Development of High-rate Nano-scale Offset Printing Technology for Electric and Bio Applications

A Dissertation Presented

By

Hanchul Cho

to

The Department of Mechanical and Industrial Engineering

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy in the field of

Mechanical Engineering

Northeastern University

Boston, Massachusetts

April 2014
Dedicated to my parents, family and friends
Acknowledgement

I am very happy to acknowledge the people who helped and supported me to complete this research. First of all, I would like to thank my mentor and adviser, Prof. Ahmed Busnaina, for his guidance, encouragement and patience over last 5 years at CHN. He gave me many research opportunities and scientific support during my Ph. D studies. This work would not have evolved into such an interdisciplinary research without his efforts and insight. In addition, I appreciate my committees, Prof. Moneesh Upmanyu, Prof. Marilyn Minus and Prof. Youngmin Liu, for giving me heartfelt comments on my research. I sincerely appreciate the time Prof. Somu, my good friend and teacher, spent giving me advice and guidance, as well as talking about our life. I thank Prof. Heayeon Lee for encouraging and also treating me to many lunches and dinners. I am thankful to my colleagues in CHN who helped to make my time in graduate school an exciting experience, Asli Sirman, Cem Apaydin, Adnan Korkmaz, Dr. Cihan Yilmaz, Dr. Asanterabi Malima, Dr. Aditi Halder, Sharon Kotz, Ankita Shah, Hobin Jeong and Jukyung Lee. I am thankful to Dr. Jinyoung Lee, my biggest device customer, for getting good results from my sensors. In addition, I really thank Jungho Seo. My research life would have been bored without him. In addition I must also acknowledge Richar DeVito, David Mckee and Scott McNamara for helping and training me. The CHN budget coordinator, Matthew Botti, deserves recognition for making sure ‘shipping today’. My church community members deserve many thanks for being always with us and praying for us. They gave us unforgettable moments such as an amazing trip, dinner and sharing. Also, I really want to say ‘thank you’ to Kevin Black and Seungyeon Han for being the best friends and helping us in our US life. You will be missed and never forgotten.

My lovely wife, Eunmil Jee, deserves special recognition for supporting me. She has
prepared more 1000 lunch boxes for my Ph.D program every morning. Really thank her for being patient and loving me. I would be failed on Ph.D without her. My cuties, Preston and Ethan, make me smile 24 hours a day. I would like to thank my parents. Every day, they pray for me and my family. When we had many difficult moments, they tried to being with us and support us even though they were many miles away from us and my research. I specially would like to pay tribute to my father in heaven. I know he is the one who will be happy and be proud of me. See Dad, the time you spent loving me drives me here and now. Also, Hansoo Cho, big brother, had supported me when we settled down in Boston. I really thank Eunchong, my lovely sister, for visiting here and helping us.

**Lastly, Praise the Lord who is from everlasting to everlasting**

*For God so loved the world that he gave his one and only Son, that whoever believes in him shall not perish but have eternal life (John 3:16)*
Abstract

Printing technology with precise alignment and orientation is expected to accelerate large-scale production of nano-scale devices such as transistor, biosensors and chemical sensors. Various templates have been fabricated through bottom-up and top-down processes for the printing. Assembly and transfer techniques have been used to achieve precise and high resolution printing results. However, despite the high-rate directed assembly techniques such as electric and magnetic field assistance assembly, absence of extremely versatile and reusable template for high throughput directed assembly and transfer have hindered the progress of fabricating flexible devices using nanomaterials.

We have developed high-rate offset printing technology for achieving a high-rate production of flexible devices based on nanomaterials. In the dissertation, we have newly developed ‘damascene template,’ reusable and versatile template, for high-rate directed assembly and transfer of nanomaterials. In addition, a flexible damascene template based on a polymer substrate has been developed to apply to the roll to roll system for continuous assembly and transfer. The governing parameters for assembly and transfer were investigated to achieve the uniform assembly and high transfer yield. Our approaches demonstrate that the combination of reusable damascene template and directed assembly and transfer is significantly compatible with various nanomaterials such as polymer, silica, semiconductor nanoparticles and SWNTs by controlling the surface energy of the template, assembly and transfer parameters. This process and template will enable high-rate manufacturing of flexible devices such as a flexible transistor, display, bio and chemical sensors, energy harvesting.
# Table of Contents

Abstract ........................................................................................................................................... i

List of Figure ...................................................................................................................................... v

Chapter 1 Introduction ......................................................................................................................... 1
  Research Objectives .......................................................................................................................... 4
  Outline of Dissertation ....................................................................................................................... 5

Chapter 2 Background and Literature Review ..................................................................................... 7
  2.1 Assembly and Printing Techniques ............................................................................................... 7
    2.1.1 Convective Assembly ............................................................................................................... 7
    2.1.2 Fluidic Assembly .................................................................................................................... 10
    2.1.3 Spin Coating ........................................................................................................................ 11
    2.1.4 Inkjet and Gravure Printing .................................................................................................... 12
    2.1.5 Dielectrophoresis Assembly .................................................................................................. 13
    2.1.6 Electrophoresis Assembly ...................................................................................................... 15
  2.2 Transfer Techniques .................................................................................................................... 19
  2.3 Applications Using Nanomaterials ............................................................................................... 21

Chapter 3 Damascene Template Fabrication ......................................................................................... 24
  3.1 Rigid Damascene Template ......................................................................................................... 24
    3.1.1 Introduction ........................................................................................................................... 24
    3.1.2 Patterning Process ............................................................................................................... 27
List of Figure

Figure 2.1 Schematic of the coating apparatus. The inset above illustrates the process of convective assembly driven by the evaporation flux, J_E. 12 ................................................................. 8

Figure 2.2 (a) Convective assembly mechanism on the patterned surface. (b) SEM images of 500 nm PS particles assembly on the patterned PDMS template. 2 ........................................... 8

Figure 2.3 Cross-sectional schematic illustrating the slip-stick mechanism responsible for self-assembly of the superlattice of single-walled carbon nanotubes (CNT) and SEM image of aligned CNT. 15 ................................................................................................................................. 9

Figure 2.4 A typical examples of assembly using fluidic assembly. (a) SEM images of assembled Au particles, (b) SEM image of assembled SWNTs on the trenches. 5 7 ............... 11

Figure 2.5 (a) Photograph of a 3D ordered nanocomposite film on a 4-inch silicon wafer and SEM image of a spin coated colloidal crystal-polymer nanocomposite film. (b) A typical process of spin coating for SWNT deposition and AFM image of spin coated SWNTs network. 23 24 ................................................................................................................................. 12

Figure 2.6 (a) Schematic of inkjet printing system, AFM image of printed SWNTs and micrograph of device. 28 (b) Illustration of gravure printing process for fabricating flexible TFT. 35 ........................................................................................................................................... 13

Figure 2.7 (a) Assembly of highly dense aligned SWNTs using DEP. 37 (b) Schematic of the high-density array of single-tube devices and the electrode array showing five adjacent devices, with each electrode pair bridged by one carbon nanotube, visible as fine white lines within the dark central areas. 38 ......................................................................................................................... 14

Figure 2.8 Electrical double layer. 46 ....................................................................................................................... 17

Figure 2.9 Previous EPD assembly results (a) silica particles, 51 (b) PS particles, 52 (c)
MWNTs, (d) SWNTs. 54  .................................................................................................................. 18

Figure 2.10 Most common transfer method; (a) SWNTs transfer using sacrificial layer (SiO$_2$), 65 (b) PDMS stamps transfer, 66 (c) Thermal tape transfer. 67 ................................. 20

Figure 2.11 (a) Illustration of a typical transfer printing technique. (b) Transferred vertical CNT on PC film using transfer printing. 68 ............................................................................. 21

Figure 3.1 The schematic of a 3-D wire template used for electrophoretic assembly. In these templates nanowire electrodes are connected to a micron scale electrodes, which are in turn connected, to a large metal pad through which the potential is applied. (b) The SEM micrographs of a typical nanoparticle assembly result obtained for configuration shown in (a). (c) The schematic of a conventional template used for electrophoretic assembly. In these templates nanowire electrodes are connected to a micron scale electrodes, which are in turn connected, to a large metal pad through which the potential is applied. .............. 25

Figure 3.2 (a) Jewelry decorated damascene process, (b) Sword decorated damascene process, (c) Copper multi-layer interconnector using damascene process. 98 ................. 26

Figure 3.3 Schematics of a rigid damascene template fabrication using CMP and microfabrications. Inset is SEM image of preliminary results of damascene template using tungsten as conductive material. Level of SiO$_2$ and tungsten is same after CMP process. .... 27

Figure 3.4 (a) ES100 film thickness change as function of spinning speed, (b) Line dose amount to make features on different thickness of ES100. ................................................................. 30

Figure 3.5 SEM images of pattern on ES100 made by EBL. (a) 3 μm, (b) 1 μm, (c) 500 nm, (d) 200 nm and (e) 100 nm feature size ................................................................................................... 30

Figure 3.6 EBL results on ES100. Very complex shape can be patterned on ES 100. .......... 31
Figure 3.7 Fabrication procedure of 3-D conductive structure using NIL .......................... 32
Figure 3.8 Nano-scale pattern array on 3" wafer obtained by NIL. SEM images show 300 nm square pattern arrays. Zoom-in image (top) and general view (bottom).................. 32
Figure 3.9 Schematic of procedure of Si mold fabrication........................................ 33
Figure 3.10 SEM image of Cr mask. (a) Before the piranha and megasonic cleaning with SC-1. The Cr residues are still remained on Si surface and attached to Cr mask. (b) After the piranha and megasonic cleaning with SC-1. There is no Cr residue as well as other contaminations ................................................................. 34
Figure 3.11 SEM image of cross section of anisotropic etching on Si substrate. Etching rate was 450 nm/min. .................................................................................................................. 35
Figure 3.12 SEM image of square mold (300 nm*300 nm)........................................ 35
Figure 3.13 (a) schematics of CMP system. (b) Map of thickness measurement for determining CMP performance ................................................................. 37
Figure 3.14 Illustration of SiO₂ removal mechanism in CMP process...................... 37
Figure 3.15 MRR as function of rotation velocity of platen and head at 2.5 psi; (a) 60 rpm/60 rpm, (b) 90 rpm/90 rpm (c) 120 rpm/120 rpm........................................ 40
Figure 3.16 MRR as function of pressure at 90 rpm of head and platen velocity; (a) 2.5 psi, (b) 3.5 psi (c) 4.5 psi.......................................................................................... 41
Figure 3.17 (a) Schematic of definition of dishing after CMP process. (b) The profile of damascene template and change of dishing amount as increase of the CMP time............. 42
Figure 3.18 Damascene template using tungsten as conductive material; (a) 4” wafer damascene template using tungsten, (b) Artificial colored SEM image of cross section of damascene template. The surface level of tungsten (gray) and SiO₂ (green) is same after
Figure 3.19 Defect generation as increase of pH of the solution. From pH 10.5 pinholes were generated on tungsten surface due to the ammonium hydroxide used as pH adjustor to increase of zeta potential of nanomaterials in the suspension.

Figure 3.20 SEM of 50 nm PSL particles and SWNTs assembly on the damascene template using tungsten; (a) SEM images of 50 nm PSL particles assembly, (b) SEM images of SWNTs assembly. PSL particles and SWNTs were assembled on tungsten and even on SiO$_2$ surface.

Figure 3.21 SEM images of PSL particles (50 nm) and SWNTs assembly on damascene template before the functionalization on the template. (a) PSL particles (50 nm) and (b) SWNTs were assembled on the gold surface and even on the SiO$_2$ surface.

Figure 3.22 Contact angle measurement on SiO$_2$ and gold surface (a) Contact angle of SiO$_2$ after SAM coating, (b) Contact angle of gold surface after SAM coating, (c) Contact angle of SiO$_2$ surface after second piranha process. The piranha process does not affect the contact angle and disturb the SAM layer. (d) Contact angle of gold surface after second piranha process. Non-covalently attached SAM layer was removed by the second piranha.

Figure 3.23 (a) SEM of PSL particle assembly on the damascene template without the application of the post treatment process to remove the non-covalently bonded SAM on the gold surface. Only few particles were assembled on the gold surface. (b) SEM image of PSL particle assembly on the template treated with the post treatment process. Full assembly results were achieved.

Figure 3.24 (a) SWNTs were fully assembled on gold surface not on the SiO$_2$ due to the low surface energy by SAM. (b) Shown is the plot of the contact angle measurement of the OTS
SAM coated SiO$_2$ surface as a function of the number of assembly and transfer cycles. 50

Figure 3.25 Schematic of procedure of flexible damascene template fabrication using PEN as substrate without CMP process. 52

Figure 3.26 3" wafer scale flexible damascene template. Insets are microscopy images of gold patterns and SiO$_2$ surface. 53

Figure 4.1 Schematic illustration of an offset printing approach to fabricate flexible devices. The insulating (SiO$_2$) surface of the damascene template is selectively coated with a hydrophobic SAM (OTS). Using electrophoresis nanomaterials are assembled on the conductive patterns of the damascene template (“inking”), which are then transferred to a recipient substrate (“printing”). After the transfer, the template is ready for the next assembly and transfer cycle. 55

Figure 4.2 Configuration of the assembly system. (a) schematic of the system, (b) photography of our system used in the experiments. 57

Figure 4.3 Cross section view of physical geometry and specific dimension used in electric field simulation. (a) 3-D wire template, (b) damascene template. 58

Figure 4.4 Electric field contours on 3-D wire template during the electrophoresis assembly at 2.5 V. (a) Cross sectional view of the electric field, (b) Zoom–in view of corner, (c) Top view of the electric field. The electric field strength on the edge of wire is higher than that on the center. The side wall of the wire has significant electric field strength to be able to attract the nanomaterials. 59

Figure 4.5 SEM images of PSL NPs assembly on 3-D wire template composited with micro/nano wires. (a) NPs were assembled on the side wall of micro and nano wires. (b)
Figure 4.6 Electric field profiles on the 3-D wire template during the electrophoresis assembly at 2.5 V. Electric field profile was obtained at 25 nm away from the top surface of conductive wires. Electric field difference between the edge and center is 244 kV/m, which is 50% of the maximum electric field strength on the wire template.

Figure 4.7 Modeling results indicating the electric field strength near the insulator and conductive pattern during the electrophoresis assembly. (a) Top view of electric field contour, (b) cross section view of electric field contour. The electric field near the insulator and the conductive pattern have the same order of magnitude.

Figure 4.8 Electric field contours and profiles at 25 nm away from the top surface of the conductive pattern. (a) 0 dishing, (b) 25 nm dishing and (c) 50 nm dishing.

Figure 4.9 (a) Electric field of damascene template as a function of dishing amount. (b) Normalized electric field non-uniformity as a function of dishing amount.

Figure 4.10 (a) Shows SEM micrograph for assembly at the edges of the pattern using 2 V and 1 mm/min withdrawal speed (the gold nanowire grains are also shown in the center of gold pattern). 100 nm silica particles assembled only on the edge of gold pattern. (b) Contour of the electric field strength at 25 nm away from the surface of the conductive pattern during the electrophoresis assembly at 2.5V. The electric strength on the edge of the conductive pattern is stronger than that on the center. (c) SEM micrograph of a typical high-density 100 nm silica nanoparticle assembly result for assembly parameters voltage (2.5 V) and withdrawal speed (1 mm/min).

Figure 4.11 The applied voltage effect on the assembly of silver NPs at the fixed pulling speed (10 mm/min). (a) 2.25, (b) 2.5, (c) 3, (d) 3.5 V. As increase of the applied voltage,
denser assembly results were obtained.

Figure 4.12 Full assembly of the silver NPs. The agglomerated silver NPs were concentrated on the edge of the conductive pattern at 3.5 V and 10 mm/min pulling speed.

Figure 4.13 SEM images of assembly results at different concentration of NPs (30 nm silica particles). (a) 0.01, (b) 0.2, (c) 0.1 and (d) 1 wt%.

Figure 4.14 Fluorescence microscopy images of assembly results at different concentration of NPs. (a) 1, (b) 0.2, (c) 0.1 and (d) 0.01 wt%.

Figure 4.15 Shows top viewed SEM micrographs of the damascene template after SWNT assembly for various applied potentials. (a) 1.5 V (b) 2 V (c) 2.5 V and (d) 3 V. The rest of the assembly parameters are kept constant. As can be seen from the images, assembly efficiency on the metal electrode increases as a function of the applied electric field and beyond a critical value the SWNTs begins to assemble everywhere including the insulator.

Figure 4.16 Shown are top viewed SEM micrographs of the damascene template after SWNT assembly for various withdrawal speeds. (a) 3 mm/min, (b) 5 mm/min, (c) 10 mm/min and (d) 20 mm/min. The rest of the assembly parameters are kept constant. As the images, assembly efficiency on the metal electrode decreases with increasing withdrawal speed, which indicates the effect of removal moment acting on the SWNTs during withdrawal.

Figure 4.17 (a-d) AFM image of before and after assembly at different withdrawal speed (top is before and bottom is after. (b) Thickness changes as function of withdrawal speed.

Figure 4.18 (a) SWNTs alignment as a function of withdrawal speed at 3 mm/min, 5 mm/min, 10 mm/min and 15 mm/min. As increase of withdrawal speed, the SWNTs networks are more disordered. (b) AFM image of different withdrawal speed.
Figure 4.19 Plots of angular alignment of individual nanotubes versus length of the nanotube for trenches of three different widths (W=200 nm, 100 nm, 70 nm). Inset: schematic showing how the angular alignment θ is defined (0° is perfect alignment in a trench). By reducing the trench width to 70 nm, the angular variation was reduced from ±75° to less than ±30°.

Figure 4.20 (a) schematic diagram of SWNTs assembly on hydrophilic surface between two hydrophobic surfaces. (b) SEM image of SWNTs (600 nm ~1 µm length) assembly into the trench of 3 µm width using fluidic assembly. (c) SEM image of SWNTs into the trench of 500 nm width. (d) High magnification image of figure (c).

Figure 4.21 (a) The schematics of proposed hypothesis of SWNTs assembly and alignment during the electrophoresis assembly (b) SWCNT-assembly and orientation in response to an applied dc electric field. The left to right sequence corresponds to an ON-OFF-ON cycle of the field with magnified sections at the bottom.

Figure 4.22 (a) SEM image of assembled SWNTs on the gold pattern of 10 µm width with the high alignment. (b) High magnification image of figure (a). SWNTs are highly aligned even though the ratio of the width of the pattern to the length of nanotubes is larger than 10.

Figure 4.23 Left: synthesis of water soluble pentacene 4; right: a solution of 4 in water.

Figure 4.24 Optical images of electrophoretic assembly of water soluble pentacene 4 onto damascene template at various conditions (a-d). The AFM image of water soluble pentacene 4 NPs (d).

Figure 4.25 Versatility of assembly on damascene template using electrophoresis assembly; polymer NPs (PSL, 50 nm), silica NPs (100 nm), SWNTs on a large scale, cellulose, MWNTs
on a large scale and SWNT with gold NPs (5 nm) ................................................................. 80

Figure 4.26 Schematic of nanoimprint tool chamber. 116 ................................................................. 82

Figure 4.27 Procedure of deposition of metal electrode to measure the electrical property of transferred nanomaterials ...................................................................................................... 83

Figure 4.28 Optical images of the setup being used to measure the electrical properties at the desired bending radius .............................................................................................................. 83

Figure 4.29 Shown images are top viewed SEM micrographs of the damascene template after transfer of SWNTs for various temperatures. (a) 135 °C, b) 150 °C and (c) 160 °C. The rest of the transfer process parameters are kept constant. As can be seen from the images transfer efficiency (absence of SWNTs on the metal electrode after transfer) increases as increasing temperature and ~100% transfer is achieved at process temperatures higher than Tg (155 °C) of the flexible substrate (PEN) on which it is transferred to ........................................ 85

Figure 4.30 (a) Shown is SEM micrograph of the assembled SWNTs on the template before the transfer. (b) The damascene template after the transfer. (c) Transferred SWNTs on recipient substrate ......................................................................................................................... 86

Figure 4.31 MWNTs assembly and transfer result using the optimized transfer condition. (a) MWNTs assembly on the damascene template. Dimension of gold patterns has 10 µm width and 1 mm length. (b) The microscopy image of the damascene template after transfer. The gold patterns are clear, which means that MWNTs are completely transfer onto recipient substrate. (c) The microscopy image of recipient substrate (PEN) after transfer. The black lines are transferred MWNTs ............................................................................................................................................. 87

Figure 4.32 The assembly and transfer result of 30 nm silica particles. (a) SEM image of 30 nm silica particles assembled on the damascene template (3 µm width and 100 µm length)
with high density. (b) SEM image of transferred silica particles on PEN substrate using the optimized conditions. The assembled silica particles were completely transferred onto PEN substrate without an empty area.

Figure 4.33 Optical images of patterned pentacene 4 onto damascene template (a) and onto flexible PET substrates (b), before (in case of a) and after (in case of b) transferring.

Figure 4.34 (a) I-V characteristic curves of transferred SWNTs for various channel length and fixed channel width (2.4 µm). (b) Change in resistance of SWNTs channel (2.4 µm width and 30 µm length) as a function of bending radius of PEN substrate.

Figure 4.35 (a) I-V characteristic curves for 10 devices with a fixed channel width (2.4 µm) and length (60 µm). (b) Resistances of 10 devices.

Figure 4.36 (a) Transferred silver NPs with two metal pads on PEN substrate. The distance of two metal pads is 30 µm. (b) AFM image of transferred silver NPs whose height is around 200 nm.

Figure 4.37 I-V characteristic curves of transferred silver particles for (a) 3 µm channel length with 3 µm channel width (b) 24 µm channel length with 3 µm channel width.

Figure 4.38 The printing procedure of gold electro pads onto the transferred nanomaterials on the recipient substrate. The metal pads printing method make the material selection as a recipient substrate to be free by excluding the lift off process.

Figure 4.39 (a) SiO₂ template with gold pads before the transfer, (b) After transfer, (c) PEN substrate with printed gold pads, (d) Microscopy image of printed MWNTs and gold pads.

Figure 5.1 Schematic of glucose detection mechanism.

Figure 5.2 (a) Glucose sensor based on SWNTs assembled by layer by layer assembly
method, (b) Covalently bonded GOD on SWNTs and detection of glucose. 63

Figure 5.3 Schematic of lactate detection mechanism. ................................................................. 97

Figure 5.4 Schematic of lactate detection mechanism. ................................................................. 97

Figure 5.5 (a) Photography of flexible biosensor based on PEN film. The sensor was fabricated through the offset printing process and the post processes to form the electrode metal pads. (b) Microscopy image of flexible biosensors. Two electrodes sit on top of SWNTs with 60 µm distance considering the area where the enzymes are reacted with biomaterial. (c) Illustration of functionalization with the linker and GOD, LOD and URE. 99

Figure 5.6 The resistance change of SWNTs before and after functionalization with the linker and enzyme (GOD). (a) The resistance change of metallic and semiconducting mixed SWNTs. (b) The resistance change of 90% semiconducting SWNTs before and after functionalization. In both case, the resistances gradually increase by adding the linker and enzymes................................................................. 101

Figure 5.7 TEM images of SWNTs (a) before and (b) after enzyme (GOD) immobilization. The clusters of enzyme were clearly shown in (b). ................................................................. 101

Figure 5.8 The resistance and current change of the metallic/semiconducting mixed SWNTs in (a) and 90% semiconducting SWNTs in (b). 4, 8, 12, 16 and 20 mM glucose were added on the both sensor every 60 sec ................................................................. 103

Figure 5.9 Glucose detection results on the different initial resistance. (a) is plot of glucose concentration and the corresponding current response. (b) Real time glucose detection from 4 mM to 20 mM. High responsiveness was achieved at 0.6 MΩ and 1.2 MΩ, whereas significant responsiveness cannot be obtained at 9.7 MΩ ................................................................. 104

Figure 5.10 An amperometric response of SWNTs upon successive additions of glucose
every 60 sec from 4 mM to 20 mM in the buffer. (a) A typical current change with the different concentration of glucose. (b) Real time of D-glucose detection 10 times. The response of current is linear to the concentration of glucose. Real time detection graph exhibits very clear response to the glucose without noise signal. From 1 to 10 times, the response plot is impressively similar. 

Figure 5.11 The long-term stability of the glucose sensor. (a) A current-time response of SWNTs glucose sensor every 24 hr for 14 consecutive days. (b) Real time detection curve.

Figure 5.12 Sensitivity of the developed enzyme-modified semiconductor SWNTs biosensor. D-glucose detection with various concentrations (0, 100, 100.1, 100.2, 100.3, 100.4, 100.5, 101, 102, 103, 104, 105, 110, 120, 130, 140, and 150 mg/dl).

Figure 5.13 Current-time response of SWNTs upon successive additions of glucose every 60 sec from 4 mM to 20 mM in the sweat. (a) A typical current change with the different concentration of glucose in sweat. (b) Real time of D-glucose detection 10 times. The response of current is linear to the concentration of glucose. Real time detection graph exhibits very clear response to the glucose without noise signal.

Figure 5.14 An amperometric response of SWNTs upon successive additions of lactate every 60 sec from 1 g/L to 5 g/L in the buffer. (a) A typical current change with the different concentration of lactate. (b) Real time of lactate detection 10 times. The response of current is linear to the concentration of lactate. Real time detection graph exhibits very clear response to lactate without noise signal. From 1 to 9 times, the response plot is impressively similar.

Figure 5.15 The long-term stability of the lactate sensor. (a) A current-time response of
Figure 5.16 Sensitivity of the developed lactate biosensor. The highest resolution is 0.001 mM which is high enough resolution to detect the lactate in the blood.

Figure 5.17 Current-time response of SWNTs upon successive additions of lactate every 60 sec from 10 mM to 50 mM in the sweat. (a) A typical current change with the different concentration of lactate in the sweat. (b) Real time of lactate detection 10 times. The response of current is linear to the concentration of lactate. Real time detection graph exhibits very clear response to the lactate without noise signal.

Figure 5.18 An amperometric response of SWNTs upon successive additions of urea every 60 sec from 10 mg/dL to 50 mg/dL in the buffer. (a) A typical current change with the different concentration of urea in the buffer. (b) Real time of urea detection 9 times. The response of current is linear to the concentration of urea. Real time detection graph exhibits very clear response to urea without noise signal. From 1 to 9 times, the response plot is impressively similar.

Figure 5.19 The long-term stability of the urea sensor. (a) A current-time response of SWNTs urea sensor every 24hr for 14 consecutive days. (b) Real time detection curve.

Figure 5.20 Sensitivity of the developed urea biosensor. The highest resolution is 0.001 mM which is high enough resolution to detect the urea in the blood.

Figure 5.21 Current-time response of SWNTs upon successive additions of lactate every 60 sec from 0.2 M to 1 M in the sweat. (a) A typical current change with the different concentration of urea in the sweat. (b) Real time of urea detection 10 times. The response of current is linear to the concentration of urea. Real time detection graph exhibits very clear response to the urea without noise signal.
Figure 5.22 The cross effect of glucose, lactate and urea. (a) the cross effect of lactate and urea on the glucose detection, (b) the cross effect of glucose and urea on the lactate detection, (c) the cross effect of glucose and lactate on the urea detection. ...................... 117

Figure 5.23 Schematic of Oxytetracycline detection mechanism using the aptamer on SWNTs based sensor. ................................................................. 118

Figure 5.24 Resistance change as increase of OTC concentration. ........................................... 119
Chapter 1 Introduction

Nanotechnology based on silicon and conventional top-down approaches such as etching and lithography has been faced with its own limits such as feature size and cost effect since the patterning process, which is a basic process for the conventional transistor. Semiconductor industries are also trying to scale wafer size up to 450 mm to reduce the price of products. However, the development of semiconductor equipment, consumables and facility for scaling wafer size up and shrinking features needs huge investment and time. Therefore, many researchers have been looking for an alternative technology to overcome the limit of features size and cost for manufacturing devices. Bottom-up approach is regarded as an alternative way to replace the traditional top-down method due to its feature size of molecular level and relatively easy accessibility.\(^1\) However, although considerable investment and progress for bottom-up have been made in nanotechnology over the last decade, but integration and translation of these innovative technologies into products have been considerably slower. There are now processes that are nanomaterial based and non-vacuum-based for the production of devices and other products. Template-guided assembly has been used to assemble nanomaterials to achieve desired nano-scale architectures.\(^2\) \(^3\) \(^4\) Fluidic assembly processes where capillary force is the dominant assembly mechanism is amenable to a variety of nanomaterials.\(^5\) \(^6\) \(^7\) The inking process using meniscus and evaporation enables precision assembly with single particle resolution using nanoparticles (NPs).\(^2\) Although these assembly processes have shown directed assembly with high resolution into micro and nano-scale trench, there are many shortcomings such as scalability, adaptability and cost (due to very low assembly speed). If electronic printing is to compete with current silicon based nano-scale electronics, it has to
print nano-scale patterns at orders of magnitudes faster than the method mentioned above and at a small fraction such as one hundredth of today's cost of manufacturing such electronic devices. If this can be accomplished, it could make nanomanufacturing accessible to millions of new innovators and entrepreneurs and unleash a wave of creativity in the same way as the advent of the personal computer did for computing.

In this dissertation, we have newly developed reusable templates (rigid and flexible) having damascene structures to enable nano-scale offset printing utilizing directed assembly. A concept that constitutes the first step along this path is presented; a scalable multi-scale offset printing that enables the printing of nano, micro or macro-scale structures (in minutes for small or large areas) at room temperature and pressure. The process starts with applying the “ink” which is made of nanomaterials (NPs, carbon nanotubes or polymers) that are attracted to the newly developed template using directed assembly. The assembled nanomaterials are then transferred intactly to another substrate (“printing”). After transfer process, the template is ready to be reused in the next assembly process right away.

Electric field simulation during the electrophoresis assembly allows us to understand and predict assembly results and geometric effect on the uniformity of assembly. The flexible damascene template based on a polymer substrate can be utilized for continuous process as roll to roll system. Based on the knowledge of assembly and transfer, closed to 100% directed assembly and transfer yield for various nanomaterials such as single wall carbon nanotubes (SWNTs) and NPs was achieved. Especially, assembly of highly organized and dense SWNTs was achieved by controlling the assembly parameters such as applied voltage and withdrawal speed. It is well known that electrophoresis assembly is not
suitable for large area assembly due to concentrating of the electric field. However, we show large scale assembly and transfer in a few minutes, in the study. Our technique overcome this shortcoming by controlling the parameters combined the developed template. Also, various nanomaterials can be assembled such as SWNTs, MWNTs, polymer NPs, silica nanoparticles and cellulose. Such versatile and reusable templates for high throughput offset multi-scale printing are essential for high-rate nanomanufacturing. The flexible multi-biosensors fabricated through the offset printing technology enable to detect glucose, lactate and urea with high resolution and stable and linear response was fabricated through the offset printing process utilizing the damascene template. This technology would enable fast economical multi-scale printing with the desired nano-scale precision on hard or flexible substrates using templates designed for high-yield and high-rate.
Research Objectives

The overall research goal is the development of reusable template and multi-scale offset printing technology, which enable to fabricate the flexible devices such as electronics and biosensor with high resolution, high productivity and minimal device-to-device variation. For the overall research goal, specific objectives are as follows:

- Developing the fabrication process of rigid and flexible reusable template using micro-fabrication techniques and chemical mechanical polishing.
- Selective control of the surface energy on the conductive and insulating surface using self-assembled monolayer to lead the nanomaterials to be assembled on the desired location.
- Performing the numerical analysis to understanding the geometry effect of the template on the uniformity of electric field and assembly during the electrophoresis assembly.
- Investigating the effect of governing parameters on the assembly efficiency: electrophoretic assembly of nanomaterials.
- Optimizing the transfer conditions to increase the transfer yield and fabricating 2-D nanostructures on a flexible substrate using the printing process: transfer process.
- Performing electrical characterization of printed nanomaterials on flexible devices.
- Fabricating the highly sensitive flexible biosensors for detecting glucose, urea and lactate.
Outline of Dissertation

The research objectives are described in the introduction. In Chapter 2, we will review the previous assembly and transfer techniques to address the barriers we are now being faced with and seek the way overcome these barriers. The driven forces for the electrophoresis assembly of nanomaterials will be briefly reviewed to understand easily and approach the assembly mechanism of this study. In addition, a variety of applications using nanomaterials will be introduced.

Chapter 3 will provide the motivation of developing reusable template, damascene template, and describe the advantage of damascene template for the electrophoresis assembly and transfer process. A detailed procedure of rigid and flexible template fabrication will be explained from the material selection to the fabrication processes including patterning, deposition, chemical mechanical polishing and self-assembled monolayer.

Chapter 4 will show the assembly and transfer results of nanomaterials through the developed offset printing process. Electric field simulation will explain the reason of needs of self-assembled monolayer and template geometry effect on the assembly efficiency. Also, the assembly and transfer parameters will be investigated to increase yield of a process and control the properties of assembled nanomaterial. The electrical property of transferred nanomaterials will be characterized.

Chapter 5 will show the results of the flexible biosensor fabricated by offset printing
process. Repeatability, long-term stability, scalability and selectivity will be evaluated on the detection of glucose, lactate and urea in buffer and sweat.

Chapter 6 will summarize the highlights and conclude this study. Finally, we will suggest research direction for the future.
Chapter 2 Background and Literature Review

2.1 Assembly and Printing Techniques

Assembly of nanomaterials has been used to make functional and novel nanostructures enabling superior device performance and miniaturization in electronics, optics, energy and biotechnology applications. However, barriers such as scalability, speed, yield, reliability, adaptability, low cost and integration of different components need to be addressed to make the assembly promise a reality. Although a few of these barriers have been addressed by some developed assembly techniques, we still need a commitment for overcoming these barriers to compete with existing top-down processes.

2.1.1 Convective Assembly

Convective assembly (coating) was introduced and explored by Nagayama and his coworkers in 1993. This process has been modified and improved to increase the assembly speed, yield and repeatability. Convective assembly allows the spherical micro/NPs be assembled continuously on the surface. Through this process, monolayer of well-ordered close packed micro/nano particles can be assembled over a large area. The basic concept and mechanism is very similar to the conventional dip-coating process. Convective assembly is also called as ‘evaporation-induced self-assembly’ or ‘evaporation-driven self-assembly’ due to the driven force to make NPs to be assembled. During the evaporation of the solution, the capillary force was induced and drive the NPs to be assembled itself on the surface. Attractive capillary force between the particles leads to well-ordered particle arrays. A typical system and process is illustrated in figure 2.1. When a deposition plate moves on direction keeping the angle and constant speed, the entrapped particles are
deposited from the meniscus to the substrate.

Figure 2.1 Schematic of the coating apparatus. The inset above illustrates the process of convective assembly driven by the evaporation flux, $J_E$.  

A convective assembly exhibits the capability to assemble particles on the patterned surface as well as a flat surface. Wolf et al. modified the convective assembly system and showed the single-particle resolution assembly on the patterned surface. Also, the assembled particles are transferred onto a recipient substrate by followed transfer process. Figure 2.2 shows a schematic of the assembly process in (a) and the assembled particles on the patterned surface in (b).

Figure 2.2 (a) Convective assembly mechanism on the patterned surface. (b) SEM images of
500 nm PS particles assembly on the patterned PDMS template.\(^2\)

The IBM group (Avouris et al.) demonstrates that the aligned nanotubes can be obtained through the evaporation assembly method and shows the electronic application with remarkable performance.\(^{15}\) Figure 2.3 is the mechanism of evaporation assembly for carbon nanotubes (CNT) and SEM images of aligned CNT on the substrate. In addition, various types of materials besides the particle and CNT were assembled by convective assembly such as ferrin protein, inverse opal structure.\(^{16}^{17}\) The assembled particles and its layer were applied in a field of conductive and antireflective coating, surface-enhancing Raman scattering substrate and lithographic mask.\(^{17}^{18}^{19}^{20}\) Although highly ordered particles assembly, submicron resolution with good performances and versatility on the materials have been achieved, weak adhesion force between the substrate and the nanomaterials, scalability of the assembly process and productivity to meet the industrial requirements can be potential problems.

![Figure 2.3](image)

Figure 2.3 Cross-sectional schematic illustrating the slip-stick mechanism responsible for self-assembly of the superlattice of single-walled carbon nanotubes (CNT) and SEM image of aligned CNT.\(^{15}\)
2.1.2 Fluidic Assembly

Template-guided fluidic assembly using has been used to assemble nanomaterials to achieve desired nano-scale architectures. Fluidic assembly processes where capillary force is the dominant assembly mechanism are amenable for variety of nanomaterials shown in figure 2.4. Template guided fluidic assembly is very similarly to the convective assembly on the patterned template. The mechanism and driven force to deposit the nanomaterials on the desired locations is exactly same. However, unlike that convective assembly process needs two plates to generate the meniscus and capillary force to assemble the nanomaterials, fluidic assembly can be performed by being pulled a patterned template out from the suspension of nanomaterials. The assembly efficiency of template guided fluidic assembly is strongly dependent on the surface energy of the template. Jung et al. investigates the effect of surface energy on the assembly results of SWNTs using dip-coating assembly. They used the oxygen plasma to create the hydroxylic group to increase the surface energy of SiO$_2$ resulting in the high efficiency of assembly. Despite the highly precise and highly dense assembly results, a typical withdrawal speed of dip coater to pull out the template with constant speed and generated the consistent meniscus and capillary force is 0.05 mm/min ~ 0.2 mm/min, which means that six hours should be needed to assemble the nanomaterials on 3” wafer.
2.1.3 Spin Coating

Spin coating process has been widely used in the academic and industrial fields due to the simplicity of the method. It is a very straightforward and simple technique to deposit the nanomaterials on the large scale template in a few minutes. The suspension of nanomaterials is dropped onto a rotating spinner. The strong stream from the top to the surface of template push down the suspension and also the nanomaterials are spread on the surface with uniform film thickness by centrifugal force. The solvent or water of suspension is evaporated and generates the capillary force during the spinning process. The film thickness and density are primary determined by the rotating speed, the viscosity of the suspension and evaporation rate. Figure 2.5 is the example of particles and SWNTs coating results. Through the spin coating process, the optical properties can be enhanced in use of particles and field-effect transistor (FET) and sensors can be fabricated on the rigid and flexible substrate using SWNTs. The drawback of this method is non-uniform assembly results according to the position of a wafer. Spin coating method
consumes relatively large amount of nanomaterials comparing to other solution processes such as dip coating and convective assembly. Thus, in case of spin coated SWNTs, the orientation of SWNTs is disorder and make random network resulting in the poor electrical properties and device to device variation.

Figure 2.5 (a) Photograph of a 3D ordered nanocomposite film on a 4-inch silicon wafer and SEM image of a spin coated colloidal crystal-polymer nanocomposite film. (b) A typical process of spin coating for SWNT deposition and AFM image of spin coated SWNTs network. 23 24

2.1.4 Inkjet and Gravure Printing

Printing is much closer to our life and familiar process to transfer information and data onto paper. The biggest advantage of printing technology is a process of material-conserving to deposit nanomaterials on either rigid substrate or flexible substrate, which directly results in the cost-effect on the final products. Inkjet printing for fabricating electronic devices borrows the concept from the paper printing method. Organic or inorganic electron materials are used in the field of printed devices instead of carbon black used as ink for paper printing. This technique is non-contact, direct write using a computer controlled translation system, maskless approach. Other advantages of this technique are cost-effective, minimal material consumption, scalable and productive process. Figure 2.6
(a) show a schematic of a typical inkjet printing system and results of printed SWNTs. Many applications such as transistor, light-emitting devices, solar cell and memory/magnetic storage using inkjet printing technology have been reported. Another printing approach is gravure printing techniques to be adopted large scale and highly productive process. Figure 2.6 (b) illustrates a gravure printing process and its system. Although these two approaches, inkjet printing and gravure printing technique, are useful for mass production, the device performance should be improved to meet the industrial requirements due to the limit of resolution.

Figure 2.6 (a) Schematic of inkjet printing system, AFM image of printed SWNTs and micrograph of device. (b) Illustration of gravure printing process for fabricating flexible TFT.

### 2.1.5 Dielectrophoresis Assembly

The assembly using external forces such as an electric force has been also explored in the area of nanomaterial assembly. Electric field assisted assembly can be categorized into two main techniques, dielectrophoresis (DEP) and electrophoresis by the current source. Here, we really focused on the DEP assembly and its capability, but electrophoresis assembly using DC will be explained next section (2.1.6)
DEP is generated when a polarizable particle is suspended in a non-uniform electric field. A polarized particles or tubes form a structure along the electric field line. High density and scalability to the processes to fabricate a large number of devices on a single chip are a major limitation of DEP. However, recent researches have demonstrated nanowires assembly over a large distance (>1 cm) using high aspect ratio nanowire. Also, Shashank shekhar et al. demonstrated ultrahigh density alignment of CNT assembly using DEP shown in figure 2.7 (a). Aravind Vijayaraghavan et al. demonstrates that precise assembly of SWNTs over several million devices per square centimeter using DEP coupled with a novel aspect of SWNTs shown in figure 2.7 (b). In addition, DEP shows capability to assemble the particles and form the wire between two electrodes. Cihan et al. built three-dimensional gold pillars by assembling the gold NPs using dielectrophoresis combined with electrophoresis.

Figure 2.7 (a) Assembly of highly dense aligned SWNTs using DEP. (b) Schematic of the high-density array of single-tube devices and the electrode array showing five adjacent devices, with each electrode pair bridged by one carbon nanotube, visible as fine white lines within the dark central areas.
2.1.6 Electrophoresis Assembly

Electrophoresis has been widely used and applied in the field of biochemistry and nanotechnology since electrophoresis was observed by Ferdinand Frederic Reuss in 1807. However, first practical use of electrophoresis was to deposit thoria particles on a platinum cathode as an emitter in 1993. Electrophoretic Deposition (EPD) based on electrophoresis makes charged nanomaterials in the suspension to be migrated toward oppositely charged electrodes along the uniform electric field and deposit the nanomaterials on it. In electrophoresis, electrostatic force acted on charged spherical particles is given by:

\[ F_e = q \left( \frac{Q \hat{r}}{4\pi\varepsilon_o \rho \lambda^2} \right) = q \cdot E \]  

(2.1)

\( F_e \) is the electrostatic force, \( q \) is the effective charge on particle and \( E \) is strength of an electric field between two parallel plates.

Electric double layer is the layer that appears on the surface of a particle when the particle is dispersed in liquid. The layer consists of the ions adsorbed on the surface of a particle and a layer of the countercharged dispersion medium. The electric double layer is electrically neutral. The maximum electrical potential is on the surface of particles and it quickly goes down as increase of distance from the surface of a particle shown in figure 2.8. Zeta potential is the electric potential at the slipping plane, which is critical factor on the particles interaction in electrophoresis assembly. The total charge on the surface of spherical is given by

\[ q = 4\pi\varepsilon_r\varepsilon_o(1 + \kappa \lambda)\zeta \]  

(2.2)

, where \( R \) is the radius of a colloidal particle, \( \varepsilon_r \) is permittivity of suspension, \( \varepsilon_o \) is permittivity of free space, \( \kappa \) is inverse debye length, and \( \zeta \) is the zeta potential on the
particles. The major driving force for EPD is the charge of particles and the electrophoretic mobility under the same applied DC voltage and environment. The strength of charge on the particle is strongly dependent on the value of zeta potential according to the equation 2.2. The electrophoretic mobility is given by

$$\mu = \frac{\varepsilon \zeta}{6\pi \eta}$$  

(2.3)

$\eta$ is the viscosity of suspension. The electrophoretic mobility is a function of zeta value from equation 2.3. The zeta potential is a key factor affecting the efficiency of EPD. In addition, Hamaker et al. attempted to estimate the deposit rate of EDP as function of different influence parameters such as electric field strength ($E$), the electrophoretic mobility ($\mu$), surface area ($A$) and concentration of particle ($C$) and suggest the following equation:

$$w = \int_{t_1}^{t_2} \mu \cdot E \cdot A \cdot C \, dt$$  

(2.4)

Besides the electrophoretic mobility and charge of particle, the electric field strength and concentration of particle also primary affect the yield of EPD from equation 2.4.
EDP is very simple, fast and environmentally free process comparing to other assembly techniques. Also, EPD demonstrated it is very versatile, since it can deposit most the nanomaterials such as semiconductor, silicon oxide and polymer particles for a specific application and purpose. Figure 2.9 shows the previous assembly results of nanomaterial using EPD.
Previous research shows the capability of EPD in the various applications. Sridhar et al. used EPD to coat bioactive hydroxyapatite on a metal substrate for bio applications. Yum et al. fabricated white light emitting diodes through the EPD with Y$_3$Al$_5$O$_{12}$:Ce$_{0.05}$. Chemical and biosensors also were developed by depositing the nanoparticle, wire and tubes using EDL.
2.2 Transfer Techniques

Transferring assembled nanomaterials onto other substrates is a rather cumbersome process requiring in-depth knowledge about the interaction energy between different materials and nanomaterials. Successful transfer of ordered nanomaterials onto recipient substrates can be utilized various flexible devices such as thin film transistors, gas sensors and biosensors. \textsuperscript{61} \textsuperscript{62} \textsuperscript{63} Figure 2.10 illustrates the most common transfer methods not only for transferring nanomaterials onto recipient substrate, but also fabricating flexible devices. The use of a template's sacrificial layer (such as SiO\textsubscript{2} film) shown in figure 2.10 (a) for transferring nanomaterials onto flexible or rigid substrates with good transfer efficiency has been demonstrated. In this method, assembled nanomaterials face down to the recipient substrate and the SiO\textsubscript{2} layer underneath SWNTs was then etched by HF. The transfer process was successfully completed when SWNTs were naturally remained on the recipient surface and dried. The transfer efficiency is completely independent of the adhesion force between the nanomaterials and template. The drawback with this method is that these templates cannot be reused after transfer process. \textsuperscript{64} \textsuperscript{65} To conduct another assembly and transfer cycle, the additional processes such as patterning and sacrificial layer deposition/removal are needed. In addition, the chemical solution used in the sacrificial layer removal process affects the nanomaterials and recipient, which limits the material selection of nanomaterials and substrate. Intermediate sacrificial films such as PDMS and thermal tapes shown in figure 2.10 (b) and (c) for transferring nanomaterials to recipient substrates have also been explored and demonstrated medium scale flexible integrated circuits. \textsuperscript{66} \textsuperscript{67} However, the methods introduce additional steps resulting in a complicated fabrication process and leading to higher production costs. Thus, the adhesion
force between nanomaterials/template and nanomaterials/recipient is thoroughly considered to achieve high efficient and uniform transfer results.

Figure 2.10 Most common transfer method; (a) SWNTs transfer using sacrificial layer (SiO₂) , (b) PDMS stamps transfer, (c) Thermal tape transfer.

Transfer printing technique, unlike previous techniques, is very straightforward and simple process to transfer nanomaterial onto a polymer substrate. This method does not need intermediate steps such as stamps, a removal process and thermal tape described above to transfer nanomaterials. Reducing the number of step directly affect the cost of a product and reduce the variables able to occur during the process. In addition, transfer printing process inherently enables to transfer nano-scale structures onto a polymer substrate. Tsai el al. demonstrated that the vertically growing CNTs on a silicon substrate were successfully transferred onto PC film using transfer printing technique and fabricated
flexible field emission devices shown in figure 2.11. Figure 2.11 (a) illustrates a typical procedure of transfer printing process. Vertical CNTs can be transferred onto PC substrate through one step process applying temperature and pressure. The transferred CNTs are transferred onto PC substrate keeping their original structures and density shown figure 2.11 (b). Hines et al. studied about the effect of correlation between nanomaterial/substrate and nanomaterial/recipient substrate on the transfer yield using a nanoimprint tool.

Figure 2.11 (a) Illustration of a typical transfer printing technique. (b) Transferred vertical CNT on PC film using transfer printing.

2.3 Applications Using Nanomaterials

Many effort has been invested to develop the practical and conventional application using nanomaterials to be able to replace the conventional silicon based application such electronic, biomedical, optical and energy devices. In addition, new fabrication approaches have been developed to efficiently utilize nanomaterials and overcome the limits that conventional top-down technology are being faced with over last few decades. The advanced technique combined with nanomaterials shows potential capability to
replace the conventional materials and fabrication technology.

Nanoparticle is the most popular material in the various applications due to its unique properties. Quantum dots show the excellent semiconductor behavior and performance in single-electron transistor (SET), which exploits the quantum phenomenon of tunneling to control the movement of single electrons. Photovoltaic utilizing quantum dots outperformed the conventionally designed devices. In addition metallic particles such as gold, palladium and silver NPs have been widely used in biomedical application and chemical sensor through the solution process. Assembled gold NPs and nanostructured film were used in the surface enhanced Raman spectroscopy. Recently, silver paste coupled with printing technology is getting the spotlight as alternative 2-D interconnect material to replace the use of indium tin oxide (ITO) in the area requiring transparent conductance.

CNTs have been most attractive materials in a field of electronics, photovoltaic and chemical/biosensor due to its high physical, chemical, electrical and thermal properties since it was observed and introduced in the research area. CNTs are categorized as SWNTs and MWNTs by the number of rolled layer. While SWNTs show different electrical properties, metallic and semiconducting, according to the different charities, MWNTs have excellent metallic property.

SWNTs are considered as the promising materials to replace poly or amorphous silicon in the thin-film transistors due to its inherently semiconducting property, high mobility and compatibility with room temperature. The transistor using highly aligned SWNTs achieved mobility of 80 cm²V⁻¹s⁻¹, sub-threshold slopes of 140 mV decade⁻¹, and on/off ratios as high as 10⁵. In addition, recent researches demonstrated that high
performance transistor can be fabricated on a flexible and transparent substrate with on/off ratio of $6 \times 10^6$.\textsuperscript{88,89} Many reports have shown the sensing capability of SWNTs for bio/chemical sensors utilizing advantage of high surface to volume ratio.\textsuperscript{90,91} Field effect transistor (FET) based biosensors were developed to obtain the highly sensitive sensing results and large scalability.\textsuperscript{92,93} Also, Kong et al. were the first to build a SWNT chemical sensor for the detection of NO\textsubscript{2} and NH\textsubscript{3} gas.\textsuperscript{94} Valentini et al. detected NO\textsubscript{2} gas with sub-ppm level sensitivity based on SWNTs.\textsuperscript{95}
Chapter 3 Damascene Template Fabrication

3.1 Rigid Damascene Template

3.1.1 Introduction

As mentioned previous chapter, electrophoretic assembly requires a conductive surface which is not practical for building a variety of devices. One solution is to make a template that has conductive patterns (based on the desired structure) and then transfer the assembled structures onto a recipient substrate. However, when using templates with 3-dimensional patterned structures such as wires on an insulating film shown in figure 3.1 (a), the assembly will be non-uniform due to the large potential drop in nano-scale wires (using a higher voltage will damage the nano-scale wires), and most particles will assemble on micro wires only due to the large resistance of the nanowires shown in figure 3.1 (b). In addition, NPs will also assemble on the side of the 3D wires. Another problem is that the template’s nano-scale wires can be easily peeled off during the transfer of assembled nanomaterials due to poor adhesion between the 3D wires and the template insulating surface due to the small contact area. The key to solve the problems of 3D wire template is the damascene template; its nano and micro features (or wires) are connected by a conductive film (underneath an insulator, figure 3.1 (c)) which enable all the structures to have equipotential leading to a uniform electrophoretic directed assembly. Corresponding equivalent resistor circuits are shown in figure 3.1 (a) and (c), where $R_m$ is the resistance introduced due to the micron scale electrode $R_n$ is that of the nano-scale electrode while $R_s$ is that of the solution. In 3D nanowire template, $R_n$ is much larger than $R_m$, but in the damascene template $R_n$ and $R_m$ can be approximately same.
Figure 3.1 The schematic of a 3-D wire template used for electrophoretic assembly. In these templates nanowire electrodes are connected to a micron scale electrodes, which are in turn connected, to a large metal pad through which the potential is applied. (b) The SEM micrographs of a typical nanoparticle assembly result obtained for configuration shown in (a). (c) The schematic of a conventional template used for electrophoretic assembly. In these templates nanowire electrodes are connected to a micron scale electrodes, which are in turn connected, to a large metal pad through which the potential is applied.

Damascene originates from 'Damascus', capital of Syria. The people invented the process to decorate the jewelry and sword surface with gold inscriptions shown in 3.2 (a) and (b). They made scratches on the sword surface by using diamond and filling gold into the trenches, and then polished the excess gold on the surface. In 1998, IBM invented copper damascene process and applied it to semiconductor process to overcome fabrication limit of semiconductor. Figure 3.2 (c) shows multi-layer of copper damascene structures in semiconductor devices. The most important process for achieving the damascene structure is the chemical mechanical polishing (CMP) process enabling flat surface composed two or three different material. Our invention was started at the copper damascene structures. On the contrary to the copper damascene structure in the
semiconductor industry, insulating material fills into the defined trenches on metallic material. The insulating layer is then polished by CMP until the surface of metallic material is revealed. After CMP process, the template can be completely flat if the CMP process is stopped right away when the surface of metallic materials is revealed.

![Figure 3.2 (a) Jewelry decorated damascene process, (b) Sword decorated damascene process, (c) Copper multi-layer interconnector using damascene process.](image)

Fabricating a damascene template starts with deposition of 5 nm adhesion layer (if needed) on 3 inch Si wafers as an adhesion layer to increase the adhesion force between Si and a conductive layer. A 300 nm of the conductive layer was then deposited on the adhesion layer by the deposition process. PMMA was spun on the Au layer; and e-beam lithography/ nanoimprint lithography was used to generate the nano/micro patterns. In case of micron feature, photolithography was conducted. The patterning process will be described in the next section. After development, a thin metal mask (50 nm of Cr) was deposited on the nano/micro-patterns followed by lift off process. The conductive layer was then etched (150 nm) by dry etching process and the metal mask was stripped out. SiO$_2$ (600 nm) was deposited at relatively low temperature (300 °C) by plasma enhanced vapor chemical deposition (PECVD) to fill the trenches etched previously in the conductive layer.
A second adhesion layer (5 nm) was deposited again on the conductive layer as adhesive layer between the conductive layer and SiO$_2$ layer to prevent SiO$_2$ layer from being peeled off from gold surface by the high torque generated during chemical mechanical polishing (CMP) process. Finally, excess SiO$_2$ was removed by CMP until the top of conductive patterns were revealed through the SiO$_2$ layer. The procedure of fabrication is illustrated in figure 3.3.

![Figure 3.3 Schematics of a rigid damascene template fabrication using CMP and microfabrications. Inset is SEM image of preliminary results of damascene template using tungsten as conductive material. Level of SiO$_2$ and tungsten is same after CMP process.](image)

3.1.2 Patterning Process

Patterning process to make 3-D structures in the damascene template fabrication is very crucial process because the fabrication process time, and pattern resolution mainly depends on the type of patterning process. The patterning process has to be prudently chosen as regarding the minimum feature size and process time. There are three major
patterning techniques in patterning process; Optical lithography, electron lithography (EBL) and nanoimprint lithography (NIL). Optical lithography can create the 15 nm feature using extreme ultraviolet (EUV) with mask and shows fast process speed. However, EUV and the mask for EUV are too expensive to use in a research area such as academia. The most of the optical lithography used in academia is equipped with general UV source (365 nm and 436 nm of wavelength) whose resolution is around a micron. Electron-beam lithography (EBL) has been widely used to achieve high resolution features in nanotechnology research, but has been limited to 4 nm features using conventional resists. In addition, we can create very complex design and easily change the shape and size by using commercially available design software connected to EBL equipment. However, EBL using conventional resist such as poly (methyl methacrylate) (PMMA) on wafer scale needs very long process time. In contrary, NIL has shown the advantage on the process time as well as the high resolution features. We can achieve sub-100 nm features in a few minutes through NIL. Although NIL takes two advantages from the optical lithography and EBL, we still need EBL to create the patterns for the mold fabrications and the demand of different mold design.

In this study, we primarily used EBL and NIL for sub-micron size features with a complex design. To overcome the slow process speed of EBL, we applied a new polymer, Eudragit S100 (ES100) to EBL as e-beam resist, instead of PMMA widely used as conventional e-beam resist for EBL due to the high resolution, and developed the EBL processes.

Eudragit is a trademark of Rohm GmbH & Co. KG, Darmstadt in Germany. ES100 based on PMMA and methacrylic acid (MAA) (2:1) was invented for the irritation of
stomach by the chemical properties of pharmaceutical dosage forms. ES100 can prevent the drug from being affected by the acidic gastric environment and provide the drug to be released at the same time under the specific pH condition. ES100 can be dissolved in water above pH 7 and biocompatible and has been used as coating to conventional solid oral dosage forms such as tablets and capsules.

We applied ES100 to EBL as e-beam resist. In my knowledge, there is no report that ES100 is used as e-beam resist in nanotechnology. The powder of ES100 was provided from Evonik. To prepare the test solution, the A part of ES100 was completely dissolved in seven parts of isopropyl alcohol containing 3% water using a magnetic stirrer. The test solution was then spun onto Si substrate and baked to evaporate the solvent. Figure 3.4 (a) shows the thickness change as a function of rotating speed of spinner. The thickness reduced as the increase of the rotating speed. We measured the thickness of ES100 film using an optical profiler (Nanospec 200). The process speed primarily depends on the sensitivity of e-beam providing lower dose amount to create patterns. If we can create the same size of pattern using lower line dose, the process speed will be linearly increased. The exposure time (process time) to a given area for a given dose is given by the following formula.  

\[ D \times A = T \times I \]  

(3.1)

T is the exposure time, I is the beam current, D is the dose and A is the area exposed. The process time proportionally increases as increase of dose amount at the same current and area from the equation 1. Figure 3.4 (b) shows dose decreased as increase of area and higher dose were needed for the thicker polymer. When PMMA was used as e-beam resist,
1.2 nC/m dose was needed to get 1 µm patterns, which means that the process using ES100 is 3 times faster than PMMA. Figure 3.5 is the example of 0.1, 0.2, 0.5, 1 and 3 µm patterns on black line of figure 3.4 (b).

![Graphs](image)

Figure 3.4 (a) ES100 film thickness change as function of spinning speed, (b) Line dose amount to make features on different thickness of ES100.

![SEM images](image)

Figure 3.5 SEM images of pattern on ES100 made by EBL. (a) 3 µm, (b) 1 µm, (c) 500 nm, (d) 200 nm and (e) 100 nm feature size.

In addition, figure 3.6 demonstrates that EBL using ES100 can create various pattern
shapes. ES100 can be also applied to the fabrication of imprint mold process as e-beam resist in EBL.

![Image of EBL results on ES100. Very complex shape can be patterned on ES 100.](image)

Through the newly developed polymer, the fast EBL process can be achieved. However, the more speedy process was required to increase the throughput. Here, we primarily used NIL enabling not only to fabricate the damascene template with high throughput comparing with EBL, but also make submicron scale features. Figure 3.7 illustrates the way to make the 3-D structure of conductive material using nanoimprinting. 150 nm PMMA (950PMMA, Microchem) was spun on the conductive material (e.g., gold and tungsten). The PMMA indented by Si imprinting mold with 150 nm structures. The residue of PMMA in the trenches was then removed by oxygen plasma using inductively coupled plasma (ICP, Plasma Therm 790) at 4 scm of O2, 40 W RF1 power, 100 W RF2 power and 5 mTorr working pressure for 5 second. Considering the etching ratio between the gold and Cr under the ion-milling (Veeco Microetch), metal layer was deposited by e-beam evaporation. When gold was used as a conductive material, and 70 nm Cr layer was deposited. 3-D conductive structures were accomplished by dry etching using ion-milling and then the metal mask was removed by wet etchant (CR-7, Cyantek Corp.). Megasonic cleaning with standard cleaning 1 solution (SC-1) to remove the contaminations generated.
in the previous process. Figure 3.8 shows pattern array on 3” wafer made by NIL.

Figure 3.7 Fabrication procedure of 3-D conductive structure using NIL.

Figure 3.8 Nano-scale pattern array on 3” wafer obtained by NIL. SEM images show 300 nm square pattern arrays. Zoom-in image (top) and general view (bottom).

For NIL process, the mold having specific dimension of features is required. Final pattern shapes and sizes were determined by the shapes and sizes of mold, so the mold fabrication is very critical step in the damascene template fabrication. Figure 3.9 is the
schematic of mold fabrication process. In order to get extruded nano-scale features on silicon (Si) mold, EBL using ES100 was utilized. 150 nm of ES100 was spin-coated on the 3” Si wafer and lithography was conducted to define the patterns. 50 nm of Cr as metal mask (hard mask) was deposited on the top of the patterned wafer using e-beam evaporator. The wafer was immersed into water of pH 9 to lift-off the ES100. The Cr layers remain as a metal mask. To remove the residual of Cr mask, organic contamination and other contamination, piranha cleaning and megasonic cleaning with standard cleaning (SC-1) were conducted.

Figure 3.9 Schematic of procedure of Si mold fabrication.

Figure 3.10 shows Cr mask and contaminations before (a) and after (b) the cleaning process. It was found that cleaning process has to be conducted right after lift-off process to remove the contamination (Cr and polymer residues). Si (150 nm) was etched by ICP. Cr metal mask was removed by wet etching process and vapor self-assembled monolayer (SAM) was deposited on the mold as anti-stiction layer to prevent PMMA from being stuck on the mold and help the mold to separate easily from the wafer.
Figure 3.10 SEM image of Cr mask. (a) Before the piranha and megasonic cleaning with SC-1. The Cr residues are still remained on Si surface and attached to Cr mask. (b) After the piranha and megasonic cleaning with SC-1. There is no Cr residue as well as other contaminations.

In general, anisotropic etching results for the straight side wall can be obtained by dry etching process. However, when the gas is used to etch the material chemically, the parameters of ICP such as RF1, RF2 power, the amount of gas, working pressure and temperature have to be controlled to achieve anisotropic etching result. RF1 power, involving with plasma acceleration, is located lower part, and the plasma density is primarily determined by RF2 located upper. The influence of power is very straightforward. Increase of power increases the density and the energy of free electrons. Also, working pressure and temperature influence mean free path affecting the energy and the formation of a new electron-positive ion pair. Figure 3.11 is the SEM images of cross section of Si substrate with Cr mask after etching process repeated 3 times to Si substrate. Anisotropic etching results were obtained at 250 W RF1 power, 300 W RF2 power and 5 mtorr working pressure using 6 scm SF6 and 5 scm Ar. The etch rate was 450 nm/min. Figure 3.12 shows that square
patterns (300 nm x 300 nm) were fabricated through this processes.

Figure 3.11 SEM image of cross section of anisotropic etching on Si substrate. Etching rate was 450 nm/min.

Figure 3.12 SEM image of square mold (300 nm*300 nm).

3.1.3 Chemical Mechanical Polishing (CMP)

Experimental Procedure

A CMP system consists of a polishing pad on a rotating platen, a rotating head where a wafer is mounted and a slurry supplier shown in figure 3.13 (a). The wafer face down to the surface of the polishing pad with down force and the head with wafer and the polishing pad are rotating. During the rotating, the slurry is supplied onto the polishing pad. Chemicals in slurry react with the wafer surface, and abrasives and morphology of pad mechanically polish the wafer. During the process, the roughness of the polishing pad
becomes smoother and influences the performance of CMP process. It is necessary to have a reconditioning process to recreate the roughness of the polishing pad to keep the same performance.

For CMP process, CMP process was performed with R&D CMP equipment (Poli-500s, GnP tech., Korea) and IC 1000 polishing pad (Rohm & Hass). SiO$_2$ slurry (Silco EM-7530K, pH 11, 75 nm diameter colloidal silica abrasive) was supplied on the pads with 50 ml/min flow rate during rotating a pad and a head. 3” thermally grown SiO$_2$ (1 µm thickness) wafer was used in CMP process to measure the removal rate and uniformity at different combination of the pressure and velocity. The platen (pad) and the head (wafer) rotate in the same direction and its rotating ratio is 1:1 regarding the trajectory of wafer during the CMP process. Before the experiments, the pad was conditioned by diamond conditioner to increase the roughness and remove the pad residues. A dummy wafer was then polished for 1 min and the pad was conditioned again. This process was repeated three times before the real CMP process. The thickness of SiO$_2$ was measured at 14 points on the bare 3” SiO$_2$ wafer using optical thickness measurement (Nanospec 200) before and after CMP process shown in figure 3.13 (b). Between each CMP processes, the conditioning process was conducted to keep the pad to be same roughness and properties. The most of slurry used in CMP process is water-based slurry with chemicals and abrasive particles. The type of slurry depends only on the material to be removed by CMP process. In this study, SiO$_2$ slurry was used to remove the SiO$_2$ layer. The slurry used in the experiments is KOH-based (pH 11) with 75 nm colloidal silica abrasive particles (10%). The removal mechanism of SiO$_2$ CMP can be described as follows. First, the hydroxyls are formed on both the oxide film surface and the silica particles. The hydrogen bonds between hydroxyls on the oxide surface and
the silica particles in slurry formed. Mechanical removal of the particles bonded with the wafer surface also tears away the atoms from the wafer surface. The SiO\textsubscript{2} removal mechanism in CMP is illustrated in figure 3.14.

![Figure 3.13](image)  
(a) schematics of CMP system. (b) Map of thickness measurement for determining CMP performance.

![Figure 3.14](image)  
Illustration of SiO\textsubscript{2} removal mechanism in CMP process.

**Results and Discussion**

CMP process is very straightforward and unique technique enabling global planarization and ultrafine surface through the control of nano-scale material removal. The
mechanical removal rate is governed by the applied pressure between the polishing pad and wafer and relative velocity. This relation was found by Preston in the field of glass polishing process. The Preston equation can be expressed as:

\[ R = K_p \cdot p \cdot \Delta v \]  \hspace{1cm} (3.2)

R is removal rate, \( K_p \) is Preston coefficient, \( p \) is pressure and \( \Delta v \) is the velocity. However, the Preston equation cannot explain the uniformity of wafer such as within wafer non-uniformity (WIWNU) and wafer to wafer non-uniformity (WTWNU) from CMP process. The equation is only related with the material removal rate (MRR) by physical effect. Wafer uniformity is strongly affected by the combination of pad material, the applied pressure, the velocity (rotating speed), and shape of wafer. We used a same pad and shape of wafer in all experiments, so the pressure and the velocity are the controllable parameters to improve the uniformity.

WIWNU is the barometer to determine wafer uniformity within a wafer after CMP process. WIWNU is measured as a standard deviation of the MRR expressed as a percent of the average of MRR. Low WIWNU means that very uniform topography on entire the damascene template can be achieved and chip yield increase. The geometry of damascene template significantly affects the uniformity of assembly. In order to minimize the geometry effect, minimal WIWNU has to be obtained by controlling the pressure and velocity. WIWNU can be expressed as follows.

\[ WIWNU = \frac{\sigma}{MRR_{ave}} \]  \hspace{1cm} (3.3)
WTWNU involves repeatability of CMP process under the set condition. WTWNU is a standard deviation of MRR for a number of wafers expressed as a percent of the average of MRR.

\[
\text{WTWNU} = \frac{\sigma(\text{wafers})}{\text{MRR}_{\text{ave}}(\text{wafers})}
\]  

(3.4)

Figure 3.15 shows the material removal rate (MRR) of SiO\textsubscript{2} as a function of velocity of platen and head at fixed pressure (2.45 psi). As the increase of velocity, the MRR proportionally increased. However, the change of velocity strongly affected the wafer uniformity influencing the yield of chip product. The minimum WIWNU (5%) and WTWNU (2.75%) can be obtained at 90 rpm of the head and the platen shown in figure 3.15 (b). The velocity of the platen and the head was then fixed at 90 rpm, and the pressure was changed from 2.5 psi to 4.5 psi shown in figure 3.16. At 3.5 psi, WTWNU (0.5%) was sufficiently improved with similar WIWNU to 2.5 psi. Also, higher MRR were achieved resulting in the decrease of CMP process time. This process conditions was chosen for CMP process of damascene template.
Figure 3.15 MRR as function of rotation velocity of platen and head at 2.5 psi; (a) 60 rpm/60 rpm, (b) 90 rpm/90 rpm (c) 120 rpm/120 rpm.
When the SiO$_2$ layer is over polished during the CMP process, the surface level of SiO$_2$ becomes lower than that of conductive patterns. This step height is called ‘dishing’ illustrated in figure 3.17 (a). The amount of dishing proportionally increases as increase of the polishing time after the conductive patterns revealing. Figure 3.17 (b) shows measurement of dishing amount as the increase of polishing time. When CMP process was stopped right after the conductive patterns were revealed, the amount of dishing was 10 nm (left top) in figure 3.17 (b). The change of dishing amount was measured every 10 sec.

Figure 3.16 MRR as function of pressure at 90 rpm of head and platen velocity; (a) 2.5 psi, (b) 3.5 psi (c) 4.5 psi.
We observed 60 nm dishing after 30 sec from when 10 nm dishing amount occurred. A geometry change by dishing amount influences the uniformity of the electric field during the electrophoresis assembly resulting in non-uniform assembly of nanomaterial, especially NPs. We will talk about the non-uniformity by the geometry of the template in chapter 4 in detail. Therefore, CMP process and the involved parameters affecting the wafer uniformity have to be precisely controlled and characterized.

Figure 3.17 (a) Schematic of definition of dishing after CMP process. (b) The profile of damascene template and change of dishing amount as increase of the CMP time.

3.1.4 Material Selection

There are many potential metals to be used as conductive materials in the damascene template. However, when CMP process used in the fabrication process and electrophoresis assembly used in the assembly are considered, the number of metal to be used in the template is not many. For example, copper (Cu) and aluminum (Al) are suitable material for electrophoresis assembly due to its low resistance, whereas Cu and Al are easily oxidized in the electrophoresis assembly and even in the air. The weakness to the oxidization affects electrical properties of the metal and the surface property such as roughness and surface energy. In addition adhesion force between the metal and SiO₂ has to
be significantly considered because the torque generated in CMP process makes the delamination, which can be serious defects on the template. Considering these reasons mentioned previous, tungsten was firstly used as conductive material for the damascene template. The adhesion force between the tungsten and SiO$_2$ is strong enough to overcome the delamination problem without adhesion layer increasing the adhesion force between two materials. Figure 3.18 (a) shows 4” wafer of damascene template using tungsten and SiO$_2$ as conductive and insulating material respectively. The cross section image of damascene template using tungsten is shown in figure 3.18 (b). Completely flat surface was achieved by CMP process.

![Figure 3.18 Damascene template using tungsten as conductive material; (a) 4” wafer damascene template using tungsten, (b) Artificial colored SEM image of cross section of damascene template. The surface level of tungsten (gray) and SiO$_2$ (green) is same after CMP process.](image)

However, there was an unexpected problem involving electrophoresis assembly. In order to increase the electric force between the template and nanomaterials, the ammonium hydroxide was added to increase and control pH of the nanomaterials solution. Ammonium hydroxide is well known as part of tungsten etchant. Figure 3.19 is SEM image
of defects generated during the electrophoresis assembly. Low pH value did not affect the surface of tungsten, while high pH made pinholes on the surface of tungsten at 2 V. Defect generated in the previous assembly step can affect the next assembly efficiency and the repeatability of assembly results using the same template.

![Image of pH 10.1, pH 10.3, pH 10.5, pH 10.7](image)

Figure 3.19 Defect generation as increase of pH of the solution. From pH 10.5 pinholes were generated on tungsten surface due to the ammonium hydroxide used as pH adjustor to increase of zeta potential of nanomaterials in the suspension.

In addition, when PSL NPs (50 nm) and SWNTs were used in the assembly process, SWNTs were assembled on the tungsten and even on SiO$_2$ as shown in figure 3.20 (a) and (b). In order to assemble the nanomaterials only on the conductive patterns, either the electric field near the insulator surface or the surface energy of insulator has to be reduced.
Reducing the electric field affects the strength of the electric field not only on the insulator surface, but also on the conductive patterns, which can influence the assembly results. In the electric force equation, applied voltage affect the amount of charge on the particles, which mainly determine the results of assembly such as efficiency, density and number of assembled layers.

We considered use of self-assembled monolayer (SAM) to decrease the surface energy of SiO\textsubscript{2} to prevent nanomaterials from being assembled on SiO\textsubscript{2}. However, most of SAM enabling SiO\textsubscript{2} to be hydrophobic has silane, which can be formed as SAM on the oxidized surface. If SAM with silane compound is used on the template using tungsten and SiO\textsubscript{2}, both surfaces will become to be hydrophobic. Consequently, instead of tungsten, gold was used as conductive material in the damascene template. Considering the poor adhesion force between the gold and SiO\textsubscript{2}, Ti or Cr was used as an adhesion layer to increase adhesion force between the two materials. The adhesion layer is expected to overcome the delamination issue due to poor adhesion between two layers during the CMP process.

![SEM images](image)

Figure 3.20 SEM of 50 nm PSL particles and SWNTs assembly on the damascene template using tungsten; (a) SEM images of 50 nm PSL particles assembly, (b) SEM images of SWNTs assembly. PSL particles and SWNTs were assembled on tungsten and even on SiO\textsubscript{2} surface.
3.1.5 Self-Assembled Monolayer (SAM)

We expected that nanomaterials would be assembled only on the conductive patterns, not on the SiO$_2$ by the electric field. However, the nanomaterials were assembled on the conductive patterns and even on the insulator. We investigated the reasons why nanomaterials were assembled even on the insulating surface. There are two main reasons. Although the insulator is low-k material, electric field near the insulator surface is strong enough to attract nanomaterials onto its surface. Electric field simulation result indicates that the electric field strength near SiO$_2$ surface is the same magnitude order ($10^6$ V/m) as that near gold surface. Electric field simulation using 3-D finite software will be described in more detail in chapter 4. In addition, SiO$_2$ is naturally hydrophilic (high surface energy) after piranha cleaning process for removing the organic contamination. Contact angle of SiO$_2$ surface is less than 5° after piranha cleaning process. Strong electric field near insulator surface coupled with high surface energy of insulator can significantly attract nanomaterials on insulator surface shown as figure 3.21.

Figure 3.21 SEM images of PSL particles (50 nm) and SWNTs assembly on damascene template before the functionalization on the template. (a) PSL particles (50 nm) and (b) SWNTs were assembled on the gold surface and even on the SiO$_2$ surface.
In order to assemble the nanomaterials only on the conductive patterns, either the electric field near the insulator surface or the surface energy of insulator has to be reduced. Reducing the electric field affects the strength of the electric field not only on the insulator surface, but also on the conductive patterns, which can influence the assembly results. However, the surface energy of insulator can be reduced using self-assembled monolayer (SAM) without affecting that of the conductive patterns. Previous researchers already demonstrated that silane compound with long change can be selectively reacted with SiO$_2$ surface and change the surface energy from hydrophilic to hydrophobic without affecting the surface energy of other materials. Octadecyltrichlorosilane (OTS) is the most common SAM to make the SiO$_2$ to be hydrophobic. OTS was used to selectively modify the surface energy of SiO$_2$ used as an insulator on the template. However, native oxide of the metal surface such as tungsten, copper, aluminum and chromium can react with OTS SAM, so that gold was chosen as conductive materials. To form the OTS SAM on SiO$_2$ surface, the damascene template was pre-cleaned with a freshly prepared piranha solution (sulfuric acid (2): hydrogen peroxide (1)) for 3 min. The template was then rinsed under the running deionized water (DIW) for 5 min and dried with a stream of nitrogen. OTS-SAM was prepared by immersing the substrate into a toluene (Sigma Aldrich) solution containing 1.4 vol.% OTS (Acros Organics) for 2 min. After OTS SAMs, the contact angle of SiO$_2$ increased from 5° to 105° and that of gold increase from 15° to 71° shown in figure 3.22 (a) and (b), respectively. The template was then rinsed with toluene to remove physically adsorbed OTS on the gold
surface, followed by drying with a stream of nitrogen. To remove completely OTS non-covalently attached to the gold surface and ensure the hydrophilic surface of gold, the template was again immersed into piranha solution for 30 sec, rinsed and nitrogen dried. Figure 3.22 (c) and (d) show that the contact angle measurements of OTS SAM coated SiO$_2$ and the gold surface after the second piranha treatment. Figure 3.22 (c) and (d) correspond to that of OTS SAM coated SiO$_2$ surface after the second piranha process, respectively. In order to investigate the effect of the post treatment process on assembly result, we applied the same assembly conditions two templates, one is without the post process and another one is with the post process. When the post treatment process to removed OTS non-covalently attached to the gold surface was not applied, despite enough applied voltage (2.5 V), there are few particles even on the gold surface shown in figure 3.23 (a). However, the full assembly could be obtained on the template treated with the post treatment process shown in figure 3.23 (b). It is significant evidence that the assembly efficiency is mainly affected by the surface energy, and the post treatment process using piranha makes the gold surface be hydrophilic without affecting the surface energy of SiO$_2$. 
Figure 3.22 Contact angle measurement on SiO$_2$ and gold surface (a) Contact angle of SiO$_2$ after SAM coating. (b) Contact angle of gold surface after SAM coating. (c) Contact angle of SiO$_2$ surface after second piranha process. The piranha process does not affect the contact angle and disturb the SAM layer. (d) Contact angle of gold surface after second piranha process. Non-covalently attached SAM layer was removed by the second piranha.

Figure 3.23 (a) SEM of PSL particle assembly on the damascene template without the application of the post treatment process to remove the non-covalently bonded SAM on the gold surface. Only few particles were assembled on the gold surface. (b) SEM image of PSL particle assembly on the template treated with the post treatment.
process. Full assembly results were achieved.

Through this process, the application of SAM of OTS increased the contact angle of SiO$_2$ from 10° to 103° without affecting the surface energy of the gold. The contact angle measurements for SiO$_2$ and gold surface were performed on a bare SiO$_2$ and gold template. The application of SAM of OTs deposition, the contact angle of SiO$_2$ was measured by contact angle analyzer (SEO, Korea). Through the surface modification, full assembly can be achieved on the conductive patterns only by protecting SWNTs from being assembled on the SiO$_2$ surface shown in figure 3.24 (a).

![Image](image1)

**Figure 3.24** (a) SWNTs were fully assembled on gold surface not on the SiO$_2$ due to the low surface energy by SAM. (b) Shown is the plot of the contact angle measurement of the OTS SAM coated SiO$_2$ surface as a function of the number of assembly and transfer cycles.

In addition, during the transfer, OTS SAM on the SiO$_2$ layer plays additional role of acting as an anti-stiction layer when the damascene template is separated from the recipient substrate during transfer printing. The SAM helps the template to
be easily separated from the recipient substrate without any polymer residue. This transfer process does not significantly affect the OTS layer and hence the surface energy of SiO$_2$ shown in figure 3.24 (b). The slope of the linear fit is $\sim -0.18$ indicating the robustness of the damascene template withstanding the wear and tear of multiple assembly and transfer cycles. Extrapolation of these results with the assumption that the OTS SAM layer deteriorates at the same rate in the subsequent assembly and transfer cycles, one can estimate that the contact angle would reach a value of 70° in 140 cycles while it reaches a value of 50° at $\sim 250$ cycles. The contact angle of the metal electrode would also increase as a function of the cycles and will saturate. If one assumes the saturated contact angle value of 50° then the life cycle for a single coat of OTS SAM layer would be $\sim 250$ cycles, thereby enabling the damascene template to be reused for assembly-transfer cycle without any additional surface modification for several hundred cycles. This clearly shows that this approach does not require any additional processes such as stripping, patterning, sacrificial layer removal/deposition and another surface modification.

3.2 Flexible Damascene Template

Si based damascene template can significantly show its reusable capability for the assembly and transfer with good uniformity and scalability. However, Si based damascene template still has limit for being applied to the continuous assembly and transfer process like roll to roll process. To overcome this limitation and to be adapted to the roll to roll system, we developed flexible reusable template having same structure as the Si based
damascene template. The flexible damascene templates are based on the polymer substrate such as polyimide (PI) and polyethylene naphthalate (PEN). Figure 3.25 shows the schematic of flexible damascene template fabrication using micro-fabrication technique. Adhesion layer (Ti or Cr, 5 nm) and 300 nm gold were deposited on the polymer substrate using the sputter. Photolithography was conducted to make patterns on top of gold surface. Ion-milling was then used to etch the 150 nm gold. Another 5 nm Ti and 150 nm SiO₂ layer was deposited on the top of the patterns and filled in the trench using PECVD oxide (Nexx PECVD). After that, photo resist used in the patterning process was lifted off and the surface of gold and SiO₂ have same level. Although the CMP process used in the fabrication of Si based damascene template was not used, we successfully fabricated the flexible damascene template for roll to roll system. Figure 3.26 is 3” wafer scale flexible damascene template based on PEN film and inset figures are microscopy images of the template. Other polymer such as polyimide (PI) and polycarbonate (PC) can be used as substrate on the fabrication of flexible damascene template.

Figure 3.25 Schematic of procedure of flexible damascene template fabrication using PEN as substrate without CMP process.
Figure 3.26 3” wafer scale flexible damascene template. Insets are microscopy images of gold patterns and SiO$_2$ surface.
Chapter 4 High-rate Offset Printing

4.1 Introduction

A newly developed damascene template for directed assembly and transfer of nanomaterials was introduced, and the advantage of damascene template was addressed in chapter 3. In addition, we demonstrated that the template can be reused hundreds of times with only one time functionalization, which means that the template does not need any additional processes in a cycle of assembly and transfer.

In this chapter, high-rate multi-scale offset printing process using damascene template will be introduced. First, the Electric field simulation using 3-D finite modeling tool was conducted to explain the electric field profile on the damascene template during the electrophoresis assembly. The simulation results support necessity of SAM layer on SiO$_2$ introduced in chapter 3. The Geometry effect on the assembly results is investigated, and the experimental results are confirmed by the simulation results.

Figure 4.1 shows a schematic of the offset printing process using the damascene template. The process consists of two steps; (1) directed assembly of the nanomaterials on the template using electrophoretic assembly (“inking”) and (2) transfer of assembled nanomaterials onto a recipient substrate (“printing”). In the inking process, the template immersed into the suspension containing dispersed nanomaterials with a DC voltage applied between the damascene template (typically positive) and bare metallic counter electrode. The negatively charged nanomaterials are assembled only on the conductive patterns (wires and structures) of the template. The template is then pulled from the suspension at a constant speed. The main assembly parameters such as voltage,
nanomaterial concentration and pulling speed were experimentally investigated to understand the mechanism of electrophoresis assembly on damascene template.

In the printing process, the assembled nanomaterials are then transferred onto recipient substrate. After the transfer process, the template is immediately ready for the next assembly and transfer process without any additional process such as functionalization, patterning, removal and deposition process. In order to improve the transfer yield, the transfer condition was studied.

Figure 4.1 Schematic illustration of an offset printing approach to fabricate flexible devices. The insulating (SiO$_2$) surface of the damascene template is selectively coated with a hydrophobic SAM (OTS). Using electrophoresis nanomaterials are assembled on the conductive patterns of the damascene template ("inking"), which are then transferred to a recipient substrate ("printing"). After the transfer, the template is ready for the next assembly and transfer cycle.
4.2 Assembly of Nanomaterials (Inking)

4.2.1 Nanoparticles Assembly

4.2.1.1 Experimental Procedure

The EPD deposition is generally conducted with organic solvent as dispersing media despite needs of high applied voltage, because there is problem related to electrochemical reaction when the water-based suspension is used in the process. However, use of water-based suspension has many advantages comparing to the organic solvent. The process can use relatively low voltage and allow us faster kinetics. Thus, water-based process gives us environmental and cost benefit. In this study, we mainly use water-based suspension with minimal electrochemical reaction during the EPD process by using the low voltage.

PSL particles (50 ± 2 nm diameter, 1 wt% suspended in DIW) obtained from Duke Scientific were used for the assembly. Silica particles (100 nm ± 20 nm and 30 nm ± 5 nm diameter, 5 wt% suspended in DIW) obtained from G. Kisker-Products. Both particle suspensions were diluted with DIW to investigate the nanoparticle concentration effect. Desired pH value (10.8) for the particle suspension was achieved by adding NH₄OH. Silver nanoparticle suspension (35 nm with 35% size distribution, 5.0 mg/ml in DIW with Polyvinylpyrrolidone (PVP) surfactant for dispersion) was obtained from Nanocomposix. For the voltage effect test, the applied voltage was varied from 2 V to 4 V. To assemble the nanomaterials, the damascene template and a plain gold template were used as electrode and counter electrode, respectively and DC 2~5 V was applied to two electrodes for 20~60 sec. For multi-time assembly test, the same assembly condition applied to the same template couple of times to investigate the thickness change and obtain thicker assembly
layer. The templates were then withdrawn with a constant speed. The damascene template and counter electrode were dipped into the nanomaterial suspension. The counter electrode is plain Cr/Au (5 nm/150 nm) layer. The distance between two electrodes was maintained at 5 mm. A Keithely 2400 DC power supply was used to apply the potential (2-4 V) between the two electrodes. The two electrodes were withdrawn using a dip coater (Single vessel system, KSV NIMA) after assembly with constant speed (1-25 mm/min) keeping voltage on. Figure 4.2 shows the configuration of the experimental system, (a) is schematic and (b) is the system used in the experiments.

![Configuration of the assembly system. (a) schematic of the system, (b) photography of our system used in the experiments.](image)

### 4.2.1.2 Electric Field Simulation

**Physical Model and Geometry**

The calculation of the electric field in 3-D Flow required several steps. The geometry of the system is specified as a side view of the wire template and damascene template as shown in Figure 4.3. The thickness of gold and SiO₂ is 150 nm respectively. The width of
gold wire on both templates is 1 μm. DI water was used as a medium. The electrical property of deionized water (DIW, conductivity, σ=5*10^{-6} S/m), SiO₂ (relative permittivity, εᵣ=3.9) and gold (conductivity, σ=4.1*10^{7} S/m) was used in the simulation. The same voltage (2.5 V) was applied to the both template. The top boundary is at 200 μm away from the surface of conductive patterns. The left and right boundaries are electrically symmetrical. The mesh for the solution started on the top surface of SiO₂ layer with 25 nm space up to 500 nm and with 500 nm up to 10 μm. The solver is then initialized to solve the Laplace equation for all elements to obtain the electric field strength. The step height between the gold and SiO₂ on damascene template was changed from 0 to 75 nm by 25 nm step to investigate the geometry effect on the electric field distribution and uniformity.

Figure 4.3 Cross section view of physical geometry and specific dimension used in electric field simulation. (a) 3-D wire template, (b) damascene template.

Result and Discussion

The contour of the electric field on the wire template is shown figure 4.4(a) and a zoom-in view of the gold wire corner is in figure 4.4 (b). Figure 4.4 (c) is the top view of the electric field strength contour on the wire template. The electric field on the edge of wire is much higher than that of center shown in figure 4.4 (a, c). Thus, the sidewall of gold wire
has stronger electric field than the center and the NPs can be assembled on the side of conductive wires if the electric field is high enough to attract NPs. Our assembly results shown in figure 4.5 (a) and (b) is in good agreement with predictions made by the electric field simulation using 3-D Flow. The electric field profile shown in figure 4.6 was obtained at 25 nm away from the surface of gold wire. The electric field difference between the center and edge is around 244kV/m. This number is around 50% of the maximum electric field strength (500kV/m) on the wire template. The difference of the electric field between the center and edge strongly impacts on the uniformity of assembly. The simulation results indicate that the uniformity of the electric field on the wire template is generated across the wire as well as length direction shown in figure 3.x in chapter 3. In addition, the particles assembled on the side wall cannot be transferred onto a recipient substrate and occur non uniform assembly result.

Figure 4.4 Electric field contours on 3-D wire template during the electrophoresis assembly at 2.5 V. (a) Cross sectional view of the electric field, (b) Zoom–in view of corner, (c) Top view of the electric field. The electric field strength on the edge of wire is higher than that on the center. The side wall of the wire has significant electric field strength to be able to attract the nanomaterials.
Figure 4.5 SEM images of PSL NPs assembly on 3-D wire template compositied with micro/nano wires. (a) NPs were assembled on the side wall of micro and nano wires. (b) Zoom-in image from image (a).

Figure 4.6 Electric field profiles on the 3-D wire template during the electrophoresis assembly at 2.5 V. Electric field profile was obtained at 25 nm away from the top surface of conductive wires. Electric field difference between the edge and center is 244 kV/m, which is 50% of the maximum electric field strength on the wire template.

The magnitude of the electric field near SiO$_2$ and conductive patterns of damascene template was obtained under the specific conditions. Figure 4.7 shows the electric field magnitude contour of a cross-sectional view and the top view of the damascene template.
when DC 2.5 V is applied between the two electrodes. The contour indicates that the electric field magnitude near SiO$_2$ and conductive pattern are the same order of magnitude during the electrophoresis assembly. This result can explain the reason that nanomaterials were assembled even on the SiO$_2$ surface. The experimental assembly results were shown in chapter 3. The electric field near SiO$_2$ coupled with high surface energy of SiO$_2$ surface is high enough to attract nanomaterials and retain them on the SiO$_2$ surface. In chapter 3, we suggested alternative and overcome this problem by controlling the surface energy of SiO$_2$ selectively using SAM.

Figure 4.7 Modeling results indicating the electric field strength near the insulator and conductive pattern during the electrophoresis assembly. (a) Top view of electric field contour, (b) cross section view of electric field contour. The electric field near the insulator and the conductive pattern have the same order of magnitude.

The damascene template topography plays a significant role on the efficiency and yield of assembly and transfer process. Ideally a flat topography provides a uniform electric field from edge to the center of each conductive pattern with minimal variation facilitating
uniform assembly shown in figure 4.8 (a). The dishing amount between the conductive patterns and the insulator increase the non-uniformity of the electric field from edge to center of the conductive pattern. The increment of dishing amount between the metal and the insulator increases the non-uniformity of the electric field from edge to center of the electrodes as shown in figure 4.8 (b) and (c). At 50 nm dishing amount, the difference of the electric field strength between the center and the edge is 44 kV/m, which is 4.4 times larger than that at zero dishing amount. However, 44 kV/m electric field difference of damascene template with 50 nm dishing is still 6 times lower than that of 3-D wire template. These results can explain how suitable the damascene template is for the uniform assembly using electrophoresis comparing with 3-D wire template. Figure 4.9 (a) shows the electric field strength at 25 nm away from the top surface of the conductive pattern with 0, 25, 50 and 75 nm dishing amount. Figure 4.9 (b) is normalized electric field non-uniformity (NEFNU) according to the amount of step height between the insulator and electrode. The NEFNU is given by

\[ \text{NEFNU} = \frac{E_e - E_c}{E_c} \]  

(4.1)

\(E_c\) and \(E_e\) are the electric field strength of center and edge of the electrode respectively.

To minimize the electric field non-uniformity on the conductive patterns due to the geometry effect and prevent the recipient substrate from being indented, the CMP process on the template has to be precisely controlled.
Figure 4.8 Electric field contours and profiles at 25 nm away from the top surface of the conductive pattern. (a) 0 dishing, (b) 25 nm dishing and (c) 50 nm dishing.

Figure 4.9 (a) Electric field of damascene template as a function of dishing amount. (b) Normalized electric field non-uniformity as a function of dishing amount.
4.2.1.3 Effect of Applied Voltage

The applied voltage between the template and the counter electrode governs the assembly process of the nanomaterials. Yuan-Chung Wang et al. demonstrated that the amount of deposition increases with the increase of applied voltage in Zinc oxide deposition. At low voltages, the assembly takes place at the edge of the conductive pattern only because the electric field strength at the edge of the conductive patterns is much strong there compared to the center of the conductive pattern. For example, at an applied potential of 2V and a withdrawal speed of 1 mm/min, 100nm silica NPs (suspended in deionized waters) assemble only at the edge of the conductive patterns as shown in figure 4.10(a). This experimental result is also confirmed by the electric field contours simulation results using finite volume modeling as shown in figure 4.10(b). The contour of the electric field strength indicates that the electric field at the edge of the conductive pattern is stronger than that at the center. However, when the applied potential is increased to 2.5 V, the 100nm silica particles are fully assembled on the surface of conductive patterns across the damascene template as shown in figure 4.10(c). This result indicates that the specific voltage ranges exist to achieve the full assembly result.

Figure 4.10 (a) Shows SEM micrograph for assembly at the edges of the pattern using 2 V
and 1 mm/min withdrawal speed (the gold nanowire grains are also shown in the center of gold pattern). 100 nm silica particles assembled only on the edge of gold pattern. (b) Contour of the electric field strength at 25 nm away from the surface of the conductive pattern during the electrophoresis assembly at 2.5V. The electric strength on the edge of the conductive pattern is stronger than that on the center. (c) SEM micrograph of a typical high-density 100 nm silica nanoparticle assembly result for assembly parameters voltage (2.5 V) and withdrawal speed (1 mm/min).

The effect of applied voltage was observed also in the silver NPs assembly process. The applied voltage was varied between 2.25 and 3.5 V for the silver NPs. Figure 4.11 shows the SEM images of silver NPs assembly on damascene template at the different voltage and the fixed pulling speed (10 mm/min). At 2.25 V, few silver NPs were assembled on the gold surface, whereas full assembly was achieved at 3.5 V. Unlike assembly of silica NPs, silver NPs were assembled on the center of gold surface even at low voltage 2.25 V, because the size of silver NPs is small enough to be attracted on the center of gold surface at 2.25 V. However, figure 4.12 shows clearly that the edge of gold pattern has stronger electric field resulting in the more assembly of silver NPs. The agglomerated silver NPs were assembled more on the edge of gold surface than on the center of gold surface. It is strong evidence that applied voltage is a dominant parameter on the result of assembly and geometry of the pattern is very effective on the uniformity of assembly of NPs.
Figure 4.11 The applied voltage effect on the assembly of silver NPs at the fixed pulling speed (10 mm/min). (a) 2.25, (b) 2.5, (c) 3, (d) 3.5 V. As increase of the applied voltage, denser assembly results were obtained.

Figure 4.12 Full assembly of the silver NPs. The agglomerated silver NPs were concentrated on the edge of the conductive pattern at 3.5 V and 10 mm/min pulling speed.
4.2.1.4 Effect of Nanoparticle Concentration

The concentration of nanomaterials in the suspension is also main parameter affecting the assembly result. In order to demonstrate the effect of nanoparticle concentration on assembly results, 30 nm silica NPs are diluted at different ratios. Figure 4.13 shows the assembly results when silica NPs suspension is diluted a) 100 times b) 50 times c) 10 times D) without dilution. The concentrations of NPs are 0.01 wt%, 0.02 wt%, 0.1 wt% and 1 wt%, respectively. The pH of the solution is fixed at pH 9. 2.5 V DC voltage and 10 mm/min pulling speed were applied for 20 seconds for all the experiments. There is no remarkable difference as the difference of the concentration of NPs shown in figure 4.13. However, when the gold pattern shape change to more complex and the space between the gold patterns is tiny, the concentration of nanoparticle is a crucial factor for achieving a precise assembly shown in figure 4.14. Figure 4.14 is fluorescence microscopy image of assembled fluorescent silica at different concentration of silica particles. At high concentration (figure 4.14 (a), the silica particles were assembled everywhere even though SiO$_2$ was hydrophobic surface by SAM. Decrease of the concentration improves the accuracy of assembly on the gold patterns. The precise assembly results can be achieved at 0.1 wt% concentration shown in figure 4.14 (c). Concentration of 0.01 wt% gives us partial assembly results shown in figure 4.14 (d). The concentration of NPs impacts more greatly on the complex designed than on the simple design. The concentration effect on the assembly should be thoroughly studied to obtain the precise assembly results.
Figure 4.13 SEM images of assembly results at different concentration of NPs (30 nm silica particles). (a) 0.01, (b) 0.2, (c) 0.1 and (d) 1 wt%.

Figure 4.14 Fluorescence microscopy images of assembly results at different concentration of NPs. (a) 1, (b) 0.2, (c) 0.1 and (d) 0.01 wt%.
4.2.2 SWNTs Assembly

4.2.2.1 Experimental Procedure

SWNTs (1~1.5 diameter and 600 nm ~ 1 µm length, 0.042 wt% suspended in DIW) obtained from Brewer Science were used for the assembly. 90% semiconducting SWNTs for biosensor application were obtained from SWeNT. For the voltage effect test, the applied voltage was varied from 1.5 V to 3 V. To assemble the SWNTs, the damascene template and a plain gold template were used as electrode and counter electrode, respectively and DC 2~5 V was applied to two electrodes for 20~60 sec. The damascene template and counter electrode were dipped into the nanomaterial suspension. The counter electrode is plain Cr/Au (5 nm/150 nm) layer. The distance between two electrodes was maintained at 5 mm. A Keithely 2400 DC power supply was used to apply the potential (1.5-5 V) between the two electrodes. The two electrodes were withdrawn using a dip coater (Single vessel system, KSV NIMA) after assembly with constant speed (1-25 mm/min) keeping voltage on.

4.2.2.2 Effect of Applied Voltage

SWNTs in the suspension have terminated carboxylic acid groups due to their purification process. When SWNTs are suspended in deionized water, these carboxylic acid groups impart a negative charge to the SWNTs. Electrophoretic force on the nanomaterials due to applied potential is directly proportional to the charge on the nanomaterials and the electric field strength. When the applied voltage is increased, the electrophoretic force increases proportionally resulting in increased amount of nanomaterials assembled on the conductive pattern. Figure 4.15 (a)-(d) clearly shows the significant effect of voltage on the SWNTs assembly. From these results, SWNTs started being assembled on the electrodes.
between 1.5 V and 2 V at fixed withdrawal speed (5 mm/min). Beyond a critical value of the applied potential, the barrier introduced by SiO$_2$ fails and nanomaterials can assemble on them as shown in figure 4.15 (d)

Figure 4.15 Shows are top viewed SEM micrographs of the damascene template after SWNT assembly for various applied potentials. (a) 1.5 V (b) 2 V (c) 2.5 V and (d) 3 V. The rest of the assembly parameters are kept constant. As can be seen from the images assembly efficiency on the metal electrode increases as a function of the applied electric field and beyond a critical value the SWNTs begins to assembly everywhere including the insulator.

4.2.2.3 Effect of Withdrawal Speed

Withdrawal speed is another main parameter to be able to determine not only the number of assembled SWNTs, but also alignment of SWNTs. Figure 4.16 shows the efficiency of SWNT assembly at different withdrawal speed. The SEM images which are shown in figure 4.16 exhibit the results of assembled SWNTs at the different withdrawal speeds. As increase withdrawal speed, the amount of assembled SWNTs was gradually
decreased. At 20 mm/min, only few SWNTs were involved in the assembly. Low withdrawal speed allows longer time SWNTs to be assembled on the template. Basu et al. already found that the amount of deposition increases with the increase of the assembly time. Thus, during the pulling the template out from the suspension, the high enough capillary force due the surface tension of water to be able to wash the SWNTs from the surface is generated, which affect the assembly efficiency of SWNTs.

![Image](image.png)

Figure 4.16 Shown are top viewed SEM micrographs of the damascene template after SWNT assembly for various withdrawal speeds. (a) 3mm/min, (b) 5 mm/min, (c) 10 mm/min and (d) 20 mm/min. The rest of the assembly parameters are kept constant. As the images, assembly efficiency on the metal electrode decreases with increasing withdrawal speed, which indicates the effect of removal moment acting on the SWNTs during withdrawal.

We have focused on the film thickness controllability by playing with the withdrawal speed. To investigate the thickness change as function of withdrawal speed, the withdrawal speed was varied from 3 to 15 mm/min, and AFM was used to measure the thickness before and after the assembly at the same position shown in figure 4.17 (a-d). Thickness
measurements were conducted on 5 devices at each condition. The thickness of assembled SWNTs decreases as increase of the withdrawal speed shown in figure 4.17 (e). The film thickness controllability directly leads to the resistance controllability. The resistance controllability is necessary in the biosensor to improve the sensitivity, but it will be fully explained in chapter 5.

Figure 4.17 (a-d) AFM image of before and after assembly at different withdrawal speed (top is before and bottom is after. (b) Thickness changes as function of withdrawal speed.
When SWNTs were assembled on a substrate, it is very important to control alignment of SWNTs. SWNTs network leads to a corresponding variation in the number of tube-to-tube junction, percolation and number of electron pathway, affecting the performance variation of device-to-device. Prashant et al. demonstrate the surface tension of water determine the alignment of SWNTs and direction as well. \cite{106, 107, 108} Figure 4.18 (a) shows how the alignment improves as a function of withdrawal speed. When the theta is closed to zero, the direction of assembled SWNT is parallel to the withdrawal direction. Low speed makes better alignments, but there is a trade-off to the process time. The angles of most SWNTs at 3 mm/min are reduced to less than 30 °. The angular changes at the different condition were characterized in 1µm x 1µm area by AFM as shown in figure 4.18 (b). The length of SWNTs used in the experiments is from 600 nm to 1 µm. Although the average length of SWNTs is shorter than the width of the conductive patterns on the damascene template, SWNTs located on the conductive pattern shows to be highly aligned with high density. Previous researches using self-assembly and fluidic assembly have reported that the alignment of SWNTs strongly depends on the relation between the length of SWNTs and the width of the pattern (trench) \cite{110, 111}. Park et al. assembled SWNTs on the desired position by an ion-exchange process \cite{110}. Figure 4.19 shows the angular alignment change of individual SWNTs as a function of tube length and the trench width. When the tube length is shorter than the width of trench, SWNTs is misaligned. To obtain the angle less than 30 °, the ratio of the tube length to the trench width has to be less than one.
Figure 4.18 (a) SWNTs alignment as a function of withdrawal speed at 3 mm/min, 5 mm/min, 10 mm/min and 15 mm/min. As increase of withdrawal speed, the SWNTs networks are more disordered. (b) AFM image of different withdrawal speed.

Figure 4.19 Plots of angular alignment of individual nanotubes versus length of the nanotube for trenches of three different widths (W=200 nm, 100 nm, 70 nm). Inset: schematic showing how the angular alignment \( \alpha \) is defined (0° is perfect alignment in a trench). By reducing the trench width to 70 nm, the angular variation was reduced from ±75° to less than ±30°. ¹¹⁰

The effect of ratio of the tube length to trench width on the alignment of SWNTs is clearly shown in the fluidic assembly using the capillary force and meniscus to put SWNTs down the hydrophilic surface defined on the hydrophobic surface. Figure 4.20 (a) shows the
schematics of alignment of SWNTs when SWNTs are diffused onto on the hydrophilic/hydrophobic surface by convective assembly. Figure 4.20 (b) is SEM image of assembled SWNTs using fluidic assembly which is very similar to the schematics shown in figure 4.20 (a). The trench width is 3 µm and the SWNTs used in this assembly are exactly same as SWNTs used in my experiments. Figure 4.20 (c) and (d) show the better alignment of SWNTs into 500 nm width of trench, which is shorter than the length of SWNTs. As shown figure 4.20 (b), (c) and (d), the alignment of SWNTs using fluidic assembly is disordered when the width of the trench is larger than the length of SWNTs.

The hypothesis is framed to explain the reason that the SWNTs were highly aligned even though the length of SWNTs is shorter than the width of the conductive pattern shown in figure 4.21. First, when DC voltage is applied to two electrodes (damascene template and counter electrodes), the SWNTs form the bundle of SWNTs and are aligned perpendicularly to the damascene template. It was already reported that the bundles of SWNTs are aligned perpendicularly to the electrode in DC voltage shown in figure 4.21 (b). Second, one end of SWNTs are anchored on the gold surface due to the charge of the carboxylic group on the end of SWNTs. Finally, the template is pulled out from the suspension and the surface tension force stretches out and aligns the anchored SWNTs. Aligned assembly results can be obtained even on the gold pattern of 10 µm width shown in figure 4.22. This result demonstrate that the alignment can be controlled even at large scale pattern and independent to the ratio of the length of SWNTs and the width of the pattern.
Figure 4.20 (a) schematic diagram of SWNTs assembly on hydrophilic surface between two hydrophobic surfaces. (b) SEM image of SWNTs (600 nm ~1 µm length) assembly into the trench of 3 µm width using fluidic assembly. (c) SEM image of SWNTs into the trench of 500 nm width. (d) High magnification image of figure (c).
Figure 4.21 (a) The schematics of proposed hypothesis of SWNTs assembly and alignment during the electrophoresis assembly (b) SWCNT-assembly and orientation in response to an applied dc electric field. The left to right sequence corresponds to an ON-OFF-ON cycle of the field with magnified sections at the bottom. 109

Figure 4.22 (a) SEM image of assembled SWNTs on the gold pattern of 10 µm width with the high alignment. (b) High magnification image of figure (a). SWNTs are highly aligned even though the ratio of the width of the pattern to the length of nanotubes is larger than 10.
4.2.3 Versatility of Assembly

Pentacene has been considered as alternative semiconductor material for the flexible devices such as a flexible display, a solar cell and a transistor due to its high charge carrier mobility and flexibility. However, the utilization of pentacene in the practical application is severely limited due to the poor solubility and photodegrade in a few minutes in solutions by the white light and oxygen in the air. Parmanik et al. introduce and synthesize water soluble pentacene to be able to adopt solution based processing methods such as ink-jet printing, drop casting and spin coating shown in figure 4.23. Newly developed water soluble pentacene is negatively charged in the water and can be attracted to the positive electrode using electrophoresis. Miller group supplied us the water soluble pentacene, which was used in our directed assembly as ink.

Figure 4.23 Left: synthesis of water soluble pentacene 4; right: a solution of 4 in water.

As shown in Figure 4.24 (b), that using high voltage pentacene 4 was over assembled and using low voltage much thinned assembly can be achieved (a, c or d). The best uniform assembly of pentacene 4 was achieved when 1.5 V was applied, for 5 second of assembly and 20 mm/min of pulling speed as shown in figure 4.24 (d). The AFM image shows some interesting nanoparticle formation during electrophoretic assembly using this particular condition.
Our assembly technique is adaptable and versatile to the various nanomaterials on the different pattern sizes and design shown in figure 4.25. It is strong evidence that most of the nanomaterials can be used as ink for the assembly and the assembly process can be used in broad areas. We have demonstrated that the offset printing technology can assemble and transfer various type of nanomaterials regardless of its electrical property (conductive, non-conductive and semiconductor) and shapes (cylindrical, spherical and molecule).
Figure 4.25 Versatility of assembly on damascene template using electrophoresis assembly; polymer NPs (PSL, 50 nm), silica NPs (100 nm), SWNTs on a large scale, cellulose, MWNTs on a large scale and SWNT with gold NPs (5 nm).
4.3 Transfer of nanomaterials

4.3.1 Experimental Procedure

Transferring onto a polyethylene naphthalate (PEN) substrate was accomplished using a Nanonex 2000 imprint tool, which uses a sample configuration as shown schematically in Fig. 4.26. This machine utilizes nitrogen gas as the pressure medium, allowing imprint pressures up to 600 psi, and three, 500 W tungsten-halogen lamps as the heat source, allowing a maximum temperature of 300 °C. A recipient substrate (PEN) is placed bottom and the damascene template is placed on top of recipient substrate. The substrates are placed in the imprinting machine between two silicone rubber sheets. The imprint process consists with three steps, pumping down, pre-imprint and main imprint. The nanomaterial is transferred onto a recipient substrate in the main imprinting step. The difference of temperature and pressure between the pre and main steps should be kept at 30 °C and 30 psi. For example, when the main temperature and pressure is 170 °C and 180 psi, the pre-temperature and pressure is adjusted at 140 °C and 150 psi. The desired pressure and sample temperature is controlled by N₂ gas and the tungsten halogen lamps. The thermocouple is located underneath the recipient substrate and monitors the change of temperature to feedback to the PID controller. Pumping time is two min and main imprinting process was conducted for two min. The chamber cooled quickly down keeping the pressure. After transfer process, a microscopy and SEM were used to check the transfer results on the recipient substrate.
To measure the electrical property of the transferred SWNTs, MWNTs and silver NPs, two electro metal pads were deposited on the ends of the transferred SWNTs and silver NPs. Figure 4.27 shows the procedure of metal pads deposition. A positive photoresist (S1813, MicroChem) was spun onto PEN substrate and optical lithography was conducted to define the patterns on the end of the transferred nanomaterials. 5 nm Ti and 150 nm gold were then deposited on the top of PEN surface using electron beam evaporation (MDC E-beam evaporator) considering the step coverage and lift-off process. The PEN substrate was immersed into acetone to lift-off the PR for five hrs. In our study, the post process including lift-off process for depositing the metal pads was successfully conducted.
Figure 4.27 Procedure of deposition of metal electrode to measure the electrical property of transferred nanomaterials.

Cylindrical objects such as those shown in the inset of figure 4.28 are used for the bending test. The PEN film with transferred SWNTs and deposited electrodes is taped to the circumference of the cylindrical object and measurements were taken in the bent state.

Figure 4.28 Optical images of the setup being used to measure the electrical properties at the desired bending radius.
4.3.2 Transfer of Nanomaterials

The efficiency of the transfer process is primarily determined by the differential adhesion strength between nanomaterials/template (NT) and nanomaterial/recipient substrate (NR). If the adhesion force between the nanomaterials and the template, $F_{NT}$ is smaller than adhesion force between nanomaterial and recipient substrate, $F_{NR}$, the nanomaterials could be transferred onto the recipient surface. However, if $F_{NT} > F_{NR}$, the nanomaterials will remain on the template surface. During the transfer process, the OTS SAM on the SiO$_2$ layer plays an additional role of acting as an anti-stiction layer when the damascene template is separated from the recipient substrate during transfer. The SAM helps the template to be easily separated from the recipient substrate without any polymer residue. This transfer process does not significantly affect the OTS layer and hence the surface energy of SiO$_2$, thereby enabling the damascene template to be reused without any further surface modification for several hundred cycles.

The adhesion force is also strongly affected by the surface energy and contact area between the nanomaterials and the recipient substrate. Therefore, the control of the surface energy is essential for a successful offset printing process. In general, the contact angle of the recipient substrate used is $\sim 70^\circ$, (moderately hydrophobic). In order to improve the adhesion force between assembled nanomaterials and the polymer recipient substrate ($F_{NT}$), a plasma treatment was used to enhance the hydrophilic nature of polymer surface. This surface treatment created of hydroxyl groups on the polymer surface increasing the surface energy on the polymer surface. After the surface treatment, the contact angle of polymer was reduced to less than $5^\circ$.

Once the surface energy of the recipient substrate was increased, the transfer
process was conducted by applying a pressure between the template and the recipient substrate and heating the substrate to a temperature regarding the thermal properties of the polymer. The temperature applied to the substrate during transfer process has an important effect on the transfer efficiency. Transfer process temperature needs to be higher than the glass transition temperature of the polymer onto which the assembled nanomaterials are transferred to. This temperature will cause the polymeric recipient substrate to engulf the assembled nanomaterials such that the contact area between the nanoelements and the substrate is sufficiently large resulting in a large adhesion force and a complete transfer of nanomaterials. This is demonstrated in figure 4.29. At lower than the glass transition temperature, the assembled SWNTs were partially transferred onto PEN film and most of the assembled SWNTs remained on the damascene template. 160 °C was chosen to be slightly higher than the glass transition temperature of the polymer substrate used (155 °C for PEN) in order to engulf the assembled nanomaterials such that a full transfer of the assembled nanomaterials can be achieved. Engulfing the assembled nanomaterials will significantly increase the contact area between the nanomaterials and recipient substrate and results in a sufficiently large adhesion force and a complete transfer of the assembled nanomaterials.

Figure 4.29 Shown images are top viewed SEM micrographs of the damascene template after transfer of SWNTs for various temperatures. (a) 135 °C, b) 150 °C and (c) 160 °C. The rest of the transfer process parameters are kept constant. As can be seen from the images transfer efficiency (absence of SWNTs on the metal electrode after transfer) increases as
increasing temperature and ~100% transfer is achieved at process temperatures higher than $T_g$ (155 °C) of the flexible substrate (PEN) on which it is transferred to.

Engulfing the assembled nanomaterials will significantly increase the contact area between the nanomaterials and recipient substrate and results in a sufficiently large adhesion force and a complete transfer of nanomaterials. Figure 4.30 (a), (b) and (c) show the damascene template before and after transfer, and PEN recipient substrate with transferred SWNTs, respectively. The transfer yield is close to 100%.

Figure 4.30 (a) Shown is SEM micrograph of the assembled SWNTs on the template before the transfer. (b) The damascene template after the transfer. (c) Transferred SWNTs on recipient substrate.

The optimized transfer condition studied in SWNTs transferring process was applied to the MWNTs transfer process. Figure 4.31 (a) is the assembly results of MWNTs on damascene template before the transfer process. MWNTs were fully assembled on the gold patterns and shows black color under microscopy. Figure 4.31 (b) shows the damascene template after transfer process. The color of gold patterns changed to the golden color, which means most of the assembled MWNTs were transferred onto recipient substrate shown in figure 4.31 (c). Figure 4.32 shows how the optimized condition works on the transfer process of silica particles. The gold pattern of damascene template was completely
covered with 30 nm silica particles through the assembly process shown in figure 4.32 (a). Figure 4.32 (b) is SEM image of transferred silica particles on PEN film. The assembled silica particles were completely transferred onto PEN substrate keeping the high density.

Figure 4.31 MWNTs assembly and transfer result using the optimized transfer condition. (a) MWNTs assembly on the damascene template. Dimension of gold patterns has 10 µm width and 1 mm length. (b) The microscopy image of the damascene template after transfer. The gold patterns are clear, which means that MWNTs are completely transferred onto recipient substrate. (c) The microscopy image of recipient substrate (PEN) after transfer. The black lines are transferred MWNTs.

Figure 4.32 The assembly and transfer result of 30 nm silica particles. (a) SEM image of 30 nm silica particles assembled on the damascene template (3 µm width and 100 µm length) with high density. (b) SEM image of transferred silica particles on PEN substrate using the optimized conditions. The assembled silica particles were completely transferred onto PEN.
substrate without an empty area.

In addition, pentacene 4 was successfully transferred from damascene template to flexible PET substrate using a temperature slightly above the glass transition temperature (100 °C) and a pressure (using N₂, 180 psi for 1 minute) utilizing a nanoimprint tool. The images of patterned pentacene 4 onto damascene template and flexible PET substrates before and after transferring respectively are shown in Figure 4.33 (a) and (b). In the future, the characterization of electrical properties will be needed.

Figure 4.33 Optical images of patterned pentacene 4 onto damascene template (a) and onto flexible PET substrates (b), before (in case of a) and after (in case of b) transferring.

4.3.3 Characterization of Transferred Materials

To measure the electrical property of these transferred SWNTs metal electrodes were fabricated by standard microfabrication processes (see the experimental procedure section). Figure 4.34 (a) shows the I-V measurement of the transferred SWNTs (2.4 µm channel width) on a PEN film as a function of channel length. The measured resistance is 3.2 kΩ and 12.2 kΩ for channel lengths 2 µm and 17 µm respectively. Figure 4.34 (b)
exhibits the robustness of the assembled SWNT structure under bending. The resistance increases linearly as a function of bending radius with a maximum change of 13% to that of the initial value. Figure 4.35 is a typical I-V curve of the transferred SWNTs. All 10 devices show a complete ohmic behavior between -100 mV and 100 mV. The average resistance of 10 devices is 270 kΩ and standard deviation is 36.1 kΩ. The resistance uniformity (1σ) is 15.9%.

Figure 4.34 (a) I-V characteristic curves of transferred SWNTs for various channel length and fixed channel width (2.4 µm). (b) Change in resistance of SWNTs channel (2.4 µm width and 30 µm length) as a function of bending radius of PEN substrate.
Figure 4.35 (a) I-V characteristic curves for 10 devices with a fixed channel width (2.4 µm) and length (60 µm). (b) Resistances of 10 devices.

Figure 4.36 (a) shows the transferred silver NPs with the gold pads on PEN substrate. The distance between the pads is 30 µm. The AFM results informing the profile of transferred silver NPs is shown in figure 4.36 (b). The thickness of the transferred silver NPs is around 250 nm regarding the embedded part of silver NPs. Figure 4.37 (a) and (b) are typical I-V curves of 4 µm and 30 µm channel length, respectively. In the case of 4 µm channel, the resistance is 15 Ω and 124 Ω is of 30 µm channel. The resistance proportionally increases as the increase of the channel length. The resistivity can be calculated based on the dimension of transferred silver NPs. The resistivity is around 310 x 10^{-8} Ω·m, which is similar to the commercially available silver paste.

Figure 4.36 (a) Transferred silver NPs with two metal pads on PEN substrate. The distance of two metal pads is 30 µm. (b) AFM image of transferred silver NPs whose height is around 200 nm.
The lift-off process using solvent such as acetone to lift off the photoresist limits the selection of the materials for the recipient substrate. For example, the poly carbonate (PC) or PMMA is dissolved in acetone in a few minute, so these polymers are not suitable as recipient substrate when the lift off process is carried out. In addition, a physical force to remove the PR in the lift off process could disturb the transferred nanomaterials on the recipient substrate, which directly affects the electrical properties of transferred materials. Therefore, we invented new post process to be able to deposit the metal pads without affecting the recipient substrate and the transferred nanomaterials. The two electro metal pads are also printed onto a recipient substrate using nanoimprint tool under the similar transfer condition as that of nanomaterials. Figure 4.38 shows the printing procedure of metal electrodes on the transferred nanomaterials. 100 nm gold electro pads are obtained on SiO\textsubscript{2} through the photolithography, e-beam deposition and lift off process. Unlike the lift-off process, adhesion layer (Ti or Cr) between the gold and the polymer is not necessary for this printing process. The recipient substrate where nanomaterials are already transferred
sits on the SiO$_2$ with gold pads and both are aligned under the microscope. The gold pads are then transferred onto the recipient substrate under the specific temperature and pressure considering the polymer properties using the nanoimprint tool. The adhesion force between the SiO$_2$ surface and gold pad is weaker than that between the recipient substrate and gold pad. The difference of adhesion force between two interface mentioned above drives the successful transferring the gold pads onto recipient substrate.

Figure 4.38 The printing procedure of gold electro pads onto the transferred nanomaterials on the recipient substrate. The metal pads printing method make the material selection as a recipient substrate to be free by excluding the lift off process.

Figure 4.39 (a) is the gold pad on SiO$_2$ surface fabricated by the post process including the photolithography, e-beam evaporation and lift-off process. The gold pads were aligned with the MWNTs which are already transferred onto PEN polymer in the previous step. The top of the PEN was down and then put it on the pre-patterned chip (a). The transfer process was conducted under the same conditions used in nanomaterial transfer process. Figure 4.39 (b) shows the template after transferring the gold pad. Most of
the gold pads were transferred. The transferred gold pad on PEN is shown in figure 4.39 (c) and (d) is the microscopy image of transferred MWNTs and gold pads. The fact that the deposited gold pads can be printed on top of the transferred MWNTs implies that a multi-layer can be built up using offset printing process if we assemble the gold particles on another damascene template having pads design.

![Figure 4.39](image)

Figure 4.39 (a) SiO$_2$ template with gold pads before the transfer, (b) After transfer, (c) PEN substrate with printed gold pads, (d) Microscopy image of printed MWNTs and gold pads.
Chapter 5 Applications

5.1 Background

SWNT is promising material for needs requiring high resolution and scalable detection range due to the high weight-normalized surface area (1600 m²·g⁻¹). The high weight-normalized surface area of SWNTs enables very sensitive response during the detecting biomaterials. In addition the excellent mechanical properties of SWNTs are another important feature to be utilized in the flexible device applications. The Young’s modulus is in the range of 1-2 TPa and the fracture stress is up to 50 GPa for bundles. A density-normalized strength of SWNTs is 50 times larger than that of steel wires.

The detection of glucose concentration is very critical not only to diabetes diagnosis but also to the food industry and environmental monitoring. Enzymatic sensors using glucose oxidase (GOD), an enzyme catalyst, is most common method to detect glucose and demonstrates high sensitivity, selectivity and promising speed. In addition there has been tremendous progress on the development of glucose sensor using SWNTs with immobilization of enzymes. Redox enzymes undergo a catalytic reaction cycle where groups in the enzyme temporarily change their charge state and conformational changes occur in the enzyme. This enzymatic activity can potentially be monitored during the sensing process. Figure 5.1 is an illustration of redox enzyme reaction, glucose sensing mechanism using the enzyme (GOD) on SWNTs.

In order to immobilize the enzyme on the SWNTs, covalent bonding and embedding method have been introduced and applied. For covalent functionalization of SWNTs the most common method involves generating the carboxylic acid groups on the
surface of SWNTs. The carboxylic acid groups are created by oxidation using strong acid like nitric acid. The strong acid introduces open end or defect on the side surface of SWNTs. The created carboxylic groups, defects and covalent bonding with enzymes can affect the properties of SWNTs. To prevent SWNT from being affected by covalent bonding processes, non-covalent bonding (π-π stacking) has been introduced. The large aromatic (π-electrons) hydrophobic surface of carbon nanotubes is suitable material for non-covalent interactions with suitable complementary molecules and macro(bio)molecules. These interactions can take place both on the inside and outside of carbon nanotubes. The non-covalent bonding method can keep the electrical properties of SWNTs and make response to the targeted biomolecules. Lee at al. demonstrated low cost, transparent and flexible glucose sensor using layer-by-layer assembly of SWNTs in figure 5.2 (a). GOD was covalently immobilized on the assembled SWNTs and detected glucose as shown in figure 5.2 (b).

![Figure 5.1 Schematic of glucose detection mechanism.](image-url)
Figure 5.2 (a) Glucose sensor based on SWNTs assembled by layer by layer assembly method, (b) Covalently bonded GOD on SWNTs and detection of glucose. 63

Few research have focused on the lactate sensor using SWNTs even though the lactate detection is very crucial in the evaluation of the severity of peripheral occlusive arterial disease and in assessing the efficiency of vasoactive drug treatment. Weber at al. demonstrated lactate sensors using SWNTs and lactate oxidase (LOD) for skin and sweat analysis, but more test involving repeatability, sensitivity and selectivity are needed. 132 In addition the sensing performance in a redox reaction strongly depends on the network of SWNTs. It is known that the electron transfer kinetics of the aligned SWNTs is 40 times faster than that of randomly disperse SWNTs, which is an advantage of well aligned SWNTs for achieving efficient electron transfer to bound redox active species in case of bioelectronics. 133 134 135 The primary sensing mechanism of lactate using enzymes (LOD) is same as that of glucose sensor described above. During the reaction between the lactate and LOD, the electrons are produced, which affect the current of working electrode. Figure
5.3 is the illustration of detection mechanism of lactate with LOD on SWNTs.

![Figure 5.3 Schematic of lactate detection mechanism.](image)

Urea detection is very crucial to diagnose various kidney diseases such as renal failure, urinary tract obstruction, hepatic failure and nephritic syndrome. Urea biosensors based on graphene was introduced very recently. However, despite an importance of urea detection, there is still lack of researches on the high resolution biosensor based on nanomaterials. Our urea sensor is also based on enzyme (urease) as glucose and lactate, but sensing mechanism of urea is a little bit different from that of glucose and lactate. In the case of urea reaction with urease, generation of hydroxyl group (OH-) change the current of working electrode instead of electron generated in the glucose detection. The reaction mechanism is illustrated in figure 5.4.

![Figure 5.4 Schematic of lactate detection mechanism.](image)
Table 5.1 is the concentration of glucose, lactate and urea in the human blood and sweat. The concentration of glucose in the blood is much higher than that in the sweat. However, the concentration of lactate and urea in the blood is lower than that in the sweat. Our goal to the developed biosensor is that the sensing resolution and range can cover the minimum concentration of blood and sweat for three biomaterials. In addition, we will improve the sensing stability well known as disadvantage of most of the enzymatic sensor.

<table>
<thead>
<tr>
<th></th>
<th>In Blood</th>
<th>In Sweat</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-glucose</td>
<td>&lt;3.89 mM</td>
<td>3.89-5.56 mM</td>
</tr>
<tr>
<td>L-lactate</td>
<td>&lt;70 mg/dl</td>
<td>70-100 mg/dl</td>
</tr>
<tr>
<td>Urea</td>
<td>&lt;1.17 mM</td>
<td>1.17-8.33 mM</td>
</tr>
</tbody>
</table>

5.2 Experimental Procedure

A flexible multi-detecting biosensor based on SWNTs was successfully fabricated through the offset printing technique. 2-D SWNTs structures were printed on the PEN substrate and two electro metal pads were deposited on the ends of SWNTs by microfabrication and lift-off process illustrated in figure 4.27. Figure 5.5 (a) is photography of the flexible biosensors used in the biosensor experiments. The SWNTs were located between two metal electro pads shown in figure 5.5 (b). The distance between two electro pads is 60 µm.
Figure 5.5 (a) Photography of flexible biosensor based on PEN film. The sensor was fabricated through the offset printing process and the post processes to form the electro metal pads. (b) Microscopy image of flexible biosensors. Two electrodes sit on top of SWNTs with 60 µm distance considering the area where the enzymes are reacted with biomaterial. (c) Illustration of functionalization with the linker and GOD, LOD and URE.

For the non-covalent functionalization of the SWNTs surface, transferred SWNTs (90% semiconducting SWNTs, SWeNT) on PEN were incubated with 6 mM of 1-pyrenebutanoic acid succinimidyl ester (PASE) as a linker in a pure organic solvent dimethylformamide (DMF) for 2h at the room temperature. The SWNTs were rinsed with pure DMF and DI water to wash away any excess reagent. To immobilized covalently GOD, LOD, and URE on the linker functionalized on SWNTs, each SWNTs bundle device was exposed to 1 mM of each enzyme in bicarbonate buffer (pH 7.4) overnight at the room temperature, rinsed thoroughly in DI water and phosphate buffer saline (PBS, pH 7.4), and then gently dried with nitrogen gas. To deactivate and block the excess reactive groups remaining on the CNT surface, 100 mM ethanolamine was added onto the channel region of the SWNTs template and incubated for 30 min. The PASE modified assembled SWNTs template was then rinsed with PBS buffer (pH 7.4). Fig. 5.5 (c) shows a basic structure of the modified biosensor with GOD, LOD, and URE-immobilized SWNTs plate using non-covalent bonding with a simple device for detecting D-glucose, L-lactate, and urea. The
current change of the biosensor during real time detection was measured by a probe station (4156C, Agilent Technologies Co., Ltd., USA) at an ambient condition. 100 mV was maintained between the source and the drain, and then the current was detected while the different concentrations of biomaterials in either the buffer or the artificial sweat was successively added on the working electrode (SWNTs) of the biosensors using micro pipet.

As we mentioned early, to prevent the electrical property of SWNTs from being affected by covalent bonding process, non-covalent bonding (π-π stacking) was used in this study. When SWNTs were functionalized with PASE by π-π stacking, the stacked PASE on SWNTs interrupts the movement of electron on SWNTs resulting in the increase of resistance of SWNTs. After the functionalization process, the enzymes immobilized on the linker by covalent bonding also influence the resistance of SWNTs. Figure 5.6 shows the resistance changes of SWNTs after the functionalization with linker and immobilization with glucose oxidase. C, L and G stand for SWNTs, linker and glucose oxidase, respectively in figure 5.6. As the linker and glucose oxidase were added on SWNT, the resistance was gradually increased. Figure 5.6 (a) is the resistance change of metallic/semiconducting mixed SWNTs. The ratio of the resistance of the bare SWNTs (R_o) and the resistance of SWNTs with the linker and GOD (R_i) is 1.3 in the case of mixed SWNTs. Semiconducting SWNTs shows larger ratio (1.7) than the mixed SWNTs shown in figure 5.6 (b), which implies that the biosensor based on semiconducting SWNTs could be more sensitive and stable. Figure 5.7 is transmission electron microscopy (TEM) images before (a) and after (b) the immobilization of GOD on SWNTs. Figure 5.7 (b) shows that GOD was immobilized onto SWNTs by covalent bonding.
Figure 5.6 The resistance change of SWNTs before and after functionalization with the linker and enzyme (GOD). (a) The resistance change of metallic and semiconducting mixed SWNTs. (b) The resistance change of 90% semiconducting SWNTs before and after functionalization. In both cases, the resistances gradually increase by adding the linker and enzymes.

Figure 5.7 TEM images of SWNTs (a) before and (b) after enzyme (GOD) immobilization. The clusters of enzyme were clearly shown in (b).

Figure 5.8 is the resistance change of mixed SWNTs (figure 5.8 (a)) and current change of semiconducting SWNTs (figure 5.8 (b)) when the different concentration (4 mM,
8 mM, 12 mM, 16 mM and 20 mM) of glucose was injected on the device every 60 sec. The response of mixed SWNTs is very noisy and not sensitive to the glucose, but semiconducting SWNTs based device exhibits clear response to the injection of glucose with minimal noise. The responsiveness of mixed SWNTs is 0.16 when the 20 mM glucose was injected, whereas that of semiconducting SWNTs is around 1.25. The responsiveness of semiconducting SWNTs based sensor is eight times higher than that of mixed SWNTs based sensor. The initial data obtained from the detecting test using the two different types of SWNTs indicates that the original resistance of SWNTs should be high enough to detect with high sensitivity and clear response signal. Consequently semiconducting SWNTs were used as based materials in this study.

Previous results indicate that use of semiconducting SWNTs provides more sensitive and stable response during the glucose detection due to the initial resistance. Although low resistance can give us high current value and decrease the power consumption, the change of current is not sensitively responded to the electron generated in the redox enzyme reaction. Figure 5.9 exhibits the correlation between the initial resistance and the responsiveness of the glucose sensor. The initial resistance of transferred SWNTs was controlled in the assembly process by adjusting pulling speed as described in chapter 4. When the initial resistances were 0.6 MΩ and 1.2 MΩ, the responsiveness to the glucose was not only highest, and also clear: ΔI/I₀ increased to one when 20 mM concentration was injected. The responsiveness was decreased as increasing resistance up to 4.5 MΩ. The real time detection graph (figure 5.9 (b)) exhibits the signal has noise resulting in the error of final value. At 9.7 MΩ, the current was not changed despite the glucose addition. The reason that the initial resistance significantly affects the responsiveness of the sensor can be
explained by the correlation between the area of SWNTs and the amount of electron generated in redox enzyme reaction. If the resistance is very low which means that many carbon nanotubes have enzymes, although the huge number of electron will be generated during the enzyme reaction, the influence of electron on the current could be low due to the very low initial resistance. If the resistance is very high, closed to 10 MΩ, the current could be sensitively responded to the generated electron, but the number of electron generated in the reaction process is not enough to increase the current value. Thus, the effect of the noise which can be come from the equipment or environment on the current could be high enough to disturb the responsiveness and make the signal be very noisy. These results are strong evidence that the window of the initial resistance to be able to obtain high and clear responsiveness and sensitiveness as well exist in the field of sensor. In conclusion, most of the tests were conducted using a device whose resistances were in our resistance window for this study.

Figure 5.8 The resistance and current change of the metallic/semiconducting mixed SWNTs in (a) and 90% semiconducting SWNTs in (b). 4, 8, 12, 16 and 20 mM glucose were added on the both sensor every 60 sec.
Figure 5.9 Glucose detection results on the different initial resistance. (a) is the plot of glucose concentration and the corresponding current response. (b) Real time glucose detection from 4 mM to 20 mM. High responsiveness was achieved at 0.6 MΩ and 1.2 MΩ, whereas significant responsiveness cannot be obtained at 9.7 MΩ.

5.3 Glucose Sensor

5.3.1 Detecting Glucose in Buffer

The sensing repeatability is an important parameter for a glucose sensor, because the strip used in most of the commercially available glucose sensor is one-time-use. A SWNTs-based sensor is continuously characterized 10 times under the same experimental conditions. 4 mM ~20 mM glucose was added on the SWNTs every 60 sec. Figure 5.10 shows the typical amperometric response at SWNTs electrode during the successive addition of different concentration of glucose. All amperometric response plots demonstrate similar behavior in figure 5.10 (a) and (b). In addition, the amperometric response was linearly increased as increasing concentration of glucose shown in figure 5.10 (a). The SWNTs electrode exhibits a fast and sensitive response to the glucose variation and
immediately reached steady-state current shown in figure 5.10 (b).

Figure 5.10 An amperometric response of SWNTs upon successive additions of glucose every 60 sec from 4 mM to 20 mM in the buffer. (a) A typical current change with the different concentration of glucose. (b) Real time of D-glucose detection 10 times. The response of current is linear to the concentration of glucose. Real time detection graph exhibits very clear response to the glucose without noise signal. From one to 10 times, the response plot is impressively similar.

Long-term stability is another important factor in the field of biosensor, because the sensors are operated in an aqueous environment or real human blood which contains various chemical components to affect the enzyme itself and enzyme activity. The ideal case is that the responsiveness of biosensor should be maintained for a long period of time, but the stability is the disadvantage of enzymatic biosensors. In order to investigate the stability of the glucose biosensor, the amperometric response was recorded every 24 h for 14 consecutive days at 100 mV under the same experimental conditions. The glucose diluted with PBS buffer used in the experiments was freshly prepared for the every test. The responsiveness to the glucose is relatively consistent up to two weeks shown in figure 5.11 (a). The slopes from the first day to six days are comparatively paralleled and the responsiveness is also relatively high. After a week, the responsiveness was slowly decreased as shown in figure 5.11 (a). Figure 5.11 (b) is real time detection recorded every
24 hr. A short response time and steady-stable time maintained until two weeks.

A sensitivity of the developed glucose sensor was investigated in the range of 0~150 mg/dl. The different concentrations of glucose from 100 mg/dl to 100.5 mg/dl by 0.1mg/dl were injected on the working electrodes in the first. After that, 1 mg/dl was added from 101 mg/dl to 105 mg/dl and 10 mg/dl was added from 110 mg/dl to 150 mg/dl every 60 sec successively. In the beginning, despite low concentration change, the current response to the glucose is relatively high shown in figure 5.12. However, the current response was gradually decreased in the range of 110~150 mg/dl even with high concentration change (10 mg/ml). The reason that the current responsiveness according to the concentration was not linear is attributable to the process of real time detection. During the real time detection, the different concentrations of glucose were accumulated on the working electrode. First injecting amount is exactly same as the original concentration, but from the second injection, the real concentration is lower than the injected concentrations. Another reason involves enzyme activity. The enzyme activity dramatically goes down during the real time detection test.

Figure 5.11 The long-term stability of the glucose sensor. (a) A current-time response of SWNTs glucose sensor every 24hr for 14 consecutive days. (b) Real time detection curve.
5.3.2 Detecting Glucose in Sweat

As we mentioned in the background, the human sweat contains glucose, so if we detect the glucose from the sweat, this technique will have huge potential in the field of glucose monitoring system. The sweat, unlike to buffer, has many chemical components such as sodium, calcium and potassium which could affect the enzyme activity and disturb the reaction between the glucose and enzyme. Figure 5.13(a) and (b) are a typical amperometric response to the glucose concentration in the artificial sweat. The sensor was characterized continuously 10 times. All current responses are considerably linear to the concentration of glucose. However, the detecting variation in the sweat is larger than the detecting result in the buffer shown in figure 5.10. The response time and sensitivity are still short and high enough to detect 0.1 mM glucose in the sweat. In the background, we already showed the range of glucose concentration in the sweat (0.04 mM~0.06 mM). The minimum detectable concentration of our sensor (0.1mM) is too large to detect glucose in
sweat. Therefore, an additional experiment to improve the resolution should be conducted in the future.

Figure 5.13 Current-time response of SWNTs upon successive additions of glucose every 60 sec from 4 mM to 20 mM in the sweat. (a) A typical current change with the different concentration of glucose in sweat. (b) Real time of D-glucose detection 10 times. The response of current is linear to the concentration of glucose. Real time detection graph exhibits very clear response to the glucose without noise signal.

5.4 Lactate Sensor

5.4.1 Detecting Lactate in Buffer

A SWNTs-based sensor is continuously characterized 9 times under the same experimental conditions. 1g/L ~5 g/L lactate was successively added on the working electrode (SWNTs) using a micropipette every 60 sec. Figure 5.14 shows the typical amperometric response at working electrode during the successive addition of different concentration of lactate. All amperometric response plots demonstrate similar behavior in figure 5.14 (a) and (b). In addition, the amperometric response was linearly increased as increasing concentration of lactate shown in figure 5.14 (a). All linear lines are considerably paralleled. The SWNTs electrode exhibits a fast and sensitive response to the lactate
variation and immediately reached steady-state current shown in figure 5.14 (b).

Figure 5.14 An amperometric response of SWNTs upon successive additions of lactate every 60 sec from 1 g/L to 5 g/L in the buffer. (a) A typical current change with the different concentration of lactate. (b) Real time of lactate detection 10 times. The response of current is linear to the concentration of lactate. Real time detection graph exhibits very clear response to lactate without noise signal. From 1 to 9 times, the response plot is impressively similar.

In order to investigate the stability of the lactate detection, the amperometric response was recorded every 24 h for 9 consecutive days at 100 mV under the same experimental conditions. The different concentrations of lactate were prepared diluting it with PBS buffer and it was freshly prepared for the every test. Although the slope in I-Concentration graph has small difference among the lines, the responsiveness to the lactate is relatively consistent up to 9 days shown in figure 5.15 (a). 5.15 (b) is real time detection recorded every 24 hr. A short response time and steady-stable time maintained until 9 days.
A sensitivity of the developed lactate sensor was investigated in the range of 0~100 mM. The detecting resolution of the lactate sensor is 0.001 mM shown in figure 5.16. When 0.001, 0.002 and 0.005 mM were successively injected onto the working electrodes, the fast response and short reaching time to the steady-state was exhibited in figure 5.16. In the most of the range, the reaction is very fast in reaching a dynamic equilibrium upon each addition of the sample solution, generating a steady-state current signal within 2 to 3 sec. However, the current response was gradually decreased in the range of 10~50 mM even with high concentration change. The reason that the current responsiveness according to the concentration was not linear is attributable to the process of real time detection. During the real time detection, the different concentrations of lactate were accumulated on the working electrode. First injecting amount is exactly same as the original concentration, but from the second injection, the detected concentration is lower than the injected concentrations. The sensitivity of lactate sensor can cover the normal range of lactate.
concentration in the human blood and even the sweat.

Figure 5.16 Sensitivity of the developed lactate biosensor. The highest resolution is 0.001 mM which is high enough resolution to detect the lactate in the blood.

5.4.2 Detecting Lactate in Sweat

Figure 5.17(a) and (b) a typical amperometric response to the lactate concentration in the artificial sweat. The sensor was characterized continuously 10 times with the different concentrations of lactate regarding the range of lactate concentration in the sweat (approximately 20~60 mM). All current responses are considerably linear to the concentration of lactate and the change of current is high enough to detect the lactate. However, the linear lines are more spread out comparing the results in the buffer shown in figure 5.14. Figure 5.17 (b) shows very short response time and steady-stable time even in the sweat. The very sensitive current responses were observed in the whole range from 10 mM to 60 mM, which can deal with the range of lactate concentration in sweat.
Figure 5.17 Current-time response of SWNTs upon successive additions of lactate every 60 sec from 10 mM to 50 mM in the sweat. (a) A typical current change with the different concentration of lactate in the sweat. (b) Real time of lactate detection 10 times. The response of current is linear to the concentration of lactate. Real time detection graph exhibits very clear response to the lactate without noise signal.

5.5 Urea Sensor

5.5.1 Detecting Urea in Buffer

A SWNTs-based sensor is continuously characterized 9 times under the same experimental conditions. 10 mg/dl~50 mg/dl urea was successively added on the working electrode (SWNTs) using a micropipette every 60 sec. Figure 5.18 shows the typical amperometric response at working electrode during the successive addition of different concentration of urea. All amperometric response plots demonstrate similar behavior in figure 5.18 (a) and (b). In addition, the amperometric response was linearly increased as increasing concentration of urea shown in figure 5.18 (a). All linear lines are considerably paralleled. The SWNTs electrode exhibits a fast and sensitive response to the urea variation and immediately reached steady-state current shown in figure 5.18 (b).
Figure 5.18 An amperometric response of SWNTs upon successive additions of urea every 60 sec from 10 mg/dL to 50 mg/dL in the buffer. (a) A typical current change with the different concentration of urea in the buffer. (b) Real time of urea detection 9 times. The response of current is linear to the concentration of urea. Real time detection graph exhibits very clear response to urea without noise signal. From 1 to 9 times, the response plot is impressively similar.

In order to the stability of the urea detection, the amperometric response was recorded every 24 h for 9 consecutive days at 100 mV under the same experimental conditions. The different concentrations of urea were prepared diluting it with PBS buffer and it was freshly prepared for the every test. Although the slope in I-Concentration graph has small difference between the each line, the responsiveness to the urea is relatively consistent up to two weeks shown in figure 5.19 (a). Figure 5.19 (b) is real time detection recorded every 24 hr. A short response time and steady-stable time maintained until two weeks.
A sensitivity of the developed urea sensor was investigated in the range of 0~100 mM. The detecting resolution of the urea sensor is 0.001 mM shown in figure 5.20. When 0.001, 0.002 and 0.005 mM were successively injected onto the working electrodes, the fast response and short reaching time to the steady-state was exhibited in figure 5.20. In the most of the range, the reaction is very fast in reaching a dynamic equilibrium upon each addition of the sample solution, generating a steady-state current signal within 2 to 3 sec. However, the current response was gradually decreased in the range of 10 ~50 mM even with high concentration change. The reason that the current responsiveness according to the concentration was not linear is attributable to the process of real time detection. During the real time detection, the different concentrations of urea were accumulated on the working electrode. First injecting amount is exactly same as the original concentration, but from the second injection, the detected concentration is lower than the injected concentrations. The sensitivity of urea sensor can cover the normal range of urea.
concentration (1~9 mg/dl) in the human blood.

![Graph showing sensitivity of the developed urea biosensor.](image)

Figure 5.20 Sensitivity of the developed urea biosensor. The highest resolution is 0.001 mM which is high enough resolution to detect the urea in the blood.

### 5.5.2 Detecting Urea in Sweat

Figure 5.21 (a) and (b) a typical are amperometric response to the urea concentration in the artificial sweat. The sensor was characterized continuously 10 times with the different concentrations of urea regarding the range of urea concentration in the sweat (approximately 50~200 mM). All current responses are considerably linear to the concentration of urea and the change of current is high enough to detect the urea. However, the linear lines are more spread out comparing the results in the buffer shown in figure 5.18. Figure 5.21 (b) shows very short response time and steady-stable time even in the sweat. The very sensitive current responses were observed in the whole range from 0.2 M to 1 M, which can deal with the range of urea concentration in sweat.
Figure 5.21 Current-time response of SWNTs upon successive additions of lactate every 60 sec from 0.2 M to 1 M in the sweat. (a) A typical current change with the different concentration of urea in the sweat. (b) Real time of urea detection 10 times. The response of current is linear to the concentration of urea. Real time detection graph exhibits very clear response to the urea without noise signal.

5.6 Cross Effect in Buffer

One of unique properties of enzymes that makes them such important as diagnostic and research tools is the specificity they exhibit relative to the reactions they catalyze. However, all kinds of enzymes do not have only absolute specificity. Some of them show either group specificity or linkage specificity. The cross effect test among the glucose, the lactate and the urea is necessary to utilize the developed biosensor as a multi-biosensor to detect three different biomolecules at the same time. In order to investigate the cross effect among the three different enzymes and biomolecules detected in our study, a specific biomolecule ‘A’ mixed with either one or two different biomolecules was injected on the working electrodes functionalized with a enzymes which can react with biomolecule ‘A’. For example, the different concentration of glucose mixed with lactate, urea or lactate/urea was injected on the working electrodes functionalized with GOD. Figure 5.22 (a) shows the
cross effect of lactate and urea on the glucose detection. I-concentration line of only glucose perfectly matches the line of glucose with urea, which means that urea does not disturb the glucose detection. However, as shown in figure 5.22 (a), the response lines to glucose with lactate and glucose with lactate and urea shift, which indicates that the glucose detection is affected by the lactate, but is not strong enough to disturb the detecting the glucose. Figure 5.22 (b) shows the cross effect of the glucose and urea on the lactate detection. There is no remarkable effect on the lactate detection. The effect on the urea by the glucose and the lactate is shown in figure 5.22 (c). There is imperceptible change among the graphs. In the results, the developed biosensor can detect D-glucose, L-lactate, and urea at the same time.

Figure 5.22 The cross effect of glucose, lactate and urea. (a) the cross effect of lactate and urea on the glucose detection, (b) the cross effect of glucose and urea on the lactate detection, (c) the cross effect of glucose and lactate on the urea detection.

5.7 Oxytetracycline Sensor

A flexible aptamer-based single walled carbon nanotubes (SWNTs) biosensor containing probe deoxyribonucleic acid (DNA) immobilized on functionalized SWNTs was also developed for detecting Oxytetracycline (OTC), which is antibiotics, using offset printing technology. The developed sensing mechanism of the SWCNTs aptamer-based
biosensor for detection of OTC is represented in Figure 5.23. We employed an indirect detection method including a pre-mixing step to incubate samples containing different concentrations of OTC with a fixed amount of OTC-aptamer. Upon the completion of binding between OTC and its specific aptamer, the remaining free aptamers concentration is inversely proportional to that of OTC in the water sample.

Figure 5.23 Schematic of Oxytetracycline detection mechanism using the aptamer on SWNTs based sensor:

A typical resistance change at different concentration of OTC is shown in figure 5.24. The increase of OTC concentration proportionally reduced number of free aptamer resulting in increasing the resistance of SWNTs.
Figure 5.24 Resistance change as increase of OTC concentration.
Chapter 6 Summary and Future work

Summary

In this dissertation, we developed reusable template having damascene structures, which can be reused more than 100 times in the directed assembly and transfer cycle without any additional process. We have demonstrated that a reusable damascene template can be successfully used to conduct multi-scale offset printing of different types of patterned nanomaterials efficiently and accurately. Flexible multi-biosensor and chemical sensors are successfully fabricated through the developed printing technology with high throughput.

A damascene template was invented to overcome the shortcomings of the previous templates (3d wire template and trench template) for electrophoresis assembly such as not reusability, non-uniform electric field and peeling off in the transfer process. All conductive structures of damascene template are connected to the conductive film underneath insulating layer and the template is completely flat. In order to fabricate the damascene template, CMP process was added on the general micro-fabrication. In the template fabrication process, the patterning process was carefully chosen regarding the processing speed, pattern size and purpose. NIL shows not only high process speed but also capability to nano-scale feature size. CMP process was investigated to minimize the geometry effect on the uniformity of an electric field during the assembly process through the control of velocity and pressure. In addition, self-assembled monolayer was applied to the damascene template to prevent the nanomaterials from being assembled on the SiO$_2$ due to the electric field coupled with high surface energy on SiO$_2$. This selective surface energy control process allows the nanomaterials to be assembled on the desired locations.
NPs were successfully assembled at the desired locations with high density and good uniformity by controlling assembly parameters such as the applied voltage, concentration of nanomaterials and withdrawal speed of the template. Increase of applied voltage increases the efficiency of assembly of NPs and SWNTs. Electric field contour obtaining from the modeling results matches well to the experimental results. Also, the geometry effect of damascene template on the uniformity of the electric field was simulated and predicted using modeling tool. SWNTs were also uniformly assembled on the damascene template. We demonstrate that the change of withdrawal speed influences not only the thickness of assembled SWNTs, but also alignment of SWNTs. Random network of SWNTs was obtained at relatively faster withdrawal speed (15 mm/min), whereas highly aligned SWNTs was shown at lower speed (5 mm/min). In addition, these excellent template and assembly process have enabled to assemble other materials such as MWNTs, cellulose, pentacene molecule and polymer/metallic particles at large scale with good uniformity. The versatility of assembly implies that this printing process can be applied to the most of nanomaterials and various applications according to the properties of nanomaterials.

The assembled nanomaterials are then transferred onto a flexible substrate without the need for sacrificial layer or any intermediate steps. The simplicity of the transfer process enables to minimize the variables, which could be generated during the process. When we applied the temperature higher than Tg of the polymer, 100% transfer yield could be achieved on the assembled NPs, SWNTs and MWNTs, which is strong evidence that the temperature higher than Tg makes the polymer to 3-dimensionally grab the assembled nanomaterials. Electrical characterization to the transferred materials was conducted to
evaluate the device to device variation, controllability of SWNTs resistance and conductivity of silver NPs.

The flexible biosensors based on SWNTs were fabricated through the developed printing process and the post process. We learned that the sensitivity of the sensor strongly depends on the first resistance and number of SWNTs. The best resolution results were obtained from the range of 4 kΩ~1 MΩ. This result explains why resistance controllability of transferred SWNTs is critical for the sensing devices during the assembly and the transfer. In order to detect glucose, lactate and urea, the enzymatic biosensor was used in our experiment. The enzymes were non-covalently immobilized on the transferred SWNTs to avoid the complicated chemical treatment steps and side effect generated when the enzymes are the covalently attached to the SWNTs. The developed flexible biosensor show excellent sensitivity, repeatability, scalability and selectivity on glucose, lactate and urea in the buffer and the artificial sweat. The obtained sensitivity of glucose using our device is 0.1 mM, which is 10 times higher than that of commercially available glucose sensors. In addition the sensitivity (0.001mM) of lactate and urea can cover the range of concentration of lactate and urea in the human sweat. We demonstrate that the sensor can be reused up to 10 times at the same day with uniform detection signal and be reused up to two weeks. The repeatability and stability of the sensor overcome the general shortcomings that enzymatic biosensors show before. Besides, simple chemical sensor based on the same platform used in biosensor with aptamer DNA was developed and showed high sensitivity results on oxytetracycline detection.
Future work

We developed a reusable template, which is specially designed for directed assembly and transfer, and the multi-scale offset printing technology. This study successfully demonstrates that developed template and printing process enables high-rate manufacturing of flexible devices such as a biosensor and chemical sensor. Although the potential and capability of this technology for fabricating flexible device with high throughput have been demonstrated, there are still plenty of research topics to be able to pave the way for the flexible device fabrications. Several suggestions for future research are as follows:

- Fundamental study on SWNTs alignment mechanism as function of pulling speed.
- Simple logic device using multi-layer printing process.
- Nano-scale device fabrication using nanoscale assembly and transfer.
- All assembly and transfer process were conducted on a chip scale not 3 inch wafer-scale even though the damascene templates were fabricated using 3 inch wafer. We need to conduct assembly process on the wafer scale.
- For commercialization and ramping of process speed, fully automatic tool for offset printing process should be developed.
- Development of various applications of nanomaterials through the offset printing such as flexible transistor using SWNTs and pentacene, chemical sensor using SWNT with gold particles and transparent conductance using MWNTs or metallic NPs.


82. Pop, E.; Mann, D.; Wang, Q.; Goodson, K.; Dai, H., Thermal conductance of an individual single-wall carbon nanotube above room temperature. *Nano Letters*
2006, 6 (1), 96-100.


93. Byon, H. R.; Choi, H. C., Network single-walled carbon nanotube-field effect transistors (SWNT-FETs) with increased Schottky contact area for highly sensitive biosensor applications. Journal of the American Chemical Society 2006, 128 (7), 2188-2189.


97. Andricacos, P. C.; Uzoh, C.; Dukovic, J. O.; Horkans, J.; Deligianni, H., Damascene copper electroplating for chip interconnections. IBM Journal of Research and


