWCNT-polymer architectures were coated with a very thin layer (several-nanometer thick) of Au/Pd to eliminate the charging of polymer except for the cases where metal layer is deposited before the transferring process or mentioned otherwise.
3.3 Mechanism

3.3.1 Heterogeneous and homogeneous interface

Figure 22. The microscale interface for wet-contact printing method (left route) and convention MEMS/NEMS method (right route).

It is essential to understand the role of superhydrophobic surface in wet-contact printing method and its relation with the status of SWCNT (suspended or collapsed). The mechanism is proposed in Figure 22. As shown in Figure 22 (top), the polymeric substrate patterned with
arrays of micro-strips with the width, $x$, center distance between the nearby strips, $y$, and height, $z$, is applied as an example. A characteristic phenomenon of a superhydrophobic surface is the formation of heterogeneous SLV interface on patterned substrate and air pockets trapped in the trenches (left route, Figure 22). This will become the core idea of the formation of suspended SWCNT architectures. The target of wet-contact printing process is to place the SWCNT architectures at the heterogeneous interface. Since no solution can penetrate into the air pocket between suspended SWCNT and the bottom of the polymeric substrate due to the strong solution repelling nature of the substrate, suspended SWCNT architectures can be obtained after removing the solution on the top. To the opposite, if a homogeneous interface (only solid-liquid interface, right route, Figure 22) was formed, usually happened in the conventional wet MEMS and NEMS processes, a collapsed SWCNT architecture is expected for a regular evaporation process because the meniscus force from solution sandwiched between SWCNT and ground of the substrate can drag the suspended architectures down to the substrate$^{38,40,123,124}$. Therefore, except for those “dry methods” such as direct growth$^{45}$ and contact printing method$^{3,4,93}$, wet methods to obtain suspended SWCNT architectures need to employ a supercritical drying process to overcome the meniscus force$^{125,126}$. The supercritical drying process has to be processed in an isolated chamber at deliberately controlled pressure and temperature with the assistance of another gas. Therefore, compared with our method, conventional MEMS/NEMS processes are less effective, more expensive and higher energy consuming.
Figure 23. The contact angle measurement of water on polymeric substrates (PDMS and SU-8) with constant $x$ and $z$ ($x = z = 6 \, \mu m$) but changing $y$ from 9 to 120 $\mu m$.

(a) The contact angle measurement of undisturbed water droplets on PDMS (left column) and SU-8 (right column) with flat substrate (upper panel), and patterned substrate from the front view (middle panel) and side view (lower panel). The undisturbed droplets were deposited very gently on the substrate without any momentum. (b) Dependence of contact angle (from front view) on micropatterned substrate with the same strips width ($x = 6 \, \mu m$) but different center space ranging from $y = 9$ to 120 $\mu m$ for both PDMS (upper panel) and SU 8 substrate (lower panel). Theoretical calculations from heterogeneous and homogeneous interface are shown as black dash line and red dash lines respectively. The contact angles for undisturbed droplets were summarized as red squares. To mimic the disturbance during the transferring process, the droplets were released at elevated height of 20 mm from the head of needle to the substrate (green square). A clear transition from heterogeneous interface to homogeneous interface can be seen for the PDMS sample with $y = 120 \, \mu m$, indicating the instability of the water-polymer interface of the substrate with larger strip center distance.

As mentioned above, the contact angle measurement can be used to probe the type of SLV interface. The type of SLV interface is dictated by the surface structure. A series of substrates with constant $x$ and $z$ ($x = z = 6 \, \mu m$), but changing $y$ (varies from 9 to 120 $\mu m$), have been designed from two different polymers (PDMS and SU-8). There are two releasing modes of the
water droplet: gently releasing with no momentum to the substrate termed as undisturbed droplets and releasing the droplet from elevated height (20 mm from head of needle to the substrate) to mimic the disturbance during the transferring process. The measurements from undisturbed droplets are close to ideal case indicating the limit of the system. On the other hand, the measurement from elevated droplets can provide more realistic information of SLV interface during the transferring process. However, the real transferring process is much more complicated and there are several source of disturbance such as the detaching process of donor substrate, the fluidic field when removing the solution, vibration during handling and etc. Therefore, the measurements from elevated droplet can only provide qualitative compare with respect to the ideal case. The predicted theoretical curves of heterogeneous interface (black dash line) and homogeneous interface (blue dash line) for two polymers are plotted in Figure 23b. In the case of micro-strips $r = (y+2z)/y$ and $\varphi = x/y$. $\theta_{i0}$ is measured to be 109.6 for PDMS and 71.1 for SU-8 by gently depositing the water droplets (undisturbed droplet) on flat PDMS substrate and flat SU-8 substrate. The flat PDMS substrate is fabricated by casting uncured PDMS (3 ml) into a stainless steel mode followed by baking at 115 °C for 8 min and the top surface flattened by gravity is used as the test plane. The flat SU-8 substrate is fabricated following the exact recipe for making the patterned substrate including the developing process, except that transparent mask is used for exposure.

A typical contact measurement of undisturbed droplet was shown in Figure 23a in which both flat and micro-patterned substrate ($y=12 \mu m$) were measured. For the micro-strips patterned substrate, the wetting of the surface is anisotropy and the measurement from front view is more meaningful, since less confinement has been exert on the solution along the strip direction (side view) (Figure 23a). For the safety reason, DI water has been used here to substitute the diluted
HF acid solution. Diluted HF acid solution does not change the surface morphology of supporting substrate within the short period of transferring process, which will be addressed later in the same section.

For a specific design, a lower contact angle indicates lower potential energy of the corresponding SLV interface and therefore a more stable status\textsuperscript{159}. For example, for PDMS substrate (Figure 23c, upper), when $y$ is less than 12 µm, heterogeneous interface (black dash line) is energetically more favorable, while beyond that, the homogeneous interface (blue dash line) is more favorable. For SU-8, the homogeneous interface is more favorable for all the designs. However, in a real wetting process, the kinetics of wetting process has to be considered and a heterogeneous interface will form first if the solution is put on the surface very gently (no momentum) even though the homogeneous interface is energetically more favorable\textsuperscript{144,152,159}. This statement is supported by our experiment using undisturbed droplets, in which heterogeneous interfaces were formed for almost all the designed substrates including both PDMS and SU-8 (Figure 23c, red dot), even at a very large center distance $y = 120$ µm, where the homogeneous interface has a much lower energy level and a large driving force exists between the two kinds of interfaces. It seems an exception for PDMS substrate with $y = 9$ µm in which the contact angle measurement agrees better with homogeneous interface. However, the transfer experiment proved that $y = 9$ to 12 µm is the most stable transferring regime for suspended SWCNT (Figure 21b), and the resultant suspended structures can survive even after rinsing and slight disturbing in the water solution. For these two samples, the data of elevated droplets could not be collected because the droplets bounce away with the initial momentum. This will be further addressed in the following section (3.3.2 Potential energy analysis). In more
realistic case with elevated droplets (green dots), a gradual transition from heterogeneous interface to homogeneous interface can be seen.

![Image](image.png)

**Figure 24.** Direct evidence for heterogeneous interface and the influence of HF acid solution on surface roughness.

(a) Optical (upper) and SEM (lower) images of the deposition of fluorescent nanoparticles on patterned PDMS substrate by mixing the fluorescent particles into HF acid solution and depositing the droplet on the surface of PDMS substrate. Scalar bars: 15 µm for upper panel, 10 µm for lower panel, 200 nm for inset. (b) The surface roughness of PDMS (monomer/curing agent = 10:3) substrate before and after the HF acid etching for 1 min.

Note that, HF acid solution can react with PDMS in a slow manner. Therefore, HF acid solution might not be able to form heterogeneous interface as pure water does. Due to the safety reason, we could not perform contact angle measurement using HF acid solution. Alternatively, a
simple experiment has been performed to check the effect of acid solution. Fluorescent nanoparticles (Green fluorescent, ~450 nm in diameter, Duke Scientific Corp.) were mixed into the HF acid solution before transferring process and then an identical transferring process on the surface of PDMS substrate \((x = 9 \text{ and } y = 15 \text{ µm})\) was processed. Fluorescent particles should be deposited on the surface that wetted by HF acid solution. The formation of heterogeneous interface is evident, because both optical and SEM images show that all the particles are located on the top of strips and no particle can be found in the trenches (Figure 24a). Also, the surface roughness of PDMS before and after transferring process has been studied by AFM showing no apparent change after the HF etching (Figure 24b). Therefore, it is reasonable to believe that the slow interaction between HF acid solution and PDMS would not influence the wetting mode significantly since processing time of wet-contact printing is short (1 or 2 min).

3.3.2 Potential energy analysis

It is important to note that heterogeneous and homogeneous interfaces are transformable to each other depending on the substrate structure, kinetics of wetting process, and the environmental effects\(^{152,159,163}\).
Figure 25. Potential energy schematic of homogeneous (Wenzel’s theory) and heterogeneous interface (Cassie-Baxter’s theory).
(a) Relative potential energy comparison of SLV interface for substrate with different center distance (Courtesy from Patankar)\textsuperscript{159}. (b) Experimental results for PDMS substrate with \(x = 6\) and \(y = 9\) to 120 \(\mu\)m with undisturbed droplet (red dot) and elevated droplet (olive dot). (c) Potential energy defined working windows for suspending SWCNT: stable regime with potential energy of heterogeneous interface no less than that of homogeneous interface and large energy barrier between the two energy levels, meta-stable regime with lower potential energy for homogeneous interface but moderate energy barrier between two energy levers and unstable regime with much lower potential energy for homogeneous interface and small energy barrier.

Partankar \textit{et al.}, further developed the theory for forming heterogeneous interface and brought out the potential energy schematic for hydrophobic surface such as PDMS as shown in Figure 25a\textsuperscript{159}. Even though it is very hard to define the exact potential energy of each state, the relative potential energies of different interfaces for the same substrate can be compared qualitatively. The absolute value of \(\cos \theta_i\) indicates the potential energy. Higher absolute value indicates higher potential energy. When \((y-x)/x = 1\), the potential energy of heterogeneous interface equals that of homogeneous interface, while \((y-x)/x < 1\), indicates a lower energy for heterogeneous interface and \((y-x)/x > 1\) indicates a lower energy for homogeneous interface. Both theoretical calculation and experimental results (gentle deposition and elevated deposition) are summarized in Figure 25b. Based on the relative potential energy, three working windows can be defined for the formation of heterogeneous interface: stable regime (olive regime), meta-stable regime (orange regime) and unstable regime (black regime) in Figure 25b and 25c. In the stable regime, the potential energy for heterogeneous interface (black dot) is lower or equal to homogeneous interface and there are large energy barrier between the two states. Based on the wetting kinetics, the heterogeneous interface is formed first. It is very hard for the system to transfer to homogeneous interface (blue dot) with higher energy lever through large potential barrier. Therefore, this is the most promising working window for transferring suspended SWCNT. In the meta-stable regime, even though the potential energy for heterogeneous interface
is higher, the potential barrier can prevent the transition of interface. As shown in Figure 25b, for elevated droplets, slightly decreased contact angles (about 10 ° lower than undisturbed droplets, but still high above predicted contact angles of homogeneous interface) indicate a partial transition which stopped at somewhere in between the two states. Therefore, this is a possible working window to form suspended SWCNT. However, the successful rate strongly depends on the \((y-x)/x\) and the energy barrier. It is unlikely to have 100% successful rates due to this metastable heterogeneous interface. But if the energy barrier can be increased, a more stable heterogeneous interface and thus suspended architectures can be expected. The unstable regime is not the working window for transferring suspended SWCNT architectures. A small vibration can initiate the transferring process from heterogeneous interface to homogeneous interface because of the combination of large potential drive force and small potential barrier\(^{160}\). As shown in Figure 25b, a clear transition happened for the sample with \((y-x)/x=19\) or \(y = 120 \, \mu m\). As we know, disturbances from transferring processes such as the contacting process and the process to remove donor substrate are inevitable. Therefore, it will be extremely difficult to obtain suspended architectures in this regime. This will be further demonstrated in the following section with real transferring results of SWCNT architectures. Please note that, potential energy and energy barrier are not only related to the \((y-x)/x\) value, but also related to some other factors such as the height \(z\) of the supporting architecture of receiving substrate, the edge condition of the supporting structure, as well as the material of the substrate (surface energy)\(^{152,159,164}\). Therefore, the energy profile provided here can only explain part of the fundamental mechanism. Detailed experimental results will be discussed in the following sections.

From the contact angle measurement results (Figure 23b and 25b), it seems an exception for PDMS substrate with \(y = 9 \, \mu m\) in which the contact angle measurement agree more with
homogeneous interface. However, considering the kinetics of the wetting process, heterogeneous interface with lower energy can form first and there is no reason to transfer to homogeneous interface. This statement is proved by the well-defined suspended SWCNT micro-lines with nearly 100% yield on this substrate (Figure 21b).

### 3.3.2 Interfacial energy analysis

![Diagram](image)

Figure 26. Interfacial energy analysis of wet-contact printing method. Left, state before etching, and right, state after etching. The wavy curves indicate the diluted HF acid solution.

Since HF acid can react with SiO₂ layer actively and fresh exposed Si has very high surface energy (2130 dynes/cm or mJ/m²), the solution (solid wavy lines) can penetrate easily into the interface between Si and SWCNT, and SWCNT can be released to the receiving substrate. On the other hand, the interface between SWCNT and polymeric substrate becomes the key in controlling. If solution (dash wavy line) can penetrate in this interface, SWCNT can be detached.
from polymer substrate when removing the solution as shown in Figure 26, right. The interfacial energy \( \gamma_{12} \) between two different materials (1 and 2) can be expressed by:

\[
\gamma_{12} = \left( \sqrt{\gamma_1^d} - \sqrt{\gamma_2^d} \right)^2 + \left( \sqrt{\gamma_1^a} - \sqrt{\gamma_2^a} \right)^2,
\]

where \( d \) and \( a \) refer to the dispersion forces and \( a \)-scalar forces (the combined polar interactions: dipole, induction, and hydrogen bonding for a polar liquids/solids interface)\(^{166,167}\).

Since there is no direct reference about surface energy of SWCNT, the surface energy of MWCNT was applied in the calculation due to the similarity of outer shell carbon lattice. The reference value water, MWCNT and PDMS are list in Table 2.

**Table 2.** Summary of surface energy of water, carbon nanotube, PDMS and epoxy resins.

<table>
<thead>
<tr>
<th></th>
<th>( \gamma ) (dynes/cm)</th>
<th>( \gamma^d )</th>
<th>( \gamma^a )</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>51</td>
<td>(^{168})</td>
</tr>
<tr>
<td>MWNT 1</td>
<td>27.8</td>
<td>17.6</td>
<td>10.2</td>
<td>(^{169})</td>
</tr>
<tr>
<td>MWNT 2</td>
<td>45.3</td>
<td>18.4</td>
<td>26.9</td>
<td>(^{170})</td>
</tr>
<tr>
<td>PDMS</td>
<td>19.8</td>
<td>19</td>
<td>0.8</td>
<td>(^{171})</td>
</tr>
<tr>
<td>Epoxy(^e)</td>
<td>32.9</td>
<td></td>
<td></td>
<td>(^{172})</td>
</tr>
<tr>
<td>Epoxy(^f)</td>
<td>44.0</td>
<td></td>
<td></td>
<td>(^{172})</td>
</tr>
</tbody>
</table>

\(^{e}\) Amin curing agent: diethylaminopropylamine (DEAPA)\(^{172}\)

\(^{f}\) Amin curing agent: diethylenetriamine (DETA)\(^{172}\)

Based on Eq. 3.3, the calculated interfacial energies are summarized in Table 2. It is clear that the interfacial energy between water and PDMS is the highest. Moreover, considering the kinetics of transferring process, the PDMS was first brought in contact with SWCNT before
etching (SWCNT-PDMS interface form first), extra energy has to be provided to overcome barrier for the separation SWCNT-PDMS interface and then form two new interfaces: SWCNT-water and PDMS-water. Therefore, from both thermal dynamic and kinetic analysis, SWCNT-PDMS interface is stable during wet-contact printing. Another question of interest is the influence of chemistry on the surface of CNT on the interfacial energy. As we known, the surface of CNT can be either hydrophobic or hydrophilic depending on the surface chemistry originated from growth method and chemical treatment after growth. We have compared two different MWCNTs here. For MWCNT1, there is no doubt that nanotubes tend to stay on the surface of PDMS because $\gamma_{\text{MWNT1-PDMS}}$ is the lowest among the three interfacial energies. However, for MWCNT2, the calculated result for $\gamma_{\text{MWNT1-PDMS}}$ is higher than $\gamma_{\text{MWNT1-water}}$. This result might raise the debate of the stability of transferring process. But since $\gamma_{\text{PDMS-water}}$ have higher energy, it is still hard to create a new water-PDMS interface by separating MWCNT and PDMS. Note that, if the disturbance during the transferring process is large enough and the contact area between SWCNT and PDMS is small, it is possible to detach the SWCNT from PDMS and even break the SWCNT structures. This will be further discussed in the following experimental sections.

**Table 3. Calculated interfacial energy.**

<table>
<thead>
<tr>
<th>Interface (1-2)</th>
<th>$\gamma_{12}$ (dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-PDMS</td>
<td>39.12</td>
</tr>
<tr>
<td>Water-MWNT1</td>
<td>15.81</td>
</tr>
<tr>
<td>Water-MWNT2</td>
<td>3.97</td>
</tr>
<tr>
<td>PDMS-MWNT1</td>
<td>5.31</td>
</tr>
<tr>
<td>PDMS-MWNT2</td>
<td>18.43</td>
</tr>
</tbody>
</table>
3.4 Results and Discussions

3.4.1 Influence of center distance, \( y \)

Table 4. Sample code for micro-strip patterned polymeric substrate. In sample code, the word “Line” indicates the substrate is patterned with micro-strips. The first number denotes the value of \( x \) and the second number denotes the value of \( y \). There is no information about \( z \) in the code, because it is a constant \((z = 6)\) in all the designs unless mentioned otherwise.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>( x ) (µm)</th>
<th>( y ) (µm)</th>
<th>( z ) (µm)</th>
<th>Sample Code</th>
<th>( x ) (µm)</th>
<th>( y ) (µm)</th>
<th>( z ) (µm)</th>
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<td>6</td>
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</tr>
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<td>Line 20 60</td>
<td>20</td>
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<td>6</td>
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A fundamental understanding of the relation among surface structure-interface morphology-status of SWCNT is essential and meaningful in both fabrication and application point of views. On one hand, the SLV interface and thereafter the status of SWCNT can be tailored by changing the surface geometries related to the potential energy of heterogeneous and homogeneous interface. On the other hand, the applications of suspended structures are directly related to its geometries. For example, the resonating frequency of suspended unit is proportional to \( l^2 \), where \( l \) is the suspended length. As discussed in section 3.3.2, large center distance is not favorable for heterogeneous interface (when \( y \) or \((y-x)/x\) is large, and \( x \) and \( z \) are constants) and a transition from heterogeneous interface (corresponding to suspended SWCNT) to homogeneous interface (corresponding to collapsed SWCNT) can easily happen, even though heterogeneous interface can form first\(^{152}\). Here, the influence of center distance, \( y \), is investigated by designing the substrates with constant \( x \) and \( z \), but changing \( y \). The sample codes are summarized in Table

83
4 depending on the geometry of micro-pattern. For example, Line 6_9 denotes that the patterns are strips and the width (x) is 6 µm and the center distance (y) is 9 µm. There is no information about the height z because the height z is 6 µm unless mentioned otherwise. To minimize the experimental variation, an integrated substrate has been designed containing all the designed patterns and for each pattern, there are 10 repeated units.

**Figure 27.** Suspended SWCNT architectures on an integrated PDMS substrate (x = z = 6 and y = 9 to 120 µm) at right angle.

Well-defined suspended SWCNT architectures can be obtained till the sample with y = 36 µm with nearly 100% yield. SWCNT architectures begin to miss and collapse for the sample with y = 60 µm and beyond. For y = 120 µm, no suspended SWCNT architectures can be obtained. Scalar bars: 100 µm for the integrated chip, (a) and 10 µm for the individual panels (b) to (g).

The experiment results of suspended SWCNT architecture over integrated PDMS substrate (Line 6 series) clearly defined the real regimes of transferring as shown in Figure 27. These results can be correlated with the contact angle measurements on the same substrates in Figure 25b to develop a comprehensive understanding between the status of SLV interface and status of transferred SWCNT. The stable suspended SWCNT (nearly 100% yield) can be obtained from Line 6_9 (Figure 27b) to Line 6_36 (Figure 27d), and collapsed SWCNT and missing SWCNT can be found in both Line 6_60 (Figure 27e) and Line 6_80 (Figure 27f). For Line 6_120 sample
(Figure 27g), all the SWCNT micro-lines were found in the collapsed style. As we have discussed in section 3.3.2, Line 6_9 and Line 6_12 are located in stable regime where nearly 100% suspended SWCNT are expected. Line 6_18 to Line 6_36 are located in early meta-stable regime and due to the large energy barrier, the heterogeneous interface can sustain the disturbance during the transferring process leading to nearly 100% suspended SWCNT. However, Line 6_60 to Line 6_80 are located in late meta-stable regime, where heterogeneous interface is vulnerable to the disturbance during the transferring process leading to partly missing and collapsed SWCNT architectures. It is clear that Line 6_120 is in the unstable regime and no suspended SWCNT can be obtained. This matches the predication from contact angle measurement where a complete transition from heterogeneous interface to homogeneous interface happened with elevated droplets (Figure 25b, green dot at y = 120).

Figure 28. Suspended SWCNT architectures on an integrated PDMS substrate (x = 20, z = 6 and y = 30 to 120 µm) at right angle.

Perfectly suspended SWCNT architectures can be obtained till the sample with y = 30 and 40 µm. SWCNT architectures begin to miss and collapse for the sample with y = 60 µm and beyond. For y = 120 µm, few suspended SWCNT architectures can be obtained. Scalar bars: 20 µm for (a) to (e), 2 µm for (f) to (h) and 10 µm for (i) to (j).
For PDMS substrate with constant $x = 20 \, \mu m$ (Figure 28, Line 20 series), the transition from stable regime (Line 20_30 and Line 20_40) with nearly 100% yield to metastable regime (Line 20_60, 80 and 120) with missing and collapsed SWCNT is evident. However, there is no completely unstable regime in Line 20 series. We believe the energy gap between the two states is actually related to ratio of center distance to the width of supporting strip, $y/x$ (or $(y-x)/x$)\(^\text{159}\). Line 20_30 ($y/x = 1.5$) and 20_40 ($y/x = 2$) have good transferred architectures. Line 20_120 ($y/x = 6$) has a small number of suspended SWCNT micro-lines, compared to Line 6_120 ($y/x = 20$) having no suspended architecture. Therefore, it is reasonable to state that the Line 20_120 is in the meta-stable regime.

In summary, the structure of receiving substrate dictates both the energy state of the SLV interface and the working window of wet-contact printing method. The best working window falls in the stable regime and early meta-stable regime defined by contact angle measurement. It is still possible to have suspended SWCNT architectures for late meta-stable regime with low yield. Unstable regime is not a working window due to difficulty in maintaining the heterogeneous interface. Current results not only address the importance of maintaining heterogeneous interface, but also indicate the route for improvement: if we are able to stabilize or maintain the heterogeneous interface by tailoring surface chemistry\(^\text{152}\), creating nanoscale structures\(^\text{151}\), applying eternal force such as electrical field\(^\text{175}\), magnetic field\(^\text{176}\) and \textit{etc.}, it is possible to further improve the transferring technique and push forward the limit. This will be the future direction of our work.
3.4.2 Influence of different polymeric materials and its fabrication technologies

![Figure 29](image)

**Figure 29.** Suspended SWCNT architectures on an integrated SU-8 substrate at right angle to the supporting strips.

(a) Line 6 series with \(x=6\) and \(y=9\) to 120 µm, and (b) Line 20 series with \(x=20\) and \(y=30\) to 80 µm. \(l\), in upper right panel, denotes the real suspended length of SWCNT architectures, which is not necessarily equal to the trench width (\(y-x\)) depending on the substrate condition.

If the SU-8 was as substrate material, well-defined suspended SWCNT micro-lines (nearly 100% yield) can be only obtained until Line 6_12 µm for Line 6 series as shown in Figure 29a, since the energy level for homogeneous interface is much lower over the entire designed regime.
(Figure 23b, lower panel). It is clear that the transferring of SWCNT to SU-8 substrate is not as good as that on PDMS substrate. There might be a few reasons.

First, SU-8 surface has higher energy (44 dynes/cm in table 2) compared to PDMS and contact angle measurement shows that the contact angle of water on flat SU-8 substrate is 71° much lower than that on PDMS (109°) as shown in Figure 23a. The predicted potential energy (proportional to value of contact angle) of homogeneous interface is much lower than that of heterogeneous interface over the entire range (Figure 23b, lower panel) indicating that all the design for SU-8 substrate is either in the meta-stable regime or unstable regime. The heterogeneous interface is subjected to large driving force to migrate to homogeneous interface. And the disturbance during the transferring process can easily initiate the interface transition and lead to the collapsed SWCNT.

Figure 30. Influence of sharp edge on suspended SWCNT micro-line.
(a) 3D optical image of SU-8 substrate ($x = 7.5$ and $y = 15 \, \mu m$). (b-d) Direct observation of suspended SWCNT film over the edge of Au coated SU-8 substrate ($x = 18$ and $y = 24 \, \mu m$). Red
dash line indicates the designed edge of supporting substrate and green dash line indicated the real edge that in contact with solution.

Moreover, micro-patterned SU-8 substrates fabricated by the method of optical lithography have smoothed the edges of the supporting strips during the developing process. Figure 30a, obtained by 3D optical profilometer (Zygo), shows the edges of SU-8 micro-strips (Line 7.5_15) fabricated on SiO₂/Si. A reflective metal layer (Au 150 nm) has to be coated on the surface to reflect the laser for imaging. Since a polarized filter was applied to straighten the UV light during exposure, the side wall of the strip is almost perpendicular to the supporting SiO₂/Si substrate. However, the edge of top plane of strips is significantly wired out forming a curved surface rather than a shape edge. The smooth edge is not favorable for the formation of heterogeneous interface. Extrand brought out the theory of contact line density to further clarify the influence of edge of the supporting substrate and found that sharp edge is helpful in forming the heterogeneous interface. In this study, the influence of blurt edge is significant. SEM images of suspended SWCNT strips over Au coated SU-8 substrate (Figure 30b to 30d) show that, l, length of suspended SWCNT region (bright contrast SWCNT film embraced by two olive dash lines) is slightly wider than the designed width of the trench, (y-x), embraced by two red dash lines. Similar effect can be found in Figure 29a (Line 6_12, upper right) over the SU-8 substrates. Combined with 3D optical profile, it is reasonable to believe the region of SU-8 strip that in contact with SWCNT film are the small flat regions on the very top of the strip. Therefore, we can define the real contact width as \(x'\) and \(x'+l = y\). Blurt edge will lead to smaller \(x'\) and larger \(l\) and thereby enlarge the potential energy difference between the heterogeneous and homogeneous interface leading to unstable transferring process and suspended SWCNT architectures. To the opposite, PDMS substrate molded using this SU-8 substrate will have the
reversed geometry where the blurt edges are located the bottom of the trench while the sharp edges can be formed on the top plane in contact with SWCNT and solution. Therefore, in the case of PDMS substrate, a sharp edge can be found on the supporting structures with real contact width equaling the width of supporting substrate, $x' = x$.

In summary, from both theoretical analysis and experimental results, it is clear that lower surface energy and sharp edge are very important factors that enhance the formation of suspended SWCNT architectures. These results provide the guidance for the choice of supporting materials and the fabrication technologies.

### 3.4.3 Influence of height, $z$

The height $z$ is directly related to the energy barrier between the two types of interfaces and thus the transition kinetics\textsuperscript{152}. The transition from heterogeneous interface to homogeneous interface is a wetting process of the side walls and the bottom of supporting strips. Assuming unchanged interface between liquid and vapor as the droplet wet downwards (transition from heterogeneous to homogeneous interface), the energy barrier can be expressed as the changed energy, $\Delta E$, per unit area corresponds to the wetting of side walls of the supporting strips:

$$\Delta E = (\gamma_{SL} - \gamma_{SA})(r - 1) = -\gamma_{LV}(r - 1)\cos\theta \approx \frac{z}{y} \gamma_{LV}\cos\theta. \tag{3.4}$$

Correspondingly, the changed energy can be obtained from geometry parameters directly, $\Delta E \approx \frac{z}{y} \gamma_{LV}\cos\theta$ (in the case of strips) and $\Delta E \approx 2\pi b z / y^2 \gamma_{LV}\cos\theta$ (in the case of post) where $b$ is the radius of the post. Therefore, it is evident that the energy barrier between the two statuses is proportional to the height of support structures in spite of their shapes. If the value of $z$ is larger, it takes longer time and higher energy to wet through.
Figure 31. Suspended SWCNT architectures on an integrated PDMS substrate with high $z$ ($z = 65$, $x = 20$, and $y = 30$ to 120 $\mu$m) at right angle.

Integrated chip with all the designed patterns for Line 20 series (a) and individual SEM image for each design with $y$ increase from 30 to 120 $\mu$m (b) to (f). Perfectly suspended SWCNT architectures can be obtained till the sample Line 20_60. SWCNT architectures begin to miss and collapse for the sample Line 20_80. For Line 20_120, few suspended SWCNT architectures can be obtained.

Moreover, the potential energy of homogenous interface is also influenced by $z$ as shown in Eq. 3.1, where $r$ is the ratio of actual area ($A$) and the projected area ($A_0$) and in the case of strip design $r = (y+2z)/y$. As discussed in mechanism section, $|\cos \theta_i|$ represents the potential energy and the higher the value is, the higher potential energy would be. Increasing $z$ will leads to the increase of $r$ and thereby increasing $|\cos \theta_i|$ and finally elevated the potential energy of homogeneous interface. As we known, the $|\cos \theta_i|$ in heterogeneous interface is independent of $z$. Therefore, in the regime where potential energy for heterogeneous interface is much larger than homogeneous interface, higher $z$ leads to a smaller potential energy gap between the two states and further reduces the driving force initiating the transition.
Figure 32. Influence of height of supporting pattern (z) on the yield of suspended SWCNT architectures over the PDMS substrate with same x (20 µm) and y (60 µm) but different z: z = 65 µm (a) and z = 6 µm (b).

After all, increasing z does not only enlarge energy barrier but also decrease the potential energy gap (driving force) of the transition leading to more stable heterogeneous interface and thereafter more stable suspended SWCNT architectures. Figure 31 shows the transferring of SWCNT micro-lines to PDMS substrate (x = 20, y = 30 to 120 µm) with high z (z = 65 µm) and stable suspended SWCNT micro-lines can be obtained till y = 60 µm. The yield for substrates with the same x and y (Line 20_60) but different z was compared in Figure 32, and a higher yield (97%) can be obtained for substrate with a higher z (z = 65 µm), compared to that of 84% for substrate with a lower z (z = 6 µm).

Another important issue related to the height, z, is the transition process from heterogeneous interface to homogeneous interface. As evidenced by our results and previous results obtained by other researchers, this transition can be tailored by the choice of z and its combination with in-plane design (x and y). However, a comprehensive understanding of the transition and the morphology of SLV interface is still in debate due to difficulty in imaging the SLV interface at small scale. There are two modes describing the SLV interface: curve mode (Figure 33a) and flat
mode (Figure 33b). As shown in Figure 33a, Extrand suggested a wavy interface in which the solution over the suspended region can extend towards the bottom of the substrates and the solution exhibits a true advancing angle with respect to the side of supporting strips. The extended distance, $d$, is defined as the distance between the lowest point of solution frontier (light blue curve) and the top plane of the supporting substrate. The solution exhibits a true advancing angle, $\theta_{a,0}$, on the side of supporting strips. If the side wall of the supporting strip (Line $x\_y$) is perfectly perpendicular to the horizontal plane, $d$ can be expressed as:

$$d = \frac{(y - x)}{2}\tan\left(\frac{\theta_{a,0} - 90^\circ}{2}\right),$$

(3.5)

in which $(y - x)$ is the width of the trench, $\theta_{a,0}$ is 118° for PDMS substrate. If $d$ is larger than $z$, a transition between heterogeneous interface will automatically happen since the solution will touch the bottom of the substrate. The state of interface can dictate the status of SWCNT strips since SWCNT strips are placed at the SLV interface. In a reversed manner, the shape of SWCNT strip after the transferring, can probe the shape of SLV interface.
Figure 33. Models of heterogeneous interface.

(a) Curved model with extended frontier of solution over suspended region. The extended distance, \( d \), is defined as the distance between the frontier of solution and the top plane of supporting structures. (b) Plain model with no extended distance. (c) Calculated extended distance with respect to the width of the trench (\( y-x \)). (d) Experimental results from samples with trenches larger than critical value (Line 6_60, Line 6_80 and Line 6_120). SEM images show that straightened suspended SWCNT can be obtained for samples Line 6_60 and Line 6_80. Collapsed SWCNT micro-lines in Line 6_120 clearly indicate a transition from heterogeneous interface to homogeneous interface.

Based on Extrand’s deduction (Figure 33c), if the height, \( z \), is 6 \( \mu \)m as the PDMS substrate in our design, and when \( z = d \), the critical width of the trench, (\( y-x \)), is 48.13 \( \mu \)m. It suggests that once the trench size is larger than 48.13 \( \mu \)m, it is impossible to obtain suspended SWCNT architecture due to the formation of homogeneous interface. Therefore, to obtained suspended SWCNT over the substrate with \( z = 6 \mu \)m, for \( x = 6 \mu \)m series, \( y \) should be less than 54.13 \( \mu \)m and for \( x = 20 \mu \)m series, \( y \) should be less than 74.13 \( \mu \)m. Interestingly, in our experiment, suspended SWCNT architectures can be obtained far beyond the limit from advancing angle model as shown in Figure 33d. Also, from the prediction of the Extrand’s model, the suspended
architectures may mimic the wavy shape of the solution frontier. However, the suspended SWCNT micro-lines are straightened even over large trenches (x = 6 and y = 60 and 80 µm). Supposed that SWCNT architectures sandwiched between solution frontier and the substrate will follow the shape of heterogeneous interface, the experimental results suggest a flat heterogeneous interface with no wavy shape for the samples such as Line 6_60 and 6_80 as shown in Figure 33d.

The morphology of SWCNT sandwiched at SLV interface can help us understand the shape and the transition of interface. The straightened suspended SWCNT strips suggest a plain model for heterogeneous interface as shown in Figure 33b and 33d while the collapsed SWCNT strips follow the frontier of liquid surface of homogeneous interface. The absence of intermediate status (such as curved suspended SWCNT closed to the ground) between the straightened SWCNT and fully collapsed SWCNT suggests a bumped transition from flat heterogeneous interface to fully collapsed homogeneous interface.

For the sample Line 6_120, the collapsed SWCNT micro-lines should follow the frontier of liquid surface where solid-liquid contact nucleate for triggering the transition (Figure 33d, right). It is interesting to see that the SWCNT micro-lines are not fully collapsed leaving suspended regions over the corners of supporting strips suggesting an intermediate state between heterogeneous interface described in Cassie-Baxter’s equation and homogeneous interface described in Wenzel’s equation. It is still a heterogeneous interface with air-pockets trapped in the corners but the apparent contact angle (θ_i) follows the prediction for homogeneous interface (Green dot for y = 120 in Figure 23b and 25b).
However, it is hard to draw a conclusive description of heterogeneous interface at current moment due to the lack of direct evidence at the interface. Other possibilities might exist. For example, SWCNT film is brought in contact with supporting strip forming an air pocket which is hard to wet through the two open endings on the sides. Also, nanotube film is very strong and it might resist from the force pushing downward from the wavy frontier. Therefore, further experiment is required to find direct evidence.

3.4.4 Transferring on substrates with micro-posts

Figure 34. Suspended SWCNT architectures on an integrated PDMS substrate patterned with circular posts.
The notation “Circle” in the figures indicates the substrate is patterned with circular micro-posts. The diameter $x = 6$ and center distance ($y$) between nearby micro-posts in the alignment direction of SWCNT micro-lines ranges from 12 (a) and (d) to 60 µm (i) and (l). And the center distance between the nearby micro-posts in the perpendicular direction is 12 µm for all the designs.

Heterogeneous interface can be formed on substrates with suitable designs. For example, the surface of lotus leaf is patterned with arrays of micro-post with the diameter of 10 to 15 µm and the height of the same range$^{140}$. I have demonstrated the transfer of SWCNT over substrate patterned with micro-strips. Here, the ability to form suspended SWCNT architectures is further demonstrated on PDMS substrate with arrays of circular micro-posts with the same diameter $x = 6$ µm and increasing center distance, $y$, along the alignment direction of transferred SWCNT micro-lines from 12 to 60 µm as shown in Figure 34. The center distance between the nearby micro-posts in the perpendicular direction is fixed at 12 µm for all the designs.

![Figure 35](image)

**Figure 35.** Miss-alignment of suspended SWCNT micro-lines during transferring to micro-posts. (a) and (d) Circular micro-posts ($x = 20$ and $y = 30$ µm), and (b) and (d) square micro-post ($x = 20$ and $y = 30$ µm). (c) and (f) Transferring of SWCNT micro-lines on the edge of circular micro-posts.
Unlike the substrates pattered with strips, the requirement for nice alignment is critical. If the distance between SWCNT micro-lines does not match that of supporting substrate, the misalignment can be found in the transferred samples as shown in Figure 35 and if there is no supporting micro-structure under SWCNT micro-lines, SWCNT cannot be transferred leaving empty spaces indicated by red dash lines in Figure 35a (35d) and 35b (35e). In some cases, the transferring of SWCNT micro-lines on the edge of micro-post can be found (Figure 35c and 35f).

3.4.5 Transferring on flexible substrate with pre-strain

Figure 36. Arrays of SWCNT micro-arches on pre-stretched PDMS substrates.

(a) Schematic of fabrication. (b) Integrated chip with all the pattern designs for Line 6 series and SWCNT arches on Line 6_18 sample (c) and (f), Line 6_30 sample (d) and (g), and Line 6_60 sample (e) and (f). Scalar bars: 100 µm for (b), 10 µm for upper panels (c to e) and 2 µm for lower panels (f to h).
Flexible electronics is one of the major targets of current research. The flexible electronic does not only require building electronics on flexible substrates but also stable device under deformation. Semiconductors with wavy geometries have been created to accommodate deformation by changing the amplitudes and periods of the waves. John Rogers’s group in UIUC first creates wavy semiconductor nanoribbons by transferring flat nanoribbons to pre-stretched PDMS substrate utilizing contact printing method\textsuperscript{7,15,17,18}.

Following the similar concept, suspended SWCNT micro-lines can be transferred to PDMS substrate with 33\% pre-strain following the procedures described in Figure 36a. After the transferring process, the substrate was released to its original size and arrays of beautiful arches with prescribed height can be formed over a wide range of distance (Line 6\_9 to Line 6\_60 in Figure 36 from 36b to 36h). There are two advantages of our structure in terms of material choice and substrate design. First, SWCNT network structure is more flexible than those single-crystal semiconductor nanoribbons especially in bending and twisting. As shown in Figure 36, the 33 \% prestrain can be easily accommodated by the SWCNT arches and no fracture can be found. In some cases, twist film other than arch can be formed, in which extreme defamation of SWCNT film can be achieved (Figure 37c). Second, the micro-patterned polymeric substrate is heterogeneous with alternating thicker strips. There is little deformation of thick strips during pre-stretching, evidenced by the fact that SWCNT micro-lines sitting on the strips have little buckling after releasing the substrate. Since little deformation can be applied to these “thick” strips, these strips not only provide a solid support for SWCNT architecture during the deformation, but also provide the surfaces to build interconnects in real flexible applications. These arch structures can find immediate application in flexible electronics since at least 33\% strain can be achieved without breaking the suspended SWCNT network.
Figure 37. Other forms of deformation of SWCNT architectures after releasing the pre-stretched substrate.

(a) Horizontal buckling, (b) buckling downwards and touching the bottom, (c) twisting and (d) buckling on substrate.

At current moment, it is hard to control the direction of buckling. The buckling can happen in any direction as shown in Figure 37. Sometimes, it can buckle within the horizontal plane as shown in Figure 37a. The height of supporting strip, z, is critical when the SWCNT micro-line is buckling downwards, and if the buckling height or depth is larger than z, the SWCNT micro-line can touch the bottom of the substrate (Figure 37b). Therefore, the combination of pre-strain and height of strip has to be carefully controlled to realize fully suspended SWCNT arches. In rare case, a complete twist other than buckling can happen (Figure 37c). For very large trench (Line
6_{120}, y = 160 \mu m with pre-stain), collapsed SWCNT micro-lines can be formed on the bottom of the substrate forming wavy buckling on the substrate after releasing the prestrain (Figure 37d).

This experiment demonstrates a very useful prototype of ultra-flexible electronics with both material choice (SWCNT) and substrate design with patterned strips. The height of supporting strip should be carefully designed to accommodate the buckling of suspended SWCNT. Also, it would be better if the buckling direction can be controlled even though it will not influence the flexibility significantly.

3.4.6 Transferring at arbitrary angle

![Figure 38](image)

**Figure 38.** Suspended SWCNT architectures on PDMS substrate at the angle of 138 °. Suspended SWCNT micro-lines on square micro-posts (a) and on micro-strips at 138 °. Scalar bars: 20 \mu m for all.
Suspended architectures can be aligned at an arbitrary angle with respect to the supporting substrate as shown in Figure 38. Figure 38a demonstrates the transferring of SWCNT micro-lines on square micro-post patterned substrate \((x = 20, y = 40 \, \mu m)\) at the 138 ° with respect to the alignment direction of micro-posts. Since it is no longer a right angle, the cross section of supporting post in contact with SWCNT as well as the suspended length of SWCNT will change. However, as long as heterogeneous interface can form and SWCNT can find the supporting post, suspended SWCNT architectures can be obtained. Therefore, the suspended length of SWCNT can be controlled by changing the alignment angle. Moreover, SWCNT micro-lines can be transferred to micro-strip patterned substrate (Line 20_60) as shown in Figure 38b. The trench size is only 40 µm, but the suspended length can be extended to 62 µm by tilting the transferring angle to 138 °.

Note that the cracks on the pre-deposited metal layer (Au/Pd) (for SEM imaging) are caused by slight bending during the sample handling. The well-defined suspended SWCNT micro-lines after handling indicate flexible nature of the suspended architectures.

3.4.7 Transferring 100-µm-wide SWCNT micro-lines

As discussed in the mechanism, the key controlling factor for wet-contact printing method is the geometry parameters of the receiving substrate. Therefore, the size of SWCNT film will not influence transferring results (suspended or not). Here, the 100-µm-wide SWCNT micro-lines (compared with 6-µm-wide SWCNT micro-lines used in the former sections) have been used to demonstrate this concept as shown in Figure 39.
Figure 39. 100-µm-wide suspended SWCNT architectures on PDMS substrate: (a) $x = 7.5$ µm and $y = 15$ µm, and (b) $x = 20$ µm and $y = 40$ to 120 µm

Figure 39a shows the optical image of arrays of 100-µm-wide SWCNT micro-lines transferred to PDMS substrate patented with micro-strips ($x = 7.5$ µm and $y = 15$ µm). In Figure 39b, 100-µm-wide SWCNT micro-lines are transferred to PDMS substrate with constant $x = 20$ µm, and the transition from stable regime ($y = 30$ and 40) to meta-stable regime ($y = 60$, 80 and 120 µm) can be seen. There is no apparent difference from results of 6-µm-wide SWCNT micro-lines on the same design. Therefore, the size of the SWCNT architecture will not influence its final status after the transferring process. However, larger films have better shape stability after the transferring process which will be discussed later.
3.4.8 Transferring on substrate with metallic surface

(a) homogeneous Au surface, in which a homogeneous Au layer (150 nm) was deposited on the top of the SU-8 substrate; (b) micro-patterned SU-8 substrate with arrays of 100*100 µm² square contact pads (Ti/Au) and (c) metallic surface with SU-8 trenches, Pd (left) and Ti/Au (middle).

Figure 40. Transferring of SWCNT micro-lines to substrate fully or partly covered with metallic surfaces.
The multiple choices of surface coating on the substrate can greatly enrich the transferring technology and the application of suspended SWCNT architectures. Moreover, the fabrication of MEMS and NEMS system also requires the ability to transfer SWCNT to both homogeneous and heterogeneous surface. The heterogeneous surface should be patterned with different materials: such as semiconductor, metal and polymer for different functions\textsuperscript{5,13}. For example, semiconductor thin film can be used as a functional unit, while metallic surfaces are applied as contact pads and connections. In Figure 40a, the transferring of SWCNT to Au layer coated SU-8 substrate has been demonstrated proving the feasibility of wet-contact printing method on metallic surface. The structure is schematically shown in the inset of Figure 40a. This result is significant because the fact that SWCNT can stick to the metallic surface makes the flexible electronic device on polymeric substrate possible. The electronic device was further demonstrated in Figure 40b, in which square Ti/Au contact pads were deposited on the SU-8 substrate patterned with micro-trenches. Continuous SWCNT micro-lines can be transferred to the heterogeneous surface and form suspended SWCNT architectures over both Au surface and SU-8 surface. Figure 40c further demonstrates the 100% suspended SWCNT device with SWCNT suspending over SU-8 trenches and sitting on different metals covered surface Pd (left) and Ti/Au (right). 100% suspended SWCNT device denotes the structure with metallic contact pads covering the top surfaces of supporting strips completely such that the SWCNT film that is not in contact with contact pads are completely suspended. In such device, the influence from supporting substrate on the electrical and thermal properties can be greatly diminished leading to potential applications in ultrasensitive sensor, bolometer, photoluminescence device and actuators.
3.4.9 Multiple transfers

The multiple transferring is very useful and sometimes necessary in building real device with multiple components from different donor substrates. However, the key issue is whether the suspended SWCNT architectures transferred onto the polymeric substrate in the first place can sustain following transferring processes or not.

Figure 41. Hierarchy SWCNT architectures obtained through repeated wet-contact printing processes.

(a) to (c) SEM images of multiple transferring of SWCNT micro-lines on the same PDMS substrate \((x = 20, y = 60 \, \mu m)\) to form SWCNT cross. (d) to (f) Optical images of SWCNT micro-lines were transferred first on PDMS substrate \((x = 6, y = 12 \, \mu m)\) and then SWCNT square shape contact pads \((100*100 \, \mu m)\) were transferred onto the same PDMS substrate. Scalar bars: 10 \, \mu m for (a) and (b); 1 \, \mu m for (c); and 100 \, \mu m for (d) to (f).

Arrays of SWCNT micro-lines were transferred to PDMS substrate (Line 20_60) in one direction and after drying the sample, another layer of SWCNT micro-lines were transferred onto the same substrate in another direction forming “X” shaped crosses of SWCNT (Figure 41a to 41c). Conformal contact between two SWCNT micro-lines can be identified (Figure 41c).
experiment demonstrates the ability to build hierarchy SWCNT architecture on polymeric substrate through multiple transferring steps. Another example is an all-SWCNT device as shown in Figure 41d to 41f, in which arrays of SWCNT devices with SWCNT micro-lines (first transferring) and SWCNT contact pads (second transferring) were built on PDMS substrate (Line 6_12). The meaning of fabricating hierarchy SWCNT architecture through multiple transferring is significant. On one hand, it demonstrates the compatibility of wet-contact printing method to the existing MEMS/NEMS technologies involving multiple solution processes such as etching and cleaning. The suspended architecture can survive after multiple solution processes. On the other hand, it demonstrates the ability to build hierarchy device simply based on multiple wet-contact printing processes, since different functional units from different substrates can be transferred the desired substrate and positions in a layer-by-layer manner.

3.4.10 Transferring SWCNT to nanoscale patterned polymeric substrate

Figure 42. Suspended SWCNT film on nano-patterned PMMA substrates. (a) AFM image of the topology and (b) line profile along red line in (a).
The mechanism of wet-contact printing method has been demonstrated on microscale patterned substrate, and it is clear that suspended SWCNT cannot be obtained beyond certain $y$ value. However, the lower boundary of wet-contact printing has yet been investigated. Would the mechanism of wet-contact printing method still work on nanoscale patterned substrates? Nanopatterned PMMA substrates pattern with nano-strips has been fabricated on Si substrate using electron-beam lithography with $x = 600$, $y = 1400$ and $z = 250$ nm. Very thin SWCNT network was obtained by directly spinning SWCNT solution (0.23wt%) on SiO$_2$/Si substrate (spinning: 200 rpm for 20s and then 2000 rpm for 1 min). Figure 42a shows a SWCNT network (bright contrast) located on the top of the strip with exposed trench shown as dark contrast. The large distance between SWCNT and ground substrate (around 200 nm, in Figure 42b) demonstrates the suspended status of SWCNT film. It is clear that the scale of several hundreds of nanometers is not the lowest limit of wet-contact printing method. The method has the potential to fabricate even smaller devices. This result implicates immediate application of SWCNT based flexible NEMS device.
3.4.11 Transferring graphene

**Figure 43.** Suspended graphene on various substrates with micro- to nanoscale patterns.

(a) Tilted-angle SEM image of graphene transferred to SAM coated Si (a) and micro-patterned PDMS substrate (x = 7.5, y = 15 and z = 6 µm) (b). (c) AFM image of nano-patterned PMMA (x = 500, y = 1000 and z = 220 nm). (d) The 3D profile of graphene on PMMA substrate and 1D profile along the red line in (c).

As a unique one atomic layer material, graphene shows striking electrical, mechanical and optical properties. Here, suspended graphene structures on various patterned substrates with different scales have been demonstrated using the wet-contact printing method. The graphene/SiO₂/Si sample is obtained from Dr. Xiaohong An from Prof. Swastik Kar’s group in the Department of Physic at Northeastern University. The graphene layer was first synthesized on Cu substrate by CVD method and transferred to PMMA film by cast and etching method.
followed by placing the graphene/PMMA film on SiO$_2$/Si substrate and removing the PMMA using acetone at elevated temperature (80 °C). Figure 43a shows suspended graphene on self-assembled monolayer (SAM) protected Si substrate. Usually, Si is a hydrophilic substrate, and to successfully transfer graphene, a hydrophobic SAM (Trichloro(1H,1H,2H,2H-perfluoroctyl)silane) was coated on the top through a vaporized self-assemble process at 150 °C for 3 hours. This experiment further addresses the importance of the hydrophobicity of the receiving substrate. More importantly, it points out the method to obtain suspended architectures over originally hydrophilic surface. Figure 43b shows a typical transfer process to micro-patterned PDMS substrate. Figure 43c and 43d further demonstrate the possibility to construct suspended graphene over nano-patterned substrate. The width of supporting strip is 500 nm and the center distance is 1000 nm leaving the 500 nm trenches in between shown as the arrays of bright strip in the image. The graphene pieces, shown as the irregular bright regions, usually cover several supporting strips. The nano-trenches between the strips are shown as dark contrast strips. The 3D image and the line profile in Figure 43d, illustrate that the distance between suspended graphene equals the height of the strip, $z$. These results further demonstrate the scalability of wet-contact printing method over different target materials, substrate and micro- to nanoscale patterns.

**3.4.12 Wetting of solution on anisotropic surface**

The anisotropic pattern design for polymeric substrate, e.g., arrays of micro-strip patterns, leads to wetting anisotropy of solution$^{180-184}$. In the discussion of potential energy analysis (section 3.3.2), only the data of front view was plotted to compare with the theoretical prediction (Figure 23). The contact angle from the side view is lower than that in the front view and its
value is strongly influenced by the material of the substrate. Here the relation between contact angle in the front view and side view will be discussed. Please note that, our measurements are based on sessile droplets.

![Graphs showing contact angle measurement with data from both front view and side view.](image)

**Figure 44.** Contact angle measurement with data from both front view and side view.

- (a) The contact angles of water droplets (undisturbed droplets and elevated droplets) on micro-patterned PDMS substrates from both front view and side view as a function of increasing center distance, y. (b) The contact angles of undisturbed droplets on micro-patterned SU-8 substrates from both front view and side view as a function of increasing center distance, y. (c) The image of real contact angle measurements for undisturbed droplets on both PDMS and SU-8 substrates.

As shown in Figure 44a, contact angles of water on patterned PDMS substrate (Line 6 series) from side view were plotted as a function of y for both undisturbed droplet (front view, red squares and side view, blue triangles) and elevated droplet (front view, green dots and side view, pink triangles). For undisturbed droplets on PDMS, both front view and side view angles have
higher value than that on the flat substrate (109°). This result is similar to the observation by Chen et al.\textsuperscript{180}. The high contact angle in the front view can be considered as the result of confinement from the supporting substrate, since the droplet is trying to wet in the perpendicular direction crossing alternating solid and air interface. The high contact angle in the side view indicates that the confinement from the micro-strips along the perpendicular direction can also prevent the solution from spreading in the longitudinal direction. While for elevated droplets, both front view and side view angles shift downwards. The side view data follow the predicted homogeneous line closely (Pink triangles). This downwards shift indicates the disturbed heterogeneous interface as evidenced by transferring results. For undisturbed droplets on SU-8 substrates having higher surface energy in nature compared to PDMS, the side view data follow the predicted homogeneous line closely (Figure 44b, blue dot). Comparing with PDMS, the water spread on SU-8 substrate in the longitudinal direction (side view) is not strongly influenced by the confinement in the perpendicular direction.

It is evident that wetting anisotropy on an anisotropically patterned substrate is influenced by chemistry nature (surface energy) of the substrate. For a surface with lower surface energy, such as PDMS with $\theta_{i,0} = 109^\circ$, the water confinement in the perpendicular direction strongly influence the water spread in the longitudinal direction leading to high contact angle in both direction and thus less anisotropy in wetting. However, for a less hydrophobic surface, such as SU-8 with $\theta_{i,0} = 71^\circ$, less interaction exist in the two directions, leading to large anisotropy during in wetting.

However, according to our transferring results, the wetting anisotropy does not influence the formation of heterogeneous interface and the resultant suspended SWCNT. This is in accordance
with the criteria given by Extrand, in which the contact line density (the density of the edge of
the supporting feature) plays an important roll regardless of the shape of supporting substrate\textsuperscript{163}.

3.4.13 Deformation and folding of suspended SWCNT network

One important issue of wet-contact printing method is shape stability of suspended 2D film
during the transferring and drying process. In Figure 45, a direct observation of suspended
SWCNT micro-lines, shown that along with increased $y$, the center width of suspended SWCNT
became smaller and smaller. To make clear observation of the deformed SWCNT micro-lines,
the SWCNT micro-lines were transferred to a SU-8 substrate coated with 150-nm-thick Au layer.
For a conductive Au coated substrate, there is no need to deposit additional the conductive layer
on the top leading to clear image of suspended SWCNT film with detailed morphology
information. As shown in the left panel of Figure 45a, $w_{\text{susp}}$ is the center width of suspended
SWCNT micro-line (bright contrast region), and $w_{\text{org}}$ is the original width of the SWCNT sitting
on the substrate (dark contrast region). Suspended length, $l$, has been defined as the length of real
suspended region which is not necessary the width of the trench ($y-x$) depending on the sharpness
of edge of supporting structure (see discussion in section 3.4.2). A close observation at the
suspended region (Figure 45a, middle and right panel) shows folding of the film can happen
from the two free-standing edges of the suspended region. The overlapped region of suspended
film is embraced by two dash lines as shown in the right panel of Figure 45a.
**Figure 45.** Deformation of suspended SWCNT network during the transferring process.

(a) SEM image of suspended SWCNT on Au layer coated SU-8 surface and schematic describing the definition of geometry parameters. The suspended SWCNT regions are shown as bright contrast. The width of SWCNT micro-lines at the center of suspended region ($w_{\text{susp}}$), original width ($w_{\text{org}}$), suspended length ($l$) and the folded region of suspended SWCNT micro-lines is embrace by two dash lines, right panel. (b) Deformation of 6-μm-wide SWCNT micro-lines transferred to both PDMS (left panel) and SU-8 (middle panel) substrates with fixed $x$ ($x = 6 \, \mu m$) and changing $y$ ($y = 9$ to $36 \, \mu m$). $w_{\text{susp}}$ and $w_{\text{org}}$ are plotted with respect to suspended length, $l$. Deformation rates ($w_{\text{org}} - w_{\text{susp}}$)/$w_{\text{org}} \times 100\%$ with respect to $l$ for both substrate are plotted in the right panel. (c) Extreme folding of suspended SWCNT over large trench (40-μm-wide): large area folding (left), multiple folding (middle) and twist (right).

In Figure 45b, the $w_{\text{susp}}$ and $w_{\text{org}}$ of 6-μm-wide SWCNT micro-lines transferred to both PDMS (left panel) and SU-8 (middle panel) substrates with fixed $x$ ($x = 6 \, \mu m$) and changing $y$ ($y = 9$ to $36 \, \mu m$) are plotted with respect to suspended length, $l$. For both substrates, $w_{\text{susp}}$ decreases
rapidly with increasing \( l \), while little change of \( w_{\text{org}} \) can be observed. Right panel summarizes the deformation rate \( (w_{\text{org}}-w_{\text{susp}})/w_{\text{org}} \times 100\% \) with respect to suspended length, \( l \). There is no significant difference between the two types of substrates indicating the deformation is mainly influenced by the suspended length, \( l \), rather than the material of the substrate.

The data for the designs with \( y \) larger than 36 \( \mu \)m are not summarized because extreme folding can happen and the deformation rate is impossible to summarize. Figure 45c summarizes three types of extreme folding of suspended SWCNT micro-line on 40-\( \mu \)m-wide trenches \((l = 40)\). In the left panel, the large area folding is happening over the whole film and in the middle panel, multiple folding leads to a very narrow strip of 400 nm. In the right panel, a twisting film can be seen.

Similarly, other suspended 2D films such as graphene fabricated by wet-method are subjected to folding\(^{185}\). The similarity indicates that folding is related to the existence of solution during the processing. For the wet-contact printing method, previous interfacial energy analysis shows that \( \gamma_{\text{water-PDMS}} \) is the highest among all the existing pairs of interfacial energy which warrants a stable SWCNT-polymer interface. However, solution can still interact with SWCNT and penetrate into the SWCNT network. There are functional groups existing on the surface of SWCNT, provided that the SWCNT was chemically treated and solved in DI water solution. Therefore, it is possible for the solution to intercalate between nanotube bundles and individual nanotubes. The following drying process can initiate tension to the suspended SWCNT network. A direct evidence of the inert tension of SWCNT network is provided in Figure 45c (left and middle), in which the PDMS surfaces in contact with the edge of suspended SWCNT films are stretched. Based on the SEM image of folded sample, for the suspended SWCNT film, the center part is tightened by constrain force from deformed PDMS strip while the edges are free to move.
The combination of meniscus force during the drying and the disturbance during the transferring process might initiate the folding behavior. For stable heterogeneous interface (stable regime and early meta-stable regime, \( y \leq 36 \, \mu\text{m} \)), the simply folding from edge might happen due to meniscus force. Extreme folding can happen with these additional influences: less confinement from the edges of the supporting structures, unstable heterogeneous interface over large trenches \((i.e., l \geq 40 \, \mu\text{m})\), and disturbance from transferring process.

Even though the size of SWCNT network cannot dictate its status during the transfer (suspended or collapsed) as shown in section 3.4.7, it does influence its shape stability. Compare Figure 28 with Figure 39, in which 6-\(\mu\text{m}\)-wide and 100-\(\mu\text{m}\)-wide SWCNT micro-lines were transferred to the sample PDMS substrate (Line 20 series). For all the range, there is no apparent deformation of 100-\(\mu\text{m}\)-wide SWCNT micro-lines. Also, Figure 45b (right) shows that less than 10\% deformation can be achieved for \( l \leq 6 \, \mu\text{m} \). This result indicates that the ratio \( \frac{w_{\text{org}}}{l} \) is critical. To achieve better stability \((\leq 10\%)\), wider SWCNT film is recommended with \( \frac{w_{\text{org}}}{l} \geq 1 \).

3.5 Summary

In this chapter, a CMOS compatible, high effective and controllable transfer technology, wet-contact printing, has been developed to fabricate large scale suspended SWCNT architectures over micro- to nano-patterned polymeric substrates. The fundamental mechanism of wet-contact printing method have been studied focusing on the micro- to nano-scale interaction among structures of polymeric substrate, the SLV interface and the status of SWCNTs (suspended or collapsed). The superhydrophobic surface design of the receiving polymeric substrate is the key to obtain suspended SWCNT architectures. The conclusion remarks are summarized as follows:
i) The status of SWCNT is directly related to the status of SLV interface and its stability. A heterogeneous interface is necessary for suspended SWCNT architectures. Since there is air-pocket (no solution) trapped between SWCNT and ground substrate, the solution on the top can be easily removed by titling the sample without influencing the status of SWCNT. Therefore, no special treatment, such as supercritical drying, is required leading to a high effective transferring process.

ii) The SLV interfaces (homogeneous and heterogeneous interface) are transformable to each other depending on the relative potential energy and energy barrier for the transition. The potential energy as well as the energy barrier is dictated by the structure of receiving polymeric substrate. The potential energy of heterogeneous interface increases with the increase of center distance (y) or ratio of center distance over width of strip (y/x). The energy barrier is proportional to the height of supporting structures, z. Smaller y (or y/x) and larger z will enhance the stable heterogeneous interface and thereafter the suspended SWCNT architectures.

iii) The chemical nature (surface energy) of the polymeric substrate is important for the stability of heterogeneous interface and thereby suspended SWCNT architectures. For the substrates with the same pattern design, heterogeneous interface on substrates with lower surface energy, e.g., PDMS (surface energy = 19.8 dynes/cm, water contact angle = 109 °), is much more stable, compared to SU-8 (surface energy ≈ 33 dynes/cm, water contact angle = 71°). As a result, suspended distance for SWCNT on PDMS is much larger than that on SU-8 substrate. Note that heterogeneous interface can be formed on patterned SU-8 even for substrate with large y, i.e., y = 120 µm, if the droplet is deposited very gently. However, such heterogeneous interface is very unstable, and tiny disturbance during the transferring process can initiate the transition leading to collapsed SWCNT architectures.
iv) The wet-contact printing method can be scaled to different combination of substrate materials (PDMS, SU-8, PMMA, Au, Pd and SAM coated Si), supporting patterns (up to microscale 100 µm trenches and nanoscale down to 500 nm trenches), target materials (SWCNT film, individual SWCNT and patterned graphene). The target materials can be transferred to polymeric substrate at arbitrary alignment with solid support.

v) Super flexible suspended SWCNT arches have been constructed on polymeric substrate with pre-strain. This structure has the potential to be an ultra-flexible electronic unit.

vi) Multiple transferring can be applied to the same polymeric substrate and suspended architectures can survive through the multiple solution processes indicating good compatibility with industrialized CMOS processes where repeated etching and cleaning are required.
Chapter 4. Highly Organized 2D and 3D SWCNTs-Polymer Architectures

4.1 Introduction

On the basis of capability of fabricating highly controlled SWCNT film on the donor substrate (in our case, SiO$_2$/Si substrate), various transfer techniques have to be integrated to build highly organized 2D to 3D flexible SWCNTs-polymer hybrid architectures. To a large extent, these architectures also represent a significant advance in the fabrication of either randomly arranged or aligned nanotubes (horizontal or vertical) stamped on, or embedded within a chosen polymer or similar matrix$^4,29$, optoelectronic$^89$, and field emission devices$^8$. However, despite of these progresses the fabrication of scalable and tightly controlled multi-dimensional microscale functional flexible systems that harness horizontal as well as vertical architectures of organized SWCNTs has remained largely elusive. Such methodologies would allow a seamless integration of SWCNTs based functional elements (e.g., field-emission pixels$^9$ and active sensing arrays$^{186}$) with the possible flexible SWCNTs-based circuitry constructed in a flexible matrix, enabling highly functional all-SWCNTs flexible devices. Developing and fine-tuning methods that not only maintain multi-dimensional structural integrity, but also high-quality electrical properties (especially at junctions and interfaces) of the said hybrid structure has so far remained a considerable practical challenge. Further, maintaining scalability of such a process up to macroscopic dimensions that would enable realistic devices is an additional roadblock.
4.2 Highly organized 2D SWCNTs-polymer architectures

![Image of a diagram showing the process of embedding 2D SWCNTs-polymer hybrid structures.](image)

**Figure 46.** Embedded 2D SWCNTs-polymer hybrid structures.

(a) The schematic of cast-etching method. The polymer (PMMA, pink layer) was casted onto the SWCNTs/SiO$_2$/Si substrate, followed by etching the SiO$_2$ layer and peel off the SWCNTs/PMMA film. The final image shows the top view after the SWCNTs/PMMA was turned upside down. (b) The SEM image of a folded region of flexible SWCNTs/PMMA film. An inset image shows the boundary between SWCNTs and PMMA. (c) An optical image of SWCNTs micro-lines transferred on the thin PMMA film together with gold contact pads (100 μm by 100 μm, 150-nm-thickness). The gold pad was patterned on SiO$_2$/Si substrate before the assembly of SWCNTs. Therefore, after transferred film was turned upside down, Au micro contact pads (squares) are placed on the top of SWCNTs-PMMA film. Scalar bars are (b) 20 μm, (A scale bar of inserted SEM image is 200 nm), (c) 100 μm.
2D SWCNT network with controlled structure and properties is a popular building block for flexible electronics. In this study, horizontally aligned SWCNTs micro-lines fabricated by the method of fluidic assembly could be transferred into polymer films such as PMMA as shown schematically in Figure 46a. This transferring method is well known as cast-etching method. For this, a layer of PMMA was casted on SWCNTs micro-lines and cured such that the SWCNTs were held by the PMMA polymer. Then, the PMMA polymer layer with SWCNTs micro-structures could be peeled off from the donor substrate by etching the SiO$_2$ sacrificial layer in the diluted HF acid solution. The mechanical flexibility of such structures can be seen in Figure 46b, which shows the curved end of SWCNTs micro-lines-PMMA film, and the inset figure clearly indicates the well-defined boundary between assembled SWCNTs micro-lines and the PMMA substrate. Along with SWCNTs micro-lines, we were also able to simultaneously transfer gold (Au) micro contacts, deposited on the initial SiO$_2$ surface before the assembly of SWCNTs forming the flexible device ready for electrical measurement. (Note that our developed SWCNTs fluidic assembly method can be applied not only to silicon based substrates, but also to other metal surfaces). Figure 46c shows an optical micrograph of these structures, where the dark squares represent the Au-contacts formed on SWCNTs micro-lines and PMMA film.
4.3 Highly organized 3D SWCNTs-polymer architectures

![Diagram showing 3D SWCNTs-polymer architectures](image)

**Figure 47.** Embedded 3D SWCNTs sandwiched between two polymers (PR and PMMA).

(a) Schematics showing transferring process of ultra-thin and anisotropic SWCNT film resulting in SWCNTs/PR/PMMA hybrid composite structure. (b) A SEM image of the transferred composite film. A scale bar is 10 μm. (c) An enlarged SEM image clearly shows well defined boundary between SWCNT film and PR. Note that PR lines are inserted on trenches of SWCNT film and both SWCNT film is placed on the thin PMMA layer. A scale bar is 200 nm. (d) The optical micrograph showing transferred SWCNTs/PR/PMMA hybrid composite film. A scale bar is 100 μm.

The cast-etching method is usually used to transfer 1D to 2D SWCNT architectures. However, if the architecture of SWCNT can be smartly controlled, 3D SWCNT architectures can be achieved on polymeric substrate. As discussed in chapter 2, the 3D SWCNT film with controlled electrical and thermal anisotropy has been demonstrated on flexible polymeric
substrates. A hybrid structure composing both PR strips and SWCNT can be transferred together to PMMA as shown in Figure 47: first, a layer of Poly(methyl methacrylate) (PMMA) was spin coated on the SWCNT film; second, the SiO$_2$ layer under SWCNT film was etched by HF solution; finally, the PR/SWCNTs/ PMMA film can be peeled off from the original substrate and transferred onto any other target substrates. Due to the unique 3D morphology, our assembled SWCNT films can be transferred together with arrays of PR micro-lines embedded into the trenches of 3D SWCNT films. Figure 47b shows the SEM image of the transferred SWCNT film, in which the black color regions are exposed to SWCNT film while the bright color regions are PR micro-lines. A well-defined boundary between SWCNTs and PR micro-lines can be seen in Figure 47c. Figure 47d shows the optical image of the transferred PR/SWCNTs/ PMMA hybrid film.
Figure 48. Embedded 3D SWCNT-PMMA film without PR.
(a) Schematic, (b) and (c) SEM images of 3D SWCNT film, and (d) and (e) AFM images of SWCNT at the boundary between removed PR and SWCNT film.

The PR can be selectively removed without damaging the PMMA substrates by exposing to developer (MF 319) for 5 min forming 3D SWCNT-PMMA architectures as shown in Figure 48a. SEM images show that PR strips embedded in the 3D SWCNT film were removed in Figure 48b and 48c. A close observation at the boundary between the removed PR and SWCNT film shows both exposed SWCNT surfaces. AFM images in Figure 48d and 48e at the boundary show that
the most of PR can be removed with well exposed SWCNT. A step height of 360 nm is the thickness of PR before removing. AFM images (Figure 48d) on SWCNT film at two different regions indicate that the PR was not removed completely even in the clear region where no PR residue can be observed by SEM. This indicates good interaction between SWCNT and PR at nanoscale. Further cleaning is required if PR has to be removed completely.

4.4 Combined 2D and 3D SWCNTs-polymer architectures

4.4.1 Morphology of combined 2D and 3D SWCNTs-polymer architectures

Further, the potential of combining lateral and vertical SWCNT structures has been developed to construct three-dimensionally ordered electrically conducting networks inside of polymer materials. Figure 49 shows schematics and micrographs of vertically aligned SWCNT line-patterns impregnated into a thick transparent PDMS matrix and interconnected with horizontally aligned SWCNTs micro-lines and gold contact pads placed on the top and bottom of the PDMS substrate. To fabricate such an architecture, firstly three columns of vertically aligned SWCNT line structures were inserted inside a bulk PDMS matrix by casting a thick layer of PDMS covering the length of vertically aligned SWCNTs and then curing it. Then, the top and bottom surfaces of a PDMS substrate were mechanically polished to expose both ends of vertically aligned SWCNTs. Each side of this polished PDMS/vertically aligned SWCNTs substrate was used as a stamp to transfer a layer of optically transparent ultra thin horizontal SWCNT micro-lines (9 μm width) together with gold contact pads on each end, using the wet-contact printing method. Finally, the whole sample was sealed in the PDMS. The optical image as well as the schematic is shown in Figure 49a. The horizontal SWCNT micro-lines are invisible since their thickness is around 10 to 20 nm.
Figure 49. A combined lateral SWCNTs micro-lines and vertically aligned SWCNTs arrays inside of PDMS substrates.

(a) The optical image and schematic (inset) of combined three dimensional lateral SWCNTs micro-lines and vertical SWCNTs-polymer hybrid structures. The horizontal and vertical SWCNT networks along with gold contact pads are sealed inside a centimeter thick PDMS matrix. Note that vertically aligned SWCNTs line structures (3 mm height, 7 mm length, and 700 μm width) are shown in black inside of a transparent PDMS substrate and physically contacted by arrays of SWCNTs micro-lines (9 μm in width and 6 μm in space, transparent in the optical image) with a 90° angle on the top and bottom of a PDMS substrate. (b) The schematic of combined three dimensional SWCNTs-polymer hybrid structures for electrical measurement with only one column of vertically aligned SWCNTs and 100 μm wide SWCNTs micro-lines. (c) An optical microscopy image of centimeters long and 100 μm wide SWCNTs micro-lines interconnected to the vertically aligned SWCNTs structure inside of PDMS matrix. Pure PDMS region are shown in a bright contrast, while the PDMS vertically aligned SWCNTs composite structures are shown in a dark contrast. (d) SEM images of interface between laterally aligned SWCNT and vertically aligned SWCNT arrays before final packaging in PDMS. The lateral SWCNT films are in contact with vertically aligned SWCNT through protruded tips.

We have shown that despite the mechanical polishing applied to the vertically aligned SWCNTs, their mechanical interface with the horizontal SWCNT architectures showed
surprisingly low contact resistance. This is indeed very encouraging, since no extra process steps were undertaken to improve the physical proximity of the vertical and horizontal nanotubes, other than the mechanical contact obtained directly through the transfer process. For electrical measurement, we used a simpler structure with only one column of vertically aligned SWCNTs and 100 μm wide SWCNTs micro-lines as illustrated in Figure 49b. Figure 49c is the optical microscopy image showing continuous and aligned 100 μm wide SWCNTs micro-lines lying across the boundary between pure PDMS and PDMS vertically aligned SWCNTs composite regions. The good contact between vertically aligned SWCNT and laterally aligned SWCNT are warranted by exposing the tips of vertically aligned SWCNT through the mechanical polishing vertical SWCNT-PDMS surface as shown in Figure 49d. Many tips of vertical SWCNTs can be exposed by grinding the surface using sand paper with the number of 3000. Interestingly, both chemical mechanical polish and O₂ plasma treatment were processed after mechanical polishing and no improvement can be found. Even the O₂ plasma can remove the tip of SWCNT leading to very poor contact.
4.4.2 Electrical contact between 2D and 3D SWCNT architectures

Figure 50. *I-V* measurement of the combined three dimensional SWCNT device.

(a) The line graph shows the measurement from contact pad A to all the other contact pads in a macroscopic SWCNTs network inside of the PDMS substrate. (b) A cross-sectional schematic of three dimensional horizontal and vertical SWCNTs network and (c) its circuit model indicating a device resistance and contact resistance between the horizontally aligned SWCNTs and vertically aligned SWCNTs.
The current-voltage ($I$-$V$) measurements conducted between the contact pad $A$ and all other contact pads are plotted in Figure 50a, showing a linear dependence of current with voltage, indicating that well defined conductive paths are built from the contact pad $A$ to other contact pads, and Ohmic interfaces have been established at every single SWCNT junction. The labeling of the contact pads is shown in the inset. The values of electrical resistances between any two existing contacts are summarized in the table 5. Note that for all measured pairs of contact pads, the conducting paths are a combination of lateral SWCNTs micro-lines and vertically aligned SWCNTs, except the conduction path along the same lateral SWNTs micro-lines (e.g. between the contact pad $A$ and $B$). The average electrical resistance measured between contact pads that included both horizontal and vertical architectures was found to be 14.16 kΩ. The average electrical resistance only for the lateral SWCNTs structures within the same plane was 13.03 kΩ. This indicates that the total resistance was largely dominated by the ultrathin lateral nanotube lines, which is not surprising since the vertical columns have much larger cross-sections. Since the vertically aligned SWCNTs structure was interconnected with the lateral SWCNTs micro-lines, the resistance in the combined three dimensional networks is higher than that of the horizontally assembled SWCNT structures. In addition, uniformly distributed electrical resistances within the three dimensional SWCNTs network indicate that contacts between lateral SWCNTs micro-lines and vertically aligned SWCNTs is quite stable for the most of macroscopic conduction paths.

To demonstrate the linearity of $I$-$V$ measurement in the combined structure, a typical dataset ($R_{AB}$) was fit to a linear equation:

$$I = G \cdot V + c,$$

(4.1)
where $G$ is the conductance, $1/G$ is the resistance, $c$ is a constant caused by an instrumental offset error. A perfect linear fit was shown in Figure 51, and $G$ is calculated to be $8.55 \times 10^{-5}$ S and the instrumental offset error is $2.68 \times 10^{-8}$ A which is very small compared to the measurement range.

**Figure 51.** Linear fit of $I$-$V$ measurement of $R_{AB}$.

**Table 5.** Resistance between all the existing pairs of contact pads calculated from the $I$-$V$ Measurement in Figure 50.

<table>
<thead>
<tr>
<th>Resistance (kΩ)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
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<tbody>
<tr>
<td>A</td>
<td>11.73</td>
<td>14.61</td>
<td>15.72</td>
<td>13.44</td>
<td>18.52</td>
<td>20.03</td>
<td>15.00</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>10.89</td>
<td>10.19</td>
<td>8.08</td>
<td>11.99</td>
<td>13.79</td>
<td>9.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>13.10</td>
<td>17.51</td>
<td>16.84</td>
<td>18.61</td>
<td>13.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>10.84</td>
<td>16.02</td>
<td>17.74</td>
<td>12.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>13.21</td>
<td>15.51</td>
<td>10.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td></td>
<td>18.45</td>
<td>14.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>
As shown in Figure 50b and 50c, the circuit model of combined SWCNTs structure of ABba consists of four SWCNTs leads (R₁, R₂, R₃ and R₄) and the junction resistance (R_c₁ and R_c₂) between horizontal and vertical SWCNTs networks (R_P). The measured resistance between the contact pads A and a can be written as

\[ R_{Aa} = R_1 + R_3 + R_c, \]  

(4.2)

where \( R_c = R_{c1} + R_P + R_{c2} \). Correspondingly, resistance of other existing pairs can be written as follows.

\[ R_{Bb} = R_2 + R_4 + R_c, \]  

(4.3)

\[ R_{Ab} = R_1 + R_4 + R_c, \]  

(4.4)

\[ R_{Ba} = R_2 + R_3 + R_c, \]  

(4.5)

\[ R_{AB} = R_1 + R_2, \]  

(4.6)

\[ R_{ab} = R_3 + R_4. \]  

(4.7)

Combining Eq. 4.2 to Eq. 4.7, lead resistances as well as the contact resistances can be calculated: \( R_c = 0.5 \times (R_{Aa} + R_{Bb} - R_{AB} - R_{ab}) = 0.245 \ \text{kΩ} \) and \( R_c = 0.5 \times (R_{Ab} + R_{Ba} - R_{AB} - R_{ab}) = 0.83 \ \text{kΩ} \). Therefore the average \( R_c = 0.5375 \pm 0.2925 \ \text{kΩ} \). The SWCNTs leads resistances (R₁, R₂, R₃ and R₄) were summarized in Table 6.

**Table 6.** Resistance estimation for the combined SWCNTs structure from A–a, A–B, a–b, and B–b.

<table>
<thead>
<tr>
<th>R_c (kΩ)</th>
<th>R₁ (kΩ)</th>
<th>R₂ (kΩ)</th>
<th>R₃ (kΩ)</th>
<th>R₄ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5375±0.2925</td>
<td>8.84</td>
<td>2.89</td>
<td>4.36</td>
<td>8.85</td>
</tr>
</tbody>
</table>
In the same way, we were able to estimate the contact resistance together with the nanotube resistance for the pairs of $C-c$, $C-D$, $c-d$, and $D-d$ as shown in Figure 52 and Table 7.

**Figure 52.** The circuit model between the horizontally aligned SWCNTs and vertically aligned SWCNTs from $C-c$, $C-D$, $c-d$, and $D-d$.

**Table 7.** Resistance estimation for the combined SWCNTs structure from $C-c$, $C-D$, $c-d$, and $D-d$ where $R_c = R_{c1} + R_p + R_{c2}$.

<table>
<thead>
<tr>
<th>$R_c$ (kΩ)</th>
<th>$R_1$ (kΩ)</th>
<th>$R_2$ (kΩ)</th>
<th>$R_3$ (kΩ)</th>
<th>$R_4$ (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.095±0.03</td>
<td>7.02</td>
<td>6.09</td>
<td>9.53</td>
<td>4.56</td>
</tr>
</tbody>
</table>

Since the resistance of the pillar is additive to the junction resistance, it was not possible to eliminate its value, and hence the quantity $R_{c1} + R_p + R_{c2}$ represents the absolute upper limit to the junction resistance. In reality, the junction resistance was even smaller, since we know that the pillar resistance is never $= 0Ω$. With the measured resistance of $R_{Aa}$ or $R_{Bb}$, we calculate the
percentage of pillar + junction resistance by dividing $R_{c1} + R_p + R_{c2}$ and found that the percentage of contact resistance is 4.0 % or 4.5 %, respectively. On the other side of the structure, the percentage of contact resistance is 11.2 % or 16.5 % depending on the measured resistance for $R_{Cc}$ or $R_{Dd}$. Even though we assume that contact resistances are much higher than the resistance of a pillar structure, horizontal and vertical SWCNTs junction contact resistances are within 3.0 to 16.5 % of the total resistance in this three dimensional network, showing stable and low electrical contacts between horizontal and vertical SWCNTs structures.

Flexible electrical device with minimized electrical contact resistance is valuable in building low energy consuming system for future flexible electronics. Our experiment demonstrates the possibility to integrate different transport units into one system with robust connections. As a proof-of-concept, the vertical aligned SWCNT can be used to substitute the Cu lead and vertically aligned SWCNT architectures can be developed into functional unit such as smart membrane system. The minimized contact resistance is originated from the robust physical contact between the lateral and vertical SWCNT architectures.

4.5 Summary

In the future flexible electronics, it is necessary to combine multiple transferring methods to integrate different SWCNT architectures through a step-by-step procedure. In Chapter 4, various mechanically and electrically robust novel 2D and 3D organized SWCNT networks-polymer hybrid structures have been demonstrated. SWCNT micro-lines with contact pads and 3D anisotropic SWCNT network are transferred into PMMA film by the method of cast-etching. Moreover, complex SWCNT network with vertically aligned SWCNT strips sandwiched between two layers of laterally aligned SWCNT micro-lines is embedded into PDMS substrate
through a multiple transferring process combining conventional cast method and new wet-contact printing method. A robust electrical contact (contact resistance as low as 3%) can be found between the two SWCNT architectures. Our fabrication methods are scalable and use CMOS compatible methods, and hence are extremely valuable for integration with the current micro-fabrication technology. These multi-dimensional micro-scale SWCNT networks-polymer hybrid structures have immediate and immense implications for the development micro-scale multifunctional flexible systems such as sensors, actuators, interconnects, transparent flexible electrodes, advanced micro-fluidic devices, and smart membrane systems.
Chapter 5. Properties and Application of Suspended SWCNT Architectures

5.1 Mechanical and electromechanical properties

5.1.1 Introduction

To realize the application of suspended SWCNT architectures, it is important to understand its mechanical and electromechanical properties. Individual nanotube based devices have attracted major attentions due to the possibility to approach nanotube’s theoretical potential\textsuperscript{52,60}. However, the individual nanotube devices suffer from poor repeatability, difficulties in handling and low efficiency in fabrication\textsuperscript{21,48,63}. In current research, suspended SWCNT network has been investigated. As discussed in Chapter 2, highly organized SWCNT film from micro- to macro-size can be achieved with desired location, orientation and electrical and thermal properties. However, the fundamental mechanical and electromechanical properties of SWCNT network are not fully understood. Especially, when SWCNT is sitting on the substrate, the substrate will influence the apparent properties of SWCNT forming some composite affects such that the real properties of SWCNT are hidden\textsuperscript{45}. The highly organized suspended SWCNT network provides the ideal prototype for investigating its original properties. This work was collaborated with Dr. Xin Wang and Prof. Kai-tak Wan at Northeastern University.

5.1.2 Experimental

As shown in Figure 53a, an electromechanical test system has been constructed combining an AFM to apply line load to suspended SWCNT network with displacement and force resolution in nm and nN and an \textit{in-situ} electrical measurement device (Keithley 2400) to investigate the real-time relation among force, displacement and electrical current passing through the suspended SWCNT as shown in Figure 53a.
Figure 53. Set-up of mechanical and electromechanical measurement on suspended SWCNT.

(a) Schematic of experimental design for mechanical and electromechanical test. (b) The SEM images of tipless cantilever before (upper panel) and after focused ion beam cutting (lower panel).

As shown in Figure 53b, the tipless cantilever (TL-NCL, Nanosensors, Inc.) made of highly doped N-type Si with resistivity of 0.01-0.02 Ω·cm have been machined by focused ion beam (JEOL JIB-4500, JEOL USA, Inc.) to chop the head and apply line-load to suspended SWCNT film, and to avoid dissipating charge on the SWCNT film, an oxidization has been process in air at temperature (1000 °C) for 5 hours to form a 140-nm-thick SiO₂ layer. The focused ion beam cutting was performed by Dr. Gregory McMahon from Boston College.

The samples for mechanical properties measurement were fabricated through the template guided fluidic assembly with the dip-coating speed of 0.1 mm/min as described in chapter 2 and 3. Fresh SWCNT/DI water solution was used to obtain well separated SWCNT micro-lines (6 μm in width). The thickness of the micro-lines ranges from ~ 14 nm to 36 nm from center to the
edge. To eliminate such non-uniformity in electromechanical measurement, a whole SWCNT film was assembled on bare plasma treated SiO2/Si substrate using the dip-coating process with the speed of 0.05 mm/min, followed by photoresist patterning (S1818) to selectively protect the SWCNT film. The expose the area of SWCNT film was removed by an O2 plasma etching process. O2 plasma etching (power = 64 W, flow rate =16 sccm) was processed for 4 min to fully remove the exposed SWCNT. Finally, the protective photoresist was stripped off by acetone, rinsed in fresh isopropyl alcohol and dried using N2. By this method, SWCNT micro-lines with different width (~ 5 and 10 μm in our experiment) can be fabricated with a uniform thickness depending on the dip-coating speed. To process the electrical measurement, the 50-nm-thick Pd contact pads were deposit on SWCNT micro-lines utilizing the sputter coater (EMITECH K575X). The contact pads were then connected to copper leads using silver paint (PELCO® CONDUCTIVE SILVER 187, Ted Pella, Inc.).
5.1.3 Mechanical properties of suspended SWCNT film

**Figure 54.** Mechanical property measurement of suspended SWCNT micro-lines.
(a) Ten identical indentation loops on the SWCNT micro-lines transferred to Line 6.9 substrate, (b) five loading curves with different indentation depth on the same sample and (c) indentation on samples SWCNT micro-lines transferred to substrates with different center distance, y. (d)
Calculated normalized applied load versus normalized central deflection of SWCNT film and (e) calculated Young’s modulus and the thickness of the suspended SWCNT films with respect to different center distance of the supporting polymer strips.

For mechanical measurement, arrays of suspended SWCNT micro-lines (about 6 µm in width) have been transferred to SU-8 substrate patterned with micro-strips (Line 6 series). The width of supporting strip, \( x \), is 6 µm and the center distance, \( y \), ranges from 9 to 18 µm. The height of the strip, \( z \), is also 6 µm leaving enough space for the indentation process. Great repeatability can be found during different indentation and contraction loops (Figure 54a and 54b). Three representative loops of three substrate designs are shown in Figure 54c.

The calculated force-displacement curves are shown in Figure 54d and a clean transition from bending dominant to stretching dominant can be found. Based on linear elastic theory, in the bending dominant, \( F = \frac{24bDw_0}{l^3} \) and \( D = \frac{Eh^2}{12(1-v^2)} \), and in the stretching dominant, \( F = \frac{EhbD w_0^3}{(1-v^2)} \), where \( F, b, w_0, l, E, h \) and \( v \), are applied force, width of suspended membrane, center deflection of the membrane, half suspended length of membrane, Young’s modulus, thickness of the membrane and Poisson ratio, respectively\(^{187,188}\). The cross-section of the film is not perfect rectangle with the center thickness of 14 nm and the edge thickness of 36 nm, due to the nature of guided fluidic assembly. Therefore, for the calculation, we set both thickness and the Young’s modulus as the variables and the calculated results (Figure 54e) indicate that the Young’s modulus of suspended SWCNT is more than 30 GPa among the highest values reported for random aligned SWCNT network\(^{53}\). This value is close to recent reported graphene paper (\( E = 31.70 \) GPa)\(^{189}\). No apparent dependence on the center distance (\( y \)) has been found. This is reasonable because elastic modulus should be independent of suspending geometry. The
calculated thicknesses also fall into the range of real thickness measured by AFM indicating average thickness across the whole width of SWCNT thin film.

5.1.4 Electromechanical properties of suspended SWCNT film

To achieve better thickness uniformity, the sample for electromechanical measurement has been fabricated by O$_2$ plasma etching of a whole film assembled on SiO$_2$ substrate. The SWCNT film was first assembled on SiO$_2$/Si substrate using the same procedure for surface treatment and dip-coating except that there was no pattern on the surface. The dip-coating speed is 0.05 mm/min. And then surface was patterned using photoresist (S1818) and exposed area was etching using O$_2$ plasma for 4 min (16 sccm, 64 W). The protective photoresist was stripped off using acetone followed by IPA rinsing leaving uniformed SWCNT micro-lines having the same thickness from center to edge. Two different widths ($b = 10$ and $5 \mu$m) of the resultant SWCNT micro-lines have been made. The thickness of the film is measured to be 45.7 nm. For a typical test of six minutes, indentation process was performed every one minute and the period for each indentation ranges from 1 to 5 seconds. Five indentation loops with both force and deformation can be recorded. During six-minute test, electrical conductance was recorded continuously.
Figure 55. Electromechanical test for 10-μm-wide suspended SWCNT film over 20-μm-wide trench.

(a) A representative test with five indentation loops. Both displacement and force are plotted with respect to real time. For each loop, the plot for displacement is stacked above the force plotted. (b) In-situ electrical measurement corresponding to the indentation test. The electrical conductance was plotted with respect to time. (c) A zoomed view of first indentation loop with force, deformation and conductance in one graph.

Figure 55 shows a representative test for 10-μm-wide suspended SWCNT film over 20-μm-wide trench. Five indentations were summarized in Figure 55a, in which for each indentation loop, deformation data were stacked above the force data with respect to time. Figure 55b summarized the electrical conductance with respect to time during the six-minute test. In Figure 55c, the time dependences of force, deformation and conductance of first indentation (1st) loop
were displayed in the same graph. At first when there is no indentation, the conductance follows a baseline which does not have to be perfect stable. During the indentation (cantilever pushing downwards), a decrease of conductance can be observed in conductance-time curve. As soon as the cantilever begins to move upwards, a recover of conductance can be seen. Once the cantilever is detached from the SWCNT film, the conductance goes back to baseline. 5-μm-wide suspended SWCNT film shows the similar response as shown in Figure 56.

![Graph showing conductance changes during indentation test](image)

**Figure 56.** Electromechanical test for 5-μm-wide suspended SWCNT film over 20-μm-wide trench.

(a) A representative test with five indentation loops. Both displacement and force are plotted with respect to real time. For each loop, the plot for displacement is stacked above the force plot. (b) In-situ electrical measurement corresponding to the indentation test. The electrical conductance is plotted with respect to time. (c) A zoomed view of first indentation loop with force, deformation and conductance in one graph.
By changing the indentation depth, different electromechanical responses are recorded and summarized in Figure 57 in which a linear decrease of change of current ($\Delta I$) with respect to elongation of the film ($\Delta l$) has been observed for suspended SWCNT film with different widths ($b \sim 5$ and $10 \, \mu m$ in width) over $20 \, \mu m$ wide trench.

![Figure 57](image)

**Figure 57.** Change of current ($\Delta I$) with respect to elongation of the film ($\Delta l$) for both $b=10$- and $5$-µm-wide suspended SWCNT film over $20$-µm-wide trench.

The electrical conductivity can be calculated as follows:

$$ G = \frac{I}{U} = \sigma \frac{A}{l}, $$

(5.1)

where $G$, $I$, $U$, $\sigma$, $A$, $l$ are conductance, current, voltage, conductivity, cross section area and length of the film between contact pads. Change of current, which can be directly obtained in the measurement, can be expressed as
\[ \Delta I = |I_1 - I_0| = |U(G_1 - G_0)| = \left| U\sigma \left( \frac{A}{l_1} - \frac{A}{l_0} \right) \right| = U\sigma A \left[ \frac{l_1 - l_0}{l_1l_0} \right], \tag{5.2} \]

where subscripts 1 and 0 indicate the status during indentation (1) and the initial status before indentation (0). Since the change of length is small, the expression for \( \Delta I \) can be simplified as:

\[ \Delta I = \frac{\Delta l}{l_0^2} U\sigma A, \tag{5.3} \]

The slope from the fitted curve in Figure 57 can be expressed as:

\[ \text{Slope} = \frac{1}{l_0^2} U\sigma A. \tag{5.4} \]

As shown in Figure 57, the slopes for 10- and 5-\( \mu \)m-wide suspended SWCNT film are 0.662 and 3.58 respectively. Therefore, the conductivity can be calculated as 3.236 MS/m and 3.155 MS/m for 10- and 5-\( \mu \)m-wide suspended SWCNT film respectively. The similar conductivity indicates the suspended SWCNT is uniform and there is little dependence of conductivity with respect the width of the film. Most importantly, the linear dependence of \( \Delta I \) on deformation (\( \Delta l \)) indicates a very stable and sensitive device for immediate applications in displacement sensing and force sensing.

### 5.1.5 Summary

In summary, mechanically robust and electrically stable suspended SWCNT network has been demonstrated through the in-situ measurement combing both mechanical and electromechanical tests. The Young’s modulus (~30 GPa) of suspended SWCNT network is among the highest values reported on random SWCNT network. The stable sensing curve of displacement indicated immediate applications in motions sensing and force sensing.
5.2 Ethanol sensor based on suspended SWCNTs-polymer structure

5.2.1 Introduction

The mechanically and electrically robust suspended SWCNT-PDMS array structures form an ideal platform for the development of highly sensitive chemical sensor due to the fully exposed surface. In such architectures, the influence of support substrate can be minimized and both top and bottom surfaces can be used for chemical detection.

5.2.2 Experimental

A SWCNT-PDMS channel architecture has been designed as shown in Figure 58a, which consists of parallel arrays of aligned and suspended SWCNT 2D micro-lines placed orthogonally across arrays of microscale PDMS trenches. The PDMS cell with trenches at the bottom was fabricated by casting uncured PDMS onto a SiO$_2$/Si substrate patterned with SU-8 strips (7.5 μm in width and 7.5 μm in space between the strips and 6 μm in height). After curing, the PDMS cell was peeled off from the substrate leaving trenches with reciprocal size on the bottom. A set of four 100-μm-wide SWCNTs micro-arrays were then transferred to the trenched region of PDMS cell by the method of wet-contact stamping following by depositing Ti/Au (5 nm/150 nm) contact pads at the end of SWCNTs micro-line structures leaving 1.5 mm gap between the two contact pads. Reference sample with SWCNT micro-lines confined to the PDMS substrate were fabricated following the same procedure except that the PDMS substrate is flat. Since it is difficult to image the SWCNTs on PDMS due to the charging and deformation of PDMS under electron beam, the SEM images were taken from the SWCNTs region coated with Ti/Au.

The ethanol sensing experiment is processed in a well-sealed chamber and the electrical data is real-time collected using Agilent 4156C. For the measurement of electrical response as the function of ethanol concentration, the ethanol vapor was infused into the chamber which was
kept closed until the resistance reached the peak value. And then the chamber was open to the atmosphere to release the ethanol. Five different concentrations (32, 75, 188, 342 and 492 ppm) were tested in our experiment. The sensitivity \( ((R_{\text{peak}} - R_0)/R_0) \) was calculated by normalizing the difference between peak resistance and the initial resistance \( R_0 \). For the test of reproducibility, two concentrations have been selected (70 ppm and 30 ppm) and four continuous running circles were processed for each concentration. For each circle, the exposing time (on status in Figure 58f) and the recovery time (off status in Figure 58f) were set to be 120 s and 240 s respectively.
5.2.3 Ethanol sensing of suspended SWCNT film

Figure 58. An ethanol sensor based on suspended SWCNTs.

(a) Schematic of suspended SWCNTs ethanol gas sensor. (b) A SEM image of the suspended SWCNTs gas sensor. (c) SEM image of the edge of suspended SWCNTs micro-lines. (d) I-V curve of gas sensor before the gas sensing experiment. (e) The electrical response of suspended SWCNTs micro-lines with respect to four different concentrations of ethanol. The SWCNTs was exposed to ethanol until the resistance reached the peak value followed by releasing the ethanol in atmosphere. The resistance difference (R-R₀) was normalized with respect to the initial value (R₀) of each run. (f) The test of reproducibility for two different concentrations (70 ppm and 30 ppm). Scalar bars are 100 μm for (b) and 5 μm for (c).
As shown in Figure 58b, the arrays of SWCNTs micro-lines sit at right angle with respect to the PDMS trenches and a higher magnification image in Figure 58c clarifies that the SWCNTs are suspended across the trenches of PDMS. Although in principle the SWCNT network structures could be independently attached to electrical contact pads, for the ease of demonstration they were electrically shorted at each end as shown, using Ti/Au contact pads. Previous work has shown that interaction with ethanol molecules can change the electrical properties of SWCNTs, leading to fast response and good reversibility. We utilize this fact to test our highly organized, flexible and suspend SWCNT micro-architecture as an ethanol sensor using varying concentrations of ethanol vapor.

The initial resistance of our sensor was 15.86 kΩ as shown in Figure 58d and the linear $I-V$ curve indicates good Ohmic contact between SWCNTs and contact pads. The electrical response as a function of ethanol concentration as well as the reproducibility is shown in Figure 58e and 58f respectively. In Figure 58e, the electrical response to four different concentrations, ranging from 30 ppm to 500 ppm, are presented. The sensitivity ($\frac{(R_{\text{peak}}-R_0)}{R_0}$) of sensor (inset in Figure 58e) increases from 3 % to 9 % with the increase of concentration from 30 ppm to 500 ppm. The electrical response in Figure 58e shows good reproducibility for four continuous cycles under two different concentrations. The on and off time were set to be 120 s and 240 s. The results feature a rapid response and almost a complete recovery of the suspended SWCNTs sensors, indicating that there was no chemical bonding between the ethanol molecules and the sensing surface; since such bond formation is usually associated with large time-scale and no recovery. It has been shown that the absorption efficiency of the polar organic molecules with hydroxyl groups in substances involving carboxyl molecules increases due to electrostatic dipole-dipole interactions. The SWCNTs micro-lines were fabricated from SWCNTs-DI water solution by the
method of guided fluidic assembly. To achieve good dispersion of SWCNTs in DI water, the surface of SWCNTs was functionalized with -COOH groups. From this fact, the main sensing mechanism in our sensor system appears to be hydrogen bonding between a hydrogen atom with a positive partial charge on the -OH group of the ethanol and a negatively charged oxygen atom within the -COOH functional groups on the SWCNTs. Therefore, the increase in resistance we have observed in all measurement is most likely due to hydrogen bond formation.

5.2.4 Ethanol sensing of SWCNT film confined to the substrate

![Figure 59](image)

**Figure 59.** Comparison between suspended and confined SWCNTs micro-lines on ethanol sensing.

(a) The electrical response on time with respect to different concentrations of ethanol. The dependences of (b) sensitivity \((R-R_0)/R_0\) and (c) saturation time (defined as the time that resistance reach the peak value) on the concentrations of ethanol.
The results of suspended SWCNT film are compared with SWCNT film confined to the substrate shown as confined SWCNT in the Figure 59. The confined SWCNT were tested simultaneously with suspended sample in the testing chamber to eliminate any possible system variation. Figure 59 shows the sensing response of both samples to five different concentrations. Both sensitivities increase with increased concentration, while the saturation times increase first and then decrease beyond 400 ppm. The sensitivity of suspended SWCNT (Figure 59b, red dot line) is higher than that of confined SWCNT (black square line). The saturation times are close for both samples.

![Figure 60](image)

**Figure 60.** Comparison of resistance response between suspended and confined SWCNTs micro-lines on ethanol sensing at low concentration 70 ppm and 30 ppm.

(a) Absolute value and (b) normalized value with respect to the initial \( R_0 \).

The repeatability tests for both samples at low concentration were shown in Figure 60. Both samples have good repeatability and fast responding. As expected, the sensitivity for suspended SWCNT is always higher than that of confined SWCNT. However, it is clear that the improvement of suspended SWCNT compared to confined SWCNT is not significant. It can be
attributed to the surface area exposed to the ethanol molecules. As we know, the substrate is patterned with strips with \( x = 7.5 \) and \( y = 15 \) \( \mu m \) and the exposed area for the top surface is the same for both samples. If the overall exposed surface (OES) defined as surface that in direct contact with chemical is normalized with the area of the top surface, for confined SWCNT film, the OES is 1 and 1.5 for confined SWCNT and suspended SWCNT.

![Graph showing the changing of relative sensitivity with respect to ethanol concentration.](image)

**Figure 61.** The changing of relative sensitivity \( \frac{\text{Sensitivity}_{\text{suspended}}}{\text{Sensitivity}_{\text{confined}}} \) with respect to ethanol concentration.

Evidently, the sensitivity of SWCNT is not proportional to its exposed area since calculated ratio result only shown average value of 1.1, rather than 1.5. Even though the improvement for gas sensing is not very much, the concept of changing the sensitivity by enlarging the exposed
area has been proved. Future improvement can be made by increasing the exposed area and choosing suitable gas.

5.2.5 Summary

The application of suspended SWCNT as gas sensor has been demonstrated with fast responding and recovery, good reproducibility and sensitivity. Compared to SWCNT sensor sitting on the substrate, the improvement of suspended SWCNT is not remarkable due to the unique sensing mechanism which is related to the exposed surface area. To further enhance the sensitivity, a structure with even more exposed areas is required. Therefore, the future direction of exposure area based sensor should be building not only suspended architecture, but also constructing delicate structure within the suspended part to create more surface areas.
Chapter 6. Conclusions

This study was set out to achieve highly organized SWCNT-polymer hybrid architectures for next generation flexible electronics. Even though remarkable progresses are made towards the assembly and transfer technologies of SWCNTs, highly controllable and affordable SWCNT-polymer hybrid system is still largely exclusive from real applications. This study sought to approach the goal through two most important aspects: i) miniaturized functional unit (SWCNT) with deliberately controlled properties and ii) high-rate and large scale integration technologies to construct the functional unit into or onto flexible, transparent and insulating polymeric substrates at desired location with prescribed orientation. A bottom-up strategy has been followed: on one hand, a facile method, template guided fluidic assembly, has been developed to achieve directional property control of SWCNT network; on the other hand, a novel transfer technology, wet-contact printing, has been invented to achieve high-rate and large scale integration of SWCNT and polymer substrate with micro to nanoscale precision. The study has further sought to combine both the assembly and transfer technologies to achieve mechanically and electrically robust flexible device and realize sensing applications.

In the first aspect, the direction property control of SWCNT network has been investigated. The structure of SWCNT network dictates its electrical and thermal properties. However, in general, the alignment control is the only principle applied by the existing methods with the help of external fields such as electrical, magnetic, fluidic and etc. In this study, a new principle, 3D morphology control, has been brought out to tailor the electrical and thermal anisotropy of the SWCNT film in a well-controlled manner. The concept of 3D morphology control is to create anisotropy with additional control in the height (z axis), while alignment control is mainly a 1D (x axis) or 2D (x-y plane) concept. The 3D morphology control has been achieved in two steps:
1) a heterogeneous substrate is created with alternating hydrophobic (photoresist patterns) and hydrophilic (plasma treated SiO$_2$) micro-strips and 2) the substrate is then used as the template for fluidic assembly in water based SWCNT solution. The different surface chemistry leads to different wettability and then 3D SWCNT film with alternating thin (over hydrophobic photoresist strips) and thick (over hydrophilic SiO$_2$ strips) SWCNT strips. If each strip can be treated as a resistor, the resistance along the strips direction, treated as a parallel circuit of all the resistors, is much lower than that transverse to the strips direction, treated as a series circuit. This study extends the controllability of SWCNT network into 3D regime which has never been investigated before and will enrich the method for structure-properties control for network system with different materials.

In the second aspect, a wet-contact printing method has been developed to integrate highly organized and large scale suspended SWCNT architecture on the various polymeric substrates and its fundamental mechanism has been studied. It is extremely challenging to integrate suspended SWCNT architectures over polymeric substrate due to the difficulty in handling the SWCNT and the incompatibility between polymeric substrate and existing MEMS/NEMS technologies where complicated interaction among solution, substrate and suspended device at micro to nanoscale is not fully understood. The principle in wet-contact printing is to intentionally control the solid-liquid-vapor (SLV) interface by creating micro- to nano-structure on the surface of receiving polymeric substrate such that a superhydrophobic polymer surface with a heterogeneous (Cassie-Baxter) SLV interface in the solution process is formed. During the wet-contact printing process, SWCNT architectures are sandwiched at the SLV interface between solution and polymeric substrate and suspended SWCNT architectures are naturally formed at the trenches where air-pockets are trapped underneath. For the same reason, solution
can be removed by simply tilting the substrate without changing the status of suspended SWCNT. Since no specify treatment is required for removing the solution, wet-contact printing method is highly efficient and can be processed in a continuous manner. Mechanism investigation reveals that structure and material of the substrate are important: smaller center distance between supporting structures, $y$, large height of supporting structures, $z$, and lower surface energy of polymer are preferred for stable suspended architectures. Moreover, the wet-contact printing method can be scaled to different combinations of substrate materials (PDMS, SU-8, PMMA, Au, Pd and SAM coated Si), supporting patterns (up to 100-µm-wide trenches and nanoscale down to 500-nm-wide trenches), target materials (SWCNT film, individual SWCNT and patterned graphene).

The ultimate goal of this study is to construct mechanically and electrically robust SWCNT-polymer hybrid devices. In most of the fabrication processes, only one transferring method is applied for each device. However, to construct a complex SWCNT-polymer hybrid architecture, different SWCNT components are required such as the functional units and leads, and correspondingly, related transferring technologies have to be applied depending on the structure of SWCNT, the material of substrate and other limitations. In this study, a combined 3D SWCNT architecture with vertically aligned SWCNT forest (3D) sandwiched between two layers of SWCNT micro-lines (2D) and casting method and wet-contact printing method were applied, respectively. A robust contact between the two SWCNT architectures can be found with a contact resistance as low as 3%. This research suggests that for the future flexible electronics, multiple transferring processes are inevitable and the integration between different transfer technologies will become the key issue in constructing robust flexible electronics.
This study has offered a CMOS compatible transfer method to achieve suspended SWCNT architectures over micro/nano-patterned polymeric substrate with desired controllability and efficiency. However, the limitation of wet-contact printing has yet been defined. On one hand, the lower limit in nanoscale patterned substrate is not clear. A transition from heterogeneous SLV interface to homogeneous interface might happen when the support features become really small. On the other hand, it will be extremely meaningful to challenge the upper limit where gap is too large and suspended architecture is no longer achievable. Moreover, as a direct consequence of wet process, the suspended 2D SWCNT network folds on both free edges leading to poor shape stability and thereby unstable performance of suspended SWCNT network. Therefore, to achieve general strategy for stable suspended SWCNT architectures over large scale, the method to break the current limit need to be developed such as nanoscale patterning, external force assisted transfer, surface decoration and etc.

Finally, it is important to address that the scale of SWCNT-polymer hybrid system is multifaceted. It is impossible to cover the whole area. In this study, only direction property control and method to construct suspended architectures have been addressed. But the method and principle developed in this study can be extended to a wide range of nanomaterials and polymeric substrates.
Chapter 7. Future Works

This study has investigated the fundamental mechanism of wet-contact printing method. However the limitation of wet-contact printing has yet been clarified especially in nanoscale. The tasks of future works will focus on three directions:

1) Define the lower limit of wet-contact printing method in nanoscale;
2) Stabilize the heterogeneous interface and explore the upper limit of wet-contact printing method;
3) Stabilize the shape of suspended SWCNT network.

For the first direction, it will be interesting to see if the increased surface area will initiate the transition from heterogeneous interface to homogeneous interface at certain point, since a lot more surface area will be created compare to microscale pattern. The suspended SWCNT network has been demonstrated on nano-patterned PMMA substrate with both widths of strip and trench around hundreds of nanometers. In the proposed research, the fabrication of receiving substrate will be further scaled down to sub 100 nm. Correspondingly, individual SWCNT will be required to build device in such a small scale. The difficulties will be the fabrication of nanostructure with a sharp edge and high aspect ratio, which are helpful for stabilizing the heterogeneous interface. Electron beam lithography and nanoimprint will be applied for the substrate manufacturing. The goal of this research is to define when the principle for stable heterogeneous interface will not work at nanoscale.
Figure 62. Schematic of wet-contact printing method without (left and middle) and with (right) the assistance from external field.

The second direction is to break the upper limit of wet-contact printing: how far the suspended SWCNT can bridge. The transition from heterogeneous SLV interface to homogeneous interface leads to the broken down of suspended architectures. The surface structure and surface energy of receiving substrate can strongly influence the transition. Researches reveal that it is possible to control the transition more actively by applying external force such as electrical field and magnetic field\textsuperscript{175,176}. Therefore, it is possible to stabilize the SLV interface through external force even though it is in the unstable regime where suspended SWCNT will be theoretically unavailable. In the proposed research, both electrical field and magnetic field will be applied and their interactions with SLV interface will be studied. Finally, the practical extreme of wet-contact printing method will be defined.
The third direction targets another limitation of the wet-contact printing: the folding of free-standing film at the existence of solution. As a direct consequence of wet process, the suspended 2D network folds on the free edge during the drying process since the solution can penetrate in the network of SWCNTs as discussed in section 3.4.13. The folding will influence the shape stability and thereby properties of suspended SWCNT network, because the extent of folding increases with the suspended length. For example, for 6 μm wide SWCNT micro-lines on PDMS substrate, multiple folding and twisting leads to less than 1 μm wide cross-section of SWCNT micro-lines when the trench width is over 40 μm. One method to attenuate folding effect is to increase the ratio width of original width of SWCNT micro-lines over the width of trench, i.e., for 100 μm wide SWCNT micro-lines no apparent change can be found for the same 40 μm wide trench. However, increase the size of the SWCNT network will increase the size of device and therefore is not preferred for miniaturized device. We believe the interaction between SWCNT network and solution, such as capillary force is the driving force of the folding. Therefore, to achieve general strategy for stable SWCNT over large scale, the methods to tailoring the interaction between SWCNT and solution, such as the chemical decoration of SWCNT need to be considered.

Ultimately, the comprehensive understanding of wet-contact printing method and fully control over the shape and size of suspended SWCNT architecture will be achieved.
Bibliography


Harkins, W. D. & Brown, F. The determination of surface tension (free surface energy), and the weight of falling drops: The surface tension of water and benzene by the capillary height method. *Journal of the American Chemical Society* **41**, 499-524 (1919).


Van Krevelen, D. W. & Te Nijenhuis, K. *Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions.* (Elsevier Science, 2009).


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