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DETERMINISTIC ASSEMBLY OF

FUNCTIONAL NANODEVICES ONTO SILICON CIRCUITS

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by

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ABSTRACT

Bottom-up integration of nanostructures offers a promising method to achieve material diversity for chemical and biological applications, often considered unattainable by conventional top-down fabrication. Thus, deterministic integration of nanostructures such as nanowires and nanoshell spheres on silicon CMOS circuitry represents a significant step toward cross-reactive silicon CMOS chip where different types of offchip synthesized sensory materials are merged. Applying this deterministic bottom-up integration to substrate or circuit eliminates the constraints of thermal budget, chemical compatibility, lattice mismatch between nanostructures to be assembled and substrate. This thesis discusses a deterministic assembly strategy for nanowires and spheres and their integrations onto silicon CMOS circuitry for electronic microsystem applications.

The nanowire assembly structure was designed to create a dielectrophoretic attractive force toward the electrode gap, resulting in uniformly-spaced rhodium nanowire array due to mutual electrostatic interaction between assembled nanowires. Systematic investigation reagarding nanowire array formation reveals that stronger longrange dielectrophoretic forces attract more nanowires at the electrode gap, forming lessspaced array while stronger electrostatic nanowire interaction results in the larger spacing within the array. Thus, their interplay tends to determine the average spacing between the assembled nanowires.

Based on understanding the electrostatistic interaction between assembled nanowires, lithographically defined wells with a localized electric field determines the final alignment position of assembled rhodium nanowires on a substrate. Post-assembly process using electrodeposition and subsequent lift-off process completes monolithic integration of rhodium nanowires while preserving nanowires assembled only within the recessed region. Individual rhodium nanowire assembly yields exceeding 95% were obtained at nanowire densities $>10^5$ /cm² with a submicron registration accuracy. PEDOT/ClO₄ nanowire chemical sensors are also fabricated to demonstrate functional nanowire integration for on-chip sensing.

This thesis also describes a bottom-up strategy for fabricating ultra-high-density cross-point sensor arrays (>10⁷ elements/cm²) that uses fluidic assembly to position the functional nanoshell microspheres between lithographically-defined electrodes on-chip. Cross-point array structure is designed to accommodate single spherical particles at each cross-point and make them electrically connected to upper and lower access electrodes. As proof-of-concept, PEDOT nanoshell microspheres are assembled to fabricate chemical sensor devices for on-chip application. Individually addressing each PEDOT nanoshell sphere enables monitoring of an array of sphere for conductance change by chemical gas, solvent, humidity.

Due to upper and lower electrodes format and intrinsic form factor of spheres, it is advantageous to achieve high integration density compared to nanowires with a high aspect ratio. Additionally, this architectural framework combines the advantages of large surface-to-volume ratio particle-based sensor elements with high sensor redundancy to enhance performance metrics such as detection sensitivity and signal-to-noise ratio.

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Chapter 1

INTRODUCTION

1.1 Heterogeneous Nanostructure Integration: An Introduction

Last decades have witnessed that the continued scaling of complementary metaloxide-silicon (CMOS) devices has been a mainstream of semiconductor research and industry. This continuous downscaling of minimum dimensions of CMOS transistors led to integration of their increasing number for better performance in digital function-based chips such as microprocessor, memories, and logic devices, as described by Moore's law. One can expect that this trend, More-*of*-Moore, will be continued to extend Moore's law over next decades until its fundamental limit is met.

In addition to this conventional scaling of CMOS transistors, as shown in Figure 1-1, adding non-digital functionality to silicon-based CMOS circuitry represents post-CMOS technologies in next decades. Figure 1-1 also suggests that this functional diversification on a single chip, More-*than*-Moore, will be continuously innovated and gain further momentum toward realization of system-on-chip (SOC) and system-onpackage (SIP) while keeping pace with device scaling. Non-digital functionalities include RF communication, power control, sensors, actuators, and biological functionality which often favors the use of non-silicon based materials. For instance, narrow bandgap semiconductors¹ that operate at lower voltages than silicon will give digital logic circuits with lower power consumption without sacrificing operation speed. Polymeric² and metal oxide materials³ designed to produce a large electronic response to chemical or biological agents offer unpredescented sensing capabilities to silicon-based CMOS circuit.





Bandgap-engineered compound semiconductor materials with a direct bandgap^{5, 6} could be integrated to add photodetecting capabilities, from infrared to ultraviolet, to CMOS circuitry. Integration of CMOS and non-CMOS based technolgies reduce the cost-perfunction and revolutionize the performance of integrated circuits. To realize this, thus, new manufacturing and integration paradigms as well as devices with diverse functionalties will be required.

Among these diverse functonalites, there has been a growing interest in chemical sensing primarily due to its significance in environmental monitoring, defense, and medical diagnosis. Conventional approaches to chemical sensors take advantage of "lock-

and-key" sensing strategy. In turn, specific sensing material is designed to detect a target chemical with a high selectivity. This approach has been useful to detect target analytes in controlled environment. In practical application, however, most chemical sensors suffer from some degree of interference by responding to chemical species that are structurally or chemically similar to target chemicals.

Alternative approach to conventional sensing strategy involves the use of array of different sensing materials or/and devices for chemical sensing as shown in Figure 1-2 (a).



Figure 1-2 Cross-reactive sensors. (a) Sensing material and transduction-diversified cross-reactive sensor. (b) Responses of cross-reactive sensor consisting of sensor elements with different sensitivities to different analytes.

In particular, multi-material cross-reactive sensor array mimics odor detection

mechanism found in the biological olfaction system. It has been known that

approximately 1000 different olfactory receptor cells in mammalian olfactory system

possess partial or non-specific sensitivities to any given analytes in which their collective response pattern is a basis of odor recognition^{7, 8}. In this cross-reactivity approach, every sensing element in the array is configured to contain as much chemical diversity as possible instead of high selectivity toward specific chemicals. Combining this cross-reactive sensor array with a pattern recognition technique will discrimate target chemicals to be dected from similar chemical species⁹.

Integration of different sensing materials for cross-reactive sensor array was demonstrated by several groups. Neotronics NOSE has electrochemically grown 12 different polypyrrole-based conducting polymers between 10µm-spaced metal electrodes by either changing the dopant ion or the polymerization conditions¹⁰. The use of 12 different polypyrroled-based sensors enables discrimation between chemically similar organic solvents. Lundstrom reported that thin film-based metal-oxide-silicon field effect transistor (MOSFET) sensor array with a different gate metal can be used to construct the cross-reactive sensor¹¹. It was shown that array of MOSFET with three different gate metal of palladium, platinium, and iridium can be used to identify four different chemical analytes including hydrogen, ammonia, ethylene, and ethanol.

Rather than just sensors, monolithic integration of cross-reactive sensor devices on silicon-based CMOS chip provides several performance advantages. Integrated sensor system intrinsically has a reduced form factor, minimize noisy interconnection between sensor device and data acquisition system, and consumes less power^{12, 13}. More importantly, realization of cross-reactive sensor on a CMOS circuitry dramatically revolutionizes its capability beyond simple environmental sensing. Silicon-based CMOS circuitry permits control and monitoring of individual sensor functions, and enables onchip signal conditioning that notably improves the overall sensing performance. CMOS circuit can also process the sensing data, collected from cross-reactive sensor array, for the pattern recognition, resulting in discrimination a wide variety of chemical analtyes. This sensor system is also capabile of incorporating analog-digital converter circuit and digital data transmission for remote analyte monitoring. Thus, combining cross-reactive sensor array with silicon CMOS technology will bring remarkable advances in the field of sensing technology.

Performance of cross-reactive sensor devices can be improved in several perspectives. First, sensing materials with a high surface-to-volume ratio deliver higher sensitivity and shorter sensing response time compared to their macroscopic counterparts such as thin and thick film¹⁴. For instance, nanowires possess relatively short distance, orthogonal to their longitudinal direction, for chemical analytes to be diffused, causing percolation effects to be sharpened. As this dimensionlaity is further reduced, one can expect sensor devices to have better sensing performance with some degree of proportionality. Second, large number of identical sensor devices can lead to the improved sensor sensitivity with an assistance of post-signal processing. Massive redundancy allows signal averaging over many replicates of each sensor type. As predicted by signal-averaging theory, averaging over *n* sensor elements improves signalto-noise ratio (SNR) to approximately \sqrt{n} times that of an individual sensor element, which in turn lowers the detection limit proportionally^{15, 16}. Third, high-density integration of sensor devices is beneficial in that sensor array consumes less area in silicon CMOS chip, making it ultrasmall. This high density integration of sensor devices will be also favored by large collective response where each sensor devices might show

very small or defective signal or signal change. Walt group immobilized massive number of flurescent spherical particles at the ends of etched optical fiber, demonstrating highdensity sensor integration and massive redundancy for enhacements in the overall sensitivity of the array¹⁷.

Conducting polymer materials offers a great chemical diversity suitable for constructing chemoresistive cross-reacitve sensor arrays⁹. In principle, chemical sensing of chemoresistive conducting polymers is based on their conductivity change arising from electron/hole exchange or bulk mobility change by interacting chemical species². A diverse set of polymers such as poly(pyrrole), polyaniline and poly(ethylenedioxythiophene) is available via the electrochemical or chemical polymerization of a range of monomer types while further diversification or sensitivity enchancement accessible via introduction of molecular recognition groups^{18, 19}. The use of the membrane with a specified nanopore size enables batch-synthesis of conducting polymer nanowire sensors with a high surface-to-volume ratio. Following synthesis of different sets of conducting polymer nanowires, their subsequent integration on a substrate will be an excellent basis of cross-reactive sensor array toward chemical diversification with a high sensitivity and rapid response.

Figure 1-3 illustrates the schematic approach for high-density cross-reactive nanosensor array which incorporates different types of conducting polymer-based nanosensor on a silicon CMOS chip. Upon off-chip synthesis of chemoresistive polymer nanowires, sensor A, B, and C, at their optimized conditions, their sequential bottom-up assembly determines final alignment positions on a CMOS circuitry while preserving their sensing functionalities during process. This bottom-up integration also eliminates





process incompatibilities, lattice mismatch, thermal budget between sensing materials and CMOS fabrication process. Following nanowires assembly, their monolithic integration can be completed by metal deposition technique such as evaporation or electrodeposition, ensuring low-noise interconnection between sensor devices and CMOS circuitry. Chemically diverse nanowires with different partial seletivities and temporal responses by a given analyte can be well-suited in fabricating cross-reactive sensor arrays on a single chip. Sensing data collected from different sensors permit subsequent pattern recognition, resulting in discrimination of chemical species using a chemical crossreacitivity. As depicted in Figure 1-3, underlying silicon-based CMOS circuitry can perform amplification, processing, and transmission of collected sensor data, which consists of driving and signal-conditioning circuitry, analog-to-digital converters, sensor control and power management unit, and a digital logic circuitry. Thus, this type of crossreactive sensor array on a CMOS chip represents significant step toward realization of complete SOC chemical sensor.

Spherical particle devices platform can replace nanowires for higher integration density as shown in Figure 1-3. Recent development in fluidic assembly can be used to integrate the spherical sensor particles at the locations defined by topological features such as dielectrics and photoresist^{20, 21}. Their electrical connection to underlying CMOS circuit could be accessible via cross-point array structure where the assembled beads make physical and electrical contacts to the top and bottom electrodes (not shown).

Recently, a significant advance was made toward the goal of chemically diversified nanowire array by sequential biasing to discrete metal electrode array as shown in Figure 1-4. Prior to the nanowire assembly, three different populations of nanowires were first functionalized with different biorecognition probes off-chip, and then each population was directed to a different region of the chip with programmable electric-field forces. Lithographically defined wells along the metal electrode gap determine final locations of assembled nanowires. Fluorescence optical microscopy confirmed that bioselective target binding was retained after on-chip assembly and nanowire device integration. Optical microscopic analysis revealed that only few, less than 1% nanowires had assembled into the unintended region of the chip .Within lithographically recessed well, individual nanowires were positioned with submicron registration accuracy to features on the chip. The overall array containing all three populations had a 71% yield of individual nanowire devices while farily small number of



Figure 1-4 Programmed biofunctionalized nanowire assembly on a substrate. (a) Suspensions of nanowires carrying different DNA sequences were injected sequentially, while sinusoidal biases were applied between the specific pairs of guiding electrodes. (b) Spatial electrical field distribution. Contour plots show $\nabla |\mathbf{E}|^2$ measured at the surface of the microwells for the peak value of voltage. (inset) Crosssection of a single microwell, plotted as $\log_{10} \nabla |\mathbf{E}|^2$; arrows indicate the direction of dielectrophoretic force. (c) Fluorescence optical microscope images of nanowire arrays. Placement of different populations in different columns is shown using this technique. Schemes and images are from a publication of Morrow and colleagues²².

empty devices and multiple nanowires are found within alignment location. Consequently, this type of programmed nanowire assembly can be used to accomplish chemical diversity on a fully-process silicon CMOS chip for cross-reactive sensor array system.

Although this deterministic programmed assembly has a potential to achieve chemical diversity on a single chp, their seamless and monolithic integration with modern CMOS circuitry presents a unique challenge. Due to the nature of freestanding nanodevices in suspension, their deterministic integration on complex silicon CMOS chip need to address following technical issues which are often considered drawbacks of bottom-up approach. First of all, yield of deterministic assembly on complex CMOS circuitry is the most important factor in fundamental research and manufacturing perspectives. Structural complexity of CMOS circuitry can affect the assembly yield of sensor devices. As a result, development of sophiscated deterministic assembly needs to take into account of this complexity as well as integration density. This bottom-up deterministic assembly typically involves misaligned and strayed nanowires off to the desired locations. These misaligned nanowires could affect the performance of nanosystem or make it even defective if aligned at the critical location of circuitry. Thus, misaligned nanowires need to be minimized during the assembly process or removed by post-assembly process.

Secondly, seamless integration of nanowire devices with an underlying silicon CMOS circuitry requires their accurate registration in a reliable and controlled manner. In other words, registration accuracy of off-chip synthesized nanowires relative to the features such as interconnects and transistors should be tolerant of nanowire alignment error within a CMOS circuitry. Since lithographical features in current CMOS platform are comparable to or even below quarter-micrometers in the last decade, capability of deterministic assembly with sub-micron translation and rotation alignment offset is highly desired to keep pace with a state-of-art top-down fabrication. Furthermore, accurate positioning of nanostructures enables this deterministic assembly to integrate them at the small pitch, achieving high density on a CMOS chip.

Last, mechanically strong and electrically low-resistant contacts between assembled nanowire and underlying CMOS devices need to be made during assembly or by additional post-assembly process. In particular, monitoring conductance change in massive number of sensor devices requires electrically low-resistant contact, ensuring that peripheral CMOS circuit readouts the conductance change of device itself, not by contacts. Also, noise from contacts between sensor devices and interconnects of CMOS circuitry could impair the improvement of signal-to-noise ratio in high-density nanosensor array. Therefore, post-assembly contact formation, if necessary, needs to address mechanical stability and electrical property of assembled nanodevices on CMOS circuit for their seamless and monolithic integration.

1.2 Organization of Thesis

This thesis primarily investigates the electric field-assisted assembly of nanowires toward on-chip integration of functional nanostructures. Bottom-up integration of spherical devices, another popular form factor, at specific locations on a chip using a capillary force is also discussed in this thesis. These integration methods deliver a way to integrate functional nanostructures at precise locations assisted by features of substrate while making an electrical contact to assembled nanostructures with or without postassembly process. Isolating the synthesis of nanostructures from their assembly into devices has many benefits, which include preserving the established reaction conditions of nanostructures without compromising other materials within a final device or underling CMOS circuit.

Importantly, this method offers a promising way to position the individual functional nanodevices in CMOS circuitry with the accurate registration, facilitating onchip integration of off-chip synthesized functional nanowires. Furthermore, this strategy including nanowire integration method and back-end process is generic and can be extended to many other types of functional nanowires for achieving the chemical diversity on a chip. Similarly, fluidic assembly of functionalized spherical particles and its integration with the cross-point array structure also represents another aspect of technology combination of bottom-up assembly and top-down fabrication, which will extend the geometrical scope of on-chip integration of nanostructures.

Investigation of dielectrophoretic nanowires attraction and related electrostatic interaction denotes an essential prerequisite for deterministic nanowire alignment at the desired locations on a substrate. This preceding fundamental investigation optimizes the nanowires alignment conditions to organize them into uniformly-spaced array, and also can assist to transform it into an array of deterministic nanowire alignment. Thus, Chapter 2 focuses on a fundamental study of nanowire alignment at high electric field gradient region, investigating effects of dielectrophoretic and electrostatic forces on nanowire attraction and orientation at different bias conditions. Nanowire assembly experiments were conducted with parallel electrodes, creating spatial field intensity and coated with a thin dielectric layer. Applied AC bias between adjacent pairs of electrodes creates a long-range dielectrophoretic force that attracts and orients the polarized nanowires to span the electrode gap in which the degree of their attraction and orientation depend on the amplitude and frequency of bias.

Several important features of the assembled nanowires such as self-centering at the electrode gap, uniformly-spaced array formation, and end-to-end nanowire chain configuration are observed and discussed with the assistance of electromagnetic simulation. It was proved that electrostatic interactions between the neighboring nanowires as well as the nanowires and the electrodes cause the nanowires to organize into a uniformly spaced array in which each nanowire is centered across the gap.

The parametric study of internanowire spacing of uniformly-spaced nanowire array is carried out in Chapter 2. Theoretical model accounting for the charge distribution of assembled nanowires was used to predict the relation of the electrostatic repulsion between the neighboring while varying geometry of structure and material parameter such as the electrode gap width and the nanowire length. The alignment of nanowires with different length (7, 13, and 24μ m) on different electrode gap (3 and 6μ m) show that longer nanowires on smaller gap width tend to be assembled with larger internanowire spacing at the same bias conditions, which is fairly consistent with theoretical expectations. It was suggested that the dielectrophoretic attraction and electrostatic interaction of nanowires contribute to the determination of internanowire spacing by the number of nanowire to be assembled and repulsive interaction, respectively. As a result, the experimental results varying the voltage of applied bias and thickness of dielectric layer, backed by theoretical simulation, reveal that their relative ratio plays an important role in establish the average nanowire spacing within an array.

This parametric study for long-range dielectrophoretic attraction and short-range electrostatic interaction should be a fundamental basis for deterministic nanowire integration on a substrate. Lack of accurate registration to features on a chip will be overcame by controlling the electric field intensity along the electrode gap by adding topographical and non-topographical features in next chapter.

Chapter 3 extends the understanding of nanowire alignment on the electrode gap to achieve the high-yield deterministic assembly of nanowires with the accurate

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registration. To realize this precise positioning of nanowires, the electric field intensity was increased in specific positions along the electrode gap by adding an array of recessed photoresist well on top of the first dielectric layer. Experimental results confirmed that the increased field intensity, and hence dielectrophoretic force, results in preferential assembly of individual nanowires within the wells. Individual nanowire assembly yields exceeding 90% were obtained at metallic and semiconducting polymer nanowire densities of approximately 10⁶ /cm². Electrical characterization of assembled nanowires and relevant electron microscopy are carried out to correlate the resistance of individual nanowires.

This deterministic assembly process and post-assembly metallization using the electrodeposition was used to fabricate arrays of electrically-contacted conducting polymers (e.g., PEDOT/ClO₄ and PEDOT/PSS) nanowire chemical sensors. The chemical sensing response from individual nanowire sensors are also measured by the exposure to the chemical solvent, the chemical toxic gas, and nerve gas simulant.

It was also presented in Chapter 3 that the monolithic integration of nanowires the determined locations within a circuit structure where assembled nanowires can be connected to features of transistors. This precise placement of functional nanowires on a substrate or circuit structure represents a significant advancement toward future miniaturized multi-functional chips with chemical diversity. Furthermore, this assembly and unique post-assembly schemes are a generic approach, not limited to the specific nanowires, and thus can be employed to the multifunctional chip using the sequential assembly of different types of functional nanowires.

Chapter 4 describes the fluidic assembly of microspheres on the patterned substrate. The capillary force at the meniscus of receding solution confined in the fluidic cell places the spherical entities into the recessed photoresist well where their configuration within the well can be determined by the ratio of dimension of sphere diameter and well depth. Array of photoresist well whose dimension is comparable to the diameter of spheres preferably traps the single spheres within it, leading to the selflimiting deposition because of structural constraint. Functionalized the microsphres with thin chemically sensitive nanomaterials and its fluidic assembly on the cross-point array structure completes the nanoelectronic device where the address to the device can be made via the top and bottom contact geometry. The electrical characterization of assembled nanoshell microspheres and subsequent sensing measurement suggest that it can be used to construct the chemical sensor with high surface-volume ratio. Its integration with CMOS circuitry is also discussed.

Chapter 5 summarizes this work and presents the future work for realization of functional nanowires integrated on CMOS circuitry. Preliminary experimental data of silicon nanowire assembly is also presented.

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Chapter 2

ELECTRIC FIELD-ASSISTED NANOWIRE ASSEMBLY

This chapter investigates the long-range dielectrophoretic forces that attract and align nanowires to span narrow gaps that separate pairs of electrically-isolated interdigitated electrodes on oxidized silicon substrates and the short-range electrostatic interactions between adjacent nanowires along the gap. These long- and short-range forces eventually lead to dense arrays of uniformly-spaced individual nanowires. Chapter 2 also describes the electrostatic interactions between the assembled nanowires and the biased interdigitated electrodes that determine both the minimum spacing between the adjacent nanowires in the array as well as the centering of each individual nanowire across the electrode gap. This combination of long- and short-range forces provides an efficient way to direct the nanowires toward desired locations on the substrate and to organize them in a controlled fashion, which in combination with additional lithographic features that are described in Chapter 3, facilitates post-assembly integration of high-density nanowire device arrays.

Section 2.1 briefly discusses the dielectrophoretic motion of spherical and anisotropic particles (*e.g.*, nanowires) in an inhomogeneous electric field. The expression for the dielectrophoretic force, based on the dipole moment of the nanowires in inhomogeneous electric fields, predicts that the highly polarizable nanowires in a liquid medium experience a positive dielectrophoretic force due to the permittivity difference between the conductive nanowire and the liquid medium, thereby directing them toward the high electric field gradient region, namely the electrode gap. Section 2.2 describes the experimental setup used in the electric-field assisted nanowire assembly.

The results of an experimental and theoretical study that investigated the nanowire assembly mechanisms appear in Section 2.3 and 2.4. By varying the amplitude and frequency of the AC bias applied to the interdigitated electrodes, it was determined that the long-range dielectrophoretic forces exerted on rhodium (Rh) nanowires become effective at polarizing and attracting the nanowires at a bias of $>1\times10^6$ V/m and >10kHz. Capacitive coupling between the nanowires and the underlying electrodes induce charge on the assembled nanowires that causes adjacent nanowires to repel each other and to span the electrode gap symmetrically. This repulsive electrostatic interaction between the adjacent nanowires gives rise to the uniformly-spaced nanowire array. A theoretical simulation of the nanowire offset from the center of the electrode gap indicates that any longitudinal shift of the nanowires induces an asymmetry in the charge and electric fields at the ends of nanowires. This asymmetry results in a net Coulombic force in the opposite direction, which causes the nanowires to center across the electrode gap. At high nanowire concentrations, mutual dielectrophoresis creates nanowire chains that limit the minimum separation between nanowires in the array. The use of a ~3µm deep dielectric well minimizes the mutual dielectrophoresis to produce arrays that are nearly free of chained nanowires.

2.1 Dielectrophoretic Nanowire Attraction and Alignment

In the electric-field-assisted nanowire assembly process, the long-range attractive force that directs individual nanowires to the surface of the substrate is due to dielectrophoresis of the nanowires in an inhomogeneous electric field. Dielectrophoresis refers to the motion of polarized objects toward either a higher or lower electric field gradient region depending on the polarization of the object and the medium. In other words, if the objects are more polarizable than their environment, they experience an attractive force toward a high electric field gradient region and also orients itself parallel to the electric field lines as shown in Figure 2-1 (a) and (b). This well-known



Figure 2-1 Dielectrophoretic (a) attraction and (b) rotation of nanowires in the electric field. (c) Nanowire is directed toward the electrode gap.

phenomenon is known as "positive" dielectrophoresis, typically employed in cell separation and manipulation of materials in solution^{4, 5}. Contrary to the above case, if the objects are less polarizable than their environment, they are driven to the low electric field gradient region because the suspending medium is attracted to the high electric field gradient region; this is known as "negative" dielectrophoresis.

The general expression for the dielectrophoretic force $(\mathbf{F}_{\text{DEP}})$ exerted on a spherical particle is⁷:

$$\mathbf{F}_{\text{DEP}} = \frac{3}{2} \upsilon \epsilon_1 \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} \nabla |\mathbf{E}|^2 , \qquad (2-1)$$

where v is the volume of spherical particles; ϵ_1 and ϵ_2 are, respectively, the permittivity of liquid medium and spherical particles, and **E** is the electric field. For anisotropic particles, such as nanowires, the frequency-dependent dielectrophoretic force experienced by them in an AC electric field can be modified to ^{7, 8}:

$$\mathbf{F}_{\text{DEP}} = \frac{\pi r^2 \ell}{3} \,\epsilon_1 \,\text{Re} \,(\text{K}) |\mathbf{E}|^2, \qquad (2-2)$$

where r is the radius of a nanowire, ℓ is the nanowire's length, and Re(K) is the real part of the Clausius-Mossotti factor. The Clausius-Mossotti factor that accounts for the screened polarizability of the nanowires along the longitudinal direction in a liquid medium is: $K = (\epsilon_2^* - \epsilon_1^*)/\{\epsilon_1^* + (\epsilon_2^* - \epsilon_1^*)L_I\}$. The complex permittivity, (ϵ^*) is $\epsilon_{1,2}^* = \epsilon_{1,2} - i(\sigma_{1,2}/\omega)$, where σ is the electrical conductivity; ω is the frequency of electric field, and *i* is an imaginary number. $L_I \approx 4r^2/\ell^2[\ln(\ell/r) - 1]$ is the depolarization factor for the nanowires^{7, 8}.

The transverse component of dielectrophoretic force, perpendicular to the nanowire's length, becomes almost negligible compared to the longitudinal component for the frequency range used in this research, which limits the nanowire motion to the longitudinal direction. If the depolarization factor, L_I is very small, valid for the high aspect ratio of nanowires, Re(K) can be rewritten as:

$$\operatorname{Re}(\mathbf{K}) = \frac{\sigma_1(\sigma_2 - \sigma_1) + \omega^2 \varepsilon_1(\varepsilon_2 - \varepsilon_1)}{\sigma_1^2 + \omega^2 \varepsilon_1^2} .$$
(2-3)

In most of non-ionic solution, the conductivity of the medium σ_1 is quite small compared to the conductivity of the metal nanowires σ_2 . For example, σ_1 for isopropanol and σ_2 for Rh nanowires are 6.0×10^{-5} S/m and 2.1×10^6 S/m. For this case, $\sigma_2 \gg \sigma_1$, Re(K) can be rewritten as:

$$\operatorname{Re}(\mathbf{K}) = \frac{\sigma_1 \sigma_2 + \omega^2 \varepsilon_1(\varepsilon_2 - \varepsilon_1)}{\omega^2 \varepsilon_1^2} = \frac{\sigma_1 \sigma_2}{\omega^2 \varepsilon_1^2} + \frac{(\varepsilon_2 - \varepsilon_1)}{\varepsilon_1} . \quad (2-4)$$

The sign of Re(K) depends on whether or not the nanowires are more or less polarizable than the liquid medium at the frequency of applied bias. Because the permittivity of metal approaches infinity, the Re(K) is positive, driving the polarized nanowires to the high electric field gradient region. Equation (2-4) also suggests that the dielectrophoretic force of conducting nanowires tends to become more dependent on their permittivities rather than their conductivities as the frequency of applied bias increases^{9, 10}.

Following the pioneering work of Pohl in late $1950s^{11}$, dielectrophoretic manipulation of polarizable materials has recently been adapted to direct nanowires to microfabricated electrodes as shown in Figure 2-1 (c)¹²⁻¹⁴. Since the liquid suspension medium can contain ionic species, the formation of an electrical double layer on top of the biased electrode and around the nanowire needs to be avoided via AC dielectrophoresis. This electrical double layer can effectively screen the charges on the biased electrodes, making it difficult for the electric field to be extended toward the nanowires in the solution. Thus, the frequency of the applied AC bias must exceed the critical frequency of ionic species in the solution in which they start to form the electrical double layer formation^{15, 16}.

2.2 Electric-Field Assisted Assembly Experimental Setup

The nanowire assembly structure used in this thesis research is composed of an interdigitated metal electrode array as shown in Figure 2-2;



Figure 2-2 Cross-sectional view of nanowire alignment structure. Parallel biased electrodes intended to form the high electric field gradient region directing the polarized nanowires toward the electrode gap.

the electrode gap region creates a high electric field, leading to positive dielectrophoresis of nanowires toward the electrode gap. As indicated by equation (2-2), the magnitude of the dielectrophoretic force needed to attract the nanowires to the electrode gap depends on the AC bias conditions and the design of electrode structures¹. Because this force varies with the distance from the substrate surface and into the fluid medium, it is first necessary to transport the nanowires to the vicinity of the electrode gap area to achieve effective alignment and assembly. The flow of the fluid medium that suspends the nanowires is also an important factor in the assembly process. The interdigitated electrode structure used in the nanowire assembly experiments, illustrated in Figure 2.5, was fabricated on a silicon (100) wafer coated with a 1µm thick silicon dioxide layer. The electrodes were defined by thermally evaporating Ti/Au (20nm/50nm) onto a pattern defined by optical photolithography in double layer photoresist (0.7µm BPRS 100(OCG Microelectronic Materials) / 0.3µm PMGI SF-6 (MicroChem Co.)) followed by metal lift-off in Microposit[®] 1165 Remover (Shipley Co.) In this design, pairs of 50µm wide metal electrodes were separated by 3µm or 6µm wide gaps, where the electric field intensity and gradient is the highest. A dielectric layer of PMGI photoresist (MicrochemTM) with a thickness that varied between 0.3µm to 4.2µm was deposited on the electrodes by spin casting and baking at 250°C for 5 minutes. As shown in Figure 2-3 (a)-(d), fluidic microchannels have been used previously to assist in the assembly of nanowires and biological cells by guiding them toward a



Figure 2-3 Fluidic flow-assisted dielectrophoretic assembly of nanowires (a), (b) and biological cells (c), (d). The direction of fluid flow assisted the nanowires and cells to assemble at the dielectrophoretic attraction sites with a preferred orientation and chain formation, respectively. The images are from publications of (a) Liu^1 , (b) Matsue², (c) Bashir³, and (d) Knapp⁶ groups.

biased electrode where they become trapped by the dielectrophoretic force^{1-3, 17, 18}. These eports show that the shear force resulting from the fluid flow in the microchannels transports the nanowires with a preferred direction parallel to the fluidic flow. This improves the deposition yield and influences the orientation of the nanowires in the electrode gap.

Figure 2-4 (a) shows a schematic illustration of the fluidic cell structure used in the nanowire assembly experiments described in this thesis. The interdigitated microelectrode array, patterned on 1µm thick thermally oxidized silicon substrate, is covered by a thin layer of Polymethylglutarimide (PMGI) photoresist. This dielectric



layer prevents the nanowires from shorting the pairs of interdigitated electrodes during

Figure 2-4 (a) Illustration of fluidic flow-assisted nanowire assembly setup used in the experiment (not in scale). (b) The fluid velocity profiles inside the fluidic cell with a channel height of $100\mu m$ and channel width of 5mm. This fluidic channel with a high aspect ratio of width to height intends to make the flow horizontally uniform over the nanowire alignment locations except the edges.

assembly. It also influences the short-range electrostatic forces that determine the final position of the nanowires along the electrode gap. A fluidic assembly cell is formed by affixing a cover slip to the substrate with an adhesive spacer. A suspension containing a low concentration of metal or semiconductor nanowires dispersed in either an ethanol or

an isopropanol fluid medium is injected at one side of the coverslip using a micropipette. Similar to earlier work, this cell assists the nanowire assembly by controling the fluid flow direction and confining the nanowires near the surface of the substrate. It also reduces the evaporation rate of the fluid medium to allow the complete assembly of nanowires in suspension. This fluidic cell provides a controlled and reproducible fluidic flow across the channel width, except near the edges of the spacer.

The flow velocity inside the fluidic cell was simulated using COMSOL Multiphysics¹⁹ and is shown in Figure 2-4 (b). The simulation confirms that a cell with a channel height of 100 μ m (defined by the spacer thickness) and a channel width of 5 mm gives a uniform flow over the patterned surface of the substrate²⁰. Additionally, the inset in Figure 2-4 (b) shows that the flow has a lower velocity near the surface of the substrate. This suggests that the nanowires in the vicinity of the substrate surface tend to be attracted toward highly gradient region, or between the biaed electrodes.

Rh nanowires used in this thesis were synthesized by Tom Morrow from Keating group at The Pennsylvania State University. The nanowires that were used in the assembly experiments were fabricated by electrodepositing rhodium (Rh) into the pores of commercial anodized aluminum oxide (AAO) membranes (Anodisc25, Whatman Scientific Inc.). The nanowires are released by selectively etching the membrane in 3.0 M NaOH with a sonication for 30 mins. The synthesized nanowires had nominal diameters of 200 nm and lengths of ~7 μ m, which were determined by the pore diameter of the template and the electrodeposition time, respectively. The nanowires were rinsed 3 times in ethanol and then transferred into isopropanol (IPA) for the experiments. Nanowire concentration is diluted down to approximately 1×10⁴ nanowires/µL. Immediately prior

to assembly, the nanowire suspension was sonicated for 10s to ensure that nanowire bundles and aggregates were separated and that the nanowire concentration was uniform throughout the suspending IPA fluid.

After the nanowire suspension is introduced into the fluidic cell, a sinusoidal bias with V_{pp} =10V, peak-to-peak voltage at fixed frequency ($\omega = 100 \text{ kHz}$) is applied between the electrodes, which creates an inhomogeneous electric field in the electrode gap. The electric field strength ($|\mathbf{E}|$) calculated using COMSOL Multiphysics¹⁹ is plotted as a function of distance from the electrode surface in Figure 2-5 (a). This simulation



Figure 2-5 (a) Simulation of electric field strength ($|\mathbf{E}|$) at the cross-section of z-x plane for the long-range dielectrophoretic force directing the polarized nanowires, within a distance less than the characteristic decay length of the AC electric field, toward the electrode gap. (b) $\nabla |\mathbf{E}|^2$ in the vicinity of the electrode gap showing the magnitude (contour map) and direction (arrow map) of dielectrophoretic force.

shows that the electric field produced by the biased electrodes extends well into the fluid medium. If the nanowires flowing across the surface enter the high electric field gradient region, they become polarized and are directed to the electrode gap. The magnitude (color) and direction (arrows) of the long-range dielectrophoretic force responsible for the nanowire alignment and attraction is shown in Figure 2-5 (b). As reported elsewhere^{14,}

²¹, the simulation results predict that the dielectrophoretic force will direct the nanowires to align across the biased electrodes. Because a thin dielectric layer covers the interdigitated electrodes, the strong electric field still remains in the regions between adjacent nanowires following their assembly. This enables the subsequent attraction and alignment of additional nanowires across the same electrode gap. The nanowire assembly process is rapid, with the nanowires aligning across the gap almost immediately after biasing the electrodes. Once aligned, short-range electrostatic interactions between the adjacent nanowires and between the nanowires and the underlying electrode control the position and density of the nanowires in the gap. The electrostatic force between the assembled nanowires and the interdigitated electrode allows the fluid to be removed without changing the position of the nanowires after the assembly process is complete.

In this thesis research, two methods were used to study the nanowire assembly process: (1) Real-time video collected durning the nanowire assembly process using an optical microscope, and (2) Optical and electron microscopy of the assembled nanowires after the suspending fluid and the cover slip were removed.

2.3 Regimes of Electric-Field Assisted Assembly

2.3.1 Attraction and Orientation of Nanowires

Effective attraction and alignment of the nanowires across the electrode gaps is achieved when the dielectrophoretic force exceeds all other forces on the nanowires, including gravitational forces, hydrodynamic forces, charge-charge interactions between the nanowire and substrate, and Brownian motion. Representative dark field optical microscope images of the nanowire attraction and alignment across the electrode gap for different amplitudes (V_{pp}) and frequencies (ω) of AC biases (appear in Figure 2-6 (a) and



Figure 2-6 Representative dark-field optical microscope images of the nanowires assembled on the electrode structure at different (a) amplitudes at 100kHz and (b) frequencies at 3×10^6 V/m of the appliedAC bias. The scale bar: 30µm. The plots are for nanowire attraction (Y) and orientation (S) as functions of (c) amplitude and (d) frequency of applied bias. The insets show the uniformly-spaced nanowire array at 1.7×10^6 V/m (left) and 1 MHz (right).

(b). For all of the AC bias frequencies investigated, only a weak dielectrophoretic force is exerted on the nanowires at low peak-to-peak electric field strength, converted from peak-to-peak voltage (V_{pp}), of ~0.1 – 0.5 MV/m, resulting in poor nanowire attraction

toward the electrode gap. At these applied AC biases, the gravitational forces cause the nanowires to settle in random positions on the substrate. As the peak-to-peak electric field strength is increased to greater than $\sim 1 \times 10^6$ V/m, the dielectrophoretic force becomes dominant, and nearly all of the nanowires are aligned across the gap. Intermediate electric field intensities result in the attraction and the alignment of a portion the available nanowires.

The dependence of the nanowire attraction with peak electric field strength at a constant frequency of 100 kHz is plotted in Figure 2-6 (c). In this plot, Y is defined as the ratio of the number of nanowires attracted to the electrode gap to the total number of anowires in the image field, and varies from Y = 0 (no nanowires at the electrode gap) to Y = 1(all nanowires at the electrode gap). The value of Y becomes equal to 1 at a peak-to-peak electric field strength of ~10⁶ V/m. At this critical field strength, the dielectrophoretic force overcomes the Brownian motion of the nanowires and the medium's dynamic flow ²² and effectively can trap the nanowires in the gap. This value is consistent with the critical field strength at which the dipole alignment energy overcomes the random Brownian motion of nanowires and is consistent with other electric field-assisted particle assembly literatures²²⁻²⁴. After the polarized nanowires are attracted and aligned across the electrode gap by dielectrophoretic force, the electrostatic interactions between the nanowires and underlying electrode binds them to the substrate.

The frequency of applied bias also affects the dielectrophoretic force because the Clausius-Mossotti factor (K) depends on frequency⁷. As shown in Figure 2-6 (b), for the high electric field strength of 3×10^6 V/m, most of the nanowires adhere to the surface of the biased electrode while only a few align across the electrode gap for low AC bias

frequencies of 0.1 kHz. This occurs because an electrical double layer forms on the surface of the biased electrode at a low frequency, which typically causes the applied potential to drop a few nm from the metal-suspension interface^{15, 16}. At frequencies higher than 100 kHz, this electrical double layer becomes more diffuse due to its long relaxation time, and thus the dielectrophoretic force becomes dominant at these higher frequencies. The dependence of the nanowire attraction with AC bias frequency at a constant electric field strength of 3×10^6 V/m is plotted in Figure 2.6 (d). In accordance with theory, the value of Y becomes 1 at a frequency of 10 kHz.

In addition to the translation motion of nanowires in an inhomogeneous electric field region, the nanowires also experience a torque unless they are perfectly aligned parallel to the direction of the electric field. This torque arises from the interaction between the induced dipole within the polarized nanowire and the external electric field, which eventually causes the nanowires to align along the field lines. The effective dipole moment of the ellipsoidal object under the external electric field can be expressed as⁸:

$$\mathbf{P}_{\text{eff}} = \upsilon(\epsilon_2 - \epsilon_1) \, \mathbf{E}_i \,, \tag{2-5}$$

where υ is the volume of the nanowire, and \mathbf{E}_i is the electric field inside the nanowire that is related to the external field \mathbf{E} through a depolarization factor, L_I , by $\mathbf{E}_i = \mathbf{E}/(1 + (\epsilon_2 - \epsilon_1)/(\epsilon_1 L_I))$. Thus, the torque exerted on the nanowire with long axis oriented at an angle of θ with respect to the applied electric field, \mathbf{E} , can be expressed as⁷:

$$T = \frac{\pi r^2 \ell}{2} \frac{(\epsilon_2 - \epsilon_1)^2}{\left[\epsilon_1 + (\epsilon_2 - \epsilon_1)L_I\right](\epsilon_1 + \epsilon_2)} \epsilon_1 |\mathbf{E}|^2 \sin 2\theta .$$
(2-6)

Introducing an orientation order parameter²⁵ allows evaluation of the degree of rotational nanowire alignment at the electrode gap, which has been used to quantify molecule orientation in liquid crystals. The orientation parameter is expressed as:

$$S = 2\cos^2\theta - 1 \tag{2-7}$$

where θ is the angle of a single nanowire relative to the direction of the electric field. To quantify the rotational alignent of nanowire arrays for different assembly conditions, S is averaged over a large number of assembled nanowires. The average value of S, which is expressed as \overline{S} , varies between $\overline{S}=0$ (nanowires are randomly oriented relative to the electric field lines) and $\overline{S}=1$ (all nanowires are perfectly aligned parallel to the electric field lines).

The dependence of the degree of nanowire orientation (\overline{S}) with electric field strength at a constant frequency of 100 kHz is plotted in Figure 2-6 (c). As expected from Equations (2-1) and (2-6), the value of \overline{S} is higher than the corresponding value of Y at the low frequencies where Y < 1. This is because the alignment torque is proportional to the square of the electric field strength, while the dielectrophoretic force depends on the square of the electric field gradient. Thus, the alignment of nanowires tends to occur more easily when the gradient of the electrical field is small. At this frequency, all of the nanowires orient parallel to the direction of electric field at a field strength of ~1 × 10⁶ V/m, which occurs when the alignment torque on the nanowires due to the dielectrophoretic force overcomes the force due to Brownian motion that randomizes their orientation. As shown in Figure 2-6 (d), similar to the dependence of nanowire alignment (Y) with electric field strength, the degree of nanowire orientation (\overline{S}) is higher than the corresponding value of Y at frequencies below 10 kHz for a constant electric field strength of 3 × 10⁶ V/m. However, at these low frequiences, the orientation of the aligned nanowires is still relatively poor due to the double-layer screening of the biased electrodes. In this case, the Brownian motion of the nanowires in the fluid medium results in a random nanowire orientation, leading to a value of $\overline{S} < 1$. As is to be expected, increasing the frequency to > 10 kHz prevents double layer formation on the biased electrodes, and improves the nanowire orientation parameter of $\overline{S} = 1$.

In summary, these experiments show that a relatively high electric field strength of $> 1 \times 10^6$ V/m and AC bias frequency of >10 kHz is needed to achieve strong attraction and alignment of the nanowires across the electrode gaps. These assembly conditions were used in the experiments described in the following sections that study the short-range forces that produce the uniformly-spaced nanowire arrays.

2.3.2 Forming Uniformly-Spaced and Centered Nanowire Arrays

After the nanowires are attracted and aligned across the gap, short-range electrostatic interactions between adjacent nanowires along the length of the gap and between the nanowires and the electrically-isolated biased electrode produce uniformlyspaced nanowire arrays in which each wire is centered across the gap. As shown in Figure 2-7 (a) - (c), the directed assembly process can be divided into three distinct phases that depend on the number of nanowires that are dielectrophoretically attracted to the biased electrode gap. In the initial phase of assembly, when few nanowires are aligned across the gap, the wires are randomly positioned along the gap (Figure 2-7 (a)).



Figure 2-7 Bright-field optical microscope images for each stage of assembly: (a) single nanowire alignment, (b) uniformly-space nanowire array formation, and (c) chained nanowire assembly. Scale bar = 10μ m. (d) Plot showing the evolution of nanowire alignment where single nanowires and chained nanowires are counted at every 10s during the nanowire assembly. Each stage is distinguished by the different configuration of nanowires at the electrode gap. I: single nanowire alignment, II: uniformly-spaced nanowire formation, III: chained nanowire formation.

As the nanowire density is increased, the distance between adjacent wires becomes

uniform, even though the absolute position of each wire along the gap is not controlled

(Figure 2-7 (b)). In the final phase of assembly, at the highest nanowire density, end-toend chains are formed (Figure 2-7 (c)). The transition between the second and third stage of assembly determines the minimum pitch between adjacent wires in the array. It should be noted that, in all cases, each single nanowire or chain is perfectly centered across the gap. For arrays containing single nanowires, as is the case in the first two phases of assembly, the right and left hand tips of each wire in the array are registered end-to-end with respect to one other.

Figure 2-7 (d) compares the number of single nanowires and chained nanowires that are created as a function of time by injecting 10 μ L of the nanowire suspension with a concentration of 10⁴ nanowires/ μ L. The dark-field optical microscope images show a snapshot of the nanowire array at 40 sec, 100 sec, and 140 sec. In the first two stages of assembly, the number of chained nanowires is negligible. The transition from the first to the second stage of assembly is distinguished by the onset of strong electrostatic interactions between adjacent nanowires assembled across the gap, which is responsible for creating uniformly-spaced arrays. In the third stage of assembly, the single nanowires are converted into end-to-end nanowire chains, and the number of chained wires increases rapidly. The nanowire chaining is due to mutual dielectrophoresis and Coulombic forces between the polarized nanowires, which dominates the assembly process at high nanowire densities.

The following subsections of this thesis provide an in-depth analysis of the forces that dominate in each stage of nanowire directed assembly process by using analytical and/or COMSOL Multiphysics modeling. The first subsection will describe the electrostatic interactions that are responsible for creating the uniform nanowire array. The following subsection will discuss the long- and short-range interactions that give rise to chaining at high nanowire densities. The final subsection will review the forces that cause the nanowires to center across the gap.

2.3.2.1 Assembly Phases I and II: Nanowire-Nanowire Electrostatic Repulsion

Analysis of the real-time video collected during the nanowires assembly process allows a more detailed understanding of the long- and short-range forces that determine the final position of the nanowires along the electrode gap. Figure 2-8 shows a series of





bring field optical microscope image snapshots captured at 0.2 second intervals during nanowire assembly process, where the arrow is tracking a wire that is being dielectrophoretically attracted and aligned across the electrode gap. The first image shows the nanowire approaching an assembled array of uniformly spaced wires. In the second image, the same wire is aligned between two adjacent wires in the array. The last image demonstrates that the nanowire dynamically rearrange until a uniform spacing between adjacent wires is re-established. The spacing between adjacent wires in the array was 11 μ m before the wire was added and 8 μ m after the wire was added. This process continues to reduce the spacing between adjacent nanowires in the array until the onset of chaining becomes dominant in the third phase of assembly.

Figure 2-9 (a) and (b) depict the dielectrophoretic (blue) and electrostatic (black)



Figure 2-9 Illustration of the relation of dielectrophoretic (F_{DEP}) and electrostatic (F_{ES}) forces for nanowires' array formation at (a) the y-z and (b) x-y planes of the electrode gap. These simulations and illustrations suggest that the dielectrophoretic force attracts the polarized nanowires toward electrode gap and the electrostatic force redistributes them for a uniformly spaced nanowire configuration.

orces exerted on the nanowires during the directed assembly process. In addition to the

long-range dielectrophoretic forces responsible for nanowire attraction and alignment

across the electrode gap, the shorter-range electrostatic interactions between adjacent nanowires in the array play a key role in determining the spacing between the assembled nanowires. Specifically, the applied AC bias on the electrically-isolated interdigitated electrodes polarizes the assembled nanowires. The net charge on the nanowires results in a repulsive electrostatic interaction between adjacent wires in the array as well as an attractive electrostatic force that holds the wires on the substrate. Because the assembled nanowires locally screen the electric field produced by the underlying electrode and because they have a repulsive electrostatic force with other polarized wires, additional wires are more likely to assemble in between the existing ones at low nanowire densities (before chaining becomes dominant).

Figure 2-10 shows cross-sectional and top-view plots of the simulated values of the $\nabla |\mathbf{E}|^2$ and the y-component of the electric field, E_y , after the initial phase of nanowire assembly. Figure 2-10 (a) and (b) clearly show that a strong dielectrophoretic force exists at the edge of the biased electrode and around the segments of the polarized nanowires that overlap with the electrode. The dielectrophoretic force between the wires is significantly weaker but extends much f urther into the fluid medium in comparison to the force in the regions surrounding the wires. Because the dielectrophoretic force around the nanowires is highly localized to the regions surrounding the wires, at low nanowire concentrations, there is a higher probability that the nanowires that are flowing in the solution will be attracted and aligned in the space between adjacent nanowires.



Figure 2-10 Cross-sectional (y-z) and top-view (x-y) plots showing (a), (b) $\nabla |\mathbf{E}|^2$ and (c), (d) E_y after the initial phase of nanowire assembly. Cross-sectional y-z and x-y planes are sliced at the edge of biased electrode and at the center of assembled nanowires, respectively. These simulations indicate that the dielectrophoretic force attracts the polarized nanowire toward electrode gap and the electrostatic force redistributes nanowires to form uniformly-spaced arrays.

Moreover, the limited spatial extent of this force indicates that it is not a dominant factor in the dynamic rearrangement of nanowires once they are assembled. Instead, the repulsive electrostatic (Coulombic) forces discussed in the following paragraphs are responsible for creating the uniformly-spaced nanowire arrays.

Based on the similarity of induced charge on the nanowires that are assembled on the electrodes, it is possible to show that the magnitude of the y-component of the electric field, E_y , from the polarized nanowires is directly proportional to the repulsive

electrostatic (Coulombic) force, F_{ES} , between adjacent wires in the array. The charges (Q) on each the nanowires is induced by the capacitive coupling between the nanowire and the electrically-isolated electrode biased at a voltage V, which is given by Q = CV. The nanowire charge can then be approximated by modeling the capacitance due to a metal nanowire that is separated from a biased metal plane by a distance equal to the dielectric layer thickness¹⁶. The electrostatic capacitance of this structure, C_{ES} , is given by:

$$C_{\rm ES} \approx \frac{2\pi\epsilon\ell}{\cosh^{-1}(2{\rm H}/{\rm d})}$$
, (2-8)

where H is the distance between the center of nanowire and the surface of the biased electrode; d is the diameter of the nanowire; ϵ is the permittivity of the dielectric layer, and ℓ is the nanowire's length.

Because each nanowire in the array possesses two oppositely-charged halves, +Q and -Q, the Coulombic repulsion between adjacent wires can be modeled by assuming that the each half of the wire is composed of a point charge (\pm Q). The repulsive electrostatic force along y-direction, F_{ES,y}, between wires is dominant in the internanowire interaction and can be estimated by:

$$F_{ES, y} \approx 2 \frac{Q_1 \cdot Q_2}{4\pi\epsilon_1 r^2} \approx 2Q_1 \cdot E_{y,2}$$
 (2-9)

where Q_1 and Q_2 are the charges on the halves of two adjacent polarized nanowires; ϵ_1 is the permittivity of the liquid medium; $E_{y,2}$ is the magnitude of y-component of electric field induced by Q_2 ; and r is the distance between the nanowires. Figure 2-10 (c) and (d) plot the simulated cross-sectional and top-view of E_y for two nanowires separated by 10 μ m. This shows that E_y is symmetric about each wire and remains near its maximum value of 10⁶ V/m for up to 3 μ m away from the wire.



Figure 2-11 (a) and (b) compare the simulated value of E_y before and after the

Figure 2-11 E_y simulations of x-y planes for (c) before and (d) after alignment of additional nanowires (3) between existing nanowires (1 & 2). The line probes for corresponding E_y along (a) a-a' and (b) A-A' in 2-11 (c) and 2-11 (d), respectively. The additional nanowires distort E_y of adjacent ones, resulting in nanowires' movement along the opposite y-direction. This repulsion occurs consecutively within the nanowire array until the E_y of the individual nanowires becomes symmetrical.

assembly of one additional nanowire that is centered in between the original two wires.

The corresponding values of E_y measured along the dashed lines near the rightmost tip of the nanowires are plotted in Figure 2-11 (c) and (d). The two nanowire configurations in the simulations correspond to the experimental assembly results shown in Figure 2-8 that

are collected at t = 0 seconds (a & c) and t = 0.2 seconds (b & d). As described previously, in the experiment, the strong dielectrophoretic force attracts and aligns the additional nanowire, which disrupts the uniform spacing of wires along the electrode gap. Similarly, Figure 2-11 (b) shows that the additional nanowire distorts the symmetry of E_y around the outer two nanowires. In accordance with the experimental result collected at t = 0.4 seconds, the asymmetry in E_y gives rise to a net electrostatic force that dynamically reorganizes the spacing between the wires to recover a symmetrical E_y around each wire in the array. In this way, the nanowire array maintains a uniform spacing as the nanowire attraction and alignment continues.

The minimum spacing that can be achieved under specified assembly conditions and electrode/wire geometries is defined by the transition from single wire alignment to chain formation. A detailed discussion of the dependence of the minimum nanowire array spacing on parameters such as the dielectric thickness, electrode gap width, AC bias frequency, and amplitude appears later in this chapter.

2.3.2.2 Centering of Aligned Nanowires Across the Electrode Gap

As observed in experimental assembly results shown as insets in Figure 2-6 (c) and (d), which employ AC bias conditions of 1.7×10^6 V/m at 100 kHz and 3.0×10^6 V/m at 1 MHz, the assembled nanowires span the electrode gap symmetrically and have excellent end-to-end registry. Figure 2-12 (a) shows that the nanowires center at the electrode gap regardless of their length, implying that nanowire length has little influence on the symmetrical alignment of nanowires at the electrode gap.



Figure 2-12 (a) Bright-field optical microscope images of nanowires of different lengths, assembled at the electrode gap, indicating that the nanowires span the gap symmetrically regardless of their lengths. Scale bar = 10μ m. (b) Schematic diagram of the nanowires' holding to the electrode gap where symmetrical alignment is sustained by the capacitive-coupling between the nanowires and the underling biased electrodes. (c) Plot of the restoring forces acting on the assembled nanowires as a function of nanowire-offset. The nanowire-offset is defined by the shift of the center of nanowires relative to the center of electrode gap. The insets indicate E_y simulations on the x-y plane through the assembled nanowires, which clearly shows that asymmetrical E_y is induced by the nanowire-offset from the center of electrode gap.

In contrast to the y-directed electrostatic (Coulombic) forces that are responsible for creating uniformly-spaced nanowire arrays, the symmetrical alignment of different length wires across the electrode gap can be explained by considering the magnitude of the x-component of the electric field, E_x , that arises from the electrostatic interaction of the wires with the biased electrode. Here it is assumed that any electrostatic forces due to the fixed surface charge on the nanowire are negligible and are not included in the analysis. Among nanowires' induced surface charges of nanowires, those normal to x-direction only gives rise to the centering of assembled nanowires, The electrostatic force $F_{ES,x}$, responsible for centering of aligned nanowires, can be expressed as:

$$\mathbf{F}_{\mathbf{ES},\mathbf{x}} = \pm \mathbf{Q}_{\perp,\mathbf{X}} \cdot \mathbf{E}_{\mathbf{x}} \,, \tag{2-10}$$

where E_x is the magnitude of the x-directed component of the electric field and $Q_{\perp,X}$ is the induced charge at the end of assembled nanowires. As shown in the simulations plotted in Figure 2-12 (b), when the position of the nanowire is translated in the +x direction relative to the center of the electrode gap, the +x-directed E_{+x} becomes smaller than the -x-directed E_{-x} . In this case, $F_{ES,x}$ is not balanced in the +x and -x directions, $F_{ES,x} + F_{ES,-x} \neq 0$, and the nanowire will experience a restoring force that causes the wire to move in the -x direction. The nanowire will continue to move in the -x direction until the balance of forces equals zero, $F_{ES,x} + F_{ES,-x} = 0$, at which point the wire will be centered across the gap.

Figure 2-12 (c) plots the restoring force, determined from the simulated values of E_x , as a function the nanowire offset (distance between the center of the electrode gap and the center of the nanowire). As expected, the magnitude of the restoring force along the long-axis of the nanowire increases linearly with increasing offset. Notably, for a population of nanowires having nominally identical lengths, this process gives excellent end-to-end registration of the wires assembled across each electrode gap. Poor registry is observed in other directed assembly methods^{26, 27}, which limits their use for chip-scale device integration. As will be discussed in Chapter 4, the end-to-end registration of

nanowire arrays facilitates the addition of metal contacts on both ends of the nanowires, yielding uniform nanowire device arrays²⁸.

, 2.3.2.3 Nanowire-Nanowire Chain Formation

In the third stage of assembly, the formation of end-to-end nanowire chains is due to a combination of mutual dielectrophoretic attraction and local dipole-dipole interactions^{21, 22}. Figure 2-13 shows a two bring field optical microscope image





snapshots captured at 0.2 second intervals during nanowire assembly process, where the arrow is tracking a wire that is being dielectrophoretically attracted and aligned. The first image shows the nanowire approaching an assembled array of uniformly spaced wires. In the second image, the same wire is aligned end-to-end with a previously assembled wire. Notably, as expected from the results presented in Section 2.3.2, the chained

nanowire is centered across the electrode gap such that the interface between the two wires is near the center of the gap. Moreover, the spacing between the two neighboring nanowires in the array increases. The dependence of nanowire array spacing with wire length will be discussed in Section 2.5.

Figure 2-14 (a) and (b) plots the simulated values of the electric field intensity measured at the tips of nanowires and at the edges of biased electrodes. As shown in



Figure 2-14 The electric field strength on the y-z planes of the alignment structure with assembled nanowires where the cross-sections are from (a) the tips of the nanowires and (b) the edges of biased electrodes. The inset in (a) also shows the electric field distribution in the vicinity of assembled nanowires (x-y plane) sliced at their center. These simulations highlight the nature of the localized stronger electric field from the tips of assembled nanowires in (a) while the electric field from the biased electrodes vertically extends toward the suspension (b).

Figure 2-14 (a), the region with the highest electric field is localized near the tips of the assembled nanowires and decays rapidly away from the surface of the nanowire. In

contrast, the plot in Figure 2-14 (b) shows that the electric field, although at least a factor of ten lower in field strength, extends much further into the fluid medium at the edge of the biased electrodes. As discussed previously, at low nanowire densities, the longerrange dielectrophoretic forces due to the electric field at the edges of the biased electrodes favor the attraction and alignment of the nanowires between the wires that are already assembled on the electrodes. Even at low concentrations, however, a small fraction of the nanowires will flow near the substrate surface and be found within the high electric field region at the tips of the assembled nanowires. These nanowires will be preferentially aligned end-to-end with the existing nanowire via mutual dielectrophoresis, which describes the attractive motion of polarized nanowires toward assembled ones. This explains the formation of chains at low nanowire density as demonstrated in Figure 2-7.

Figure 2-15 (a), (b) and (c) plot the electric field intensity as the spacing between adjacent nanowires in the array decreases. At the electrode edges, the field strength and vertical extent of the field decreases with increasing array density. In contrast, the fraction of the substrate surface area having high field strength (around the nanowire tips, field strength independent of wire density) increases. Thus, the probability of forming end-to-end nanowire chains increases as the nanowire array spacing decreases. As shown in Figure 2-7, the transition between single wire and chained wire assembly occurs gradually, eventually reaching a nanowire array density where nearly all of the additional wires in the fluid are assembled by mutual dielectrophoresis to form end-to-end chains.



Figure 2-15 The electric field strength on the y-z planes sliced at the edges of biased electrodes, demonstrating that vertical extent of electric field intensity becomes attenuated with increasing nanowire array density. The internanowire spacings are (a) 12, (b) 6, and (c) $3\mu m$.

Following the experimental results shown in Figure 2-12, Figure 2-16 (a) and (b) plots the simulated values of the electric field strength before and after the end-to-end assembly of an additional nanowire to form a two wire chain. The electric field simulation in Figure 2-16 (a) visualizes that dielectrophoretic force can continue to pull the nanowire closer to the electrode gap after nanowire array formation. Evidently from the inset in Figure 2-16 (a) that the localized electric field from the nanowire in the array tends to interact with additional nanowires within a certain interaction range. Since the



Figure 2-16 Electric field distribution on the x-y planes of the alignment structure (a) before and (b) after the chained nanowire configuration. The additional nanowires are placed $0.5\mu m$ away from the existing ones in the array.

existing nanowire array is electrostatically tied to the electrode gap, the additional nanowires should join with it, forming the nanowire-nanowire chain. Notably, the asymmetry of nanowires relative to the electrode arises again immediately after nanowire-nanowire chain formation. The resulting asymmetrical electric field distribution along the longitudinal direction of the nanowires ultimately restores the symmetry of the chained nanowires by moving them. Observations indicate that this process is instantaneous and barely observable in captured video, implying that this restoring force still remains strong after the chain formation.

2.3.2.4 Suppressing Nanowire Chains with Recessed Wells

The simulation results in the previous section showed that the probability of forming end-to-end nanowire chains increased as the electric field strength at the nanowire tips relative to the field strength between adjacent assembled nanowires increased. Thus, nanowire chain formation becomes dominant over single wire assembly when the density of wires assembled in the array is high. Because the vertical extent of the dielectrophoretic force induced by the nonuniform electric field at the wire tips is short compared to the same force at the electrode edges, it is possible to modify the design of the features on the substrate to significantly reduce the formation of nanowire chains even at high nanowire densities. In particular, as illustrated in Figure 2-17,



Figure 2-17 Illustration of nanowire array formation in the deep PMGI trench on the alignment structure where end-to-end nanowire interaction is structurally inhibited.

fabricating a recessed well in the regions surrounding the electrode gap can be used to

suppress the dielectrophoretic force from the nanowire tips.

The structure used to study the effectiveness of the dielectric well on reducing the number of nanowire chains was fabricated by lithographically patterning the PMGI dielectric layer coated on top of the assembly electrodes. The width of the well and the thickness of the surrounding PMGI dielectric layer required to suppress the dielectrophoretic forces from the nanowire tips was determined using 3D COMSOL Multiphysics simulations that investigated the dielectrophoretic forces and electric field intensity at various points in this structure. Figure 2-18 (a) plots $\nabla |\mathbf{E}|^2$, proportional to the dielectrophoretic force, for a PMGI well that is 3 µm deep and is 2 µm wider than the nanowires assembled at the base of the well. This plot shows that the dielectrophoretic force induced by the biased electrodes extends vertically beyond the top surface of the thick dielectric and thus preferentially attracts wires into the wells. Figure 2-18 (b) plots the electric field strength $(|\mathbf{E}|)$ in cross section along the tips of the nanowires assembled in the well. This demonstrates that the highly localized electric field at the tips of the wires, which is responsible for mutual dielectrophoresis and chain formation, does not extend to the top of the well. Therefore, there is a significantly lower probability of creating nanowire chains in this structure as compared to the planar structure discussed previously. Specifically, at high nanowire density, excess wires tend to flow across the surface rather than aligning into end-to-end chains. Figure 2-18 (c) plots the magnitude of the y-directed electric field, E_y, around a pair of assembled nanowires. This simulation result confirms that adjacent wires aligned across the electrode gap experience the same electrostatic forces described previously, which are responsible for producing uniformly spaced and centered nanowire arrays.


Figure 2-18 Simulations for (a) $\nabla |\mathbf{E}|^2$, (b) $|\mathbf{E}|$, and (c) E_y of the illustrated alignment at the cross-sections of z-x, y-z, and x-y planes, respectively. The distance labeled "t" in the illustration and simulation, between the top surface of the PMGI layer and the tips of the assembled nanowire, creates difficulty for interaction between an additional nanowire and one in the deep trench. This structural constraint for nanowire chain formation favors dielectrophoretic alignment in the trench, yielding a nanowire array nearly free of nanowire chains.

Figure 2-19 (a) shows a dark-field optical microscope image of a nanowire array that was assembled within the dielectric well after the fluid was evaporated. The 2.5 μ m





deep well was defined in the deep-ultraviolet PMGI resist layer by flood exposing and

developing the PMGI through a second patterned BPRS-100 photoresist mask. This

process left a 0.3 μ m thick PMGI layer at the base of the well, which is comparable to thickness of the planar PMGI layer in the previous experiments. The same interdigitated assembly electrode with a 3 μ m electrode gap and bias conditions of 10 V_{pp} at 100kHz were used for comparison. Figure 2-19 (b) shows the nanowire array along the same electrode gap as it transitions from a segment with the well to a segment without the well. The planar PMGI dielectric layer in the region without the well was 2.8 μ m thick.

As expected from the 3D electric-field simulation, the nanowire array assembly results shown in Figure 2-19 confirm that the lithographically-defined well is effective at suppressing nanowire chain formation. Nearly 100% of the wires assembled across the electrode gap along the planar segment were chains as compared to fewer than 10% of the wires assembled within the well segment. Importantly, the individual nanowires within the wells are centered across the electrode gap. The alignment of a second nanowire at the tip of a wire already assembled within the well did not result in a recentering of the end-to-end chain across the gap as observed for the chains on the planar electrode segement. Instead, the second wire is aligned on the top surface of the PMGI layer outside of the well. This is because the PMGI well constrains the lateral movement of the nanowires assembled in the well, preventing their recentering due to the electrostatic coupling with the underlying assembly electrodes.

The optical microscope images collected after the fluid evaporated show that the spacing between the nanowire arrays assembled within the wells is not as uniform as arrays on the planar surface in the second phase of assembly (e.g., see Figure 2-7). A comparison of the nanowire array before and after the fluid evaporated indicates that the capillary forces due to the receding meniscus are the primary factor responsible for poor

uniformity of the array. Thus, further optimization of the well design and contact angle between the fluid and the substrate could be used to reduce the disorder with drying. This concept of using lithographically-defined wells is extended in Chapter 4 to further improve positional registration of individual nanowires with respect to predefined features on the substrate.

2.4 Dependence of Nanowire Array Assembly on the Nanowire Length, Structure Geometry, and Assembly Conditions

The previous sections of this thesis discussed the regimes of nanowire assembly by analyzing the experimental results collected using one electrode structure (*e.g.*, electrode gap width and dielectric thickness) and one nanowire type (*e.g.*, 7 μ m long Rh nanowire). A more thorough understanding of the electric-field-assisted directed assembly process requires a correlation between the properties of the assembled nanowire array with systematic variations in the assembly parameters and structure geometry. The following subsections describe the effect of varying the nanowire length, electrode gap width, dielectric layer thickness, and AC bias amplitude and frequency.

2.4.1 Parametric Study of Nanowire Array Assembly

The nanowire assembly experiments were conducted using the same interdigitated electrode structure described Section 2-2. The following parameters were varied:

- (1) Different 250 nm diameter Rh nanowire lengths of 7, 13, and 24 μm and electrode gap widths of 3 and 6 μm. The planar PMGI dielectric layer thickness was 0.3 μm and the AC voltage was 10 V_{pp} at a frequency of 100 kHz.
- (2) Different planar PMGI thicknesses of 0.3, 0.6, 0.9, 2.1, 2.7, and 4.2 μ m. The Rh nanowires were xx nm in diameter and xx μ m long. The AC voltage was 10 V_{pp} at a frequency of 100 kHz.
- (3) Different applied AC voltage of 5 to 35 V_{pp} in steps of 5 V_{pp} . The naowire length was 7 μ m, the electrode gap width was 3 μ m, and the PMGI thickness was 0.3 μ m.

To maintain consistency in the nanowire assembly process across these experiments, the concentration of Rh nanowires was diluted to $\sim 1 \times 10^4$ nanowires/µL in isopropyl alcohol. A total volume of 10µL was injected between the subustrate surface and the cover slip until significant end-to-end nanowire chaining was observed. This transition from a uniformly spaced nanowire array to significant chaining was used to determine the minimum spacing between adjacent nanowires in the array.

2.4.1.1 Nanowire Array Spacing Dependence on Nanowire Length and Electrode Gap Width

Figure 2-20 (a) shows a series of dark-field optical microscope images collected at the minimum nanowire array spacing for the 7, 13, and 24 μ m long Rh nanowires aligned across the 3 μ m wide electrode gaps using an AC bias of 10 V_{pp}. The results



Figure 2-20 (a) Plot of internanowire spacing in the array with different nanowire lengths ($\ell = 7, 13, \text{ and } 24\mu\text{m}$) where different widths of electrode gaps, $3\mu\text{m}$ (black square) and $6\mu\text{m}$ (red circle), are employed. The inset shows dark-field optical microscope images of Rh nanowire array assembled on 3 μm -spaced electrode gap. (b) Plot for the interwire spacing as a function of nanowire length that spans the metal assembly electrodes. Inset schematic shows the length of nanowires overlapped by the biased electrodes.

demonstrate that uniformly spaced nanowire arrays having excellent end-to-end registration along the entire length of the electrode gap were obtained for all of the wire lengths investigated. The minimum spacing between adjacent nanowires as a function of nanowire length for the 3 and 6 μ m electrode gap widths is plotted in Figure 2-20 (a). In both cases, the interwire spacing increased linearly as the wire length increased from 7 to 24 μ m. However, the interwire spacing was consistently larger for the smaller gap width, increasing from 5 to 12 μ m for the 3 μ m gap width as compared to 4 to 10 μ m for the 6 μ m gap width.

As decribed in Section 2.3.2.1, the uniform spacing is achieved because of the repulsive electrostatic force between adjacent nanowires in the array, which is proportional to the charge induced on the wire by the biased assembly electrode. Figure 2-20 (b) plots the interwire spacing as a function of nanowire length that spans the metal assembly electrodes, which varies from 1 to 21 μ m for the three wire lengths and two electrode gap widths. As expected based on the simple electrostatic analysis presented in Section 2.3.3.1, the interwire spacing increased linearly as the fraction of the wire length that overlaps with the assembly electrode increased. The following subsection provides a more detailed analytical model to analyze this trend.

Importantly, the experimental data presented in this section can be used to develop design rules to optimize the assembly electrode geometry for applications that require different nanowire array spacings. For example, for a given wire length, the fraction of the wire that overlaps the assembly electrode should be minimized to give the smallest spacing for high density nanowire device arrays. It is also possible to limit the wire density by increasing the length of the wire that spans the electrode gaps. As described in Chapter 3, this control over nanowire spacing will be crucial to achieving accurate placement of individual wires along the length of the assembly electrode using arrays of lithographically defined wells.

2.4.1.2 Analytical Model to Describe Nanowire Array Spacing Dependence on Nanowire Length and Gap Width.

A more accurate analytical model that describes the electrostatic forces of attraction and repulsion for a pair of polarized nanowires is described by the illustration in Figure 2-21. The distributed charge induced on the nanowire by the underlying metal



Figure 2-21 Schematic diagram for the theoretical model for the electrostatic interaction between two adjacent nanowires. Double integration of Coulombic force of the charges in the dx' segment, experienced by the electric field from the charges in dx segment, completes the total force calculation. Taking only the y-component of the total force into account yields nanowires' repulsive and attractive behavior while bound to the electrode gap.

assembly electrodes are labeled "+" and "-" for the positive and negative charge,

respectively. The expression for the Coulombic force exerted on the nanowire segment dx' by the electric field from the charge on the adjacent nanowire at the segment dx is given by:

$$\mathrm{dF} = \frac{\mathrm{dqdq'}}{\mathrm{4q}\epsilon_1 \mathrm{r}^2},\tag{2-11}$$

where dq and dq' is the charge on the nanowires; ϵ_1 is the permittivity of the isopropyl alcohol, and r is the distance between dx and dx'.

By assuming the charge is uniformly distributed around the nanowire, the total ydirected Coulombic (electrostatic) force, $F_{ES, y}$, can be determined by integrating the equation (2-11) over dx and dx['] from -1/2 ℓ to 1/2 ℓ :

$$F_{ES,y} = \frac{1}{4\pi\epsilon_1} \int_{-\frac{1}{2}\ell}^{\frac{1}{2}\ell} \left[\int_{-\frac{1}{2}\ell}^{\frac{1}{2}\ell} \frac{\lambda(x) \cdot D}{((x-x')^2 + D^2)^{\frac{3}{2}}} dx \right] \lambda(x') dx', \qquad (2-12)$$

where ℓ is the nanowire length and $\lambda(\mathbf{x})$ is the nanowire line charge density. The nanowire line charge is induced by capacitive coupling of the wire to the underlying biased assembly electrode. Figure 2-22 (a) shows a simulation of electric field intensity plotted in cross-section along center of the wire for an electrode structure with a 3 µm gap, a 0.3 µm dielectric layer thickness, and an AC bias voltage of V_{pp} =10V. The induced line charge density along the nanowire length can then be sketched as the dashed line in Figure 2-22 (b). This shows that the charge density is nearly uniform along the segment of the nanowire that overlaps with the biased assembly electrodes and then gradually tapers to down to zero beginning at the edge of the electrode.



Figure 2-22 (a) Simulation of the electric field at the z-x plane taken along the center of the nanowire showing the capacitive-coupling between the nanowire and the biased electrode. The inset shows the y-component of the electric field from the polarized nanowire. This shows that that the charge density is uniform in the segments where the wire spans the biased electrode. (b) Schematic drawing of line charge density induced on the nanowire with a total length ℓ that spans the electrode gap symmetrically. Solid line refers to the simplified model for the line charge density.

The actual line charge density on the nanowire can be approximated by an abrupt transition from the maximum charge to zero charge near the edge of the assembly electrode. This approximation, drawn as a solid line in Figure 2-20 (b), can be expressed as:

$$\lambda(\mathbf{x}) = +\sigma$$
 for $-\frac{1}{2} \ell \le \mathbf{x} \le 0$, and (2-13)

$$\lambda(\mathbf{x}) = -\sigma \qquad \text{for } 0 \le \mathbf{x} \le +\frac{1}{2} \ell . \tag{2-14}$$

Evaluating (2-12) usuing this simplified line charge density model gives:

$$F_{ES,y} = \frac{2\sigma^2}{4\pi\epsilon_1} \left[2\left\{ \sqrt{1 + \frac{1}{4}\left(\frac{\ell}{D}\right)^2} - 1 \right\} - \left\{ \sqrt{1 + \left(\frac{\ell}{D}\right)^2} - 2\sqrt{1 + \frac{1}{4}\left(\frac{\ell}{D}\right)^2} + 1 \right\} \right]$$
(2-15)

The first and second terms in (2-15) are due to the repulsive and attractive forces between two adjacent polarized nanowires, respectively. This expression indicates that the net force exterted on adjacent nanowires is positive (repulsive) and inversely proportional to the spacing between the wires. Additionally, this repulsive force between the wires becomes larger when ratio of internanowire spacing (D) to length (ℓ) is smaller.

Figure 2-23 (a) plots the net Coulombic force determined from (2-15) as a function of the distance between the nanowires (y) and the nanowire length (ℓ) . This This plot predicts that the repulsive force (F_R) tends to become less strong as the internanowires' separation distances (D) increase. A further approximation from the previous model indicates that uniform charge density of half of assembled nanowires, can easily clarify this tendency. In other words, the polarized nanowires can be a further approximation of dumbbell dipole structures having the opposite charges, positive and negative, at the ends of the dumbbells, as shown in Figure 2-23 (b). Simply, two forces exist, the repulsive force between the charges with the same polarities and the attractive force with the different polarities. At very small distances (D) between the dumbbells, the repulsive forces dominate the attractive forces since the distances between the same polarities is much smaller than the different polarities. This strong repulsion keeps the assembled nanowires a few micrometers apart, leading to a single nanowire assembly. If the inter-nanowire distance (D) becomes much larger compared to a nanowire's length (ℓ) , the repulsive force tends to converge as the attractive force while each force is still in effect. As a result, the overall electrostatic interaction between the assembled nanowires becomes nearly negligible, making them static between the biased electrodes. Consistent with this intuitive explanation, Figure 2-23 (a) shows that the force amplitude indicates a

positive value, namely repulsive force, while this force amplitude tends to converge at zero at larger inter-nanowire spacing compared to nanowire length.



Figure 2-23 Plot for the relation between the force, F_y , and the nanowire spacing, y, while varying the nanowire length, ℓ , from $3\mu m$ to $30\mu m$. The positive value in the plot refers to the repulsive force between the nanowires, indicating that they tend to be spaced at all different length of nanowires. The vertical dashed lines are drawn to compare the forces at the constant distances.

As investigated in Section 2.3.2.1, the uniformly-spaced nanowire array begins to form as the nanowire spacing comes close to a certain value for efficient electrostatic interaction. According to the plot in Figure 2-23, this tendency becomes more significant in longer nanowires, hinting that longer nanowires can easily form a uniformly-spaced nanowire array. Also easily recognize from the plot is that the longer nanowires experience a higher degree of repulsion between them at the same inter-nanowire distance. This relation is intuitively sensible because longer nanowires have more overlapping by the underlying biased electrode, leading to higher repulsion between the

assembled nanowires primarily due to more charges within them. Additionally, repulsive forces are normalized by the maximum values of different nanowire lengths, whose functions are plotted in Figure 2-24 to investigate their relationships at fixed nanowire



Figure 2-24 Plot of the normalized force as a function of a nanowire's length, ℓ , at fixed nanowire distance, y = 1, 5, and 10µm, marked by the dashed lines in Figure 2-23. The inset illustrates a nanowire's repulsion, F_R , at the electrode gap.

spacing. This plot reveals that the repulsive force develops into an approximate linear relationship with the lengths of nanowires, particularly at small nanowire spacing. This force relates to the average spacing within the nanowire array.

The frictional interaction of nanowires with the PMGI layer might be another factor affecting electrostatic forces between the assembled nanowires and their spacing. Perhaps, in some way the nanowires slide away from each other until the repulsive interaction exceeds the friction. This friction should depend on the magnitude of capacitive-coupling between the nanowires and the biased electrode.

2.4.1.3 Dependence on Dielectric Layer Thickness

Figure 2-25 (a) shows a series of dark-field optical microscope images collected after assembling 7 μ m long Rh nanowires on the 3 μ m wide electrode gap structure at an AC bias of V_{pp} =10V with PMGI dielectric layer thicknesses that vary from 0.3 μ m to 4.2 μ m. The arrays maintained uniform nanowire spacing with end-to-end registration of the wire tips for all the dielectric layer thicknesses investigated. The minimum interwire spacing as a function of dielectric layer thickness is plotted in Figure 2-25 (b). The results demonstrate that the spacing between adjacent wires also increases linearly with increasing PMGI layer thickness, from an interwire spacing of 4 μ m at a dielectric thickness of 0.3 μ m to a spacing of 13 μ m at a thickness of 4.2 μ m. This indicates that the

This uniform nanowire array formation on a 4µm thick PMGI layer implies that the electrostatic interaction between the assembled nanowires is still valid as long as the nanowires become polarized by the electric field from the electrode gap. Understanding that electric field strength from the biased electrode covered by the thick dielectric layer becomes attenuated, inversely proportional to its thickness is easily comprehensible.



Figure 2-25 (a) Schematic diagram of nanowire alignment structure for the internanowire spacing with different PMGI thicknesses. (b) Series of dark-field optical microscopic images for the different thicknesses of PMGI layers ($t_{PMGI} = 0.3, 0.6, 0.9, 2.1, 2.7, and 4.2\mu m$), and (c) its plot for the relationship between the internanowire spacing and PMGI thicknesses.

Figure 2-26 clearly shows that the electric field in the suspension as well as in the vicinity of the electrode gap becomes weaker with a thicker PMGI layer spun on it. Evident from Figure 2-26 is that the electric field at the electrode gap decreases by nearly 2 orders as the thickness of the PMGI layer decreases from 0.3µm to 5.4µm.



Figure 2-26 Spatial electric field distribution at different thicknesses of PMGI layers (t_{PMGI} =0.3, 0.9, 2.7, and 5.4µm) exhibiting the electric field's spread toward the liquid medium. Smaller number of nanowires in the suspension will be polarized, dielectrophoretically attracted, and redistributed on thicker PMGI layers, leading to smaller inter-nanowire spacing. This is due to the electric field's decaying relatively quickly on thick PMGI layers.

In order to interpret this inter-nanowire spacing dependence on the thickness of PMGI, performing a simulation to compare the ratio of the electrostatic (F_{ES}) and dielectrophoretic (F_{DEP}) forces is necessary. Similarly, a plot of $E_y/cosh^{-1}(2H/d)$ for the inter-nanowire repulsion force and $\nabla |\mathbf{E}|^2$ for the dielectrophoretic force as functions of PMGI thickness from 0.3µm to 7.2µm appears in Figure 2-27. This plot describes that both forces at the surface of the PMGI layer diminish as PMGI thickness increases. This relationship is compatible with the theoretical expectation from Equations (2-17) and (2-18). The inset of Figure 2-27, however, shows that their ratios of F_{ES} to F_{DEP} increase

nearly linearly as PMGI thickness increases, suggesting that the electrostatic force



Figure 2-27 Plot of the electrostatic repulsive $(E_y/\cosh^{-1}(2H/d))$ and dielectrophoretic $(\nabla |\mathbf{E}|^2)$ forces as functions of PMGI thickness. The inset shows that ratios of electrostatic to dielectrophoretic forces increase nearly linearly as the PMGI thickness increases. This result coincides well with Figure 2-25.

between the assembled nanowires becomes relatively stronger compared to the dielectrophoretic nanowire attraction. Thus, the ratios of $E_y/\cosh^{-1}(2H/d)$ to $\nabla |\mathbf{E}|^2$ seem to provide an adequate account for the relationship between the electrostatic and dielectrophoretic forces, namely sensitive inter-nanowire spacing change according to differing PMGI thicknesses.

2.4.1.4 Frequency and Amplitude of Applied Bias

According to Equation (2-15), electrostatic repulsive force can be determined by the value of the charge density (σ) on the assembled nanowires. Approximation of the nanowire-electrode system to the parallel capacitor leads to modulation of the induced charges in the polarized nanowires as a function of bias conditions and the materials' parameters in the alignment structure, all of which eventually affect nanowire spacing. The charge of the nanowire using a simple capacitor model and the capacitance of the nanowire on the biased electrode approximation has the expression¹⁶:

$$Q = C V = \frac{\pi \epsilon \ell}{\cosh^{-1}(2H/d)} V , \qquad (2-16)$$

where ϵ is the permittivity of dielectric layer; H is the distance between the biased electrode and the center of nanowire; d is the diameter of nanowire, and V is the potential between the nanowire and the electrode and is proportional to the applied bias. With fixed nanowire length and diameter at a constant value due to batch fabrication, the amount of charges in the nanowires depends on the amplitude of applied bias and the thickness of the dielectric layer.

As presented in Section 2.3.1 and elsewhere²⁹, the frequency of applied bias could influence nanowire alignment on a biased electrode. In other words, the frequency response of dipole moment in the polarized nanowires determines the dielectrophoretic nanowire attraction by the real part of the Clausius-Mossotti factor ($R_e(K)$). The frequency of applied bias also affects the induced charges in the assembled nanowires resulting in the frequency-dependent electrostatic force between them. In contrast to the dipole formation in semiconducting nanowires, the metal is of very high permittivity material due to free electrons in it. Ideally an infinite value makes $R_e(K)$ almost constant over a wide range of frequencies, as discussed in Section 2.3. Without doubt, the frequency response of free electrons in the metal is instant. Thus, the induced charges in the assembled nanowires as well as the dielectrophoretic attraction of them can be considered frequency-independent factors for determining the nanowires' spacing in the array. The average spacing of 7µm long rhodium nanowires, assembled at the electrode gap in Section 2.3.1, is estimated to be about 5µm in the range of 10kHz to 10MHz. As discussed, no significant change in nanowire spacing were observed at relatively low frequency ranges compared to the relaxation time of free electrons in the metal.





Figure 2-28 Plot of average nanowire spacing as a function of the voltage of applied bias, V_{pp} . Apparently, the inter-nanowire spacing increases gradually as the voltage of applied bias ramps up from 5 V to 35 V. Dark field optical microscope images of the nanowire array are obtained from V_{pp} = 5, 15, and 35 V. Scale bar = 5µm.

peak voltage of applied bias (V_{pp}). An observation was that 7µm-long rhodium nanowires form uniformly-spaced arrays on the electrode gap for all voltage ranges. In contrast to the theoretical expectation described in Equation (2-15) and (2-16), the plot demonstrates that the nanowire spacing tends to increases very gradually as the bias voltage ramps up. This discrepancy might appear intuitively inapprehensible until the effect of voltage for trapping the nanowires from the suspension is taken into account. Previously discussed is that the electric field from the electrode gap spreads into the liquid medium, resulting in polarizing the nanowires within the decay length and directing them toward the high density electric field region. Since the strength of the electric field in the medium, as well as at the electrode gap, depend on the voltage of applied bias, higher voltage applied between the electrodes leads to more nanowires attracted to the electrode gaps while the assembled nanowires form a uniformly-spaced nanowire array.

In order to investigate the dependence of applied voltage for the nanowire assembly, visualization of the spatial distribution of the electric field from the electrode gap can be beneficial. Figure 2-29 (a)-(c) displays the spatial electric field distributions of z-x planes toward the nanowire solution at $V_{pp} = 5$, 10, and 20V. Comparison of spatical electric field distributions as a function of amplitude of applied biasclearly contrasts the critical nature of field strength spread in the suspension with almost linearly proportionality of the applied voltage. For example, predictably from Figure 2-29 (a) and (b), the minimum electric field required for nanowire attraction, namely about 10^6 V/m, at $V_{pp}=10$ V, extends toward the nanowire suspension two times further than at $V_{pp}=5$ V in



Figure 2-29 Normalized electric field simulation at different voltages of applied bias (V_{pp} = 5, 10, and 20 V) exhibiting the electric field's spread toward the liquid medium. The nanowires will be polarized and dielectrophoretically attracted toward the electrode gap if they are within the decay length of the critical electric field.

the nanowire assembly. This tendency suggests that more nanowires in the suspension are within an electric field of effective nanowire polarization at higher voltages, resulting in a nanowire array formation with less spacing.

Comparison of the dielectrophoretic force, responsible for the number of nanowires to be assembled, and the electrostatic repulsion between the nanowires, responsible for the inter-nanowire spacing, is a reasonable indication for determining the inter-nanowire spacing for given conditions. Expression of the dielectrophoretic force is⁷.

$$F_{\text{DEP}} = \frac{\pi d^2 \ell}{24} \varepsilon_1 \operatorname{Re} (K) \cdot \nabla |\mathbf{E}|^2 ; \qquad (2-17)$$

$$F_{\rm ES} = \left(\frac{2\pi\epsilon}{\cosh^{-1}(2H/d)}\frac{\ell}{2}V\right) \cdot E_{\rm y} , \qquad (2-18)$$

where ε_1 is the permittivity of the liquid medium, and Re(K) is the real part of the Clausius-Mossotti factor. Using the simulation, the ratio of the electrostatic repulsive to

the dielectrophoretic forces enables estimation of the relative inter-nanowire spacing in the array according to the chosen specific bias conditions and materials' parameters. In other words, their high ratios of electrostatic to dielectrophoretic forces at the given conditions of applied voltage provide an indication of relatively stronger electrostatic force between assembled nanowires compared to the dielectrophoretic force, leading to larger spacing between the nanowires.



Figure 2-30 shows the plot of the ratio of the electrostatic (F_{ES}) and

Figure 2-30 Plot of the electrostatic repulsive $E_y V_{pp}$ and dielectrophoretic $\nabla |\mathbf{E}|^2$ forces as functions of the applied bias strength. The inset emphasizes that ratios of the electrostatic to dielectrophoretic forces increase relatively gradually as the applied bias increases. The ratio increase is consistent with the experimental results shown in Figure 2-28.

dielectrophoretic (F_{DEP}) forces in which E_y for F_{ES} , and $\nabla |\mathbf{E}|^2$ for F_{DEP} , are extracted

from the PMGI surface above the electrode edge and the surface of the assembled

nanowires in the simulations, respectively. The peak-to-peak voltage of applied bias (V_{pp}) varied from 1 V to 35 V. As anticipated from the equations, notably, from Figure 2-30, the electrostatic repulsive force and dielectrophoretic force increase as the voltage ramps up. As explained earlier in this paragraph, comparison of the ratios is more important for clarifying the relationship between the inter-nanowire spacing and the voltage. The inset displayed in Figure 2-30 shows that the ratio of F_{ES}/F_{DEP} increases by a small increment as the voltage increases. This further suggests that the inter-nanowire spacing at varying voltages has the same relationship. Apparently, this relationship is quite consistent with the plot of the experimental results shown in Figure 2-28.

2.5 Conclusion

This research demonstrates that the combination of dielectrophoretic force and electrostatic interaction produces uniformly-spaced nanowire arrays at the electrode gap of biased electrodes. Assembled nanowire arrays feature the high degrees of nanowire attraction and orientation at the desired location, namely the electrode gap which the assembled nanowire span symmetrically due to their electrostatic interaction with the underlying biased electrodes. The nanowires in the array tend to be reconfigured into nanowire-nanowire chains, detrimental to device performance, by the injection of additional nanowires. Thus, this research demonstrates a simple, yet efficient, approach to preventing nanowires from forming nanowire-to-nanowire configurations by the structural constraint of a deep PMGI photoresist trench. These experimental results,

supported by theoretical simulation, indicate that the electric field can readily manipulate any polarizable nanowires, leading to their organization in a highly ordered fashion.

In-depth investigation regarding the dependence of nanowire spacing on the bias conditions and alignment structure presents that the average spacing within in an array can be readily controlled by the relative strength of electrostatic repulsion to dielectrophoretic attraction.

2.6 References

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Chapter 3

DETERMINISTIC NANOWIRE INTEGRATION FOR ON-CHIP APPLICAITON

Chapters 2 discussed dielectrophoretic nanowire alignment and array formation between biased electrodes. Apparently, a strong electric field gradient is responsible for attracting nanowires toward the electrode gap while the electrostatic interaction between the assembled nanowires maintains uniform spacing in the array. Furthermore, the electrostatic interaction between the assembled nanowires and biased electrodes favors the attracted nanowires' symmetrically spanning the electrode gap. Chapter 2 also discussed the detailed investigation of the dependence of nanowires' spacing on the alignment structure and biased conditions, which further clarifies the mechanism governing formation of uniform spacing in the array. The investigation indicates that the interplay between dielectrophoretic attraction and electrostatic repulsion forces determine the spacing between assembled nanowires.

As a fundamental study, the theoretical and experimental investigation regarding the uniformly-spaced nanowire array appears beneficial in that nanodevices can be fabricated by capitalizing on self-determined spacing, free of a requirement controlling nanowire registration. However, integration of functional nanowires on a circuit structure requires precise positioning at predefined locations with accurate registration. The restrictions have been addressed by many other bottom-assembly techniques but remain significant challenges for realization at commercial levels. Therefore, Chapter 3 discusses nanowires' deterministic integration at desired locations on a substrate. These assemblies demonstrate high yield and accurate registration. Section 3.1 discusses the background and motivation for developing deterministic nanowire assemblies for on-chip application. In the course of research, a potential exists for positioning nanowires or nanotubes using a microfabricated electrode array, and dielectrophoresis has shown potential for achieving high-yield integration on a substrate. This section also discusses further investigation of nanowire alignment structures and post-assembly processes for metal contact formation necessary for reproducible and reliable fabrication of nanowire device arrays.

Section 3.2 compares two different alignment structures, finger-like metal tips, and recessed dielectric wells, for spatially-controlled nanowire alignment where a strong electric field region at the tips or within the wells determines the final position of the assembled nanowires. Despite of strong dielectrophoretic force from the finger-like metal tips, their repulsive electrostatic interaction with the the nanowires assembled in their proximity resulted in < 20% assembly yield. As suggested in the simulation, a recessed photoresist well attracts the nanowires from the suspension medium and also traps them with stronger dielectrophoretic force, compared to the edges of biased electrodes, achieving > 90% assembly yield.

Section 3.3 demonstrates that the proposed high-yield assembly method which uses a recessed photoresist well is applicable to the fabrication of functional nanowire devices on a substrate. The electrical address and mechanical contact of the assembled nanowires is possible through the developed post-assembly process which includes metal electrodeposition for electrical contact and dry etch for device isolation. Thorough analysis of completed Rh nanowire devices, as control samples, reveals that >95 % of device sites are filled by a single nanowire. Furthermore, Rh nanowire devices exhibited small resistance variations compared to nanowire diameters while showing low contact resistances.

This section also describes that PEDOT/ClO₄, conducting polymer nanowires are the functional nanowire devices for on-chip sensor fabrication using the proposed approach. Analysis of completed PEDOT/ClO₄ nanowire devices demonstrates the highyield of single nanowire assemblies on a substrate. These arrays have accurate registration and retain functionality during the process. Sensing performance of PEDOT/ClO₄ nanowire device by various chemical analytes represents an example of bottom-up integration of functional devices on a substrate. Furthermore, the process also demonstrates that this approach, including the post-assembly process, can accommodate many different types of nanowires on a substrate or for a circuit structure with a specific capability. The accommodating characteristic allows material flexibility and diversity on the same substrate.

3.1 Background and Motivation

Despite of significant advance in nanowire synthesis, integration of nanowire at desired locations on a substrate or CMOS circuitry represents a major challenge toward realization of functional-diversified CMOS circuitry as illustrated in Figure 1-1. The fabrication challenges include registration accuracy of nanowire and effective metallization for robust electrical connections to the features within a substrate or CMOS circuitry. In most applications, assembly of a single nanowire at a predefined position and

orientation with submicron registration accuracy is desirable, and especially preferable is a process that facilitates post-metallization of both ends of the nanowires.

Dielectrophoretic manipulation of nanowires has shown its capability to attract, align, and position nanowires in a controlled manner. As shown in Figure 3-1, recent



Figure 3-1 Electric field-assisted nanomaterials integrations for nanodevice array fabrication. (a) Gold nanowires, (b) indium phosphide nanowires, and (c) carbon nanotubes, (d) indium arsenide nanowires. Schemes and images are publications from (a) Mayer¹, (b) Lieber², (c) Krupke³, and (d) Yu⁴ groups.

successful demonstrations of large area single nanowire or nanotube assemblies on substrates represent a bright prospect and a significant advancement for dielectrophoresis. These dielectrophoresis achieving the high yield integration take an advantage of spatially-defined strong electric fields to direct the nanowires toward the specific locations on a substrate or circuit. A finger-like protruding electrode design³⁻⁹ has been a popular technique to assemble single nanomaterials between a pair of electrode arrays where the localized electric field arises.

Following nanowire alignment between metal islands by Smith et al.¹, Duan et al.² exploited the electric field to align and position individual InP nanowires into parallel array and also demonstrated the formation of crossed nanowire devices by changing the electric field direction as shown in Figure 3-1 (b). Vijavaraghavan et al.¹⁰ investigated the assembly of carbon nanotubes between the tips of biased electrodes whose biasing toward the discrete electrodes was possible due to capacitive-coupling with the dielectricscovered, highly-doped silicon substrate. Modulating the capacitive-coupling, varying the thickness of dielectrics and varying the areas of discrete electrode pads enabled high yields (~90%) of single nanotube alignments between the tips of electrodes. Raychaudhuri *et al*⁴. investigated the precise alignment of InAs semiconducting nanowires between very narrow, prepatterned electrodes via dielectrophoresis. That research demonstrated ~70% single nanowire yield at the optimized condition bias and electrode structure. These researchers also reported that the configuration of nanowires between the tips of biased electrodes depends on the direction of an electrical field gradient rather than the direction of an electrical field of high frequency (>10MHz).

Recently, Li *et al.*¹¹ reported large-area bottom-up fabrication of a nanowire resonator on a substrate, and they demonstrated precise assembly of metallic nanowires on lithographically recessed well array rather than between a pair of protruding electrode tips. Electroplating of assembled nanowires and a subsequent lift-off process removed the misaligned nanowires and mechanically clamped the nanowires for nanoelectromechanical device application.

Both approaches, protruding electrode tip and recessed dielectric well, will be exploited and compared to achieve the precise nanowire alignment via the dielectrophoresis, necessary conditions are forming a spatially-controlled electrical field region on a substrate. In addition to the local electric field enhancement at the assembly sites, a fundamental understading of nanowire array formation at the electrode gap discussed in Chapter 2, lead the current research to extend the dielectrophoresis toward the precise positioning of nanowires on a substrate for nanoelectronical applications such as on-chip sensing. As discussed in Chapter 2, the use of a fluidic cell is also beneficial for controlling the direction of fluidic flow and lowering the evaporation rate of the nanowire suspension.

3.2 Spatially-Controlled Nanowire Alignment Using Local Electric Field Enhancement

3.2.1 Narrow Electrode Tips Array

Figure 3-2 (a) and (b) illustrate the nanowire alignment structure in which the desired nanowires' positions are between the narrow tips protruding from the parallel



Figure 3-2 (a) Top-view and (b) cross-sectional view of spatially-controlled nanowire alignment using the electrode tips protruding from the parallel electrode array structure. Stronger electric field between the electrode tips is expected to determine the final position of attracted nanowires.

electrodes. The narrow metal electrode tip structure (Ti/Au=20nm/50nm), fabricated on a silicon substrate, consists of ~1 μ m thermally grown oxide. Electrode tips, 5 μ m long and 1 μ m wide, are intended to form a 4 μ m electrode gap from which a higher electric field region is induced. In order to prevent shorting the electric field between the biased electrodes, application of a dielectric layer of PMGI with a thickness of 300nm covers the entire substrate. AC bias of 10 V_{pp} at 100kHz is applied to the electrodes following the injection of 10 μ L Rh nanowire solution (~5×10⁴ nanowires/ μ L).

Figure 3-3 (a) shows the dark-field optical microscope image of 7μ m long Rh nanowire assembly on a protruding electrode tips array patterned on a substrate. In contrast to structural design for stronger dielectrohoretic force formation between the



electrode tips; however, Figure 3-3 (a) shows that most of the nanowires assemble at

Figure 3-3 Spatially-controlled nanowire alignment using a protruding electrode tip array structure. (a) Dark-field optical microscope images of a 7µm long rhodium nanowire assembly. Scale bar = 10µm. (b) The simulation of dielectrophoretic force $(\nabla |\mathbf{E}|^2)$ at the cross-sections of x-y plane showing the strong dielectrophoretic force between pairs of protruding electrode tips. V_{pp} =10V is used for the experiment and simulation.

either of the edges of biased parallel electrodes while only a small fraction of assembled nanowires appear at the gap of the protruding electrode tips.

As expected, spatially-controlled dielectrophoretic force between the ends of electrode tip array is apparent from Figure 3-3 (b), and exhibits a relatively higher $\nabla |\mathbf{E}|^2$ value on a substrate compared to elsewhere on a substrate. This simulation result indicates that the strongest dielectrophoretic force is induced at the electrode tips which will favorably accept the attracted nanowires. Discrepancy between the theoretical expectation and experimental results appears counterintuitive. Considering another perspective of nanowire attraction and alignment on the biased electrodes could narrow the explanation of this discrepancy. That is to say, the vertical extent of dielectrophoretic

force from nanowire attraction sites and their relative area ratio on a substrate need to be taken into account.

Figure 3-4 (a) and (b) show the dielectrophoretic force simulations, proportional to $E\nabla |\mathbf{E}|^2$, at the cross-sections of the z-x plane of the nanowire alignment structure's





protruding electrode tip array. These simulations for dielectrophoretic forces from the edges of the protruding electrode tip (a-a') and the parallel electrode (A-A') indicate that the nanowire's attraction about 5µm above the substrate is barely influenced by the nanowire alignment location along the electrode edges. In other words, these simulations predict that the nanowires suspended in the solution tend to assemble at the edges of electrodes and between the protruding electrode tips with nearly the same probability of the nanowire attraction. Comparison of the proximity of the electrode edges in Figure 3-4

(a) and (b) indicates that a stronger dielectrophoretic force is induced at the edges of electrode tip, compared to the edges of parallel electrodes. This difference favors spatially-controlled nanowire alignment. Comparison of Figure 3-4 (a) and (b), however, suggests that stronger dielectrohoretic $(\nabla |\mathbf{E}|^2)$ force from the edges of protruding electrode tips appears to extend vertically within a limited range of ~2µm and becomes barely distinctive from the edges of parallel electrodes.

As mentioned earlier in this section, stronger dielectrophoretic force between electrode tips is localized within a $\sim 2\mu m$ range. A reasonable inference for the assembly result shown in Figure 3-3 (a) is that the relatively larger area of parallel electrode edges, compared to the electrodes' tip edges, can lead to more predictable nanowire alignment. As hinted in a recent report⁴, one possible way to enhance the alignment yield at the electrode tips is to make them longer, which drives their dielectrophoretic attraction to be more influential compared to the edges of parallel electrodes. Since the electrostatic repulsion between assembled nanowires still persists, this method, however, appears not suitable for achieving high-density nanowire integration.

For more detailed understanding the nanowire assembly results, taking the electrostatic force interaction between the assembled nanowires and protruding electrode tips into account is worthwhile. As illustrated in Figure 3-5 (a), consideration of the polarities of the biased electrodes and assembled nanowires reveals that the protruding electrode tip and outer half of assembled nanowires are under the same phase of AC bias. As a result, the nanowires assembled at the edges of biased electrodes experience the repulsive force from the protruding electrode tips, keeping the assembled nanowires some distance from those electrode tips. Noticeably, a considerable number of nanowires




become placed 1~2µm away from the strong dielectrophoretic force location. As a result, the likelihood exists that the polarized nanowires tend to be assembled on the electrode edge unless attracted directly toward the strongest dielectrophoretic region. A triangular-shaped electrode tip could alleviate this repulsive interaction while sacrificing the accuracy of nanowire alignment¹². Using this electrode design revealed that the nanowires assembled at the edges of parallel electrodes could be transported toward the electrode tips by dielectrophoretic attraction. Using a narrow, protruding electrode tip array structure, therefore, converted the ordered nanowire array, deterministically, led to unfavorable alignment on the electrode edges due to the repulsive electrostatic interaction between the polarized nanowires and oppositely polarized electrode tips.

Figure 3-5 (b) shows low-magnification optical microscope image of Rh nanowire assembly, indicating that the nanowires assembled at the electrode edge tend to be away from a protruding electrode tip across the substrate. Its statistical analysis regarding alignment result is summarized in Figure 3-5 (c).

3.2.2 Recessed Photoresist Well Array

An alternative to producing the spatially-controlled dielectrophoretic force on a substrate is to form a recessed photoresist well at the gap between biased electrodes. This process applies a dielectric layer of PMGI (0.9 μ m thick) on the substrate by interdigitated metal electrode fabrication. Following the lithographical patterning of a 7 μ m long and 2 μ m wide rectangle well array at the electrode gap using an imaging photoresist of BPRS-100, the subsequent ultraviolet ozone exposure of PMGI layer forms a ~0.4 μ m

deep well. The BPRS-100 photoresist layer is washed from the substrate using an acetone and isopropanol spray. The final structure of the spatially-controlled nanowire alignment using a recessed photoresist well appears in Figure 3-6.



Figure 3-6 (a) Top-view and (b) cross-sectional schematic diagram of spatiallycontrolled nanowire alignment using the electrode tips protruding from the parallel electrode array structure (not in scale). Stronger electric field between the electrode tips is expected to determine the final position of attracted nanowires.

AC bias of 10 V_{pp} at 100kHz is applied to the electrodes following the injection of 10 µL Rh nanowire solution (~5×10⁴ nanowires/µL). Representative images of an experimental nanowire assembly with this structure, as shown in Figure 3-7 (a), show that the nanowires are preferentially assembled at the locations defined by the lithographically recessed dielectric region. Not surprisingly, several nanowires are also found at the electrode gap between the assembly sites where dielectrophoretic force also exists. Importantly, the assembled nanowires at the electrode gap, not within the recessed well, still maintain the uniform spacing between them and also span the electrode gap symmetrically, which coincides with the discussion for uniformly-spaced nanowire array formation in Chapter 2. This result suggests that the electrostatic repulsive interaction



Figure 3-7 Spatially-controlled nanowire alignment using a recessed photoresist well array structure. (a) The simulation of dielectrophoretic force $(\nabla |\mathbf{E}|^2)$ at the cross-sections of x-y plane showing the strong dielectrophoretic force from a recessed photoresist well array. (b) Dark-field optical microscope images of a 7µm long rhodium nanowire assembly at the photoresist well array patterned on the electrode gap. Scale bar = 10µm. V_{pp} =10V is used for the experiment and simulation.

between the assembled nanowires remains even after the nanowires' alignment. Figure 3-

7 (b) shows the dielectrophoretic force simulation of the x-y plane of the nanowire alignment structure, creating the intended nanowire position within a recessed well. This simulation is quite consistent with the experimental nanowire assembly result shown in Figure 3-7 (a). Dielectrophoretic attraction ($\nabla |\mathbf{E}|^2$) within a recessed well reached the maximum value for highest probability to trap the nanowires while electrode gap region between recessed wells also has only two folds lower value. As a result, the attracted nanowires tend to be filled within a photoresist well. Rrelatively large number of nanowires is also found at the electrode gap between the recessed wells.

Figure 3-8 (a) and (b) show the vertical extent of dielectrophoretic force at the cross-sections of the z-x plane of the nanowire alignment structure with a recessed



Figure 3-8 The simulations of dielectrophoretic force $(\nabla |\mathbf{E}|^2)$ at the cross-sections of z-x planes, between (a) the parallel electrodes (A-A') and (b) within a recessed photoresist well (a-a') from Figure 3-5 (a), show the alignment structure in which the nanowires adopt the desired position within a recessed well region. $V_{pp}=10V$ is used for the simulation.

photoresist well. The structure achieves spatially-controlled dielectrophoretic nanowire attraction. These simulations indicate that the magnitude of dielectrophoretic force from the recessed and flat photoresist regions become similar at 5μ m above the surface of substrate.

Contrary to the protruding electrode tip structure, the recessed photoresist well favors the alignment of polarized nanowires in terms of the dielectrophoretic and electrostatic forces. The nanowires, assembling at the electrode gap, outside the desired, predetermined locations, can be attracted to the stronger dielectrophoretic region, namely that of the recessed photoresist well. Since the electrostatic repulsive interaction between the assembled nanowires remains viable, the nanowires' alignment between the recessed wells can also assist positioning nanowires at the recessed well region through dynamic nanowire redistribution. Consequently, predetermined assembly can be accomplished not only by direct nanowire alignment at the recessed well region, but also by the dynamic redistribution of aligned nanowires due to the repulsive repulsion between them.

Apparently, from observation, the hydrodynamic motion in the nanowire suspension could induce nanowire movement along the electrode gap and trap the nanowires in the recessed photoresist well. Captured video of nanowire assembly supports the mechanisms of deterministic assembly, which allows high yield precise integration of nanowires over a large area of patterned substrate.

Similar to the uniformly-spaced nanowire array formation at the electrode gap, assembly defects such as nanowire-nanowire chains and multiple nanowires in a recessed well are also present. Figure 3-9 (a) illustrates nanowire-nanowire chains and multiple nanowire formation within a recessed well while Figure 3-9 (b) shows their optical microscopic images. As discussed in Chapter 2, chained nanowires can be attributed to the mutual dielelecphoresis between polarized nanowires. Multiple nanowire attraction from the well becomes attenuated toward the nanowire suspension media, yet remains viable even after the nanowire's alignment. As a result, this dielectrophoretic force, with a moderate strength, could attract a polarized nanowire toward a photoresist well already occupied by a nanowire. Notably, the electrostatic repulsive interaction makes the assembled nanowires within a well repel each other and thus pushed against the walls of the recessed photoresist well. The nanowire bundles relate to defects of nanowire batch-synthesis in which nanowires physically join during electrodeposition.



Figure 3-9 (a) Illustration and (b) dark-field optical microscope images of nanowirenanowire chains and multiple nanowire formation within a recessed photoresist well. (c) Low magnification of optical microscope image of nanowire assembly using a recessed photoresisit well array and (d) statistical analysis for the alignment yield calculation and defect analysis. Scale bar = 35μ m. The dashed white rectangles in (c) indicate empty device sites. This image indicates that strong dielectrophoretic force determines the spatial alignment of nanowires at the electrode gap, achieving an ~95% assembly yield. Apparently, all nanowires are attracted and assembled at the gap with a good orientation relative to the direction of the electric field. Based on the low magnification optical microscopic image of 192 assembly sites in Figure 3-9 (c), conducted statistical analysis of the assembly yield and related defects is summarized in Figure 3-9 (d). The yield of a single nanowire assembly, counted as a success, is a single nanowire trapped in a photoresist well. The yield is as high as ~90% and is reproducible and reliable. A small fraction (~5%) of the chained and multiple nanowires, considered assembly defects, are also found among assembly locations.

Conceivably multiple and bundled nanowires could impact uniformity of device performance, weakening the integrity of the assembly scheme. Notably, this assembly process is a self-limiting single nanowire deposition by a repulsive force between the polarized nanowires except for pre-existing bundles. In order to minimize multiple nanowires within a photoresist well, dilution of the concentration of the nanowire solution is maintained as low as $\sim 5 \times 10^4$ nanowires/µL and repeated injection ensures that the assembly sites attain a single nanowire while rarely attracting multiple nanowires simultaneously.

Beyond positioning the nanowire in the recessed photoresist well region, the accurate registration of functional nanowires is a prerequisite for integrating them in a complex circuit structure whose devices' feature sizes and metal electrodes have been shrunk in a sub-micrometer regime. To quantify the registration accuracy of the nanowire assembly, the alignment errors of x- and y-axes are determined with high magnification optical microscopic images of the nanowires assembled within a photoresist well.

Figure 3-10 (a) illustrates the alignment error of nanowires assembled within a recessed photoresist well. As discussed in Chapter 2, the nanowires assembled on the flat PMGI layer tend to span the electrode gap symmetrically due to their electrostatic



Figure 3-10 (a) Illustration of alignment error, orthogonal shift and rotational error, of the nanowires assembled within recessed photoresist wells. (b) Dark-field optical microscopic image of 7μ m long single Rh nanowires assembled in recessed photoresist wells with lengths of 8μ m and widths of 2μ m. Scale bar = 10μ m. (c) Statistical analysis of orthogonal and rotational alignment error for the assembled nanowires. The chart shows excellent registration accuracy, almost compatible with the overlay error of a lithographic stepper used in the experiment.

interaction with both sides of biased electrodes. The electric field lines at the electrode

gap favor parallelism of the long axes of assembled nanowires with the longitudinal

direction of photoresist wells. Hydrodynamic motion in the nanowire solution during

assembly, capillary force at the meniscus, asymmetrical electric field strength between

the signal and ground electrodes at high frequency, and any possible fabrication nonuniformity, all, could shift and orient the nanowires assembled in photoresist wells.

Figure 3-10 (b) shows the optical microscopic image of 7μ m long Rh nanowires assembled within a recessed photoresist well array. The alignment errors of single nanowires relative to the predetermined location are calculated for 12 nanowires in terms of X- and Y-offsets with a rotational error. Each offset is defined as the distances between the centers of assembled nanowires and photoresist wells. Figure 3-10 (c) summarizes the alignment errors, demonstrating sub-micron registration accuracy as <0.5µm orthogonal alignment errors on both axes and a <0.1° rotational error. This excellent registration of nanowires is encouraging in that the spatially-controlled dielectrophoretic force using a micrometer-sized photoresist well allows achievement of accurate nanowire registration with a submicron alignment error. This alignment error is comparable to the lithographic stepper used in this experiment whose typical overlay error ranges from 0.25 to 0.5µm.

The ability to assemble a single nanowire at a precise position on a substrate with a high yield and submicron registration accuracy leads the way for reliable, reproducible fabrication of electronic devices on substrates or as circuit structures. Since the assembled nanowires need to be electrically connected to the underlying electrode, the relevant post-assembly process requires development. In previously reported assembly methods of exposed electrode structures^{1, 3-6}, electrical contact between the nanomaterials and the metal electrode, apparently, occur at the moment of alignment. As a result, the electrical contacts are not readily controlled, leading to variation in contact resistance, which eventually requires post metallization¹ and even thermal annealing to lower

resistance³. Due to the configuration of the cylindrical-shaped devices and the flat electrode, metal evaporation or sputtering only covers a half or two-third of the assembled nanowires, possibly implying another source of nonuniformity in large numbers of devices. Making a reproducible and low contact to the nanowires provides a new challenge in fabricating electronic device arrays from a manufacturing perspective.

3.3 High-Yield Integration of Functional Nanowires for On-Chip Sensing

3.3.1 Conducting Polymer Sensor Nanowires

Nanowires possess an attractive form factor for chemical and biological sensing platform primarily because of their high surface-to-volume ratio for the rapid sensing response and miniaturized geometry, comparable to the diffusion length of chemical analytes, for the high sensitivity¹³⁻¹⁹. Since electrical conductivity needs to be modulated by the oxidizing/reducing agents of chemical analytes for sensing, semiconducting nanowires, including those of inorganic and organic materials, have been widely employed to demonstrate ppm sensitivity with sub-second response times at room temperature²⁰⁻²². In particular, conducting polymer possesses several potentially advantageous features for use in chemical sensor devices. A diverse range of conducting polymers such as polythiphene²³, polyaniline^{17, 22}, and polypyrrole¹⁹ is available via the electrochemical or chemical polymerization of the different types of monomers. These conducting polymer nanowires are advantageous for detecting a wide range of chemical

analytes while lacking a specific chemical sensing. This non-specific sensing capabilities can be suited for the electronic nose systems²⁴.

As a chemical sensor, the conducting polymer experiences a charge exchange and/or swelling from exposure to chemical analytes. This exposure causes a change in conducting polymer's electrical conductivity, namely, a sensitivity to the environmental change²⁵. In principle, the electrical conductivity of conducting polymers depends on the concentration of existing charge carriers (carrier doping level) and the ability of those charge carriers to move along the π -conjugated backbone of the polymer chains (carrier mobility). The chemical analytes, depending on their concentrations, modify the carrier's doping level and mobility within a conducting polymer. The sensitivity of a sensor element can be readily altered by changing the polymerization conditions and the charge compensating counterions. These conducting polymers have appropriate off-state resistivity and on/off conductivity ratios for use as nanosensor elements. In particular, PEDOT and its derivatives are of much interest due to their high electrical conductivity, high environmental stability, and low band gap. PEDOT could serve as a highly sensitive sensing material for detection of chemical analytes²³.

Conducting polymer nanowires can be electrochemically grown via the template method. Conventional hard templates include anodic aluminum oxidized (AAO) membranes and track-etched polycarbonates membranes as depicted in Figure 3-11 (a). Deposition inside



Figure 3-11 (a) Electrochemical deposition setup for batch-synthesis of conducting polymer nanowires. (b) Electrochemical interaction for polymerization of monomers. (c) Process steps of electrodeposition and release of nanowires. (d) Dark-field optical microscopic images of PEDOT/ClO₄ nanowires drop-cast on silicon substrate. Scale bar: 15 μ m.

the pores can be achieved through chemical/electrochemical polymerization in solution.

Vapor deposition has also been used as an effective way to fabricate the nanostructures

with a high aspect ratio inside a membrane template.

Yanyan Cao in the Mallouk Group chose the conventional hard template method to batch-fabricate conducting polymer nanowires with dimensional uniformity because of ease of process and high throughput. A sequential deposition technique for the segmented nanowires with metal tips was used. The first segment of gold was deposited in the pores of a membrane from a cyanide based plating solution (-1.75 mA for 15 min.). Then, this segment of gold was used as part of the working electrode for electrochemical polymerization.

Electrochemical polymerization within pores in the membrane occurred place in a solution with monomers and a supporting electrolyte at anodic conditions. The PEDOT/PSS segment was polymerized from a solution of 0.05 M 3,4-

ethylenedioxythiophene, 0.1 M PSS in 1:1 v/v water/acetonitrile at 1 V vs. a saturated calomel electrode for 14 min. The PEDOT/ClO₄ segment was polymerized from a solution of 0.01 M EDOT, 0.1 M lithium perchlorate in acetonitrile at 1.4 V vs. a Ag/AgCl electrode for 7 min. A commonly accepted mechanism for electrochemical polymerization of pyrrole, aniline, and ethylenedioxythiophene is the formation of radical cations at the working electrode (anodic). Then, two radical cations experience a coupling reaction, followed by a deprotonation process to generate a dimer. The dimer can lose an electron and form a radical cation again. The polymerization of monomers propagates by the repetition of this procedure. The polymer chains can be oxidized in situ during the synthesis to form positively charged carriers such as polarons and bipolarons. The anions in the supporting electrolyte are electrochemically involved in the polymer to balance the charges. Thus, the supporting electrolyte used for oxidative electrochemical polymerization is often referred to as a dopant.

Figure 3-12 (a) shows the optical microscopic image of Au-PEDOT/PSS-Au nanowires dispersed on a silicon substrate, and the inset clearly shows the junction between metal and polymer. Figure 3-12 (b) shows scanning electron microscopic images of conducting polymer nanowires with metal tips assembled at the electrode. The image of the structure depicts nanowires' charge transport and sensing performance. Figure 3-12 (c) and (d) illustrate nanowires' test structure alignment. These figures demonstrate the charge transport mechanisms in the assembled PEDOT/PSS and PEDOT/ClO₄ nanowires according to their chemical sensing properties in the solvents²⁶. The temperaturedependent measurements of those nanowires indicate that their electric conductions are



Figure 3-12 (a) Optical and transmission electron microscopic (inset) images of multisegmented Au-PEDOT/PSS-Au nanowires. (b) Field emission scanning electron microscopy image of Au-PEDOT/PSS-Au nanowires assembled on a four-point measurement test structure. (c) Top- and (b) cross-sectional illustrations of four-point measurement structure where the assembled nanowires span the four electrodes while making an electric contact with them.

the insulating, PEDOT/PSS, and metallic, PEDOT/ClO₄, sides of the metal-insulator

on

(M-I) transition regime. Consequently, the nanowires exhibit an opposite response from exposure to the chemical solvents such as methanol and acetonitrile.

Extensive study and measurement of two different conducting polymers revealed that the charge transport in PEDOT/PSS nanowires is dominated by a rapid transition between highly conducting islands embedded in the insulating medium; conversely PEDOT/ClO₄ behaves like the metallic materials. This differing transport mechanism also contributed to the signal-to-noise level in the sensing performance, making PEDOT/ClO₄ nanowires more promising for detecting low concentrations of chemical analytes due to better sensitivity. It was also suggested that optimization of PEDOT/ClO₄ nanowire synthesis can lead to the improved sensing performance capable of detecting traces of chemical analytes.

Figure 3-13 (a) - (d) show the sensing performance of PEODT/ClO₄ and PEDOT/PSS nanowires through exposure to water and methanol. Comparison of temperature-dependent I-V measurement of PEDOT/ClO₄ and PEDOT/PSS nanowires with the sensing responses from them highlights that the different charge transport mechanisms are responsible for different sensing responses by PEDOT/PSS and PEDOT/ClO₄ nanowires. The advantages of this test structure include a relatively simple



Figure 3-13 Sensing responses of individual (a), (c) PEDOT/ClO₄ and (b), (d) PEDOT/PSS nanowires to water and methanol, respectively.

fabrication of structure and no necessary post-assembly process for metal contact formation. This structure, however, lacks uniform metal contact formation of nanowires to the electrodes, high yield, single nanowire deposition capability, and symmetry of aligned nanowires. Thus, this structure is unsuitable for oh-chip integration of functional nanowires.

As indicated in the previous section, the recessed photoresist well offers a promising method for assembling nanowires at precise locations and simultaneously providing high yield and accurate registration. Thus, a combination of chemically sensitive nanowires with a high-yield assembly scheme will be the basis for integration of bottom-up nanowires with top-down post-assembly fabrication. The compatible processes of using the assembly scheme and the relevant post-assembly process, developed in previous section, with functional nanowires of this section are the focus of the next section.

3.3.2 Integration of Functional Nanowires on a Substrate

3.3.2.1 High-yield Assembly of Functional Nanowires with Accurate Registration

Solid PEDOT/ClO₄ nanowires without metal tips were batch-fabricated via the electrochemical deposition of PEDOT monomer through the aluminum oxidized membranes (Whatman, Co.) and stored in isopropyl alcohol after purifying the nanowires with a solvent. These solid polymer nanowires rather than metal-tipped ones are favored mainly because the growth of the metal part tends to cause the nanowires to bundle, which creates difficulty for identifying nanowires. The technique use in this research applied AC sinusoidal bias (10V_{pp}, 100 kHz) to the pads connected to the interdigitated electrode structure (Ti/Au=10nm/20nm). A relatively thin metal electrode, compared to the previous nanowire alignment structures, is favored as a sacrificial metal layer which will be patterned for the post-assembly process. Prior to nanowire assembly, PMGI and BPRS 100 photoresist layers were spun, softbaked, and patterned for the recessed regions the electrode gaps so that nanowires' placement is at the desired locations in the post-assembly process. 10µL of PEDOT/ClO₄ nanowire suspension, injected through the

fluidic cell in which the spatially-controlled dielelctrophoretic force from the recessed photoresist well array, achieves the high yield and precise alignment of the nanowire sensor device in an array format on a substrate. The electrode structure is depicted in Figure 3-14 while the fluidic cell is identical to the one in Figure 2-3 (a) in Chapter 2.



Figure 3-14 (a) Top-view and (b) cross-sectional view of spatially-controlled nanowire alignment using the electrode tips protruding from the parallel electrode array structure. Stronger electric field between the electrode tips is expected to determine the final position of attracted nanowires.

As a control experiment for the newly-designed electrode structure for individual nanowire assembly and measurement using a thin metal, 7µm long Rh nanowires are assembled on a substrate. Figure 3-15 (a) shows the optical microscope images of Rh nanowires assembled in the recessed photoresist wells, located at the gaps of the interdigitated electrode array structure. Thus, the Rh nanowire assembly for testing this

alignment structure was as successful as the previous alignment structure, showing the viability of high yield of spatially-controlled alignment of nanowires within a photoresist well. Assembly of PEDOT/ClO₄ conducting polymer nanowires attempted to integrate the functional nanowires at the desired locations on a substrate. As shown in Figure 3-15 (b), the strong electric field from the electrode gap attracts virtually all the conducting polymer nanowires, while the stronger dielectrophoretic force from a recessed photoresist well determines the final position of attracted nanowires along the electrode gap.





Contrasting the metallic rhodium nanowires shown in Figure 3-15 (a), a greater number of conducting polymer nanowires appeared as bundles. This phenomenon is attributable to the polymer nanowires' tendency to grow faster on the surface of a membrane, resulting in more chance for them fuse with a neighboring one.

This precise positioning of conducting polymer nanowires at the desired locations on a substrate addresses the fundamental issue of heterogeneous integration, namely the process' incompatibilities among materials. As discussed in Chapter 1, conventional microfabrication techniques have been the mainstream of current CMOS device and circuit fabrication which typically involves high temperatures and chemically aggressive process steps. As a result, integrating functional polymer devices at predetermined locations on a circuit without sacrificing their functionality has been almost impossible. Therefore, the spatially-controlled alignment of functional PEDOT/ClO₄ nanowires on a substrate with accurate registration could be a promising method to integrate the nanowires in a circuit structure while preserving the device's functionality during the process steps.

3.3.2.2 Post-assembly Process for Electrical Contact

The functional nanowires, assembled in the recessed photoresist wells need to be connected to the underlying metal electrodes for electrical contact. As illustrated in Figure 3-16 (a), the post-assembly process using electrodeposition and dry etching is the proposed method to be accomplished following nanowire assembly. To define the electrodeposition area, a BPRS 100 photoresist layer is spun on the substrate with the



Figure 3-16 Post-assembly process for individual device fabrication. (a) Illustration of processing steps for completing a single Rh nanowire device array. Nanowire assembly at the photoresist well, the electrodeposition for metal contact, and the dry etch for device isolation appear sequentially. Purple: thermally-grown silicon oxide, yellow: the metal electrode for biasing, light blue: PMGI dielectric layer, light red: BPRS 100 photoresist, orange: electrodeposited gold, and blue: nanowires (b) Scanning electron microscopic image of a single Rh nanowire array clamped by the gold electrodeposition where the misaligned nanowires are released by PMGI removal. Scale bar: 5μ m. (c) Optical microscopic image of a measured Rh nanowire device. Scale bar: 20μ m. (d) Nanowire integration result following the postassembly process.

nanowires and patterned by a stepper (GCA 8000). The exposed PMGI photoresist layer, through the BPRS 100's window was then exposed and removed by the developer. Then, gold electrodeposition (TG-25ES-RTU, Technic Inc.) occurs by a pulsed current in the solution, leading to the formation of a surrounding electric contact area at both ends of the assembled nanowires. Electrodeposited gold grows from the biased bottom electrode and then wraps around the suspended part of the assembled nanowires. Care is necessary to prevent excessive mushrooming over the photoresist window.

The advantage of this post-assembly method is twofold: First, this wrap-around type contact, mechanically sturdy and electrically low resistant in nature, of the assembled nanowires is of great promise for integration and secure functionality of nanowires on a substrate or circuit. Since the electrodeposition process holds the assembled nanowires firmly without excessive damping, different types of nanodevices can be fabricated for a hybrid nanosystem via the same process steps. For instance, the nanoelectromechanical and nanoelectronic device arrays may populate a single chip. Secondly, the dimension of contact via window for the electrodeposition is designed to clamp the assembled nanowires within a photoresist well or less than 1µm away from it. It is very unlikely that nanowires would occupy a position within a1µm range of an existing nanowire at the electrode gap because of the electrostatic repulsion between the assembled nanowires and through control of the concentration of the nanowire suspension. As shown in Figure 3-7 (d), the attracted nanowires are prone to be positioned between the assembly sites if filled with nanowires As a result, the electrodeposition and subsequent PMGI removal process effectively removes misaligned nanowires from assembly sites.

As proof-of-concept and control studies, Rh nanowires are used to demonstrate the versatility of this post-assembly process and characterize the resistance variation in the devices by contacted the electrodeposited metal electrodes. Figure 3-16 (b) shows the scanning electron microscopic image of a single Rh nanowire array clamped by a $3\mu m$ wide electrodeposited electrode. The misaligned nanowires between the assembly sites are removed following PMGI removal. Individual addresses of the clamped devices are possible by selective removal of biased electrodes in a way that electrically isolates the devices in an array. As illustrated in Figure 3-16 (a), the dry etching of thin, sacrificial metal electrodes (Ti/Au=10nm/20nm) using an inductively-coupled plasma reactive ion etch (ICP-RIE) system completes device isolation following lithographical patterning. The etch conditions are: ICP = 50 W; RIE = 100W; pressure = 100mTorr; gas flow rate (Cl₂) = 25 standard cubic centimeters per minute (sccm), and time duration = 90sec. The intentional overetching of 10sec ensures complete removal of the metal layer.

Figure 3-16 (c) shows the optical microscopic image of a single Rh nanowire device array used for its electrical characterization, highlighting that all misaligned nanowires are released from a substrate. Prior to the electrical characterization, visual inspection of 118 nanowire assembly sites assessed the effect of the post-assembly process on the clamped Rh nanowires. Figure 3-16 (d) provides a summary. This statistical analysis demonstrates that high yields of spatially-controlled nanowire assemblies remain valid with this alignment structure and the assembled nanowires are preserved without breakage during the post-assembly process.

To measure the electrical resistances of assembled Rh nanowires, the electrical characterization of clamped single Rh nanowires occurred by probing the contact pads. A histogram for the resistances of the measured devices appears Figure 3-17 (a). The tilted scanning electron microscopic image in the inset of Figure 3-17 (a) demonstrates the representative single Rh nanowire devices, clamped by gold electrodeposition and isolated by dry etching. The current-voltage (I-V) characteristics of ~50 single clamped devices were measured, and all of them were functional, exhibiting the reliability of the developed post-assembly process.



Figure 3-17 (a) Histogram for the resistance distribution of a ~ 50 single Rh nanowire device contacted by the wrap-around gold electrode. Representative current-voltage curve of a single Rh nanowire device is the inset showing the ohmic contact. Zoom-in SEM image exhibits the measured device consisting of the suspended Rh nanowire and metal contact. Scale bar = $3\mu m$ (b) Plot of the resistance of a single Rh nanowire vs. the nanowire diameter, suggesting that the variation in Rh nanowire diameter is a major source of effect on its resistance.

The typical I-V of the measured device as shown in the inset of Figure 3-17 (a) indicates that the electrical contact to the assembled nanowires is purely ohmic as expected from the metal-metal contact²⁷. The single Rh nanowire devices exhibit a mean

resistance of ~13.4 Ω with a standard deviation of ±3.4 Ω . The measured resistivity of Rh in this device configuration (10.45×10⁻⁶ Ω -cm) seems to be almost twice its bulk value $(4.74 \times 10^{-6} \,\Omega\text{-cm}$ for bulk at 300K), which can be attributed to the microstructure of electrodeposited Rh and its contact to the electrode^{1, 5, 28}. To identify the source of resistance variation, the scanning electron microscopic images of the measured devices were thoroughly investigated and compared with their corresponding resistances. Measurement of nanowire diameter reveals that the diameters of Rh nanowires are well distributed ranging from 200nm to 350nm, which is in positive agreement with batchsynthesis of electrodeposited nanowires²⁹. A plot of the nanowire diameter vs. the resistance in Figure 3-17 (b) suggests that the diameter variation in the nanowires by the nanowire batch-synthesis predominantly accounts for device-to-device variation rather than arising from nanowire assembly and/or post-nanowire assembly processes. Similar dependence of the radii of nanowires on their resistance was found in silicon nanowire interfaced with silicon electrodes³⁰. Accordingly, improving the device variation via a tight control of the dimensions of nanowires, i.e. top-down fabrication of nanostructures³¹⁻³³ is highly possible.

Using the same post-assembly process, the fabrication of chemical nanowire sensors using PEDOT/ClO₄ nanowires was undertaken. Figure 3-18 shows the completed PEDOT/ClO₄ nanowire devices contacted by electrodeposited Au contacts and isolated by dry etch. The bright region refers to the thin Ti/Au bias electrode, contrasting the etched region. Figure 3-18 (a) exhibits a PEDOT/ClO₄ nanowire device array contacted by an electrodeposited metal layer before dry etch, while Figure 3-16 (a) shows the discrete devices for individual measurement. Figure 3-18 (b) shows the top-view of optical microscopic images of a typically measured nanowire device where dry etch of



Figure 3-18 (a) Optical microscope images of high density PEDOT/ClO₄ nanowire array clamped by the electrodeposited electrode prior to the device isolation. The scale bar: 20μ m. (b) Optical microscope image of the discrete PEDOT/ClO₄ nanowire completed by the dry etching. The scale bar: 10μ m. The inset shows the tilted-view of field emission electron microscope image of clamped Rh nanowire device. The scale bar = 1μ m.

biased electrodes completes the device isolation for individual nanowire measurement. High-magnification by electron microscopic analysis reveals that the electrodeposited metal wraps around the assembled nanowires without any crevices between them. In the inset of Figure 3-18 (b), a tilted SEM image also shows that the clamped nanowires are suspended from the bottom of the substrate with a height determined by the underlying PMGI layer. Notably, this configuration of suspended conducting polymer nanowires appears to offer a larger surface area to interact with the solvent molecules compared to one resting at the bottom of the substrate. The latter condition offers the potential for greater sensitivity.

As mentioned earlier in this section, this metal contact formation provides a useful method for reliable and reproducible contacts of assembled nanowires, while nanowire alignment on the exposed metal electrodes solely depends on how the nanowire rests on the exposed electrodes. As observable in Figure 3-18 (b), high magnification by optical microscopic imaging allows identification of the number of nanowires assembled and clamped by the electrode. Visual inspection of the nanowire devices using an optical microscope distinguishes single nanowires from multiple and bundled ones. Further analysis of the assembled nanowire devices using a field-emission scanning electron microscope confirms the geometrical shape and dimensions. For example, the fused bundle and fatty nanowires can be identified only by high electron microscopically magnified images while optical microscope barely discriminates them.

As summarized in Table 3-1, visual inspection of assembly sites using optical and

Table 3-1 Nanowire integration results of 108 device sites by visual inspection using an optical microscope and electrical measurement of the devices. Only 3 devices' sites remain empty while most of them are filled with a single or multiple PEDOT/ClO₄ nanowires. The electrical measurement reveals that the electrodeposited metal forms the physical and electric contact with the assembled nanowires, completing the functional devices. Electrical contact failure might be due to defective nanowires with breakage caused by thermal expansion differences at the metal-polymer junction.

	Single	Double	Bundle	Empty
Visual inspection	85	15	5	3
Electrical contact failure	3	2	2	

electron microscopes reveals that high-yield of single polymer nanowire device fabrication can be achieved by the spatially-controlled dielectrophoretic nanowire assembly and post-assembly process. The electrical measurement of clamped devices also confirms that most of them are electrically functional and well-contacted by the metal electrodeposition. Following device isolation by seed metal removal, I-V measurement of the single PEDOT/ClO₄ nanowires using the manual probe station to extract their zero-bias resistances was completed. The measured resistances appear as a form of histogram in Figure 3-19. As shown in the inset of Figure 3-19, representative



Figure 3-19 The histogram of zero-bias resistance of single PEDOT/ClO₄ nanowire devices. The inset shows the representative current-voltage characteristics of single PEDOT/ClO₄ nanowires contacted by the electrodeposited Au electrode. The histogram suggests that the electrodeposition provides a promising method for forming reproducible contact with the nanowires with less electrical resistances as compared to those resting on the exposed electrode structure. I-V curve shows the slight non-linearity at zero-bias, suggesting the existence of a Schottky barrier at the metal-polymer interface.

current-voltage characteristic curve of PEDOT/ClO₄ nanowire indicates slight nonlinearity at the zero bias range, suggesting a Schottky barrier between the metal and the polymer materials. large fraction of measured devices, >95%, show the similar behavior.

The zero-bias resistances of clamped single PEDOT/ClO₄ nanowires are

distributed from 8 to 43 kOhm, showing a sharp peak between 10 and 15 kOhm. This

histogram implies that the developed post-assembly process offers the advantages of low

electrically-resistant and mechanically strong contact to the assembled polymer

nanowires. Total resistance of PEDOT/ClO₄ nanowires contacted by the electrodeposited

wrap-around metal is comparable to that with metal tips assembled on exposed metal electrodes shown in Figure 3-12 (b), suggesting that this post-assembly process, demonstrated in this section, does not noticeably alter the doping concentration of PEDOT/ClO₄ nanowires. However, since PEDOT/ClO₄ nanowires experience repetitive exposure to organic solvent, photoresist, and developer during the post-assembly process, long time of baking at moderate temperature should be followed for those chemicals to be diffused without sacrificing nanowires' sensing capability. The resistances of PEDOT/ClO₄ nanowire devices were measured before and after baking (80 °C for ~12 hrs) in a convection oven in a nitrogen flow.

Figure 3-20 exhibits that the histogram of resistance changes shows a 10~20%





resistance increase partly due to solvent evaporation inside the polymer structure. This

slight increase of resistance correlates with the out-diffusion of solvents which are

incorporated during the process steps. This resistance change is also consistent with the sensing measurement of PEDOT/ClO₄ nanowires performed in previous research as represented by Figure 3-12 (a) and (c), which shows that the sensor devices become less resistant from water and solvent exposure.

3.3.3 Chemical Sensing Results

The single PEDOT/ClO₄ nanowire device was mounted in the small chemical sensor stand chamber to test this device for sensor applications. Automated measurement of resistance changes enabled by the Labview® is capable of monitoring the sensing response from the devices. Figure 3-21 shows the sensing measurement configuration for the nanowire sensor. The sensing data are recorded and saved on the computer simultaneously while the chemical analytes such as the chemical gas and solvent are introduced. The chemical analytes are diluted with nitrogen which also purges the lines between exposures.



Figure 3-21 Images showing the chemical sensing test stand system. (a) Gas bottles for delivering the chemical solvent and its dilution. Bottles for toxic gases such as NH_3 and NO_2 are stored in light yellow gas cabinet with the exhaust behind the N_2 and H_2 gas bottles. (b) Computer-automated sensing measurement system. The gas manifold cabinet houses the mass flow controllers for regulating accurate gas flow, assisted by Labview-based computer program. (c) The gas inlet and outlet for chemical exposure to the chemical sensor. Brass flat metal plate with O-ring, guided by metal, threaded pins, seals the sensing chamber of the 40-pin DIP package. (d) Zoomed-in picture of 40-pin DIP package which accommodates the sensor chip in the recessed region. Wire-bonding connects the sensor chip to the pins of package. The inset shows the nanowire sensor devices used in this experiment.

Figure 3-22 shows the sensing responses from the fabricated PEDOT/ClO₄

nanowire devices from exposure to solvent, chemical gas, and nerve gas stimulants. First, a series of the sensing responses from PEDOT/ClO₄ nanowire devices indicate that their sensing capability appears to be preserved following the post-assembly process. This can be attributed to the chemical stability of PEDOT materials. Comparing this sensing data to that of previous research suggests that the electrodeposited metal formation wrapping



around the nanowire offers competitive or even better sensitivity. Namely, this new

Figure 3-22 Sensing responses of PEDOT/ClO₄ nanowires contacted by the electrodeposited metal electrodes. (a) Methhanol, (b) acetonitrile, (c) ammonia, and (d) dimethylphosphonate (DMMP).

platform for a sensor shows an approximate 2% of relative resistance change at 460ppm of methanol. The sensing results also indicate that PEDOT/ClO₄ nanowires are able to detect acetonotrile, ammonia, and even nerve gas stimulants with a detection limit of about 300ppm.

Despite of the demonstration of versatility of PEDOT/ClO₄ nanowire sensors, a considerable fraction of them exhibit opposite responses or very low sensitivity as presented in Figure 3-22. For instance, Figure 3-23 shows the opposite responses from



PEDOT/ClO₄ nanowire sensor devices even though they experienced the same fabrication process of nanowire synthesis through the post-assembly process. This

Figure 3-23 Sensing responses of PEDOT/ClO₄ nanowires by exposure to

methanol, showing the opposite differential resistance changes.

unexpected result suggests that the post-assembly process steps, rather than the nanowire assembly, might alter the doping level or make a structural change within a PEDOT/ClO₄ nanowire. Another possibility is that as-synthesized PEDOT/ClO₄ nanowires via an electrochemical deposition method have variations in doping level and structural disorders following the nanowire's release from the membrane.

In order to minimize excessive solvent exposure to PEDOT/ClO₄ nanowires during the process, the nanowires are intended to rest on the PMGI well following the dry etch for device isolation. Figure 3-24 (a) and (b) contrast the differences between PEDOT/ClO₄ nanowires suspended (Approach I) and sitting on the PMGI layer (Approach II), respectively, between the electrodeposited metal posts. PEDOT/ClO₄ nanowire sensor using Approach I underwent less aggressive solvent exposure while Approach II includes N-Methyl-2-pyrrolidone (NMP) exposure for PMGI removal. As shown in Figure 3-25(a), resistances of PEDOT/ClO₄ nanowire devices show a barely noticeable difference between Approach I and II. This result indicates that the use of NMP has an insignificant effect on the electrical properties of PEDOT/ClO₄ nanowires.



Figure 3-24 Illustration of PEDOT/ClO₄ nanowire sensor devices (a) suspended and (b) sitting on a PMGI photoresist well between the electrodeposited Au electrode posts. A less aggressive chemical process is used in the latter device structure.

Figure 3-25 (b)-(d) show the representative sensing responses from PEDOT/ClO₄ nanowire sensor devices sitting on a PMGI layer. They exhibit mixed responses from methanol exposure. These mixed responses, negative, very low sensitivity, and positive differential resistance change from PEDOT/ClO₄ nanowires, creates difficulty for detecting chemical analytes reliably in on-chip sensing applications.


Further process development is needed to obtain consistent sensing responses from PEDOT/ClO₄ nanowires. As mentioned earlier in this section, variation of doping

Figure 3-25 (a) Histogram of resistances from PEDOT/ClO₄ nanowire sensor devices sitting on a PMGI photoresist well. Representative sensing responses from PEDOT/ClO₄ nanowire sensor devices fabricated by Approach II, showing (c) negative, (b) very low sensitivity, and (b) positive differential resistance changes by a methanol.

concentration and structural disorder could impact the sensing responses from the conducting polymer nanowires. In particular, the conductivity of this investigation's PEDOT nanowires are between the metallic and insulating transport regimes, possibly making PEDOT/ClO₄ nanowires have mixed responses due to small structural

variations³⁴. Therefore, the statistical analysis regarding the electrical and relevant sensing characteristics of as-synthesized PEDOT/ClO₄ nanowires is also underway.

3.4 High-yield Monolithic Integration of Nanowires on a CMOS circuit

3.4.1 Individual Address to the Integrated Nanowires

One possible nanowire readout strategy appears in Figure 3-26 (a) to investigate the bottom-up integration of nanowires on CMOS circuitry where the electrical address to



Figure 3-26 (a) The schematic circuit diagram for the cross-point array structure for individual addresses and readouts of assembled nanostructures. The inset indicates the unit cell of the array showing one access transistor and a serially connected nanowire (1T-1NW) scheme. (b) Illustration of 1T-1NW scheme realized on the silicon substrate where the access transistor, interconnected with nanowires, are buried under the interdielectric (Si₃N₄) layer. The nanowires could be replaced with spherical entities.

the assembled nanowires can be made through access transistors. This configuration

resembles the unit cell of dynamic random access memory (DRAM): one transistor and

one capacitor. The simple cross-point array allows addressing hundreds-to-thousands of

individual devices for off-chip electrical characterization and defect studies; the array

also serves as a building block for more sophisticated multiplexed nanosensors and imaging arrays.

In the proposed design, thin metal biasing electrodes are patterned on top of a fully processed silicon circuit, leaving gaps only in the regions where nanowires are desired. Next, lithographically-defined microwells, in which individual nanowires preferentially assemble, are superimposed across of the electrode gaps, and are aligned relative to the source region of each transistor and ground. Following assembly, windows for contacts and interconnects are patterned with a second photoresist, and only the nanowires assembled in the microwells are electrically and mechanically connected to the transistors on a chip. Here, biasing electrodes are used as seed metal for electrodepositing contacts. Finally, the seed metal is removed to complete individually-addressable nanowire devices following photoresist patterning. Importantly, the sacrificial photoresist layers completely encapsulate and protect the nanowires during the entire back-end integration process. Figure 3-27 summarizes these process steps. The detailed process conditions for n-MOSFET fabrication can be found in Appendix.



Figure 3-27 Process flow for integration of nanowires with CMOS circuit structure. Process steps largely consist of transistor fabrication, nanowire assembly, and postassembly processes. (a) Highly-doped region formation for source/drain of the transistor. (b) Gate oxide growth and metal deposition. (c) Thin metal deposition for nanowire placement at the desired locations only. (d) Deterministic nanowire assembly following the photoresist's well pattern above the electrode gap. (e) Electrodeposition of metal electrode for electrical and mechanical contacts with assembled nanowires. (f) Dry etch of thin metal electrode for device isolation. (g) Removal of photoresist layer for measurement.

Integration of nanowires on a circuit structure using an electric field gives rise to the

complexity of electric field distribution which hinders assembly yield and accurate

alignment of nanowires. This complexity is caused by the parasitic capacitor-like

interaction between biased electrodes and other devices, such as the access transistors and

interconnects, within a circuit.

3.4.2 Electrode Design for Deterministic Nanowire Assembly on a Circuit



Figure 3-28 (a) illustrates the process steps of an earlier approach to assembly of

Figure 3-28 (a) Process steps for capcitively-coupled upper and lower electrode structures integrated on an access transistor array. (b) Optical microscopic image of 7μ m long Rh nanowires assembled between upper alignment electrodes where the nanowire's position is undetermined. Obviously, considerable numbers of nanowires are assembled at the edges of upper and lower electrodes without a sacrificial photoresist layer. Scale bar = 30μ m. (c) Dark-field optical microscopic image of 7μ m long Rh nanowires assembled at the photoresist well, and exhibiting misaligned nanowires. Scale bar = 20μ m. (d) Optical microscopic image of 7μ m long Rh nanowires assembled between upper alignment electrodes free of misaligned nanowires following removal of sacrificial photoresist. Removal of the sacrificial photoresist layer releases the misaligned nanowires from the substrate. The inset shows high magnification, scanning electron microscopic image of 7μ m long Rh nanowires. Scale bar = 50μ m and 2μ m.

nanowires between pairs of discrete electrode arrays. This earlier approach takes

advantage of a capacitor-coupled alignment structure in which biased, lower electrodes

are capacitively-coupled to discrete upper electrodes. Biasing the buried lower electrodes produces a higher electric field gradient between the alignment electrodes, and directing the nanowires toward the electrode gap. Assembled nanowires are intended to make a physical and electrical contact with the alignment electrodes where the resistance of assembled nanowires can be read from the access transistor.

Figure 3-28 (b) shows the optical microscopic image of 7µm Rh nanowires assembled on a circuit structure in which upper and lower metal electrodes are fabricated without access transistors. The nanowire assembly yield appears to be as high as about ~70%. Apparently, from the assembly image, the edges of lower biased and upper assembly electrodes, as well as the assembly sites, collect considerable numbers of nanowires from the suspension. Modern CMOS chips typically consist of several stacked layers of metal and interdielectric materials for increasing the device's integration density. This complexity of interconnecting lines and devices between each layer in CMOS chips will affect the yield of nanowire alignment, making the yield even lower than simple alignment structures of upper and lower electrodes. Since, in particular, misaligned nanowires could impact performance of nanowire circuit structures and even jeopardize their entire function, spatially-controlled nanowire alignment on a complex circuit structure is a necessity.

The use of a recessed photoresist well for spatially-controlled nanowire alignment guides the attracted nanowires to assemble at the desired positions between the upper assembly electrodes. Also, this photoresist layer, BPRS-100, serves a sacrificial layer for the release of misaligned nanowires on a circuit structure. Figure 3-28 (c) shows the dark-field optical microscopic image of assembled 7µm Rh nanowires, and exhibiting

misaligned nanowires assembled at the edges of biased (BE) and upper (UE) electrodes as well as within a recessed well. In the image, biased, lower and upper electrodes are purposely and respective blue and green, making them visually discriminated. Stripping the sacrificial photoreist layer by dipping in acetone and isopropanol removes the misaligned nanowires from a substrate, leaving nanowires appropriately assembled at the photoresist well.

Figure 3-28 (d) shows the optical microscopic image of 7µm Rh nanowires assembled at the photoresist well following sacrificial photoresist layer removal. A sacrificial photoresist layer alleviates excessive nanowire alignment at undesired regions on a circuit while producing strong dielectrophoretic force from the recessed photoresist well. As a result, spatially-controlled dielectrophoretic force preferably positions the nanowires at the desired locations on a circuit structure, yet provides a relatively intermediate alignment yield of ~80% at maximum. In order to achieve high assembly yield reproducibly, a stray electric field, induced by the interconnecting metal electrodes, needs to be eliminated or at least minimized. Furthermore, the applied bias for nanowire alignment could damage gate dielectrics of the access transistor by capacitive-coupling between overlapping interconnects within a circuit.

Covering the underlying CMOS structure except the alignment sites with a thin metal film can offer a way to eliminate the stray electric field induced by the parasitic electric field interaction within a circuit. As illustrated in Figure 3-29 (a), a thin metal electrode makes a continuous film on the access transistor and forms an electrode gap with adjacent electrodes which is oppositely biased. This electrode configuration can eliminate the stray electric field of the buried interconnecting electrodes while creating a



Figure 3-29 (a) Illustration of nanowire alignment structure integrated on access transistor. A thin metal film makes a continuous layer over CMOS structure while intending to create strong dielectrophoretic force within a recessed photoresist well. (b) Optical microscope images showing the assembly of (a) 7 μ m long Rh nanowires, (c) PEDOT/ClO₄ conducting polymer nanowires on a circuit structure. Scale bars in (b) and (c) = 20 μ m.

strong dielectrophoretic force within a photoresist well.

Defining the highly doped region for the source and drain of transistors within a

circuit structure causes a substrate to be topographically different. Thin metal

(Ti/Au=10nm/20nm), sputtered on a substrate, ensures a conformal metal film on a circuit structure. A recessed photoresist well array is lithographically defined using PMGI SF-11 following patterning the imaging layer, BPRS-100. Injection of approximately 10µL of nanowire suspension using the same fluidic cell from Chapter 2 completes the nanowire assembly on a circuit structure. Figure 3-29 (b) and (c) show the optical microscopic images of Rh and PEDOT/ClO₄ nanowires assembled at the desired locations on a circuit structure. This method achieves high-vield integration of nanowires, ~95% for Rh, and 80% for PEDOT/ClO₄ nanowires on the 32×16 nanowire alignment sites. The nanowire integration density is as high as about 10^4 devices/cm². Noteworthy is that this assembly yield is quite comparable to deterministic, individual nanowire alignment without a circuit structure discussed in section 3.3. This high yield assembly suggests that thin metal electrodes successfully eliminate the stray electrical field from the underlying access transistor and interconnects. Also, the nanowires assembled at the electrode gap tend to form a uniformly-spaced nanowire array, indicating that the electrostatic repulsive interaction between the nanowires remains. Notably, a thin sacrificial biased electrode plays a critical role in guiding the motion of attracted nanowires toward the desired locations on a circuit while minimizing the parasitic electric field interaction within the circuit.

3.4.3 Post-Assembly Process for Nanowires Integrated on a Circuit Structure

The same post-assembly process from Chapter 3, including electrodeposition for electrical contact and dry etch for device isolation, completes the array of nanowires and

access transistor structure. As illustrated in Figure 3-26 (a) and (b), the assembled nanowires can be individually addressed through the access transistor with assistance from an external measurement setup. Figure 3-30 (a) shows the optical microscopic



Figure 3-30 (a) Completed 32×16 nanowire array structure fabricated on a MOSFET circuit structure. Scale bar = $300\mu m$. (b) Zoomed-in optical microscopic image showing Rh nanowires and access transistor array which are serially interconnected by electrodeposition. Scale bar = $10\mu m$. The inset shows a tilted-view of a scanning electron microscopic image exhibiting the suspended structure of nanowires. Scale bar = $5\mu m$.

images of a competed 32×16 Rh nanowire device array with the assembled nanowires contacted by electrodeposited metal. This metal electrode also interconnects the nanowires with the underlying MOS transistor in the circuit structure for individual addresses. High magnification optical microscopic image in Figure 3-30 (b) are the completed nanowire device array and highlights each individual nanowire's connection to a particular access transistor on the chip.

The process monitor allows inspection of the fabricated transistor with different ratios of channel widths to lengths, determining their transconductance, namely the channel resistance. The transistors in the process monitor are all functional when their resistances range from a few to tens of kOhms depending on the gate bias, as shown in Figure 3-31 (a) and (b). Unfortunately, the metal nanowires possess much smaller



Figure 3-31 Drain currents transistors with different gate biases from 0 to 10V. The channel width to length ratio is (a) W/L=10µm/6µm, and (b) W/L=30µm/6µm. resistances, compared to the channel resistances, which makes impossible extracting the nanowire resistance from the 1T-1NW measurement scheme. Therefore, integration of silicon nanowires with a moderate doping concentration on a circuit structure enables the investigation of the device uniformity as well as nanowires' alignment defects associated with bottom-up assembly processes where the resistances of silicon nanowires should be much less than that of the transistor channels.

3.5 Conclusion

The method described in this chapter offers a promising approach for positioning a single nanoscale building block at predefined locations. This method is possible by the combination of dielectrophoretic force from photoresist wells and electrostatic force from the polarized nanowires. The research demonstrates that the post-assembly process via

electrodepositon and dielectric layer removal can effectively transfer assembled nanowires, only trapped in the photoresist wells, to the metal electrode, producing a large array of mechanically and electrically robust nanodevices. This result can be considered a significant advancement toward commercially viable bottom-up nanodevice fabrication. In addition, this post-assembly process can readily combine functional nanowire devices, such as chemical and biological sensors, at predetermined locations in the underlying logic circuit, highlighting seamless integration of bottom-up functional nanowire assembly and top-down fabricated of CMOS circuits. A reasonably small device variation, considering distribution of nanowires' diameters, further proves the potential and versatility of this approach for integrating a large number of identical devices. Furthermore, the research demonstrates that this assembly technique can extend to the fabrication of conductive polymer nanowire sensor devices. Electrical measurement and sensing responses of PEDOT/ClO₄ nanowires, contacted by the electrodeposited metal electrodes, represents deterministic integration of functional devices on a substrate with high-yields and precise registration.

3.6 References

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Chapter 4

FLUIDIC ASSEMBLY OF FUNCTIONAL MICROSPHERES FOR ELECTRICALLY CONTACTED HIGH DENSITY ARRAYS

This chapter describes the fluidic assembly of functional spherical particles at predetermined locations on a substrate where a capillary action at the meniscus, assisted by a patterned substrate, plays an important role in positioning the particles with an electrical addressability. This integration of functional spherical particles on a circuit structure offers a promising way to fabricate high-density nanodevices in which top and bottom electrodes electrically contact assembled spheres. Similar to the electric-fieldassisted nanowire assembly described in previous chapters, fluidic assembly for the spherical particles also features the potential to achieve chemical diversity and flexibility on a substrate or a circuit structure without sacrificing optimized properties of functional spherical particles. In the current research, conducting polymer, chemoresistive nanoshell-spheres are the chosen building block to demonstrate functional electronic devices in a format that could be integrated with silicon CMOS circuits.

Section 4.1 introduces the sphere assemblies reported in the literature for controlled positioning on a substrate. This section discusses and assesses their application to the fabrication of functional electronic devices, potentially connected to the underlying circuit structure.

Section 4.2 begins with the fluidic assembly setup used in this chapter. This section describes the fluidic cell, consisting of the glass slide with a thick SU-8 photoresists spacer and substrate, for creating the sphere assembly. This fluidic cell,

clamped by a metal fixture, confines the micrometer-sized silica sphere solution and controls its evaporation direction. Capillary force at the solution's meniscus assembles the spheres at the recessed photoresist well following a hydrophilic treatment of the substrate using an oxygen plasma, 25W for 1min with an oxygen flow of 25 sccm. This section shows that > 95% single sphere assembly over large area can be achieved through a low contact angle between the sphere solution and the substrate assisted by tight control of the photoresist well dimension which accommodates a single sphere.

For this research, functional sensory spherical particles are synthesized to demonstrate the application of their fluidic assembly for fabrication of an electronic device array. Section 4.3 presents the cross-point array electrode structure designed to trap the spherical particles and electrically address them. Following the synthesis of gold and PEODT conducting polymer nanoshell spheres with a thickness of < 50nm, integration at the cross-point structure completed fabrication of the control sample and the chemical sensor. The current-voltage characteristics of functional sphere devices show that the assembled spheres make physical and electrical contact with bottom and top electrodes for an electrical address. Thin nanoshell spheres allows the chemical analytes to diffuse with a relatively short distance for rapid detection of environmental changes with a short recovery time. Furthermore, high surface-to-volume ratio sensing layer on the spheres facilitates high sensitivity for chemical detection, leading to promising building blocks for chemical sensor devices.

4.1 Introduction to the Sphere Assembly

Spherical particles ranging from a few micrometers down to tens of nanometers have begun to emerge as building blocks for various applications. Such applications exploit the quantum-confined electronic system⁸, optical interaction with the light⁹, and high catalytic activity^{10, 11}. Also, reports indicate that metal nanoparticles interact strongly with electromagnetic waves, promising surface-enhanced Raman spectroscopy¹² and surface plasmon resonance¹³. Micrometer-sized spherical particles are also hold promise for manipulating light in optical and optoelectronic devices. Whereas most research has been devoted to fabricating 2- and 3-dimensional sphere structures, electrically conducting spherical particles for electronic device applications have been investigated as a combination with microfabricated electrode structures^{7, 8, 14}. Similar to the nanowires and nanotubes, the integration of spherical particles with an electrode structure on a substrate or a circuit often requires deterministic arrangement or assembly of particles at predetermined locations over a large area.

Various techniques such as electric^{15, 16}, magnetic field¹⁷, drop-casting¹⁸, spincoating^{19, 20} and fluidic interactions^{1, 5, 6, 21} have been proposed to arrange and position the spherical particles. Among these techniques, fluidic assemblies assisted by recessed photoresist wells demonstrate the capability of precise, self-limiting placement of spheres, ranging from several nanometers to micrometers, on a substrate. As shown in Figure 4-1 (a), the Xia Group^{1, 21} demonstrated that template-assisted fluidic assembly successfully positioned submicrometer-sized spherical particles in photoresist wells and narrow photoresist trenches. The fluidic cell has been employed to control evaporation rate of





injected sphere solution and also to render capillary force dominant during sphere

placement at the meniscus. Previous reports indicate that sphere assembly, using well-

defined recessed photoresist regions, achieves heterogeneous dimer-type sphere and single sphere placement at predetermined locations on a substrate.

Cui et al. reported that capillary force at the meniscus can be used to assemble sub-100nm colloidal nanocrystals at lithographically patterned wells where the electrical measurement for the assembled nanocrystal was made possible by designing a pair of electrodes for them⁷. Evaporation of sphere solution with a patterned substrate inserted creates the capillary force at the meniscus, leading to sphere placement at the recessed region of substrate. Cui et al. also demonstrated that capillary force can even assemble tetrapod-shaped nanostructures at the photoresist trench while orienting their branches parallel to the length of the photoresist trench. In particular, demonstration showed that metallic nanoparticles can be assembled between pairs of pointing metal electrodes, showing the demonstration of electrically addressable electronic particle device array.

Kraus et al. performed extensive study of sphere assembly to investigate many experimental parameters such as the temperatures, surface properties of substrates, concentrations of particle solutions, and geometry of the photoresist well pattern^{4, 5}. The Kraus et al. study revealed that those parameters need to be optimized to organize nanoparticles in a controlled fashion and achieve single nanoparticle placement on patterned substrates.

These sphere assembly results are encouraging in that the capillary force can be used to assemble functional spherical particles at predefined locations of electrode structures to complete chemical sensor devices. In contrast to other sphere assemblies, fabricating electronic devices requires an electrical address for the assembled spheres. Thus, the structure of electrodes and the relevant dielectric layers should be designed to

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make electrical contact with the assembled spheres as well as accommodate them in predetermined locations in a controlled way.

Due to the direction of capillary force at the meniscus, as shown in Figure 4-1 (a), (b), and (c), the spheres tend to make physical contact with the sidewall as well as the bottom of recessed photoresist region. Orthogonal metal electrodes, separated by an interdielectric layer, offer a way for the assembled nanowires to be integrated between the top and bottom and electrodes.

Figure 4-2 (a) illustrates the scheme of the spherical sensor array integrated on the



Figure 4-3 (a) Schematic circuit diagram for the spherical device array integrated on the circuit structure. (b) Three dimensional illustration of unit cell of the cross-point array consisting of the access transistor and the serially connected spherical device. The spherical device makes electrical contact with the bottom and top electrodes as shown in (c).

circuit structure. The electrical address to the cross-points, namely the spherical device, can be made via the peripheral row and column decoders. This scheme enables the individual address to the cross-points in row-column format where the cross-point consists of one access transistor and one sphere (1T-1S) as show in Figure 4-2 (b). The access transistor is serially connected to the sphere for electrically addressing the specific assembled spheres while other access transistors remain closed. Capillary force assembles electrically conducting spheres at the via of the top metal electrode and the dielectric layer. The force also completes the spherical device's forming contact with the top and bottom electrodes, as shown in Figure 4-2 (c). This process features room-temperature deposition of functional devices and also enables sequential assembly of different types of functional particles by "off-chip" batch-synthesis of them. Furthermore, the ability to assemble the spherical building blocks into an integrated electronic system at narrow pitch (and thus high density) opens the possibility for fabricating high-density nanosensor arrays.

4.2 Fluidic Assembly of Microspheres

Figure 4-3 shows the procedure of fluidic assembly of spheres at the recessed region on a substrate. This procedure begins with the preparation of a patterned substrate and a glass slide for the recessed photoresist well array and channels. Thereafter, $\sim 10\mu$ L of silica sphere solution is injected on a substrate by a micropipette and sandwiched by the glass slide with channels. This fluidic cell, placed in a metal fixture, bottom and top parts, and clamped by four pins ensures that evaporation occurs only through the channels of the fluidic cell. Capillary force at the meniscus of sphere solution assembles the spheres at the recessed photoresist wells on the substrate. The process can be monitored via the aperture at the top part of the fixture using an optical microscope. Once the solution dries, the fluidic cell can be dissembled. Then, optical inspection of the



Figure 4-3 Procedure for the sphere assembly including preparation of substrate and glass slide.

substrate determines the results of sphere assembly. Substrates with assembled spheres can be processed for further analysis or measurement.

4.2.1 Fluidic Assembly Setup

A fluidic assembly fixture made of aluminum alloy ensures sealing the fluidic cell, thereby controlling contact angle, evaporation front, and evaporation rate. Figure 4-4 (a) and (b) illustrate the aluminum fixture's configuration and an example of a fluidic cell routinely used in the assembly of spherical particles. The fluidic cell consists of the lithographically patterned substrate and the glass slide with the photoresist spacer. Photoresist, 15µm thick SU-8 (Microchem Inc.) is spun on the glass slide and patterned





ensure that the liquid medium evaporates only throuh 100 μ m wide channels. Prior to assembly of the fluidic cell, the solution of silica microspheres with a mean diameter of 0.9 μ m (approximately 10 μ \ell) is dispensed onto a substrate. Thereafter, the fluidic cell is sandwiched between the aluminum fixtures and completely sealed by the four bolts at each corner of metal fixture. The top part of the fixture's design allows optical microscopic monitoring of the fluidic assembly procedure via the center aperture. Observation consistently revealed that the liquid frontline recedes from the channel area and finally disappears in about 10hrs.

4.2.2 Integration of Microspheres on a Patterned Substrate

This strategy for the controlled assembly of nanoscale building blocks exploits the capillary interaction at the water frontline while maintaining controlled evaporation. Capillary forces at the liquid/air interface have been used to assemble colloidal spheres ranging from sub-100nm to several micrometers on lithographically patterned substrates^{1,} ⁷. The contact angle at the interface between suspension and substrate plays a critical role in determining the fluidic-assembly yield¹. As depicted in Figure 4-5 (a),



Figure 4-5 (a) Schematic illustration of fluidic assembly of spherical particles at the photoresist wells using a fluidic cell where the capillary force at the meniscus confines the particles to the recessed region and leaves few on the surface of the substrate. (b) The forces exerted on the spheres during the assembly. The inset shows the low contact angle between the deionized water and the substrate where this angle determines the direction of capillary force acting on the spheres. Field emission electron microscopic images of (c) dimer-like and (d) single 0.9 μ m-sized silica spheres trapped in the photoresist well by the differential ratio of the to-be-assembled sphere's diameter and the dimensions of the photoresist well.

three major force components act on the particle in suspension during fluidic assembly.

The gravitational force (F_g) is usually not significant in the suspension because the density of the suspending medium is typically comparable to that of the spheres. The surface charges of the sphere and the substrate result in an electrostatic force (F_e) . A slight repulsive force exists between polystyrene (PS) or silica (SiO_2) spheres (both from Bangs Laboratories Inc., Fishers, IN) and the substrate because of the negative surface charges of SO⁴⁻ and SiOH⁻ and oxygen plasma treated-substrate. This condition leads to levitation of the spheres from the substrate and prevention of random sticking. The capillary force (F_e) at the meniscus pushes the spheres partially toward the substrate while evaporation of the supension continues. The particles are forced into the lithographically-defined wells and removed from unwanted areas as the meniscus passes over them.

The direction of capillary force is dependent on the contact angle or the interfacial energy between the suspension and the substrate. Thus, controlling the contact angle plays an important role in determining the fluidic-assembly yield, mainly because the capillary force dominates the other force factors. Therefore, a small contact angle, less than $\sim 10^{\circ}$, is necessary to obtain highly efficient fluidic assembly. Figure 4-5 (b) illustrates that evaporation of the sphere solution in the fluidic cell along with a low contact angle assembles the spheres at the photoresist wells by structural trapping and drags excessive, extraneous spheres away. The ratio of sphere diameter to the dimension of the photoresist well defines the geometry of assembled spheres within the well. For self-limiting deposition, the photoresist well needs to be precisely configured to accommodate a single particle only where the well's depth is between half and two-thirds of the sphere's diameter. The shape of assembled microspheres is determined by the

dimension of the well and its ratio to the spheres. By increasing the diameter of wells, producing a variety of sphere clusters is possible as has been demonstrated elsewhere.

Figure 4-6 (a) shows an example of single sphere assembly at the photoresist well, while Figure 4-6 (b) shows the dimer-like assembled spheres in the wells. As mentioned earlier in this chapter, notably, the spheres' assembly is inclined toward the direction perpendicular to the liquid's flow. Figure 4-6 (c) shows the assembled silica microspheres, with a 0.9 μ m mean diameter, at the well-defined locations, which clearly demonstrates about a 95% single microsphere assembly yield on a 150×150 μ m² area.



Figure 4-6 Field emission scanning electron microscope images of single silica spheres trapped in the photoresist wells over a $150 \times 150 \mu m^2$ area. Contrast difference of single silica spheres resulted from the variation in the diameter of photoresist wells, leading to silica spheres with different heights within the photoresist wells. Scale bar = $20 \mu m$.

The fluidic assembly begins with preparing a patterned template. Periodic wells, circle-

shaped photoresist wells of 1µm diameter and 1.1µm depth, are lithographically patterned

following application of Shipley 1811 photoresist on a silicon (100) substrate. Prior to

injecting the microsphere solution, the substrate is routinely treated with the oxygen plasma to ensure its hydrophilicity.

4.2.3 Integration of Functional Microspheres for On-chip Sensing

4.2.3.1 Fabrication of Cross-Point Array Structure

The power of fluidic assembly of spherical particles lies in its versatility allowing high density assembly of the functional microspheres at the wells between the addressable top and bottom electrodes. Unlike random deposition, the fluid technique offers a predictable and controlled assembly of spheres for device fabrication. Thus, the design for the current research is a cross-point array structure for ultrahigh density sensor integration and readout using a multiplexed row-column format. The research investigated a high-density, cross-point microshell sphere sensor array in which microshell sphere sensors are confined by wells of the top metal electrode at the crosspoints and also are electrically addressed by the top and bottom orthogonal metal lines. The approach for individual addresses of the assembled sensor will be discussed later in detail.

Figure 4-7 illustrates the process flow scheme for fabricating the cross-point array structure in which spheres locate at the wells formed by the top metal electrode and interdielectric layer. Fabrication of a cross-point array structure begins with the fabrication of bottom metal electrode (Ti/Au=15nm/60nm) followed by deposition of an interdielectric layer, as shown in Figure 4-7 (a). Figure 4-7 (b) shows that plasma



Figure 4-7 Illustration of the process flow scheme for fabrication of a cross-point array structure and fluidic assembly of spherical particles. (a) Fabrication of bottom metal electrode and interdielectric layer deposition. (b) Fabricaton of top metal electrode. (c) Via etch using a dry etch following the photoresist patterning. (d) Fluidic assembly of spherical particles at the structure's cross-point. Cross-sectional view indicates that the assembled sphere makes contact with the bottom and top electrodes.

enhanced chemical vapor deposition (PECVD)-grown silicon nitride, 1µm thick, serves as the interdielectric layer separating the top and bottom metal electrodes following the fabrication of top metal electrodes (Ti/Au=15nm/60nm). A silicon nitride layer was selectively etched from the cross-points and wire bonding pads following photoresist patterning. Overetching of the silicon nitride layer was attempted to allow forming of the reentrant profile of the dielectric layer. This ensures that the assembled spheres make contact with top and bottom electrodes. Considering the diameter of spherical particles, $0.9\mu m$, used in this experiment, $1.5\mu m \times 1.5\mu m$ for the dimension of the well with a depth of $0.7\mu m$ were determined as appropriate traps for single spheres.

Figure 4-8 (a) schematically illustrates that the spherical particles assemble at the cross-points in the array due to capillary action. As shown below, the controlled



Figure 4-8 (a) Schematic illustration of fluidic assembly of spherical particles in the cross-point array structure where the top electrode with an aperture array traps the nanowires at the cross-point. (b) Field emission scanning electron microscopic image of bare silica spheres assembled on a 4x4 array structure. Scale bar = 5 μ m. (c) A cross-sectional view at the cross-point where the assembled spheres make physical contact with the bottom and top electrodes. (d) Top-view of an assembled sphere at the cross-point where the inset image highlights the reentrant profile of the etched silicon nitride layer. Scale bar = 1 μ m.

water evaporation results with nearly unidirectional capillary force and shear force along

the flow direction. The field emission scanning electron microscopic image indicates that

the forces acting on the spherical particles are also dominant in the complicated electrode array structure and strong enough to overcome the protruding region and trenches formed by the top metal electrode array and the dielectric layer. Figure 4-8 (b) exhibits that $0.9\mu m$ silica spheres assemble at the array's cross-point array, demonstrating 100% assembly yield. Also clearly seen from Figure 4-8 (b) is that every hole had one sphere physically trapped within it, while the top surface of substrate was essentially free of any spheres. This result indicates that capillary force is sufficiently strong to trap particles in lithographically patterned wells and to remove excessive particles from unwanted regions. Figure 4-8 (b)also exhibits that fluidic assembly pushes silica spheres over protruding regions and positions them at desired sites of the cross-point structure. Notably, every self-assembled sphere is in physical contact with the sidewalls of both the top and bottom electrodes due to the direction of capillary force. Figure 4-8 (c) shows that the reentrant profile of the silicon nitride layer is intended to allow assembled spheres to make physical and electrical contact with top and bottom electrodes. Figure 4-8 (d) confirms that the overetching of silicon nitride achieves the desired reentrant profile.

In principle, individually assembled spherical devices can be addressed by selecting the corresponding bottom and top electrode lines. Thus, this structure scheme is well suited for achieving ultrahigh density in sensor arrays. Considering addressed cells and their neighboring cells, however, reveals that a leakage current path, in addition to the direct current, always remains. This condition necessitates an access transistor, as shown in Figure 4-2 (a) and (b).

As stated earlier in this chapter, electrical accessibility to the self-assembled spheres is a prerequisite for an electrically addressable, ultrahigh density, sensor array.

Au nanoshells, layered on a silica spheres synthesize the assembly and provide means for measuring them as a control devices to prove the concept of a cross-point device array. Since Au-Au forms a good Ohmic contact in nature, an Au nanoshell sphere allows investigating the electrical contact properties between the metal electrodes and assembled spheres. As shown in the upper inset of Figure 4-9 (a), the transmission electron





microscopic image shows that the Au nanoparticles with a mean diameters of 50nm

attach to the silica spheres whose mean diameters are 0.9µm. This nanoparticle

attachment is possible by treating the silica spheres with (3-aminopropyl)-

trimethoxysilane (APTMS). Resultant terminal amine groups act as attachment points for

Au nanoparticles on the silica spheres. Thereafter, a 30nm thick Au conformal overlayer

is grown from the spheres by dipping the nanoparticle-attached silica spheres in a 1% solution of HAuCl₄ in potassium carbonate for ~24hrs.

Following synthesis of Au-coated silica nanoshell spheres, fluidic assembly positions them in the wells at the cross-points. Figure 4-8 (b) and (c) show scanning electron microscopic images of an assembled Au-coated silica device and its currentvoltage (I-V) characteristics plot, respectively. Linear I-V indicates that the capillary force at the meniscus is strong enough to force the Au/SiO₂ spheres into contact with both the bottom and top electrodes and suggests that Si₃N₄ at cross-points is completely etched away by reactive ion etching. The assembled spheres inherently form point contacts for both top and bottom electrodes because of the geometrical shape of the sphere and electrodes. The total resistance of a self-assembled Au/SiO₂ device is estimated to be as low as ~16 Ohm as indicated in Figure 4-9 (c).

The small contact area between the assembled sphere and electrodes sustain nearly no high current density. Oopen-circuiting of Au nanoshell device by electron migration occurs at less than 1V. This device breakdown can also be found in metal nanowire²² or particle¹⁴ devices where their diameters appear comparable to the contact areas of assembled spheres. Importantly, the assembled Au nanoshell sphere makes Ohmic contact with the prefabricated metal electrodes, implying potential use for novel electronic components despite of the characteristic, extremely small contact area.

4.2.3.2 Synthesis of Functional Nanoshell Microspheres

Monodispersed microspheres with chemical functionality represent promising building blocks for fabrication of spherical devices using a fluidic assembly technique. The nanoshell grown on dielectric spheres appears advantageous compared to solid spheres because functionally of microspheres can be modified by the nanoshell layer. This approach offers a few advantages over solid spherical particles in terms of devices' sensing performance. First, the core-shell structure offers a high surface-to-volume ratio facilitating sensor devices' high sensitivity and the rapid response times, as compared to the counterpart, solid spheres. The thin shell on the microspheres has a short diffusion distance for chemical analytes, potentially promising rapid response time and high sensitivity. Second, microspheres serve as mechanical support for the thin shell and have chemical sensing ability and help define the dimensions of sensor devices. Silica (SiO₂) spherical particles are commercially available or synthesized in Mallouk laboratory in chemistry department.

Conducting polymer materials allow functionalizing silica microspheres for the chemical sensing applications. PEDOT is the choice due to its chemical stability and ease of synthesis. After several trials based on the literature regarding particles' coating, Dr. Yanyan Cao developed a method to batch-synthesize nanoshell coating on microspheres and to readily control thickness during the process.

Batch-synthesis of conducting polymer nanoshell microspheres for the chemical sensor follows the process of: 1) 15mg silica particles of about 900nm diameter dispersed in anhydrous hexane; 2) 1 to 3.5 mg of FeCl₃ weighed and added, exposed to strong ultrasonication, and magnetic stirred; 3) After vigorous stirring, and addition of 6.8µL ethylenedioxythiophene (EDOT) monomer; 4) The reaction mixture turned from light

yellow to green in a few minutes and after 30 minutes, collection of the colloids by centrifuging and washing with methanol for a few cycles. This method yielded continuous coating of nanoparticles on the microspheres. Figure 4-10 (a) and (b) show the transmission electron microscopic images of thick and thin polymer layers on the microspheres. The images show contrasting polymer layers with silica cores.



Figure 4-10 Comparison of (a) thick and (b) thin PEDOT nanoshell layers grown on silica spheres. The inset in (a) shows the silica spheres before PEDOT coating.

The thickness of polymer films can be controlled to some extent by varying the amount

of FeCl₃ added. Figure 4-10 (a) displays a thick coated sphere with a coating of 3.5 mg of **4.2.3.3 Integration of Sphere Chemical Sensor and Its Sensing Performance** FeCl₃ In contrast, Figure 4- 10 (b) shows a thin layer polymer coating of 1 mg of FeCl₃.

A large Figure 4-12 (3) 6%) or the transmission shert price rescarce neithing aggromeration


approximately 50nm, but not quite uniform around the silica core. This is partially due to the polymerization of EDOT, a monomer of PEDOT, which occurs not only on the surface of the silica cores but also a few nanometers away from silica cores. Following fluidic assembly of PEDOT/silica nanoshell spheres, electrical measurements analyze the contact properties of assembled nanoshell spheres. Figure 4-11 (b) indicates that the current value at 1V ranges from 1nA to approximately 10nA with non-linearity around the zero-voltage bias, which suggests that the overall electrical property is governed by the contact between the assembled spheres and the electrodes rather than the sphere itself. Repetitive measurements on the same device over 10 cycles show reproducible I-V characteristics and indicate stable contact formation. Low leakage current from this device can be attributed to a discrete device using a cross-point electrode structure.

Figure 4-12 (a) and (b) exhibit the sensing performance of a PEDOT nanoshell device in the presence of hydrogen and methanol. PEDOT conducting polymers are synthesized as p-type materials because of the oxidizing agent during their polymerization from the monomer. Figure 4-12 (a) shows that the resistance of a PEDOT



Figure 4-12 (a) and (b) show the reversible and rapid sensing responses of a PEDOT nanoshell device to hydrogen and methanol, respectively. The <5s response time to hydrogen and methanol were estimated from the insets in (a) and (b). The green and red arrows indicate the introduction of chemical analytes and nitrogen gas, respectively.

nanoshell device increases upon exposure to hydrogen gas flow. The resistance change of

known to be an electron donating gas. The diffused hydrogen into a PEDOT shell donates the electrons and compensates the positive charges of the polarons and the bipolarons along the polymer backbone, leading to reduction of the charge carriers. In addition, methanol molecules can make a conformational change to a PEDOT polymer's backbone as well as modulate the charge carrier's concentration within a PEDOT polymer by undergoing a partial charge transfer as an acceptor^{24, 25}. This change in polymer structure, within a conducting polymer, affects polymer's conjugation length and increases the resistance of a PEDOT shell, as shown in Figure 4-12 (b).

For hydrogen and methanol sensing, the magnitudes of normalized resistance change (defined by $\Delta R/R_0 = (R-R_0)/R_0$, where R and R₀ are the real-time and the initial resistances, respectively) tend to increase as the analyte's concentration increases. This is because the diffusion of an analyte into the conducting polymer governs the sensor response and strongly depends on analyte's concentration gradient at the analyte/polymer interface. As a result, the use of a thin conducting polymer layer on the silica is favored due to the short distance over which the analyte diffuses. Compared to a thick PEDOT shell sensor, a thin one shows higher sensitivity, in turn a larger normalized resistance change, to the same analyte concentration.

Figure 4-13 (a) shows the transmission electron microscopic image of a thick PEDOT nanoshell silica sphere exhibiting a PEDOT shell approximately 150nm thick. Sensing response for this thick PEDOT nanoshell sensor appears in Figure 4-13. A thick PEDOT sensor shows relatively low sensitivity to exposure to methanol solvent. Furthermore, estimates of the response time is on the order of tens seconds for 6% methanol, while a thin PEDOT sensor shows <5 second response time for a lower concentration of methanol, $\sim 3.5\%$.

The irreversibility of the sensor response, often present in conventional thin film sensors, is considered one of drawbacks for commercialization of conducting polymer sensors. Thin film sensors often require the sensing operation to occur at an elevated



Figure 4-13 (a) Transmission electron microscopic image of a thick PEDOT silica sphere and (b) its sensing response from exposure to 6% methanol. A thick PEDOT sphere sensor shows the reversible response to methanol solvent PEDOT. However, a thick PEDOT nanoshell demonstrates relatively low sensitivity and slow response compared to thin PEDOT. The green and red arrows indicate the introduction of chemical analytes and nitrogen gas, respectively.

temperature to facilitate adsorption/desorption of chemical species^{26, 27}. For both types of electronic nose system with extreme redundancy mainly due to its scalability, self-chemical analytes, a PEDOT nanoshell sensor exhibits reversible responses, which is limiting top electrode, and compatibility with CMOS fabrication techniques. The likely due to the short diffusion distance for the chemical analytes. Macroscopic thin film electronic nose fundamentally requires different types of sensor elements assembled in a type of chemical sensors tend to exhibit relatively slow response times (a few minutes) small area of a single chip. This can be achieved by the geometry ratio-dependent nature and/or irreversible sensing response²⁸.

of fluidic assembly. Namely, different sensor elements could be assembled into the holes

by controlling the geometrical size of sphere and hole. If the dimensional ratio between

holes and colloidal spheres is precisely controlled, multiple-steps of fluidic assembly makes feasible fabrication of an electronic nose. The density of the sensor array can be further increased by combining sub-100nm sensor elements with state-of-the-art lithography techniques, to achieve beyond ~billion sensor elements per square centimeter.

4.3 Conclusion

This chapter presents a versatile approach to fabrication of an ultrahigh density nanosensor array, in which the assembled sensor elements, either identical or different, over large area, are individually addressable. As a proof-of-concept work, this discussion also demonstrates that a PEDOT nanoshell sphere sensor is self-assembled, makes stable electrical contact to the electrode, and shows rapid and reversible response to the chemical analytes. This sensor fabrication scheme is scalable and fully-compatible with current CMOS fabrication technologies. This compatibility strongly suggests that the chemical sensor array can couple with micro- or nanoelectronics to not only address and readout the sensing data, but also, on a single chip, process the acquired data for analyte analysis. The technology also provides a novel method to assemble different types of sensor elements into precisely controlled locations, thereby producing a unique fingerprint response for identifying chemical analytes.

4.4 References

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Chapter 5

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

5.1 Summary

This thesis investigated bottom-up integration of functional nanostructures such as nanowires and nanoshell spheres for on-chip applications. This method offers a promising approach to integrate off-chip synthesized building blocks on a substrate or a circuit without sacrificing nanostructures' unique properties or functionality during the fabrication process. Conventional semiconductor fabrication processes for CMOS circuits often involve high temperatures (>1000°C) and application of aggressive chemicals, which could impact on the properties of nanostructures. Thus, high-yield integration of nanostructures at the desired locations on a substrate or in a circuit represents a significant advance toward heterogeneous nanosystems for various on-chip applications.

Dielectrophoretic force has attracted much attention, primarily due to its capability to manipulate high aspect ratio, polarizable nanostructures in a controlled way. Dielectrophoretic assembly of nanowires, assisted by the design of a microelectrode structure, yields spatially-controlled nanowire alignment. In particular, dielectrophoretic force and electrostatic interaction of nanowires enables positioning of metallic and semiconducting nanowires with respect to lithographically defined wells. Furthermore, combination of nanowire integration with a unique post-assembly process completes device isolation for an individual address, removes misaligned nanowires, and provides electrical connection to the underlying electrodes. Fluidic assembly of nanoshell spheres also provides a way to integrate the functional spherical entities on a substrate or crosspoint electrode structure for on-chip sensing. These integration methods are generic in nature and thus could be extended to sequential assembly of different types of nanostructures, potentially encompassing heterogeneous integration of functional nanodevices on a single, multifunction chip.

Chapter 1 introduced directed-assembly of nanowires for on-chip integration and discussed the important aspects of nanowire placement, associated with the post-assembly process and device registration.

Chapter 2 investigated the details of electric field-assisted Rh nanowire assembly used to position nanowires between biased, parallel electrodes where a high electric field gradient arises. The experimental results and relevant theoretical simulation revealed that the dielectrophoretic attractive force, assisted by the fluidic cell, directs the nanowires from the solution toward the high electric field gradient region, namely the gap between oppositely-biased electrodes. In addition to this long-range dielectrophoretic force, the electrostatic force between the assembled nanowires and biased electrodes determines their final configuration relative to the electrode and neighboring nanowires. In other words, the nanowires form a uniformly-spaced array with excellent end-to-end nanowire registration, which ensures metal contact at both ends of assembled nanowires. Continuous supply of nanowires might degrade the integrity of uniformly-spaced nanowires by forming nanowire-nanowire chains due to a localized electric field arising from the tips of nanowires. Deeply trenched dielectric layer at the electrode gap prevents this end-to-end nanowire interaction so that the nanowire array maintains uniform spacing without excessive numbers of chained nanowires.

Chapter 2 also discussed internanowires' spacing within a uniformly-spaced array which depends on the electrode's alignment configurations and the biasing conditions for Rh nanowire alignment. The chapter builds a theoretical model for electrostatic interaction between assembled nanowires and predicts the relationship of internanowire spacing as a function of nanowire length and electrode gap. The experimental results of nanowire assembly which varied nanowires causes them to space at a greater distance. This phenomenon is consistent with the theoretical expectation based on the model. The thickness of the dielectric layer and the amplitude of applied bias also play an important role in determining the uniform spacing within the nanowire array. This research proposed that the ratios of the electrostatic to dielectrophoretic forces are a convenient measure for predicting nanowires' spacing within the array. Thus, a stronger electrostatic force in the nanowire array with a lower dielectrophoretic force leads to greater spacing between the nanowires assembled at the electrode gap.

Chapter 3 presented the deterministic integration of Rh nanowires at the lithographically defined well array achieved a >90% single nanowire assembly yield with submicrometer registration relative to the center of photoresist wells. Stronger dielectrophoretic force at the photoresist well induced preferred attraction of nanowires along the electrode gap while the electrostatic repulsive interaction persisted within the assembled nanowires. Also developed was a post-assembly metallization process for nanowires' electrical contact using an electrodeposition technique. The electrical measurement of assembled single nanowire devices, clamped by an electrodeposited electrode, revealed that this unique metal contact formation provides a mechanically strong and electrically less-resistant contact to the assembled nanowires and also releases misaligned nanowires from the substrate. The techniques demonstrated a >95% discrete device fabrication yield.

As proof of the concept, functional PEDOT/ClO₄ nanowires, with lengths of about 7μ m and mean diameters of 200nm, were synthesized via the template method and assembled at the photoresist wells for fabricating chemical sensing devices. The ends of the nanowires were electrically addressed by the electrodeposited electrode. Chemically sensitive PEDOT/ClO₄ nanowires showed a conductivity change by exposure to an organic solvent, chemical gas, and nerve gas simulant in which the chemical sensing arises from structural and/or electrical modification of charge carriers within a nanowire.

Chapter 4 presented the fluidic assembly of spherical particles for on-chip sensing applications. The capillary force at the meniscus assembled the spherical particles at the photoresist wells or wells defined by the metal electrodes which are designed to accommodate a single spherical particle only by structural constraint. The proposed cross-point array structures integrated the functional spheres at predetermined locations at which the bottom and top electrodes make electrical contact with the assembled spherical particles. A developed thin functional layer on the spherical cores converted the dielectric spheres into chemical sensory building blocks. Fluidic assembly of nanoshell PEDOT spheres at the cross-points of metal electrodes completes the fabrication of chemical sensors for detecting a chemical solvent or gas. Due to the geometrical nature of the nanoshell's PEDOT sensing layer, PEDOT nanoshell sensors exhibit reversible responses to both types of chemical analytes, a consequence likely due to the short diffusion distance of them. This thin structural feature of PEDOT nanoshells also accounts for the relatively short response and recovery times (~5 seconds) to the analytes, while the thin film-type chemical sensors tend to exhibit relatively slow responses (a few minutes).

5.2 Outlook for the Deterministic Nanowire Assembly

This thesis discussed the directed-assembly of high aspectio raitio and spherical nanostructures on microfabricated electrode structures for adding new functinoalites to silicon circuit. This thesis also investigated the deterministic assembly technique as a means to integrate them on a CMOS circuit with reliability, accuracy, and reproducibility of registration. As a reasonable step, future work should include electrical field-assisted assembly of semiconducting inorganic nanowires to expand their materials' flexibility. Since different materials possess different permittivity, expectedly changes in permittivity give rise to different dielectrophoretic forces directing the polarized nanowires toward the high electric field gradient region. Applying the experimental and relevant theoretical analysis used in metallic nanowire array formation to semiconducting nanowires will validate the generic approach of electric field-assisted nanowire assembly.

5.2.1 Uniformly-spaced Silicon Nanowires Array

Vapor-liquid-solid (VLS) growth method, using metal nanoparticles, produces large numbers of nanowires, leading to the potential building blocks for the nanoelectronics¹⁻⁴. VLS growth method using metal particles, however, often lacks tight control of diameter and length of grown nanowires, partially due to variations of nanoparticles' sizes and the direction of nanowire growth. Nanowires' release from the substrate using an ultrasonication produces a nanowire solution with small, broken pieces, the result of which is difficulty in interpreting the outcomes of nanowire assembly. The doping uniformities in radial and axial directions within nanowires do not appear well-defined. As a result, these imperfections and possible non-uniformities in VLS-grown nanowires could result in performance variations among nanode vices assembled on a CMOS circuit. This variation within a circuit creates difficulty for proving the electric field-assisted nanowires assembly's suitability for high-yield nanowire integration in a CMOS circuit.

Wenchong Hu in the Mayer Group developed the method for fabricating silicon nanowires with diameters of ~100nm and with well-controlled lengths using top-down fabrication technologies. Figure 5-1 (a) briefly illustrates the top-down fabrication of silicon nanowires. Deep reactive ion etch using a Bosch process, cycling of isotropic etch and passivation, defines the high aspect ratio of pillar arrays whose diameters can be uniformly patterned by lithographical techniques. Oxidation of silicon pillars and subsequent buffered oxide etch (BOE) can shrink pillars' diameters to sub-100nm without visible variation in the diameters of nanowires, as shown in Figure 5-1 (b). The wavy nanowire surface, as seen in Figure 5-1(c), is characteristic to Bosch-processed high aspect ratio pillars or holes. The wavy characteristic could be minimized by reducing the cycle time of the etch process. Figure 5-1(d) exhibits that ultrasonication of the substrate releases nanowires without damaging them or producing an excessive number of broken pieces.

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Figure 5-4 Top-down fabrication of silicon nanowires with uniform diameters and lengths. (a) The oxidation and wet etch of silicon pillar array for sub-100nm diameter nanowire arrays following a deep reactive ion etch. (b) Field emission electron microscopic image of a nanowire array with a mean diameter of 150nm. Scale bar = 5μ m. (b) Zoomed-in microscopic image showing the wavy surface of nanowires, which is characteristic of the Bosch process. Scale bar = 3μ m. (d) The dark field optical microscope images of silicon nanowires drop-cast on silicon substrate. Scale bar = 30μ m.



Figure 5-5 (a) Low magnification and (b) zoomed-in view of dark field optical microscopic images of silicon nanowires assembled at 4 μ m-spaced electrode gaps. Scale bar = 100 μ m in (a) and 4 μ m in (b). These images demonstrate silicon nanowires' strong dielectrophoretic attraction which directs them toward the electrode gap and also suggests that the electrostatic repulsive interaction between the assembled nanowires and their capacitive coupling to the underlying electrodes still dominates during the assembly process. This eventually results in a uniformly-spaced silicon nanowire array with excellent end-to-end nanowire registration.

Obviously, nearly all nanowires are attracted and assembled at the electrode gap while

spanning it symmetrically due to the capacitive coupling between the polarized

permittivity of ~11.7 at a frequency of tens of kHz. This mutual dielectrophoresis is the outcome of polarization within the nanowires and depends on the polarizability of nanowire materials⁵. Repeating Equation (2-2) and (2-3) from Chapter 2:

$$\mathbf{F}_{\text{DEP}} = \frac{\pi r^2 \ell}{3} \,\epsilon_1 \,\text{Re} \,(\text{K}) \,\nabla \mathbf{E}^2 \,, \qquad (2-2)$$

and Re (K) =
$$\frac{\sigma_1(\sigma_2 - \sigma_1) + \omega^2 \varepsilon_1(\varepsilon_2 - \varepsilon_1)}{\sigma_1^2 + \omega^2 \varepsilon_1^2}$$
(2-3)

indicates that the dielectrophoretic force, exerted on the nanowires is proportional to the permittivity of nanowires suspended in the liquid medium. As a result, the metal nanowires possess, ideally, an infinity of polarizability, primarily due to the nature of unbound free electrons. This condition leads to the high probability of local end-end nanowire interaction and thus the formation of chained nanowires. The polarization of silicon nanowires can be considered several orders lower than metallic entities due to the relatively low permittvity of silicon, which results in the weak mutual dielectrophoresis between nanowires' ends. Notably, the capacitive coupling between the assembled nanowires and biased electrode still remains valid in this system and thus induces nanowires' charges by the biased electrodes. As a result, this repulsive interaction between the assembled nanowires keeps them uniformly-spaced within an array. Furthermore, spatially-controlled silicon nanowire integration on a substrate or circuit can be achieved by the use of a recessed photoresist well.

Dielectrophoretic attraction and electrostatic repulsion of nanowires are not restricted to the specific materials investigated in this thesis, but appears to be generic to polarizable material systems. Further study will be necessary to prove this hypothesis and need to be investigated in the near future.

5.3 References

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Appendix

TRANSISTOR-NANOWIRE CIRCUIT ARRAY FABRICATION PROCESS

Sample Number	
Date	

FABRICATION PROCESS		Date
Cleaning 3 inch p-Si wafers with standard cleaning process (SC1&SC2)		
Thermal growth of 0.7µm field oxide on Si wafers		
Lithography for defining of source and drain of transistors - Spin SPR-3012 at 4000 rpm for 45 sec		
- Bake 100°C for 1min.		
Use a stepper to pattern with an exposure time of 1.2 sec.Develop in CD-26 for 1min.		
Dry etch of field oxide using a ICP-RIE system		
- Pressure: 20mTorr		
- Power (ICP/RIE): 50W/100W		
- Gas flow (CHF3/O2): 25sccm/5sccm		
- Time:		
Removal of SPR-3012		
- Rinse in 101 remover at 120°C for ~ 1 nr.		
- Piranha etch for 10mins.		
- Acetone and IPA spray		
Predeposition for heavily doped region of source an drain		
- Use a POCl ₃ for n-type source.		
- Predeposition conditions: 100sccm O ₂ bubbling for 12mins.		
Drive-in of dopants		
- Use a wet oxidation furnace.		
- Drive-in condition:		
Standard cleaning process (SC1&SC2)		
Lithography for defining of gate oxide region		
- Spin SPR-3012 at 4000 rpm for 45 sec		
- Bake 100°C for 1min.		
- Use a stepper to pattern gate oxide region		
Dry etch of field oxide using a ICP-RIE system		
- Pressure: 20mTorr		
- Power (ICP/RIE): 50W/100W		
- Gas flow (CHF3/O2): 25sccm/5sccm		
- Time:		

Removal of SPR-3012	
- Rinse in 101 remover at 120°C for ~1hr.	
- Piranha etch for 10mins.	
- Acetone and IPA spray	
Growth of high quality of oxide	
- Use a ultrahigh purity O_2 .	
- Growth condition: 1050°C for 24min (t _{OX} ≈30nm)	
Standard cleaning process (SC1&SC2)	
Gate electrode deposition	
- Spin PMGI SF-6 at 4000 rpm for 45 sec.	
- Bake 250°C for 5min.	
- Spin an imaging photoresist, SPR-3012:a l-methyl lactate=2:1, at 4000	
rpm for 45 sec.	
- Use a stepper to pattern with an exposure time of 0.7sec.	
- Develop in CD-26 for 1min to develop an imaging photoresist.	
- UV ozone exposure for 150sec.	
$-O_2$ descum at 25W for 1min.	
- Thermal evaporation of Ti/Au=20nm/50nm.	
- Lift-off in 1165 remover at 80°C for ~30min.	
- Rinse in acetone and isopropanol.	
Interdielectric layer deposition using AMAT PECVD	
- S1 ₃ N ₄ deposition ($t_{Si3N4} \approx 180$ nm)	
Lithography for etching of interdielectric layer	
- Spin SPR-3012 at 4000 rpm for 45 sec.	
- Bake 100°C for 1min.	
- Use a stepper to pattern with an exposure time of 1.2 sec.	
Interdielectric layer etching using ICP-RIE	
Photoresist removal	
- Dip in 1165 remover at 80°C for ~30mins.	
- Rine in acetone and isopropanol	

 Spin PMGI SF-6 at 4000 rpm for 45 sec. Bake 250°C for 5min.
- Bake 250°C for 5min.
- Spin an imaging photoresist, SPR-3012:a I-methyl lactate=2:1, at 4000
rpm for 45 sec.
- Use a stepper to pattern with an exposure time of 0.7sec.
- Develop in CD-26 for 1min to develop an imaging photoresist.
- UV ozone exposure for 150sec.
- O ₂ descum at 25W for 1min.
- Sputtering Ti/Au=20nm/50nm.
- Lift-off in 1165 remover at 80°C for ~30min.
- Rinse in acetone and isopropanol.
Lithography for photoresist well (~0.3µm deep)
- Spin PMGI SF-11 at 4000 rpm for 45 sec.
- Bake 250°C for 5min.
- Spin an imaging photoresist of BPRS-100 at 4000 rpm for 45 sec.
- Bake 115°C for 90sec.
- Use a stepper to pattern with an exposure time of 0.25sec.
- Develop in PLSI 3:1 for 1min to develop an imaging photoresist.
- UV ozone exposure for 150sec.
- Remove BPRS-100 with acetone and isopropanol.
Nanowire alignment
- Use a function generator
- Alignment conditions: $V_{pp}=10V$ at 100kHz.
Clean residue on sample with isopropanol-soaked swab.
Lithography for nanowire clamping
- Spin an imaging photoresist of BPRS-100 at 4000 rpm for 45 sec.
- Bake 115°C for 90sec.
- Use a stepper to pattern with an exposure time of 0.25sec.
- Develop in PLSI 3:1 for 1min to develop an imaging photoresist.
- UV ozone exposure for 450sec.
Nanowire clamping using electrodeposition of gold.
- Prepare TG-25ES RTU at about 60°C with a magnetic stirring.
- Use a pulsed voltage at 0.5V with a 0.3ms (ON) / 0.6 ms (OFF) duty
cycle.
- Deposition rate: ~0.1µm/min
Photoresist removal
- Dip in 1165 remover at 80°C for ~30mins.
- Rine in acetone and isopropanol

Lithography for sacrificial layer removal	
- Spin BPRS-100 at 4000 rpm for 45 sec.	
- Bake 115°C for 90sec.	
- Use a stepper to pattern with an exposure time of 0.25sec.	
- Develop in PLSI 3:1 for 1min.	
- O_2 descum at 25W for 1min.	
Dry etch of sacrificial Ti/Au metal layer	
Photoresist removal	
- Dip in 1165 remover at 80°C for ~30mins.	
- Rine in acetone and isopropanol	
Sample inspection	

VITA

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Selected Publications

- Jaekyun Kim, Mingwei Li, Alexey E. Kovalev, Seokho Yun, Thomas J. Morrow, Christine D. Keating, and Theresa S. Mayer, "Controlled Assembly of Metallic Nanowire Array via Dielectrophoretic Nanowires Attraction and Internanowire Electrostatic Interaction.", (in preparation).
- <u>Jaekyun Kim</u>, Mingwei Li, Alexey E. Kovalev, Thomas J. Morrow, Christine D. Keating, and Theresa S. Mayer, "*Investigation of Spacing-controlled Nanowire Array Formation by the Electric Field-Assisted Assembly*.", (in preparation)
- Jaekyun Kim, Alexey E. Kovalev, Thomas J. Morrow, Christine. D. Keating, and Theresa S. Mayer, "Deterministic Dielectrophoretic Nanowire Assembly." (in preparation)
- Jaekyun Kim, Yanyan Cao, Thomas E. Mallouk, and Theresa S. Mayer, "*Nanoshell Sphere* assembly toward Ultra-high Density Functional Device Integration", (in preparation)
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