The Pennsylvania State University
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PATTERNED SELF-ASSEMBLED MONOLAYERS FOR NANOSCALE
LITHOGRAPHY AND THE CONTROL OF CATALYTICALLY PRODUCED
ELECTROOSMOSIS

A Thesis in
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by
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ABSTRACT

This thesis explores two applications of self-assembled monolayers (SAMs) a) for developing novel molecular assembly based nanolithography techniques and b) for tailoring zeta-potential of surfaces towards achieving directional control of catalytically induced fluid flow.

The first half of the thesis develops the process of molecular ruler lithography using sacrificial host structures. This is a novel hybrid nanolithography technique which combines chemical self-assembly with conventional fabrication methods for improving the resolution of existing lithography tools to sub-50 nm. Previous work related to molecular ruler lithography have shown the use of thiol-SAMs, placed one on top of the other like a molecular resist, for scaling down feature sizes. In this thesis various engineering solutions for improving the reproducibility, yield, nanoscale roughness and overall manufacturability of the process are introduced. This is achieved by introducing a sacrificial inert layer underneath the gold parent structure. This bilayer sacrificial host allows for preferential, easy and quick removal of the parent structures, isolates the parent metal from the underlying substrate and improves reproducibility of the lift-off process. Also it opens avenues for fabrication of high aspect ratio features. Also molecular layer vapor deposition method is developed for building the multilayer molecular resist via vapor phase to reduce contaminations and yield issues associated with solution phase deposition. The smallest isolated metal features produced using this process were 40 nm in width.
The second half of the thesis describes application of thiol-SAMs to tailor surface properties of gold, specifically the surface charge or zeta potential. Previous work has demonstrated that the direction of movement of fluid in the vicinity of a catalytically active bimetallic junction placed in a solution of dilute hydrogen peroxide depends on the charge of the gold surface. SAMs with different end-group functionality impart different surface zeta potential to the gold surface. Zeta-potential engineering via patterning various end-group functionalized SAMs on gold surface to control direction of catalytically induced electroosmotic fluid flow is demonstrated for the first time.

This work also describes the application of catalytic power to produce controlled rotational motion. Gold gears-like structures made using conventional microfabrication techniques and propelled by catalytic power are shown to rotate at speeds of 1 rotation/sec in a dilute solution of hydrogen peroxide. Fabrication of a force sensor for detection and measurement of catalytic forces is also introduced. The force sensor, with sensitivity in the piconewton range, consists of a microcantilever with a catalytically active silver post patterned on the tip. Changes in cantilever displacement and resonance frequency due to the catalytic force were monitored as a function of concentration of hydrogen peroxide.

Overall, this thesis integrates SAM deposition and patterning techniques with conventional fabrication methods to engineer and control nanoscale structures and devices. Possible future device designs are described including CMOS devices having channel width defined using molecular ruler lithography with sacrificial hosts, drug delivery device based on AFM force sensor and channeless pumps powered by catalytic reactions with SAM controlled electroosmotic fluid flow.
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Chapter 1

Self-assembled monolayers (SAMs) are a single layer of surfactant molecules that are formed spontaneously at solid-liquid or solid-vapor interfaces. One end of the surfactant molecule is designed to have greater affinity for the solid substrate and hence is preferentially chemi-adsorbed onto the surface to form a stable monolayer film.[1] The molecular self-assembly process followed by self-organization of the molecules within the film lead to the formation of a few nanometer thick, uniform, dense, highly oriented and ordered monolayer which resembles a bulk material with near crystalline properties. The film retains its properties even when the substrate is removed from the surfactant solution. These characteristics of the SAMs combined with the flexibility in design of the individual molecules through chemical synthesis has lead to the increased interest in SAM as a technological tool for advancing nanotechnology and also as a unique chemical system for fundamental research and understanding of surface phenomenon.

Historically the first mention of the self-assembly is credited to Zisman [2] who in 1946 reported the formation of oleophobic films from solution on a metal surface. This research did not generate much interest. Much later in 1983 Nuzzo and Allara [3] described the formation of monolayers on gold surfaces from organic solutions containing disulfide molecules. In 1984 J.Sagiv [4] analyzed the formation of silane monolayers on glass substrates. These two publications helped bring self-assembled monolayers into the limelight. It was around this time when scientist and researchers in all fields from electrical engineering to biology were investigating means of
miniaturization and understanding phenomenon at the micro and nanoscale. SAMs caught the imagination of the scientific community as it provided a unique and novel way to control structure and properties of surfaces using molecular films, to study interfacial properties of solids and opened avenues to build micro and nanoscale devices and assemblies from bottom-up. Since then there has been a continuous increase in the study of self-assembled monolayers and its applications, which is reflected in the exponential increase in the number related publications. For example a keyword search for ‘self-assembled monolayers’ in the web of science reveals more than 3500 hits in just the last five years. Discovery and application of improved surface analysis techniques such as the X-ray spectroscopy, vibration analysis methods and scanning probe microscopy has speeded the growth of study of SAMs, by providing better understanding of the mechanism of monolayer growth and film structure and properties.[5, 6] Several substrate/adsorbate pairs are suitable for formation of SAMs including long-chain n-alkanoic acids (CₙH₂n₊1COOH) on sliver and aluminum oxide, alkylchlorosilanes, alkylalkoxysilanes, and alkylaminosilanes on hydroxylated surfaces such as glass and quartz, alkyl chains to silicon and organosulfur compounds on gold, silver, copper platinum and other transition metals.[1] However most studies over the years have been conducted on organosulfur (HS (CH₂)ₙX) SAMs on gold surface mainly because of the ease and speed of formation of monolayers, ability to synthesize wide range of end groups, high stability of the monolayers formed leading to the displacement of more weakly adsorbed impurities, high packing density and high robustness of the films. Potential applications of SAMs are being explored in the areas of molecular and
semiconductor electronics, electro-optic devices, micro/nano electromechanical systems (MEMS/NEMS), chemical sensing, biomolecular detection etc.[7]

As the dimensions of devices shrink the surface area to volume ratio increases and the surface effects become increasingly dominant. This leads to surface and interface related problems such as adhesion, stiction and friction between the moving parts.[8] One method to solve this problem is to explore new materials with improved and desired surface properties. However this would mean developing new infrastructure and instrumentation to build these devices and the silicon technology, so readily available, can no longer be used. Instead scientists are exploring methods to tailor the surface of the devices by using ultra thin polymer films and self-assembled monolayers. For example improved wear resistance and reduced friction during the release and use of silicon, silicon nitride and polysilicon based MEMS devices is achieved by coating the surface with octadecyltrichlorosilane (OTS) self-assembled monolayer. The self-assembled monolayers are tailored to make the surface very hydrophobic and thus reducing contact between micromachined parts.[9]

Microfluidic devices are silicon or polymer based microfabricated network of channels for handling, transporting and analyzing micro/nanolitres of fluid. They are used in conjunction with the actuating and sensing parts fabricated using MEMS processes mainly for biological applications such as lab-on the chip.[10] The fluids in such systems come in contact with the surfaces of the microchannels and their interaction is governed by surface properties such as surface wettability, surface charge, zeta potential etc. The surfaces properties are altered using SAMs. SAMs are deposited on the channel wall-surface by pumping the SAM solution through the channels or flowing of adsorbate gas.
Directional pumping in the microchannels has been achieved by patterning the surface wettability with patches of hydrophobic SAM which force the fluid into certain channels while preventing movement in the others.[11] Also stabilization of the surface charge has been carried out by modifying the inner channel walls with self-assembled monolayer to regulate the direction and rate of electrophoretic flow of fluid.[12]

Another area where SAMs have found applications is for the design of templates to immobilize biomolecules such as DNA and other proteins for biomolecule sensing, proteomics, DNA detection arrays etc. For example the protein streptavidin was immobilized using thiol based SAM on the electrode of a detector array fabricated using MEMS technology. The binding of EColi to the protein was detected and measured optically and electromechanically. Such integrated systems offer the advantage of rapid detection, repeatability and portability.[13] In another example optical sensing of the acidity and pH of a solution is carried out by using a molecular switch immobilized to a glass microfluidic channel using a SAM.[14] The molecular switch alternates between the fluorescent and non-fluorescent states depending on the acidity or pH of the surrounding solution. DNA biosensors are fabricated by immobilization of DNA molecules on a SAM covered substrate while making sure that no denaturing occurs. This template of DNA then serves as probe sensor used for making the DNA chip.[15]

Broadly, application of SAMs has been two-fold: firstly to design templates to immobilize chemical and biological functional molecules and for building nanoscale devices, structures and supramolecular assemblies via bottom-up fabrication and secondly to modify physical and chemical properties of the surface at the nanoscale for
improved device performance. This thesis explores both these applications as related to molecular ruler lithography and catalytic motors.

Chapters 2 and 3 describe processes that use self-assembled monolayers as a building block for fabricating nanoscale structures. In particular advancements in molecular ruler lithography process using sacrificial host structures is discussed. Molecular ruler lithography [16] is an innovative approach currently being explored which combines chemical self-assembly based bottom-up techniques with top-down lithography methods to scale down the feature sizes achievable by conventional patterning techniques. This is accomplished by patterning functional host structures whose dimensions are tailored by systematically assembling engineered organic molecules of precise length (SAMs) on their surface, creating a template for producing features with reduced dimensions. Molecular ruler nanolithography using sacrificial multilayer host structures defined via optical or electron beam lithography, [17] described in Chapter 2 is a modified molecular ruler method which aims to improve the reproducibility and versatility such that it can be incorporated into the manufacturing environment. Chapter 3 describes the application of the process to build MOS like structures and high aspect ratio features. Preliminary results of vapor phase assembly of the molecular resist are also demonstrated.

Chapters 4 and 5 describe methods for patterning self-assembled monolayers to tailor the surface charge of gold substrates for application in catalytic motors. Catalytic motors [18] refer to a class of novel nano and microscale powering devices that operate on the principle of catalytic conversion of chemical energy available in the environment to mechanical energy. It has been observed that bimetallic junctions placed in a fuel
solution, such as dilute solution of hydrogen peroxide, produce localized forces via catalytic decomposition. The forces though small, in the range of piconewtons, have been shown capable of propelling nanorods, rotating microgears and pumping fluid. A novel method to measure the catalytically generated force using a microfabricated cantilever is described in Chapter 4. Surface and interface properties play an important role in the operation of catalytic motors. Tailoring surface zeta potential via self-assembled monolayers to achieve spatial and temporal control of the catalytically induced electroosmosis is demonstrated in Chapter 5. Catalytically powered rotation of gear-like structures by selective patterning of the bimetallic junctions on the spokes is also introduced in this chapter.

Overall this thesis explores SAMs as a resolution enhancement tool in molecular ruler lithography using sacrificial host structures and as a surface engineering tool to control surface zeta potential in catalytic systems.
1.1 References


Chapter 2

Molecular ruler lithography processes using sacrificial multilayer hosts

2.1 Introduction

Nanofabrication processes capable of producing features and devices with dimensions less than 10-50 nm are key to the production of many emerging and future devices including molecular and semiconductor electronic components and interconnects, nanoelectromechanical systems (NEMS) and related structures for biological applications including sensors, engineered surfaces and nanofluidic channels. Continuous improvements in lithography techniques over the past decade, such as advanced optical proximity corrections, phase shift masks, immersion lithography, step and flash lithography and 193 nm technology, have managed to keep optical lithography viable to the 90-nm technology node.[1] Patterning technology extending to sub-45 nm is a subject of considerable importance and debate. Further improvement in exposure tools, resist chemistries and mask designs are being researched, but new instrumentation solutions are expensive and disruptive. Other lithography tools being explored such as electron beam lithography, imprint lithography and soft lithography [2] have problem associated with cost and reproducibility. An ideal solution would involve the extension of established manufacturing capabilities to patterning smaller feature dimensions based on new but
compatible process development, reducing transition time and costs and avoiding additional investment into new instrumentation and infrastructure.

2.2 Molecular ruler lithography

2.2.1 Introduction

Molecular ruler nanolithography,[3] developed by Dr Weiss and his group in 2001, is a scalable patterning technology allowing nanoscale features to be ‘scaled down’ by assembling a molecular film consisting of multiple layers of functional organic molecules onto patterned host features. The final dimensions of features produced using the molecular film can be precisely controlled since functional organic molecules (molecular rulers) can be synthesized with lengths tailored to sub-nanometer precision. This molecular film can also be used in conjunction with other processes to create a variety of nanoscale structures.

Molecular ruler lithography processes examined to date include a variation on the well known lift-off process where the molecular film is used as a sacrificial resist. A lift-off process is a multi-resist multi-layer process used to pattern metals which are difficult to remove by wet or dry etching. In the single-layer lift-off process (Figure 2.1a) a metal film is evaporated over a single layer of patterned resist. The resist is then dissolved leaving only the patterned metal. However the single layer lift-off is irreproducible and low yielding because the metal film coats the underlying resist making it difficult for the
solvent to access and dissolve the resist layer. Also the feature edges are rough and the process is difficult to scale to smaller dimensions. In the bi-layer process (Figure 2.1b) a sacrificial layer is introduced under the resist layer to form an undercut profile. This provides a gap between the patterned metal and the excess metal allowing the solvent to easily access the underlying sacrificial and resist layer. As a result the features have smoother edges and can be reproducibly scaled down

Fig. 2.1: a) Single layer lift-off process. The process is irreproducible and features have rough edges. b) Bi-layer lift-off process. The undercut profile ensures a discontinuity in the evaporated film giving higher yield and reproducibility with reduced line edge roughness and better resolution.

Molecular ruler lithography uses a variation of the single layer lift-off process as shown in Figure 2.2 and consists of the following steps. First, a parent host material is deposited and lithographically patterned on the surface of a substrate defining a gap. This gap may represent the minimum spacing of features achievable via the lithography process employed. A three dimensional multilayer molecular film is then assembled on the host structures using alternate solution phase, selective deposition of $\alpha$,ω-mercaptoalkanoic acid (HS(CH2)xCOOH) and Cu$^{2+}$ ions. This technique exploits a
selective and orthogonal chemistry; the thiols stick only to the gold and the Cu$^{\text{2+}}$ ions bind only to the carboxylate termini of the bifunctional molecules.[4] By precise control of the length and number of the $\alpha,\omega$-mercaptoalkanoic acid molecules, the gap between the parent host structures can be accurately reduced. Once the desired molecular film thickness is achieved, the daughter material is deposited. The molecular film is then removed lifting off the unwanted daughter material and leaving behind the parent structure and the newly formed smaller daughter feature.

This process has been used to build sub-20 nm metal lines housed between the parent features.[3] Advanced generation of structures placed between the gaps formed between the parent and the daughter, called granddaughters have also been fabricated. The molecular ruler process has been further extended to parent structures fabricated using nanosphere lithography to pattern nanoscale metal dots.[5, 6] A two level photolithography technique has been developed for controlled placement of the molecular rulers on the parent structure for patterning and aligning of the nanogaps.[7] Some of the applications of molecular rulers being explored include formation of precise, electrically isolated nanogaps for measurement of electrical properties of single molecules and molecular conduction.[8-11]
Fig. 2.2: A molecular ruler nanolithography process. a) Parent host metal is evaporated on an oxidized silicon wafer. b) Photoresist is spun on the parent host surface and it is patterned using lithographic techniques. c) A gap is etched into the parent metal using the above resist as a mask. d) A molecular film, of desired thickness, is self assembled selectively on the host metal. e) The daughter metal is evaporated. f) The molecular film is removed and the unwanted daughter metal is lifted off. A nanoscale daughter feature along with the parent is left behind.
2.2.2 Issues to be addresses in the molecular ruler process

Several issues directly relating to the manufacturability of this process have been identified and addressed,[12] including issues which directly relate to the practical application of this process to silicon device fabrication. These process issues include:

1. Increased capability to pattern thick daughter materials. As the daughter material thickness exceeds the total molecular film thickness, the lift-off process becomes less reproducible since the daughter material encapsulates the molecular film preventing it from being stripped.

2. Increased flexibility in the choice of host materials. In many cases it may be necessary to remove the host structure upon completion of the lift-off process. This removal process should not adversely impact the rest of the process or device structures.

3. Isolation of the host material from the underlying substrate throughout the process flow. For example, gold, a common host material, is well known to have a negative impact on silicon based device performance.[13] In this case, new host structures may be required.

4. Improved reproducibility of the lift-off process and the potential for very high yield in a production environment.

5. Optimization of molecular ruler assembly step to reduce the number of steps and time required for formation of desired thickness of the molecular resist.

6. Improved nanoscale roughness of the final feature.
2.3 Molecular ruler lithography using sacrificial multilayer host structures

A new modified molecular ruler fabrication process, molecular ruler lithography processes using sacrificial host structures, was developed which addresses these issues by incorporating a sacrificial multi layer parent host structure. The process is shown in Figure 2.3 and consists of the following steps. First, a sacrificial material is deposited onto the wafer surface. Then a parent host structure is lithographically patterned on the surface of the sacrificial layer defining a gap. A three dimensional multilayer molecular film is then assembled onto the parent host structure as described above. The daughter material is then deposited and the entire host structure is lifted off by dissolving the sacrificial material leaving only the smaller isolated daughter feature.
Fig. 2.3: The Sacrificial bilayer Process; a) A lift-off resist (LOR) is spun on an oxidized silicon wafer. Gold is thermally evaporated on the LOR. b) Photoresist is spun on the gold and lithographically patterned. c) A gap is etched in the gold host structure using the photoresist as a mask. The LOR resist is selectively dissolved to give an undercut. d) Molecular film of desired thickness is assembled on the gold feature. e) The parent metal and the molecular film are stripped by dissolving the lift-off resist which also lifts off the unwanted daughter metal. The isolated daughter feature is left behind.
This approach potentially provides a reproducible and high yield process for removing parent host structures involved in molecular ruler lithography. It also eliminates direct contact of the host material with the substrate, which is of particular importance in the case where gold host features are desired for fabricating silicon based devices. This method also allows the preparation of thicker daughter metal layers, as the thickness now is dependent primarily on that of the sacrificial layer.

2.3.1 Experimental details

This new molecular ruler nanolithography process incorporating a sacrificial host structure implemented using photolithography. Specifically, the process consisted of the following steps. First, 250 nm of silicon dioxide was thermally grown on a 3 inch silicon wafer cleaned in a 5:1:1 water:ammonium hydroxide:hydrogen peroxide solution. The wafer was then coated with Lift-off Resist (LOR) 1A (MicroChem Corp.) using a dynamic spin-on process. The LOR was spun on at a speed of 500 rpm, which was accelerated to 4000 rpm over 10 s and maintained for 40 s. The wafer was then baked at 200 °C for 10 minutes on a contact hot plate resulting in a LOR film thickness of ~150 nm. The sacrificial material employed in this process consisted of the Lift-off Resist manufactured by Microchem corp. This resist was chosen because of the flexibility of resist thickness and undercut rates. Using the different combinations of spin-speed and resist type (LOR A and B series) the thickness of the LOR could be varied from less than 100 nm to about 5 μm. By varying the temperature and time of baking the LOR very slow and controlled dissolution rates could be achieved to obtain the desired profile. Also LOR
was inert to the process conditions for self-assembly of the molecular rulers. LOR did not dissolve in ethanol, which is used in the subsequent molecular ruler assembly process (see below), and it is a nonphotosensitive resist designed for lift-off applications.

A uniform 20 nm layer of gold was then thermally evaporated onto the LOR as a parent host material. (Figure 2.3a) No adhesion layer was used since gold adheres well to the LOR. Megaposit SPR-3012 Photoresist (Shipley) was used to photolithographically pattern the gold layer. SPR-3012 was spun onto the substrate at 4000 rpm for 40 s. The wafer was then soft baked on a contact hot plate at 95 °C for 1 minute providing a 1.2 µm thick resist layer. The wafer was then exposed for 4 s on a Karl Suss MA-6 contact aligner through a test mask containing large test features. The mercury lamp ultraviolet source was unfiltered and exhibited an output power of 12 mW/cm² at the wafer surface. A post exposure bake was performed at 95 °C for 1 minute.

The features were developed for 1 minute and 10 s in CD-26 (.26 N tetramethyl ammoniumhydroxide). (Figure 2.3b) The patterned SPR-3012 was used as a mask to etch the gold parent host structure using a PlasmaTherm PT720 reactive ion etching system. The etch was performed using 15 sccm of Cl₂, 15 sccm of CF₄, and 5 sccm of O₂ at 300 mtorr and 200 watts of RF power for 1 minute and 25 s. This process etches through the gold host layer but does not completely remove the underlying LOR layer. The SPR 3012 resist is then dissolved by sonicating the wafer for 3 minutes in acetone, which does not have an effect on the sacrificial LOR layer. The wafer was then submerged into CD-26 for approximately 10 s. This process provides a ~100 nm lateral undercut beneath the gold parent host structure aiding in the subsequent daughter metal lift-off. This undercut can be tailored for smaller features depending upon the application. (Figure 2.3c)
2.3.1.1 Molecular ruler deposition process

The molecular ruler film was then self-assembled onto the patterned gold parent host structure. The wafer was alternately submerged in 1 mM solution of 16, mercaptohexadeconoic acid in ethanol for 1 hour and 1mM Cu$^{2+}$ ions (copper (II) perchlorate) in ethanol for 15 minutes to construct the molecular film. The wafer was rinsed thoroughly in ethanol and dried using nitrogen after each step. In the first step the mercaptohexadeconoic acid molecule binds to the gold substrate preferentially at its thiol end, exposing the carboxylic acid end. Next Cu$^{2+}$ ions selectively bind to the exposed carboxylic acid termini. Immersing the wafer again into the mercaptohexadeconoic acid solution results in the thiol preferentially binding to the Cu$^{2+}$ ion, forming the second layer of rulers. The carboxylic acid group is again exposed at the surface for subsequent functionalization with Cu$^{2+}$ ions for further film assembly. (Figure 2.3d) Repeating this process 7 times produced a molecular film on the surface of the gold host feature 16.6 nm thick with a standard deviation of 1.1 nm measured at 4 different locations across the surface of the sample using elipsometry. This molecular film was used to demonstrate the new lift-off process. Figure 2.4
75 nm of platinum was then deposited as the daughter material using e-gun evaporation. (Figure 2.3e) The gold and molecular film was then lifted off by sonicating the LOR in CD-26 to leave behind the platinum daughter feature. (Figure 2.3f)

Fig. 2.4: Assembly of molecular film on a gold surface. Step 1. Substrate immersed in a 1 mM solution of mercaptohexadecanoic acid to form the first self assembled layer (~2.2 nm long). Step 2. The sample is then rinsed in ethanol and nitrogen dried and immersed in 1 mM solution of copper perchlorate solution. The Cu$^{2+}$ ions bind preferentially to the acid end group. Step 3. The sample is rinsed in ethanol and dried using nitrogen and then immersed in thiol solution again. The sulfur end group binds preferentially to the copper ion forming the second layer. This process is repeated to increase the thickness of the film formed.
2.3.2 Results and discussion

A field emission scanning electron microscope (FESEM) image of a cross section of the processed structure before final lift-off is shown in Figure 2.5. The gold parent, platinum daughter and sacrificial LOR layers are all visible in the figure, including the ~100 nm LOR undercut. The figure also depicts a clear separation between the gold and platinum layers where the molecular ruler film has been assembled. The roughness of the parent and the daughter structures are in the order of ±5 nm.

Figure 2.6 is an FESEM image of a cross section of the daughter platinum feature after lift-off of the parent host structure. The inset of Figure 2.6 depicts an FESEM image (taken at a lower magnification) of the daughter feature to illustrate that the lift off is uniform over a larger area of the substrate suggesting that this process can exhibit high yield. The deposited daughter metal is 75 nm thick which exceeds the molecular ruler film thickness by a factor of ~4.5 without impacting the lift-off process. This is due to the use of the LOR sacrificial layer, which is approximately 100 nm thick. The thickness of the LOR can be easily varied by adjusting the deposition parameters or by using different LOR compositions, allowing great flexibility in the design of the sacrificial host structure. Moreover, the parent gold structure has been isolated from the substrate surface via the introduction of the LOR sacrificial material.

Thus a new molecular ruler lithography process which addresses the needs of reproducibility and yield, simplified removal of the parent host material, isolation of the host material from the substrate surface and the capability to pattern daughter features
whose thickness exceeds the thickness of the molecular film was designed and demonstrated.
**Fig. 2.5:** Field emission scanning electron microscope cross section image of a sample processed up to Step d as shown in Figure 2.3. Silicon dioxide, LOR, gold platinum and the location of the molecular ruler film are seen in the figure. The ~100 nm undercut in LOR is also clearly visible.

**Fig. 2.6:** Cross sectional field emission scanning electron microscopy image of the daughter platinum feature after lift off is seen. Inset image, taken at lower magnification, shows uniform lift-off over larger areas.
2.4 Molecular ruler lithography using sacrificial host structures fabricated using electron beam lithography

The molecular ruler lithography process using sacrificial host patterned using electron beam lithography was employed to demonstrate the successful and exact scaling down of features.[14] Initially, a sacrificial host structures spaced at 100 nm was fabricated using electron beam patterned resists and from these 40 nm wide isolated metal lines are fabricated using a self-assembled molecular resist. Implementation of such new generation lithography techniques require expenditures in terms of new instrumentation and infrastructure and involve substantial new process development and integration into existing production facilities. Development of methods for extending the resolution of established lithography techniques to the 45-nm technology nodes and below may avoid such investment and reduce transition time and costs while also enabling the production of new nanoscale devices and structures. These include non-CMOS devices such as nano-electro mechanical systems (NEMS), nanoscale sensors, improved structures for data storage, devices for biological applications, etc.

2.4.1 Experimental details

The molecular ruler lithography process using sacrificial host structures fabricated using electron beam lithography is illustrated in Figure 2.7. The fabrication of the multilayer host stack begins with growing 250 nm of silicon dioxide thermally on a 3 inch silicon wafer. The molecular resist does not assemble on the oxide layer. The sacrificial resist LOR 1A (Lift-off Resist 1a) (Micro Chem Corp) is dynamically spin
coated at a speed of 5000 rpm for 40 s to a thickness of ~100 nm. The LOR is then baked at 200 °C for 10 minutes. This baking temperature and time combination ensures a low dissolution rate of LOR, which allows the desired undercut to be obtained in the subsequent process steps.

Gold host features are patterned over the underlying LOR layer using electron beam lithography. A bilayer of resist consisting of polymethyl methacrylate (PMMA) and copolymer methyl methacrylate (MMA) (MicroChem Corp.) is used since they provide a desirable lift-off profile upon development and, in particular, their development and removal chemistries are orthogonal to that of LOR (i.e., the sacrificial LOR layer is not modified or removed with their developers or solvents). In the case where it is desirable to use a resist to pattern the host which is not orthogonal to LOR, a barrier metal can be used to isolate these chemistries. This has been recently demonstrated using a self assembled resist on a sacrificial host structure incorporating a barrier layer patterned via contact lithography. PMMA is a modified form of polymethyl methacrylate designed to provide high resolution for electron beam lithography processes. MMA (8.5) MAA is made of a mixture of PMMA and ~8.5% methacrylic acid. For the bi-layer lift-off process the copolymer is used as the bottom layer and the PMMA as the top layer. This resist combination provides reproducible control of the size and shape of each resist layer. Developing of the PMMA/MMA resist stack after exposure to an electron beam causes the underlying MMA to develop faster than PMMA resulting in an undercut which aids lift-off of the gold. Development of the exposed resist is done in a solution of Myethyl Isobutyl Ketone (MIBK) and Iso Propyl Alcohol (IPA) and the resist is stripped in acetone. MIBK, IPA and acetone do not react with LOR. Thus
MMA/PMMA processing conditions are suitable to be used with LOR as the sacrificial layer.

The PMMA/MMA bilayer is then deposited onto the LOR coated wafer. (Figure 2.7a) The bottom layer of copolymer, is spun on at a speed of 5000 rpm for 40 s and then baked for 90 s at 150 °C. The top layer of PMMA of molecular weight 950 K and 3% dilution in anisole is spun on at 5000 rpm for 40 s and then baked for 90 s at 180 °C. A host feature pattern is then exposed using electron beam lithography at 100 KeV and a dose of 800 µC/cm². The wafer is then developed in 1:3 solution of MIBK in IPA for 30 s. It is then baked for 90 s at 100 °C. An oxygen plasma consisting of 15 sccm of O₂ at a pressure of 25 mTorr and 100 W is used to descum the wafer for 6 s. Gold is then thermally evaporated to a thickness of 25 nm. (Figure 2.7b) The wafer is placed in an acetone baths at 25 °C for 30 minutes. The PMMA/MMA layer is lifted off leaving behind gold lines separated by varying gap dimensions. The pattern consisted of gold lines 5 μm long and 0.5 μm wide. The gaps between adjacent lines were varied from 75 nm to 175 nm. The underlying LOR layer was then partially dissolved in a 1:1 mixture of CD26 (0.1N dilute TMAH(Tetra Methyl Ammonium Hydroxide) in water) and deionized water for 30 s to obtain a very small undercut. (Figure 2.7c)

The molecular resist was then assembled on the gold host structure. The molecular ruler assembly was carried out by alternate solution phase deposition as described in Section 2.3.1.1

A chrome daughter metal was then evaporated on this sample to a thickness of ~25 nm (Figure 2.7c). The host structure was then selectively lifted off by dissolving the
LOR in a solution of CD26. The final lift off took less than a minute to complete. The isolated scaled down daughter chrome lines were left behind on the wafer. (Figure 2.7 d)
Fig. 2.7: The molecular ruler nanolithography process using sacrificial host structure patterned using electron beam lithography. a) A 3” silicon wafer with 250 nm dioxide thermally grown is spin coated with Lift-off Resist (LOR), the sacrificial material, and MMA/PMMA bi-layer electron beam resists. b) The resists are exposed and developed. The gold host parent is evaporated. c) dissolution of the MMA in acetone causes lift-off of the excess gold. The LOR is then dissolved in a controlled manner to get the desired undercut. d) 15 molecular resist is preferentially assembled on the gold and the daughter chromium is evaporated. e) LOR is dissolved to lift off the parent leaving behind the daughter.
2.4.2 Results and discussion

Top-down field emission scanning electron microscope images of the process steps leading to the formation of 40 nm wide chrome lines are shown in Figure 2.8. Figure 2.8a show gold host structures patterned over an underlying LOR layer. Figure 2.8b shows the substrate after the assembly of the molecular resist and the evaporation of the daughter chromium metal layer. The gaps between the parent structures are seen to be reduced due to the molecular resist assembled on the gold feature edges. Figure 2.8c shows a 40 nm isolated chrome line left behind after preferentially removal of the host structure. The inset shows a low magnification image of the daughter feature showing uniform lift-off over larger areas of the wafer.
Fig. 2.8: Field emission scanning electron images of fabrication of 40 nm chrome lines using molecular ruler nanolithography with sacrificial host structures. a) Gold parent structure with an initial gap of 100 nm fabricated over an underlying LOR layer. b) Gold host structures with 30 nm molecular resist and daughter chromium metal evaporated in the scaled down gaps. c) 40 nm chromium feature after lift-off of the sacrificial host structure. The inset shows a low magnification image of the daughters, showing successful and uniform lift-off over large areas.
Figure 2.9 shows a high magnification cross section scanning electron microscope image of the parent, daughter and the resists. The undercut in the sacrificial LOR layer underneath the gold parent structure is clearly visible. The molecular resist of thickness of 30nm is seen on the gold edges leading to the scaling down of the gap from 100nm to 40nm. The 40nm chrome line between the sacrificial host structures is also visible.

Fig. 2.9: Cross section field emission scanning electron microscope image of step d. The gold parent, chromium daughter and LOR sacrificial resist layer is seen above silicon dioxide surface. Also seen is the LOR undercut below the gold. The molecular resist layer is also clearly visible in between the gold and chromium and on the edges of the gold (resulting in decrease of the gap size). The inset shows the cross-sectional field emission scanning electron microscope image of the daughter feature after lift-off.
2.4.3 High-aspect ratio features

The molecular ruler lithography process using electron beam was implemented to demonstrate the flexibility of the process to fabricate thicker metal daughter features by using a thick underlying sacrificial resist layer. Specifically, the thickness of the daughter metal was increased from ~25 nm to over 100 nm without impacting the lift-off of the sacrificial host.

The above process was also implemented using a 400 nm thick layer of LOR 5A which was spin coated at 5000 rpm for 40 s and cured as described previously. The sacrificial LOR layer thickness was increased to enable thicker daughter layers to be deposited. Thick LOR layers require a modification of the fabrication process. As described above, the underlying LOR layer was partially dissolved in a 1:1 mixture of CD26 and deionized water for 30 s to obtain a very small undercut. In the case where the LOR thickness is greater than the desired undercut, this solution based process is undesirable since the dissolution of the LOR is isotropic leading to a pronounced undercut which is at least as large as the thickness of the LOR. To achieve a more controlled undercut, reactive ion etching of the thicker LOR is carried out using oxygen plasma. Specifically, the LOR is etched in 20 sccm of oxygen and 7 sccm of argon at 200 W and 20 mtorr for 55 s and 10 mTorr for 15 s followed by a rinse in CD26(1:1) in water for 6 s. This results in a more directional etching of the LOR giving a smaller undercut.

Figure 2.10 depicts a high magnification field emission scanning electron cross sectional image of the structure incorporating a 400 nm thick LOR layer before final lift-
off of the sacrificial host. In this case, over 100 nm of chrome was evaporated forming the daughter metal layer. In the figure, the LOR, gold parent, molecular film and deposited daughter chrome are all visible. Thicker daughter layers can be deposited using this process. In the figure, the gold host bends upward slightly perhaps due to stress developed in the film due to the processing conditions or the increased undercut of the LOR underneath. This is augmented by the assembly of the molecular film and the chrome deposition as shown in the figure. It is believed that this results from the increased undercut of the LOR which compensates for the stress in the thermally evaporated gold film. Adhesion of the LOR to the gold film near the edges results in a more planar film. A small but noticeable upward bend can be noticed in the gold host layer in Figure 2.9. The observed bend is smaller since the undercut of the LOR is also smaller. Optimization of the reactive ion etching process for anisotropic removal of the LOR between the host structures may address this issue.

Fig. 2.10: Cross sectional field-emission scanning electron image of gold host parents fabricated over ~400 nm thick sacrificial LOR layer toward fabrication of high aspect ratio features.
Thus the molecular ruler nanolithography process using sacrificial host structures fabricated using electron beam lithography is demonstrated. In particular, a bilayer of PMMA/MMA is used to define gold parent host structures on a sacrificial layer of LOR via a lift off process. The PMMA/MMA bi-layer resists are developed in an MIBK based solution and are dissolved in acetone. Both these solutions do not affect the sacrificial LOR layer. Sacrificial host structures spaced at 100 nm are used to fabricate 40 nm metal features using a molecular resist for reducing the size of the feature. A successful lift-off of the sacrificial host is demonstrated over larger areas indicating the potential for high yield processing. Moreover, a process for implementing thicker sacrificial layers is demonstrated allowing the daughter metal thickness to be increased from ~25 nm to over 100 nm. This process opens up new avenues for fabrication of high-aspect ratio nanoscale structures. All demonstrated processes are compatible with an array of lithographic techniques for patterning the host including optical lithography, step and flash lithography, etc. The geometry and composition of the daughter structures fabricated can be easily varied. Any material capable of being deposited without compromising the host and molecular film can be used to make nanoscale daughter features. This process can be implemented to extend the achievable resolution of existing lithographic techniques to reach sub-45 nm dimensions without the need for new instrumentation, addressing needs in the semiconductor industry.
2.5 Molecular ruler lithography using sacrificial host structures incorporating a barrier layer

The most commonly used patterning tool in the industry today is the deep UV stepper. As the next logical step towards making molecular ruler lithography process better compatible with the production environment, stepper lithography was used to fabricate the sacrificial host structures. However the same process could not be used because UV5 a resist used with the stepper was not compatible with LOR. Thus in order to make the process more versatile and compatible with a wide variety of lithography tools and resists and in particular be able to utilize the stepper, a new process called molecular ruler lithography using sacrificial host structures incorporating a barrier layer was developed. In this process a very thin layer of chrome is directly evaporated on the LOR before depositing the gold host layer, to protect the LOR from the rest of the process. This barrier chrome layer is selectively removed in the regions where there is no gold host present via reactive ion etching.(Figure 2.11) This barrier layer decouples the development and removal chemistries of the lithography used to pattern the host structure and the sacrificial release layer. By using the barrier layer, virtually any lithography process can be used to pattern the host structure without compromising the underlying release layer. The process was demonstrated successfully using contact lithography. (Figure 2.12)

The barrier layer was particularly instrumental in combining Deep UV lithography with molecular ruler lithography. Due to the similar development and
removal chemistries of LOR and the commonly used deep UV resist UV5 it is essential to separate and isolate the two layers using the barrier layer chrome.

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**Fig. 2.11:** Molecular ruler lithography using sacrificial host structures incorporating a Barrier Layer. a) Lift-off of the parent gold metal on top of LOR and chromium metal barrier. b) Molecular ruler process for patterning the metal carried out after etching into the barrier layer.

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**Fig. 2.12:** Cross-section field-emission microscope of sample showing barrier layer between the LOR and gold to prevent mixing of the LOR and photoresist used to pattern the gold.
2.6 Summary

Application of self-assembled monolayers as a nanolithography tool was demonstrated by successful implementation of the molecular ruler lithography process with sacrificial multilayer host structures. The sacrificial host architecture improves the yield and reproducibility of the lift-off process. Other advantages include preferential and easy removal of the host structure to produce isolated metal lines with 40 nm width, fabrication of high aspect ratio structures and isolation of gold metal from the underlying silicon substrate. Compatibility of the modified process with contact photolithography, electron beam lithography and deep UV lithography was also demonstrated.

Next chapter introduces some of the applications and describes initial work done towards successful implementation of this process in a manufacturing environment.
2.7 References


Chapter 3

Applications of molecular ruler lithography using sacrificial hosts and future advancements

Molecular ruler nanolithography process using sacrificial host structures has potential applications in areas of many emerging and future devices including molecular and semiconductor electronic components and interconnects, nanoelectromechanical systems (NEMS) and related structures.

3.1 Application to sub-50 nm CMOS device

The process flow for fabrication of NMOS devices via molecular ruler lithography using sacrificial host structures is shown in Figure 3.1 in which isolated metal lines, the end product of the molecular ruler process is used as a metal-mask to define the polysilicon gate.[1] Firstly, isolated 40 nm wide and 100 nm thick nickel lines are fabricated on a substrate via the molecular ruler lithography process with sacrificial host structures made using electron beam lithography and using a barrier layer. The substrate used for fabrication of the NMOS device consists of boron doped p-silicon with 50 nm of thermally grown silicon dioxide, 200 nm of low-pressure chemical vapor deposited polysilicon and 25 nm of electron-beam evaporated chromium. The final chromium layer acts as a barrier to prevent non-specific binding of the molecular rulers to the underlying polysilicon.
Fig. 3.1: Process steps (top and side view) for fabrication of sub-50 nm gate length NMOS starting with the daughter feature fabricated via the molecular ruler nanolithography process using sacrificial multilayer host structures. a) Molecular ruler process using sacrificial host is used for fabrication a 40 nm Ni line. b) The Ni metal is used as a mask and the underlying Cr and Poly-Si is etched using reactive ion plasma. The Ni and the Cr are then removed. c) and d) Steps showing patterning of the source and the drain and the gates.
The next step consists of etching the underlying chromium and polysilicon using reactive ion plasma with the nickel as the mask. The nickel mask and the chromium barrier metal are then stripped using wet chemical etching, leaving behind a 40 nm wide polysilicon gate structure. Standard CMOS processes can then be used to define the drain and source regions in the silicon substrate and the electrical contacts to the gate, drain and source as shown. The final structure fabricated is a 40 nm channel length polysilicon gate NMOS device. Preliminary results demonstrating the fabrication of the nickel mask on polysilicon are shown in Figure 3.2. The nickel daughter feature is seen between 100 nm wide sacrificial host structures defined using electron beam lithography. The gate oxide, polysilicon gate, and chromium barrier layer underneath the nickel are also seen.

The process flow described for the fabrication of the NMOS device combines chemical self-assembly based molecular lithography method and conventional top-down techniques for scaling down of the channel length. This new hybrid nanolithography process has the capability of extending the resolution of conventional exposure tools to below 50 nm without any new instrumentation. However several important issues need to be addressed for this process to be made manufacturable in a production environment including the effect of gold and copper used in the molecular lithography process on the device characteristics given the presence of the protective barrier of chromium and sacrificial resist, optimization of the molecular ruler assembly to reduce the number of steps and time and the reduction of nanoscale roughness of the daughter feature.
3.2 Application for fabrication of surface plasmon structures

Collective electron oscillations known as localized surface plasmons (LSP) can be excited in metal nanoparticles (typically gold or silver) along a dielectric surface resulting in strong amplification of the local evanescent electromagnetic field and appearance of surface plasmon absorption bands. Localized surface plasmon resonance in metal nanoparticles is used in detection schemes and sensors. These nanoparticles are used to control, transmit, scatter, amplify, radiate and modify electromagnetic field of the incident light for applications in sub-wavelength optics, data storage, biophotonics, and detection and sensing.

By controlling the size, shape and spacing of the nanoparticles the electromagnetic field of light can be modified for various applications. Currently used methods for fabricating and patterning these nanoparticles, such as ebeam lithography,
suffer from drawbacks including high cost and low yield. Molecular ruler chemistry can be extended to create novel nanoscale structures and gaps for plasmon studies and to construct sensors and devices. Molecular lithography techniques can enable creation of nanogaps and nanoscale structures with high reproducibility and versatility and without the need for investment in new instrumentation. The dimensions and spacing of the structures can be varied over large length scales with relative ease and at low cost. Molecular ruler nanolithography process can be easily automated and hence these techniques are well suited for batch production. Described below are three schemes for using molecular ruler lithography to pattern the spacing between nanostructures for use in plasmon studies.

**Scheme 1:** In has been shown that dendrimer functionalized gold nanoparticles [2] can be self assembled using the dendrimers as the spacer molecules, which mechanically reinforce and cross-links the particles to the surface. The size of the dendrimers determines the inter-particle distance and can be varied depending on the type of dendrimer used. (Figure 3.3) In a similar way molecular ruler chemistry can be used in conjunction with gold and silver nanoparticles to control the spacing and placement of nanoparticles. The particles can be coated with the desired number alternating acid terminated molecules and copper linker. The distance between adjacent molecules will depend on the number of layers of rulers assembled. Also these modified particles can be immobilized on the substrate using an amino functionalized surface as illustrated in Figure 3.4.[3, 4]
Fig. 3.3: Dendrimers used as spacer molecules between nanoparticles to provide controlled spacing between particles. The blow-up of the dendrimer molecule is shown on the right. The dendrimers bind to the nanoparticles and hold them together and immobilize them to the surface forming a matrix.[2]

Fig. 3.4: Scheme 1: Molecular rulers assembled on the nanoparticles are used to space them apart in a controlled manner. Also the terminal –COOH functionalization forms an amide bond with surface consisting of –NH₂ functionalized SAMs [3, 4] and binds the particles to the surface. Replacing the single amine molecule on the surface SAM with molecular rulers allows for engineering the gap between the particles and surface. Arrows indicate the gaps that can be potentially tailored using molecular rulers.
Scheme 2: In this approach nanosphere lithography (NSL) [5] is combined with molecular ruler assembly process to help tailor the dimensions of the structures fabricated.[6] In NSL a nanosphere solution is spin coated uniformly on a surface. The solution is allowed to evaporate and a hexagonal array of spheres is left behind. Next metal is evaporated on these assembled particles and into the triangular gaps in-between the spheres. The spheres and the excess metal on the spheres are then removed by sonication in a solvent. Triangular metal nanostructures forming a hexagonal array are left behind on the surface. The size of the nano triangles can be further modified by molecular ruler assembly process. In this process gold nanoparticles are arranged on the surface and then molecular rulers are assembled on the spheres and in the inter-sphere gaps. This reduces the inter-sphere spacing by a thickness determined by the molecular ruler thickness. The metal is evaporated on these ruler covered nanoparticles into the scaled down spaces. These nanoparticles and rulers are subsequently lifted off to leave

![Scheme 2: Nanosphere lithography combined with molecular ruler assembly to fabricate metal nanostructures.][5]
behind hexagonally spaced metal dots. The gaps can be reproducibly fabricated over the whole wafer with high throughput. (Figure 3.5)

Scheme 3: Another novel approach for producing array of gold or silver nanoparticles is to preferentially and locally change the surface chemistry of SAMs such that [7] nanoparticles bind only to pre-defined regions. For example ultraviolet lithography can be used to expose certain areas of the thiol SAMs to oxidize the sulfur atom to sulfur dioxide.(Figure 3.6) These oxidized areas are readily replaced in solution by SAM with different functionality molecules suitable for nanoparticle assembly. Another method suitable for smaller areas is the use of metallized AFM/STM tips to locally oxidize SAM regions.[8] The terminal CH₃ molecules are oxidized to COOH by passing an electrical pulse through the tips. Both the above methods locally modify the surface chemistry on the SAM. After further processing, nanoparticles can be assembled only on these modified portions . The distance of the particles from the surface can be varied by using a multilayer SAM assembly underneath the particle and the inter-particle distance can be controlled by the patterning design used by AFM-probe or UV light.

Thus these novel schemes demonstrate the application of molecular rulers to fabricate precise gaps for applications in plasmon sensors.
Fig. 3.6: Scheme 3: CH$_3$ SAM is locally modified via UV exposure (a1-b-c) or by passing current through a STM probe which directly oxidizes the end-group to –COOH (a2-c). b) The sulfur end-group is oxidized in the case of a1. c) The modified SAM is replaced by another SAM with a COOH end group. If desired molecular rulers can be grown using a copper linker specifically in modified SAM regions. d) Nanoparticles are assembled on the modified SAM regions. This method give flexibility in the spacing between particles and also between the substrate and the particle. (as indicated by the arrows) [7,8]
3.3 Methods for improving molecular ruler lithography process using sacrificial host structures for manufacturing

In this section some of the remaining challenges towards making molecular ruler lithography process more manufacturable and their potential solutions are addressed.[9, 10]

3.3.1 Optimization of ruler assembly process

Existing methods employed for self-assembly of molecular rulers include alternate solution phase assembly of mercaptohexadecanoic acid and Cu\(^{2+}\) ions as shown in Figure 2.3. Both the components are in the form of 0.1 mM solution in ethanol. Several problems are encountered when carrying out this process. Firstly, contamination of the two solutions results in clumping of the rulers leading to non-specific binding and irreproducibility of molecular resist thickness.(Figure 3.7) Secondly, the assembly process requires a large number of long process steps which makes the entire process inherently low-yielding and too time consuming to be implemented by industry. For example to get a full monolayer coverage of the SAM the sample is placed in the solution for about 2 hours and then rinsed in ethanol, dried in nitrogen and then placed in the Cu\(^{2+}\) solution for 15 minutes. The process has to be repeated upto 15 times to get the desired 30 nm thick molecular resist. Moreover improper rinsing in between steps can result in the contamination of solutions leading to irreproducible film thickness. The automation of the ruler assembly process has been demonstrated on a large scale using robotic arms that move wafer cassettes in and out of baths containing the SAM solution
and rinsing agents.[6] Though this makes the process more efficient and reproducible than manual operations, the time required remains very large. A quicker, efficient and cleaner method is required to assemble thick molecular resists. Two methods are discussed below 1) By use of longer molecules, such as dendrimers, which could be tailored to work as rulers 2) By using vapor phase deposition of the SAM and the Copper.

Fig. 3.7: Scanning electron microscope image of a gold sacrificial host feature defined using contact lithography, after deposition of 7 molecular rulers. Defects in the molecular film are formed due to cross-contamination. This causes the roughening of the feature edges and non-specific binding to the silicon dioxide substrate.
3.3.1.1 Introduction to dendrimers

To reduce the number of steps and the time required for the assembly of rulers larger molecules such as dendrimers can be employed. Dendrimers are a class of monodispersed macromolecules with cascade treelike repetitive structure, well defined shape and dimensions and controllable molecular weight. Dendrimers are produced by iterative sequence of reactive steps each producing an additional ‘generation’. 3 major components of dendrimers are the core, branch and end groups and each of these parts can be tailored to have various properties and functionalizations. (Figure 3.8) It has been shown that thiol functionalized dendrimers form chemiadsorbed layers on gold surface by self assembly.[11] 15-20 nm long dendrimers self assembled on gold can be used as molecular resists in the molecular ruler process thus significantly lowering the number of self assembly steps, possibly to a single step, and thus reduce process time and complexity. Some of the potential dendrimers identified for this application are shown in Figure 3.9.[12, 13]
Fig. 3.8: Generation 2 polyphenylene dendrimer template with ~SMe groups at the outer surface showing the dendritic structure with the core, branch and end group functionality.[11]
Fig. 3.9: a) Polyether Dendron thiols of Generation 3.[12] b) Third generation disulfide-bridged dendrimers lysine-based (G3SSG3) These dendrimers have been produce up to generation 6.[13]
3.3.2 Vapor phase molecular layer deposition (VPMLD)

The main factors influencing the yield and edge roughness of the molecular ruler process using sacrificial hosts is the solution phase method of depositing the constituent layers of the molecular resist. Dipping the solution alternately in the mercaptohexadecanoic acid solution and the copper solution results often in the cross contamination of the liquids leading to thick clumps of the SAM on the film and irreproducible film thickness. Also the time required for each step is over two hours, making the process inherently low yielding with low throughput which is a major disadvantage when integration into mainstream manufacturing. One possible method for solving both these issues is the use of vapor phase molecular layer deposition (VPMLD) of the organic molecules to construct the molecular resist. VPMLD is a process also known in literature as molecular layer deposition (MLD) [14] or molecular layer epitaxy (MLE) [15] or organic molecular beam deposition (OMBD) [16] all of which belong to the family of process similar to atomic layer deposition (ALD) [17] when used to fabricate ultrathin organic multilayer films. This is achieved by stacking molecules (in vapor phase) on substrates one by one under vacuum, in a manner similar to stacking atoms in the ALD process (which is used mainly to deposit metals, metal oxides, metal nitrides, semiconductors, transparent conductive oxides, and ferroelectric materials). A setup of an MLD reactor used to deposit molecular layers is shown in Figure 3.10.(taken from reference [15]) Here, vapors of organic molecules are introduced into a vacuum chamber operated at pressures ranging from 100 mTorr to ~10^-6 Torr and allowed to react.
with the substrate to form a monolayer film in a self-limiting manner. The chamber is then purged and the second component of the multilayer film is introduced and allowed to react with the first monolayer on the substrate. The two films are alternately deposited, with intermediate purge steps to remove excess reactants and products, to form a film of desired thickness.

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Fig. 3.10: Molecular layer epitaxy reactor setup. MLE approach extends the scope of ALE techniques to thin films containing both organic and inorganic multilayers. MLE is carried out under vacuum using organic precursor materials that are heated to form vapor. These molecules in vapor phase are first purified and then carried over to the substrate by an inert carrier gas. The molecular self-assembly is a self-limiting process. The unreacted precursors are purged out before the next deposition step. [15]
The formation of self-assembled multilayer using vapor-phase processes has been carried out for anti-stiction coatings in MEMS devices (dichlorodimethylsilane (DDS) on a silicon surface) and for depositing films for nano-bio devices.[18] Here the samples are exposed to a mixture of DDS and water vapor at pressures of ~3 Torr for 10-15 minutes at room temperature. Vapor phase deposition of C₆-C₁₀ alkyl thiols on gold substrates with methyl and hydroxy end groups have been reported by Poirer and Pylant [19] and Schreiber et al.[20] Here pure alkanethiol molecules are purified, dried and degassed and then leaked into a vacuum chamber (10⁻⁵ to 10⁻⁶ Torr) and transported using carrier gases onto the surface of a clean gold substrate. Organic quantum-confined structures have been formed using a process consisting of an organic precursor, 1,8:4,5 naphthaleneteracarboxylic dianhydride (NTCDA), which is assembled on an alkylamine surface using vapor phase.[15] In this process an aliphatic or aromatic diamine spacer was used to link successive layers via covalent imide linkage. This is an example of vapor-phase formation of a multilayer structure where the linker is a covalently attached organic molecule, such as the diamine spacer shown in Figure 3.11. Self assembly from vapors of liquid thiols delivered into the chamber through a Teflon nozzle with lower dosing pressures of 200-800 mTorr has also been demonstrated.[21] Here the growth of the monolayers at both low (100 K) and room temperature (260-350 K) have been studied. Other multilayer film growth using pyromettitic dianhydride (PMDA) and 2,4-diaminonitrobenzene (DNB), both from vapor phase and using vacuum organic molecular beam deposition (OMBD), has been demonstrated by Yoshimura et al.[14] and is shown in Figure 3.12. Thus formation of self-assembled monolayers and molecular multilayers has been demonstrated in the past and has the potential to be extended further
for vapor phase deposition of molecular film for the molecular ruler lithography technique.

Fig. 3.11: Formation of organic multilayers structure using self-limiting vapor phase assembly. The successive layers are covalently bound using a diamine spacer forming an imide linkage. [15]

Fig. 3.12: Change in thickness of a polymer film formed via self-limiting vapor-phase deposition of organic precursor molecules (PMDA and DDE). [14]
Vapor phase deposition of 16-mercaptohexadecanoic acid molecule is a well-studied process for the formation of functional SAMs surfaces and once deposited on gold, it forms a stable, well-ordered monolayer that can undergo a number of chemical transformations.[22] The other component of the film assembly is the inter layer coordination which is performed with a Cu$^{2+}$ copper ion. ALD of copper films has been accomplished using Cu(thd)$_3$ (Cu(II)-2,2,6,6-tetramethyl-3,5-heptanedionate). The Cu(thd)$_3$ has been shown to selectively adsorb onto hydroxyl terminated surfaces in a self limiting manner to form copper thin films.[23] (Figure 3.13) Cu(thd)$_3$ was used as the precursor and hydrogen used as the reducing agent and nitrogen as a carrier gas, at precursor evaporation temperatures of 120 ºC and pressure of 5-10 Torr.

VPMLD was explored as a possible route for deposition of the SAM and the copper linker atom because it offers the following advantages:

1. Precise in-situ layer thickness control
2. Atomically clean environment and substrate. Due to the low pressure deposition conditions, very small amounts of impurities and defects are introduced into the assembled film.
3. Reduced cross contamination issues when depositing heterogeneous multilayer structures
4. Significantly reduced time required for deposition.

Additionally vapor phase deposition of organic thin films opens the possibility to experiment with other appropriate organic molecules (already available with know
synthesis procedures) as possible replacements of the existing multilayer molecular resist structure.

Fig. 3.13: Proposed reaction mechanism for deposition of copper on hydroxyl-terminated surfaces.[23]
To explore the feasibility of the specific vapor phase molecular layer deposition process, copper bis(6,6,7,8,8,8-Heptafluoro-2,2-dimethyl-3,5-octanedionate) is examined as a precursor to deposit the copper linker required in the forming the multilayer molecular resist in the molecular ruler process (see Figure 2.4). A basic instrument was constructed for these experiments and consisted of a vacuum chamber connected to a roughing pump and a turbo pump, two ports of entry for the precursor and the reducing gas, respectively, and a cylindrical chamber to hold the precursor. The solid precursor was placed in the 0.5 inch diameter; 2 inch long stainless steel cylindrical container and heated using heating lamps connected to a resistance control to control the temperature. The process steps consisted of the following steps: 1) pump down the chamber to ~5 mTorr using the turbo pump, 2) flow in a small amount of pure nitrogen (which will become the carrier gas for the pre-cursor deposition) until the chamber pressure was stabilized at ~12 mTorr, 3) heat the precursor to form the vapor within the cylindrical container, 4) redirect the nitrogen flow through the precursor container allowing the nitrogen to carry the precursor into the chamber and to the substrate surface, 5) after 2 minutes, discontinue the flow of the precursor and purge the chamber of the precursor with nitrogen, discontinue the nitrogen flow and pump the chamber down to 5 mTorr, 6) flow in a reducing gas containing 5% hydrogen in nitrogen at a pressure of 20 mTorr for 5 minutes, and 7) discontinue flow of reducing gas and purge the chamber with nitrogen before venting. The sample substrate was prepared by evaporating 10 nm of
Chromium and 100 nm of Gold onto a silicon substrate using physical vapor deposition.

Self-assembled monolayers were formed by immersing the sample overnight in 1 mM of mercaptohexadecanoic acid in ethanol. Figure 3.14

3.14: Rudimentary set-up for Vapor Phase Molecular Layer Deposition. The precursor is heated in a closed container and the vapors carried into the chamber using nitrogen gas. The chamber is pumped to a pressure of ~20 mTorr. Reducing gas containing hydrogen is flown in to remove the ligands attached to the copper atom.
Infrared spectroscopy was used to study the deposition of copper on the SAMs. Figure 3.15 shows the high frequency IR spectrum of three samples. Sample 1 has only the solution deposited SAM on it. Sample 2 has the SAM and copper deposited on the SAM using the vapor deposition process described above. Sample 3 is similar to the second but it has been rinsed using ethanol and water after the vapor deposition process. The d⁺ and d⁻ identified as the symmetrical and asymmetrical stretching modes of C-H are at 1852 and 1817 cm⁻¹ respectively. The d⁺ and d⁻ modes indicate the presence of SAMs on all the three substrates. Figure 3.15 shows the low-frequency IR spectra of the same three samples. Sample 1 has the C=O carbonyl stretching of the terminal CO₂H at 1740 cm⁻¹ and the CH₂ scissor deformation of the α-CH₂ and main chain CH₂ at 1458 and 1433 cm⁻¹ respectively.
Fig. 3.15: High and low frequency region of the IR spectra. Sample 1: Solution deposited SAM. Sample 2: Solution deposited SAM and vapor deposited Cu Sample 3: Solution deposited SAM and vapor deposited Cu rinsed in ethanol and water.
Sample 2 and 3 do not show the carbonyl peak that is seen in sample 1. However two other prominent peaks are present in sample 3 at 1445 and 1592 cm\(^{-1}\) which are most likely the symmetric and asymmetric stretching modes of the carboxylate (\(\text{CO}_2^-\)) due the attachment of copper to the carboxylic acid end group and possible formation of a metal ligand complex. These peaks are seen with lesser intensity in sample 2. However an additional peak in sample 2 is seen at 1250 cm\(^{-1}\) which is not present in sample 1 or 3. These peaks are associated with C-F bonds of the precursor. Rinsing the sample in ethanol and water probably removed the ligands attached to the copper as a result the peaks at 1250 cm\(^{-1}\) disappear in sample 3. However the presence of copper is indicated by the absence of the C=O stretching mode of the carboxylic acid and the presence of the stretching modes of the carboxylate anion.

This preliminary work done demonstrates that the proposed research exhibits a high chance of success, potentially enabling molecular ruler nanolithography to become a viable nanomanufacturing process for the production of molecular scale structures and devices.

### 3.3.3 Elimination of a metallic host especially gold

Metals, especially gold, have detrimental effect on electrical properties of devices, especially when used in conjunction with silicon and silicon based devices. Alternate host materials need to be developed in order to make the molecular ruler lithography process more viable and compatible to industry standards. Alternate host materials include organic hosts such as polymer layers, dielectric or insulating material like silicon dioxide,
silicon nitride or other non-reacting metals such as platinum. Non metallic host materials such as organic polymers are suitable, provided they have the following properties.

Ease of patterning of features. The polymer itself should be sensitive to either photons or electrons to allow patterning of the initial host structures. If not patternable they should be inert to and non-miscable with conventional photo-resists and electron beam resists and their developers. This will allow for patterning of the host polymer using standard patterned photoresist as masks.

Selectivity: They should have high selectivity to etch processes that are used to open the barrier layer and undercut the LOR.

Self-assembly of rulers: The organic polymer should have surface functionality such that the molecular rulers can be assembled either through solvent or vapor phase assembly preferentially on the host material without affecting the LOR or the substrate beneath.

3.4 Ideal molecular ruler process

Figure 3.16 shows the ideal molecular ruler lithography process using sacrificial multilayer host structure for fabricating isolated nanoscale structures and architecture.
Some of the key features include

- Use of long and then shorter molecules for self-assembly in order to reduce the total number of steps and at same time have precise control over the thickness of the film.

- An inert sacrificial layer compatible with the polymer and ruler chemistries and with ability to form an undercut profile.

- A non-metallic host formed with a patternable polymer to which the molecular rulers can selectively and conformably adhere.

- Deposition of molecular rules and film done via vapor phase eliminating the need for solution dipping of sample.

Fig. 3.16: Ideal Molecular ruler process using sacrificial host structures

Organic polymer patterned using conventional lithography techniques, having development chemistries orthogonal to LOR and inert to the Large Molecule (>10 nm) capable of being self-assembled on above polymer either through vapor or solution phase deposition.

Further self-assembly of molecules for precise control of final gap size through multilayer assembly.
3.5 Summary

In this chapter various applications of self-assembled monolayers when used in conjunction with conventional lithography techniques as a resolution enhancement tool are described. Initial work done to make a sub-50nm wide MOSFET structures using the molecular ruler lithography process with sacrificial host structures is presented. In this method the isolated metal line fabricated is used as a mask to define the polysilicon gate. Thus by successfully combing chemical self-assembly techniques with electron and photo-lithography the resolution of existing instrumentation was improved to below sub-50nm and a possible method for incorporation of this technique for making CMOS structures was shown.

Potential use of molecular rulers to form nanogaps for plasmon sensors is discussed. Molecular rulers offer accurate control over the placement of metal structures and also the process is easy to reproduce and scale up. Three potential schemes involving the use of molecular rulers as spacers in-between nanoparticles, used of nanosphere lithography and use of STM techniques for SAM patterning to build precisely spaced metal structures are described in detail.

Also various methods of improving the nanolithography process for better manufacturability is listed including use of longer molecules such as dendrimers, elimination of metallic host and use of vapor phase assembly. Preliminary results of assembling the multilayers of SAMs and the copper linker using vapor phase molecular layer deposition, studied using IR techniques, is presented. The successful attachment of the vapor phase deposited copper linker to the carboxylic acid end-group via a covalent
bond was shown. These preliminary results are very promising and indicate the potential elimination of solution phase assembly techniques in future. Successful implementation of the vapor phase deposition will lead to making molecular ruler nanolithography more efficient and reproducible for large scale manufacturing.
3.6 References


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Chapter 4

Self-assembled monolayers for surface engineering: introduction to catalytic powered devices

4.1 Introduction

SAMs allow for engineering surface properties at the nanometer scale in a precise and controlled manner and offer flexibility in the range of properties that could be directly transferred to the surface. In the following two chapters, application of self-assembled monolayers for surface modification, specifically for surface zeta-potential engineering for control of fluid flow in catalytically-powered nano/micro engines is discussed. The present chapter looks into the theory and background of catalytic powered devices and the forces generated by them. The next chapter describes the application of SAMs to achieve spatial and temporal control of the catalytic engines by manipulating surface properties at the nanoscale.

One of the greatest remaining challenges facing technologist today is to electrically and physically connect to nano and micro scale machinery, MEMS and NEMS devices. As devices shrink in size it is proving increasingly difficult to supply power to and harness power from these systems. Methods which rely on external sources such as magnetic, electrical, or optical fields or on acceleration forces are difficult to scale down and impose either operational limitations or significant complexity on the system design and the fabrication process.[1] Moreover this may not be the most efficient method due to the fact that dominant forces at the nanoscale are different than for those seen at the macroscale.
A potential solution to this problem can be devised by mimicking biological systems. In nature nanoscale motors are found in many places including inter and intra-cellular delivery vehicles, motion of bacteria, ATP synthesis and cell replication. These motors operate by converting chemical energy available in their immediate environment to mechanical energy through catalytic hydrolysis of adenosine triphosphate (ATP), a chemical fuel present in the intercellular solution suspending the motors.[2, 3] However there are very few examples of non-biological nano or micro scale machinery being operated using self-generated power. Whitesides et al. showed that platinum discs are propelled on the surface of hydrogen peroxide solution due to the oxygen bubbles being produced by catalytic decomposition of peroxide.[4] Translational and rotational motion has also been seen in gels because of surface tension gradients.[5] One of the oldest examples of self-generated power is the spontaneous movement of camphor discs in water because of concentration gradient and surface stresses produced by the asymmetric dissolution of camphor.[6]

In all the systems described above in-situ conversion of chemical energy to mechanical energy propels the system forward. The generation and consumption of power are on the same surface and result in autonomous motion. The movement of the object is mainly initiated due to formation of a gradient near the system via catalytic reactions, interface tension differences or concentration changes. There is no connection to an external power source. Thus developing nano and micro engines that are self-sufficient, self-contained and self-directed is the key to solving the problems associated with powering miniaturized machinery. These properties circumvent the problems associated with scaling down of macroscale machinery as no external circuitry is needed.
4.2 Motion of micro and nanoscale systems using catalytic power

For the past five years scientist and engineers at Pennsylvania State University are exploring methods to build inorganic micro and nanoscale motors that autonomously move and carry cargo using self-generated power. These motors have a built-in catalytic site which interacts with a fuel solution to produce mechanical energy via catalysis. So far, transitional motion of 2 μm long rods, rotational motion of 100 μm diameter gears and movement of fluid due to catalytic power have been demonstrated.(Figure 4.1) The last case being that of pumping of fluid in the vicinity of the catalytic site observed using tracers placed in the solution. In all cases the common prerequisite for motion was the presence of two metals with different electrochemical potentials, physical and electrical contact between the metals and an environment of dilute hydrogen peroxide fuel solution.

Autonomous non-Brownian movement due to catalytic power was first observed in the gold/platinum nanorod system.(Figure 4.1a) [7] The nanorods used were 370 nm in diameter, with 1 μm long gold segment and 1 μm long platinum segment synthesized electrochemically using template-directed growth in a porous membrane.[8] When the nanorods were suspended in aqueous hydrogen peroxide solution the rods moved along their long axis with the platinum end forward. Oxygen bubbles were seen evolving at intervals from the platinum side indicating the catalytic decomposition of the peroxide. The oxygen evolution increased with increase in peroxide concentration. The average instantaneous velocity of the rod along its axis at 3.3% hydrogen peroxide concentration was measured to be 6.6 μm/sec. Both the speed and the directionality of the nanorods increased with increasing concentration of the peroxide solution and leveled off around
5% dilution. However nanorods with gold-platinum-gold segments did not show significant movement. Thus the geometry and placement of the catalyst determined whether the system would move and in what direction it would move.

Nanorods are ideal structures for studying these phenomena since they exhibit radial symmetry, can be produced using simple fabrication methods, and modeled effectively.[9] To create more functional devices and systems, other geometries needed to be explored. Figure 4.2a and Figure 4.2b depict a geometry which could represent either a rod like structure, or a rectangular slab type structure. The object depicted in Figure 4.2a has one interface between the metallic regions. In the case where, for example, platinum and gold are used as the metals and a solution of hydrogen peroxide is used as a fuel as described above, the object would move toward the platinum end due to the forces produced at the bimetallic junction. The device in Figure 4.2b, however, contains two metallic interfaces whose orientation is symmetrical about the devices’ center of mass. Thus the forces produced by these two interfaces cancel resulting in no net positive motion of the device.

The objects shown in Figure 4.2c and Figure 4.2d represent a different geometry in that the force is located away from the objects center of mass and is not directed through the objects center of mass. In this case, the force produced is orthogonal to a line passing from the force producing area to the object’s center of mass providing a rotational motion. In Figure 4.2c, the catalyst region geometry locally is similar to that of Figure 4.2a, and thus produces a resultant net positive motion. The object in Figure 4.2d, however, will not exhibit any positive motion since the interfaces formed are symmetrical and the surface forces produced by these interfaces cancel. As can be seen from these
examples, different geometries are needed to obtain useful force generation depending upon the application.

Fig. 4.1: Optical microscope image of the three geometries used to demonstrate catalytic power: A) An optical micrograph of a platinum/gold rod. [7](500x) b) 100 μm diameter gold gear with platinum patterned on the spokes.(Scale bar = 50μm) c) A gold surface with silver disc 200 μm in diameter and 500 μm apart. 2 μm diameter negatively charged carboxyl tracers in a solution of dilute hydrogen peroxide form a pattern at a distance of 150 μm from the edge of the disc. (Scale bar = 200μm)
To begin examining new device geometries and to determine if micro scale objects can be propelled via continuously generated catalytically driven gradients, gear-like structures resembling the object shown in Figure 4.2b were produced using conventional micro fabrication processes.[10] Each of the spokes of this gear-like structure has adjacently located platinum and gold areas. Reactions that take place at each of the bimetallic junctions on the gear create gradients in the environment. The net force thus produced is perpendicular to the spokes of the gears, directed towards the platinum end as indicated by the arrows in Figure 4.1b. Thus these devices exhibited rotational motion and are interesting since they have practical implications for driving MEMS devices and represent a basic geometry which can implemented for other applications including rotary shuttles, generators, positioners, etc. As can be seen from these examples, different geometries are needed to obtain useful force generation depending upon the application. The gear structure described above was successfully fabricated and showed rotational speeds of 1 rotation/sec. This was about 100 times faster than the speed of the nanorods. Details on the fabrication steps and experimental observations using these gear-like objects are discussed in the next chapter.

Observing the motion of suspended catalytic objects in a fuel solution it can be intuitively expected by Galilean Invariance principles that a fixed catalytic site will move the fluid surrounding it.[11] Such systems will have practical applications such as channel-less micropumping and drug delivery. The bimetallic nanorod system has been inverted to demonstrate localized fluid flow and pattern formation of colloids in the vicinity of an immobilized catalytically active bimetallic junction. In particular, silver discs of various sizes have been patterned onto a gold coated surface and the motion of
tracer particles has been examined in solutions containing low concentrations of \( \text{H}_2\text{O}_2 \). (Figure 4.1c)[12] Various kinds of tracers were used including silica spheres, negatively and positively charged polystyrene spheres, and gold nanorods. The behavior of the tracers is influenced by the catalytically generated forces acting on the fluid and on the tracer itself. Details of the force generated and fluid pumping are discussed in the next section.

Fig. 4.2: Schematic illustration of two structural geometries where the catalytic region has been positioned such that a net forward motion is achieved (figures a and c) or not achieved (figures b and d). The direction of motion is shown assuming platinum and gold metals in a hydrogen peroxide solution.

To date the above discussed three geometries (Figure 4.1) rods, gears and pumps have been examined. Catalytically generated energy has been successfully harnessed to cause motion in micro and nano scale objects in all three systems. Better understanding of the mechanisms involved in conversion of the stored chemical energy to mechanical
energy by the catalytic motors is the key to achieve control of the movement produced and to build practical power generators.
4.3 Mechanism of catalytic power generation

It is not fully understood what drives the catalytic motor. From experimental observations it is seen that some of the prerequisites of motion include the presence of at least two metals in a fuel solution, asymmetry in the placement of the two metal features and physical and electrical contact between the metals. A fuel solution is defined as an environment that interacts electrochemically with one or more of the metals. In the cases seen so far hydrogen peroxide is used as a fuel solution which decomposes into oxygen in the presence of bimetallic systems such gold/platinum and gold/silver. Other fuel solutions being explored include dimethylhydrazine and hydrazine. The asymmetric design of the structures and disproportional nature of the reaction of the metals with the hydrogen peroxide solution suggests a gradient driven flow. As long as there is a supply of hydrogen peroxide to the surface of the metals the gradient is continuously formed and the system is propelled. Concentration, temperature, pressure, surface tension and chemical gradients or a combination of these factors are considered to be the cause of catalytic powered motion. Two commonly accepted theories based on the interfacial tension gradient and proton concentration gradient are discussed in detail.
4.3.1 Interfacial tension model

The interfacial tension model [7] was one of the first theories used to describe the movement of the nanorods and the gears. In this model it is assumed that the platinum serves as a catalyst decomposing the hydrogen peroxide into oxygen and water. The uniform generation of oxygen selectively on the platinum end of the nanorod creates an oxygen concentration gradient in the system such that the concentration of oxygen remains constant over the platinum surface and decreases from the platinum/gold junction towards the gold end. (Figure 4.3) The oxygen bubbles so formed get pinned onto the hydrophobic gold surface creating a liquid/vapor interface. The interfacial tension at this liquid/vapor interface decreases with the increase in the oxygen concentration in the solution. Thus the presence of an oxygen concentration gradient along the gold segment of the nanorod cause an interfacial tension gradient which increases from the platinum/gold junction towards the gold end which results in the nanorod being propelled forward towards the platinum end. Observations of this system suggest that the hydrophobicity of the region adjacent to the catalytic site is essential to create an interfacial tension gradient that causes movement.

The hydrophobicity of the gold surface was studied in detail using the gear system.[10] In initial experiments, where a fuel solution consisting of only hydrogen peroxide and DI water was used, no rotational motion of the structures was observed. It was discovered experimentally that the addition of ~3% sulfuric acid: peroxymonosulfuric acid: hydrogen peroxide (90:5:5) to the hydrogen peroxide and DI
water solution suspending the gear-like objects activated the rotational motion of the objects once the formation of significant bubbles ceased.

---

![Diagram](image)

Fig. 4.3: Schematic describing the interfacial tension model. An oxygen concentration gradient along the hydrophobic gold surface leading to an interfacial energy gradient which propels the rod.

To determine if an increase in hydrophobicity of the region adjacent to the catalytic site was the mechanism behind the activation of the interfacial tension gradient causing the objects to rotate, wetting experiments were performed on gold surfaces exposed to various wet chemistries representing different steps in the fabrication process and testing environments.(see Section 5.1.1 for fabrication steps) Though the platinum surface is exposed to the same process steps as gold any change in surface properties of platinum does not affect the rotation of the gears because the interfacial tension gradient does not exist on the platinum catalyst since the concentration of oxygen generated remains uniform throughout the platinum surface.
Specifically, to test the surface properties of gold surface, 150 nm of gold was deposited on top of a 3 inch silicon wafer coated with 25 nm of chromium. The wafer was separated into several pieces and exposed sequentially to different wet chemistries associated with those used to fabricate and test the structures shown in Figure 4.2c. Table 4-1 summarizes the solution chemistries tested, length of time the sample was exposed to the solutions and the approximate measured wetting angle for 4 samples. Optical photographs of approximately 0.02 mL droplets of DI water on the surface of

<table>
<thead>
<tr>
<th>Table 4-1: Wetting angle of samples 1-4 exposed to the different solutions used for gear fabrication.</th>
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<tr>
<td>Acetone/IPA/DI water rinse</td>
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<tr>
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*0.1:1:2:100 peroxymonosulfuric acid: hydrogen peroxide: sulfuric acid: DI water

Samples 1-4 are shown in Figure 4.4a-d respectively. Gold surfaces exposed to DI water directly after deposition were extremely hydrophilic and exhibited nearly zero contact angles in agreement with prior experiments. All samples were taken directly from solution and wetting experiments were immediately performed limiting the exposure to atmosphere before test data was collected. Samples 1-4 were rinsed in acetone, IPA and DI water as were the gear structures fabricated and tested as described above. Sample 1 was then exposed for 10 minutes to hydrofluoric acid (HF) to examine the
The gold surface is hydrophobic exhibiting wetting angles of 65°. As discussed above, the surface of gold has very high surface energy making it very susceptible to contamination by organic matter from the atmosphere and from organic solutions used during fabrication of the gear. An organic layer instantly forms on a gold surface exposed to organics making it hydrophobic at room temperatures.[13-15] Sample 2 was exposed to the same treatment of Sample 1 and then to hydrogen peroxide: DI water solution (3:10) for 10 minutes. The surface becomes hydrophilic with a wetting angle of 18°. Sample 3 was then exposed to a solution of sulfuric acid: peroxymonosulfuric acid: hydrogen peroxide (90:5:5) for 10 minutes after being subjected to the treatment of Sample 2. This sample exhibited a hydrophobic surface with a wetting angle of 48°. To ascertain if this change in hydrophobicity is reversible, Sample 4 was exposed to the same treatment as Sample 3, and then was rinsed and placed in hydrogen peroxide: DI water (3:10) solution for 10 minutes. The wetting contact angle observed on this Sample 4 after rinsing in DI water was 15°, indicating that the surface can again be made hydrophilic by exposure to hydrogen peroxide. Although we believe that organics on the surface of the gold are
playing a role in this behavior, further study is needed to determine how these solutions are impacting the surface chemistry.

The interfacial tension model successfully explains the origin of the catalytic force and predicts the correct direction of movement of the nanorods. In this model catalytic activity was considered to take place on the platinum surface while the gold did not interact with the solution. However it is commonly observed that a gold substrate immersed in a solution of hydrogen peroxide solution is covered by bubbles of oxygen, possibly due to the decomposition of hydrogen peroxide, suggesting that gold might also have a role in the catalytic activity taking place. The direction of fluid movement in the inverted nanorod system described in Figure 4.1c is observed to be dependent on the charge of the tracer particles used. The interfacial tension model was unable to explain the dependence on tracer charge. Also it was experimentally observed that the pumps and rods did not function when an oxide layer was placed in-between the two metals. Thus an electrical contact between the metals was necessary for catalysis to occur. These observations led to the development of the electrochemical model which assumes

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Fig. 4.4: Photographs of approximately 0.02 mL of DI water placed on the surface of a) Sample 1, b) Sample 2 and c) Sample 3 d) Sample 4. Samples were prepared as described in Table 4-1.
electrochemical decomposition of hydrogen peroxide on both the gold and silver surfaces leading to the formation of an electric field in the solution. This model was successfully modeled to explain the formation of tracer patterns [16] and the movement of the nanorods.[17, 18]
4.3.2 Electrochemical model

In this model disproportional electrochemical decomposition of hydrogen peroxide is considered to take place simultaneously on both metal surfaces. An ion gradient rather than an interfacial gradient is believed to be the origin of the forces. In this model it is assumed that a surface containing adjoining regions of silver and gold as shown in Figure 4.5 will decompose hydrogen peroxide via the following reactions. (Eq. 4.1, Eq. 4.2, Eq. 4.3)

\[
\text{Overall: } 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \quad \text{(Eq. 4.1)}
\]

\[
\text{Anode: } \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad \text{(Eq. 4.2)}
\]

\[
\text{Cathode: } \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad \text{(Eq. 4.3)}
\]

Observations on model systems suggest that silver is the cathode in the reaction, reducing \( \text{H}_2\text{O}_2 \) to \( \text{H}_2\text{O} \) and consuming protons (\( \text{H}^+ \)) in the process.\(^{16, 19} \) At the gold anode, \( \text{H}_2\text{O}_2 \) is oxidized which generates protons thus forming a continuous self-generating ion gradient.
The creation of an ion gradient in close proximity to the surface has the effect of producing a nonuniform electric field driving electroosmotic fluid flow. The velocity of fluid movement under the influence of an electric field is given by the Helmholtz-Smoluchowski equation Eq. 4.4:

$$U_{eo} = -\varepsilon \zeta_s E/\eta$$  \hspace{1cm} \text{Eq. 4.4}

where $U_{eo}$ is the electroosmotic velocity, $\varepsilon$ is the dielectric constant of the medium, $\zeta_s$ is the zeta potential of the surface, $E$ is the electric field and $\eta$ is the viscosity.

Fig. 4.5: Diagram describing the electrochemical model. Catalytic decomposition of hydrogen peroxide takes place on the gold and silver surfaces. Gold acts as the anode producing protons and silver acts as the cathode consuming protons. The protons move from the gold end to the silver end and this result in a proton-gradient generated electric field in solution.
If a charged particle is located within the electric field resulting from the catalytically produced ion gradient, its motion will be influenced by an electrophoretic force.

The electrophoretic movement of a particle in solution is governed by a similar equation Eq. 4.5:

\[ U_{ep} = -e\zeta_p E/\eta \]  \hspace{1cm} \text{Eq. 4.5}

where \( U_{ep} \) is the electrophoretic velocity and \( \zeta_p \) is the particle zeta potential. The catalytically generated electric field \( E \) shown in equations Eq. 4.4 and Eq. 4.5 has been evaluated theoretically based on the catalytically produced ion gradients leading to electroosmotic and electrophoresis. The theoretical predictions agree with the experiment observations of negative tracers forming a ring from the edge of the catalyst and the positive tracers performing convective motion at the edge. The behavior of the tracer is shown to be a function of the tracer zeta potential, the surface zeta potential and the electric field created.[16]

The motion of bimetallic nanorods can be explained by this model. Electrochemical decomposition of hydrogen peroxide occurs simultaneously on both ends of the rod in accordance to Eq. 4.1, Eq. 4.2 and Eq. 4.3. Due to electrophoresis the ions in the double layer of the rod migrate in response to the self-generated electric field causing the movement of the bimetallic rod in the opposite direction by Galilean invariance.[17, 18]

As mentioned in the previous section the bimetallic nanorods system have been inverted to explore localized fluid flow.[11] The electrochemical model successfully explains the direction of fluid and tracer behavior in a system consisting of silver disc
patterned on gold surface. In a dilute 0.5% solution of hydrogen peroxide exhibiting a pH of 5.5, gold exhibits a negative zeta potential of approximately -20 mV. The electric field created causes the ions in the double layer of gold to migrate at the electroosmotic velocity towards the silver feature. The ions carry along with them water molecules resulting in a surface fluid current. Tracer particles in the solution are also swept inwards due to this electroosmotic fluid flow. This fluid flow acts on the tracer particle independently of its zeta potential. Once the fluid flow brings the tracer particle close to the silver catalyst, in the vicinity of the ion charge gradient, the electrophoretic force begins to act on the particle as well. The direction of the electrophoretic force is dependent on the zeta potential of the tracer. (Eq. 4.5) In the case of negatively charged carboxyl terminated spheres, the electrophoretic force is directed outward in the opposite direction of the electroosmotic fluid flow. At the point where these forces balance, the tracer particle velocity reaches zero. The accumulation of tracer particles at that point forms a defined ring. This process is shown schematically in Figure 4.6a. Figure 4.6b shows the optical image of the silver disc in the center and the ring of tracers.

In the case of amidine terminated positively charged latex sphere, a ring is not formed around the silver catalyst. Positively charges tracers move inward toward the catalyst following the electroosmotic fluid flow. Once the tracers reach the position where the ion gradient is present, the electrophoretic force begins to act on the particle as well. Since the particle is positively charged, the direction of the electrophoretic force aligns with the direction of the fluid flow and the tracers continue to flow onto the silver catalyst and accumulate on its surface. This is shown schematically in Figure 4.6c and the optical image of the silver catalyst covered with the tracers is shown in Figure 4.6d.
Fig. 4.6: Illustration of the catalytically generated electrophoretic and electroosmotic forces acting on a latex microsphere (tracer) in the vicinity of the silver-gold interface placed in a 0.5% dilute hydrogen peroxide. Due to the negative zeta potential of the gold surface the electroosmotic fluid flow is always inward toward the silver. a) Negatively charged carboxyl functionalized microspheres experience an outward electrophoretic velocity which counteracts the inward electroosmotic fluid flow. The sphere comes to rest and forms a ring at a distance from the edge of the silver where both forces balance. b) Positively charged amidine functionalized microspheres experience an inward electrophoretic force. This combined with the inward electroosmotic force pushes the particles towards the disc and no ring formation is observed. (Scale bar = 50 μm)
Preliminary experiments were conducted to quantitatively measure the effect of the diameter of the silver disc and the concentration of hydrogen peroxide solution on the diameter of the rings formed using carboxyl tracers. Specifically silver discs 20-200 μm in diameter were fabricated on a gold surface using photolithography methods described elsewhere (Section 5.22.1). A dilute solution of hydrogen peroxide and carboxyl spheres were concocted and placed on the sample. The concentrations of the hydrogen peroxide used were 0.5%, 1%, 1.5% and 2%. Figure 4.7 shows a graph with the annulus ring area, as defined by A1 in the illustration, on the y-axis, and the concentration of hydrogen peroxide on the x-axis. The plot shows data for silver disc diameters of 20, 50, 100 and 200 μm.
Fig. 4.7: a) Graph shows the annulus ring area vs. concentration (%) of hydrogen peroxide for various ring diameters. 

b) Double ring formation around a silver dot of 20 μm diameter. Hydrogen peroxide concentration of 1%. Inner ring diameter 66 μm and outer ring diameter 240 μm.

c) Single ring formation around a silver dot 50 μm in diameter in 1% hydrogen peroxide. Ring diameter is 162 μm.
According to the graph, an increase in annulus ring area is seen with increasing disc diameter and increasing hydrogen peroxide concentration (except for the 20 μm disc). According to the electrochemical model the ring diameter depends on the electroosmotic fluid flow and the electrophoretic velocity experienced by the particle. The magnitude and distribution of these velocities along the surface depends on the electric field (Eq. 4.4 and Eq. 4.5) created in the solution which in turn depends on the rate of consumption and production of proton on the silver and gold respectively. It is assumed in the electrochemical model that the decomposition of peroxide on the silver disc is reaction limited. If this is the case then an increase in silver disc area or an increase in concentration will result in the increasing consumption of protons. Both these situations are analyzed separately below.

The actual profile of the proton gradient and electric field is not known but can be approximated as shown in Figure 4.8. In this figure the gold surface adjacent to the silver disc is divided into three regions. In region 1, closest to the disc edge, the electrophoretic velocity is dominant and in region 3, far away from the disc edge, the electroosmotic velocity is dominant. In region 2 the two opposing forces balance causing the particle to come to rest and accumulate to form the ring. A possible profile of the proton concentration gradient is charted out in Figure 4.8, where the dashed line represents a system with larger disc diameter (shown by the hashed Ag region) and the solid line represents a smaller diameter silver disc (shown by the solid Ag region). As the gold surface area is much larger than the silver surface area it can be assumed that no significant change in proton production occurs on the gold surface due to the increase in silver disc diameter and hence the profile in region 3 does not change.
Fig. 4.8: Illustration of possible proton gradient in solution (solid line) formed due to catalytic decomposition of hydrogen peroxide on gold and silver. Change in gradient profile and corresponding increase in ring diameter due to increase in silver disc diameter is shown (small-dashed line). Fluid flow due to electroosmosis is also shown by the big-dashed lines.
However an increase in silver disc diameter will result in increase in consumption of protons by the silver. In the case of the smaller silver area (the solid line) a finite concentration of unconsumed protons are seen on the silver. The dashed line is an extreme case when silver diameter is large enough to consume all the protons. This increase in proton consumption causes a steeper proton gradient in regions 1 and 2. As electrophoretic forces are more dominant in these regions the particle experiences a larger increase in outward electrophoretic velocity as compared to inward electroosmotic velocity. Thus an increase in ring diameter is seen with increasing disc diameter. This area dependence clearly proves the assumption of the reaction limited reduction of protons on the silver. More the area of the silver disc more the protons consumed from the solution.

The graph (Figure 4.7) also shows a linear increase in ring size with concentration for the larger three dots i.e. 50,100 and 200 μm diameter dots. A possible explanation is shown in Figure 4.9. An increase in concentration of peroxide causes an increase in rate of consumption and production of protons. (Eq. 4.1, Eq. 4.2, Eq. 4.3) However assuming that silver is working at maximum load no further increase in consumption of protons is possible for a given surface area of silver. The production of protons increases on the gold. This causes a steeper proton gradient in region 1 and 2 as seen in Figure 4.9 where the dashed line represents higher concentration of peroxide as compared to the solid line. Again the electric field becomes steeper in region 1 and 2 causing an increase in outward electrophoretic velocity and an increase in ring diameter.
Fig. 4.9: Illustration of possible proton gradient (solid line) in solution formed due to catalytic decomposition of hydrogen peroxide on gold and silver. Change in gradient profile and corresponding increase in ring diameter due to increase in hydrogen peroxide concentration is shown (small dashed line).
However the 20 μm diameter dots showed inconsistent behavior. The 20 μm diameter silver discs showed a double ring formation for higher concentration of hydrogen peroxide. Both the rings are formed simultaneously and at a distance of 66 μm and 240 μm from the silver edge. (Figure 4.7b) The data point for 2% concentration and 20 μm dot is taken for the inner ring and does not follow the overall trend of the graph. (Figure 4.7b) Also the stability of the rings is tested by disturbing the setup via adding more solution or shaking the microscope table. This disrupts the rings but both the rings are reformed immediately and simultaneously. The formation of the second ring cannot be intuitively explained by the electrokinetic or interfacial model. A possible explanation includes presence of other gradients such as temperature and pressure which become prominent as the silver disc size reduces and as a result the electric field created in solution decreases in magnitude. Another explanation is that perhaps such rings were not formed on bigger discs due to the closer proximity of neighboring structures. All discs of various dimensions were spaced equally apart (500 μm apart) thus resulting in increased inter-disc spacing for smaller discs as compared to the larger discs. Formation of similar rings on larger discs was possibly suppressed due to overlapping of the gradients of adjacent discs.

Better understanding and modeling of the magnitude and direction of the electric field and corresponding forces acting on the tracers will help explain the formation of the double ring.
4.4 AFM-based force sensor for quantitative measurement of catalytic force

4.4.1 Introduction

In theoretical calculations done previously on the gold/platinum nanorod system, [7] the interfacial forces produced was estimated by calculating the change in interfacial energy on the gold surface due to dissolved oxygen. This involved solving the convention-diffusion equation for oxygen to obtain the concentration profile along the gold segment and calculation of interfacial energy change along the gold surface using the Acree’s model.[20] The interfacial force acting on the rod is given by Eq. 4.6 where the gold surface was considered to be hydrophobic.

\[
F = -2\pi R - \frac{dy_{solution/\text{Au}}}{dC} \Delta C
\]

Eq. 4.6

Here \( F \) is the catalytic force produced, \( R \) is the radius of the nanorod, \( \gamma \) is the interfacial energy of the gold surface and \( \Delta C \) is the change in oxygen concentration. By equating the interfacial force to the drag forces acting on the cylindrical rod, the velocity of the nanorod was predicted to be 17 \( \mu \)m/sec in 3.3% concentration of hydrogen peroxide, which is in accordance with the experimental observations. The force was predicted to be in the \( 10^{-14} \) N range.

Except for this rough estimate, no extensive modeling or experiments have been done to determine the magnitude of the force generated by the catalytic motors. Perhaps the main obstacle towards measurement of the force is the inaccessibility of the environment in which it is generated. Catalytic motors work on forces produced
continuously in-situ on the surface of a metallic nanostructure, which at all times remains suspended in solution. The small surface area of the nanorods, in the range of micron squares, precludes the use of probes and tracking devices. The lack of electrical and mechanical connections to these catalytic motors makes it difficult to carry force measurement without disturbing the system. Moreover the catalytic forces are extremely small possibly in the piconewton range thus extremely sensitive instruments and accurate calibration methods are needed. Direct measurement of these minute forces posses a technological challenge and exact and systematic study of the magnitude of the catalytic forces produced at the surface has not been done till date. In this section a method for quantitative measurement of the force produced by the bimetallic catalytic system is introduced and the design and fabrication of a catalytic force sensor is described. Also, preliminary results of the magnitude of force is presented and compared to the available theoretical predictions carried out in reference [7].

To measure the forces with which the rods are propelled a catalytic force sensor device was built consisting of a cantilever with a catalytic site built on its tip. Catalytic force is produced when the tip of the cantilever is immersed in hydrogen peroxide. The force is detected and measured as a change in cantilever property. As the catalytic system has dimensions in nanometers and the force produced is in pico-newtons, successful and accurate detection entails the use of a micro-cantilever.

Microcantilevers have been increasingly popular in the past few years for purposes of chemical, biological and analytical detection and monitoring and biomedical diagnostics.[21, 22] MEMS process have enabled microcantilever to be mass-produced cheaply and to be easily tailored for the required application. Detection is carried out by
translating changes occurring in the environment or on the cantilever surface into a mechanical response of the cantilever. A variety of sensor structures can be used to detect mechanical motion or deformation. Such sensor architectures are based on electronic and optical responses such as capacitance, piezoresistive, piezoelectric, Fabry-Perot filters gratings, beam steering, and optical signal modulation. Figure 4.10 shows three possible configurations of a catalytic force sensor. All the cantilevers have the bimetallic post similar to the nanorod built on the tip which is immersed in the fuel solution. The catalytic force F acting on the post causes the tip to move upwards as indicated in the figure. The detection mechanisms are based on change in capacitance between the cantilever and substrate, change in transmission resonance of a Fabry Perot cavity and change in current of a piezoresistive material.
Fig. 4.10: Illustration of catalytic force sensors where gold/platinum posts similar to the nanorods are placed on the tip of the cantilever. The end of the cantilever is immersed in a solution of hydrogen peroxide. The change in cantilever response to the catalytic force $F$ (load) acting on the tip is detected using a) Change in capacitance. b) Change in transmission resonance of Fabry Perot cavity. c) Change in current in the piezoresistive material.
Atomic force microscopy [23] used to image surface topography, utilizes microcantilevers having a very sharp conical tip. The instrument scans the tip at a known height above the surface and detects the deflection of the cantilever because of interaction between the cantilever tip and surface. Off-late AFM is being increasingly being used as force sensors [24] to measure material and surface properties such as elasticity, hardness, magnetic spin, molecular interaction and cell binding.[25-27] In all these application the force experienced by the tip when approaching a surface or when influenced by an external stimuli is measured in terms of changes in cantilever parameters such as resonance frequency and quality factor. These force sensors have shown sensitivity to detect attograms of mass [28] and forces in the pico-newton range.[29] The sensitivity and availability of AFM cantilever tips encouraged the use of an atomic force microscopy (AFM) cantilever as the catalytic force sensor.

4.4.2 Fabrication of AFM cantilever catalytic force sensor

A tipless AFM cantilever coated with gold, having silver posts fabricated in place of the standard conical tip was used to as a catalytic force sensor. The silver post in contact with the gold surface forms a catalytically active bimetallic junction which when immersed in hydrogen peroxide produces catalytic force.

Fabrication of silver post on the tip of the AFM cantilever is carried out using standard photolithography and evaporation techniques. The cantilever used was purchased from SPMTips.com. The cantilever when purchased was mounted on a silicon chip along with 5 other cantilevers of varying lengths (Figure 4.11a-b). The cantilever
was made of silicon and was 90 μm long, 35 μm wide and 1 μm thick. It was uniformly coated on all sides with 10 nm of chromium and 20 nm of gold.

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Fig. 4.11: a) Photograph of tipless cantilevers mounted on a silicon chip, as purchased (spmtips.com). b) Illustration of the silicon chip on which 6 cantilevers of different lengths are mounted. The smallest cantilever was used for fabricating the post. c) The silicon chip is then fixed on a standard silicon wafer (3” diameter) using removable wax for easier handling. The entire wafer is used for performing the photolithography steps.
The silicon chip with the cantilevers is mounted onto a 3” silicon wafer using reformable wax. (Figure 4.11c) Mounting the cantilever in this fashion made it easier to handle and process the chip during the fabrication steps. Now the silicon wafer is spin coated with LOR 30B resist at speeds of 1000 rpm for 40 s. LOR 30B, purchased from Microchem Corp, is a lift-off resist with very high viscosity. The high viscosity and low spinning speeds helped the resist adhere to the cantilever during spinning. The LOR was baked at 150 °C for 5 minutes using a contact hot plate. The baking was carried out by gradually ramping the temperature to prevent wrapping of the cantilevers. Photoresist SPR 3012 was then spin coated on the LOR layer at 1000 rpm for 40 s and baked at 110 °C for 90 s. This bi-layer stack consisting of LOR 30B and SPR 3012 was exposed using a contact aligner and a soda lime mask. The mask was designed and aligned to expose a circular feature 15 μm in diameter on the tip of the cantilever. The wafer was developed in CD26 solution for 1 minute 20 s. The exposed photoresist was dissolved along with the underlying LOR layer to give a step like profile as shown in Figure 4.12. 10 nm of chromium and 100 nm of silver were evaporated on the silicon wafer and into the exposed feature. After dissolution of the photoresist in acetone and LOR in CD26, the silver feature was left behind on the cantilever edge. (Figure 4.12)
Fig. 4.12: Steps for fabrication of a catalytic post on the end of an AFM cantilever using the lift-off process. The lift-off process a) A bilayer resist stack consisting of LOR 30B and Photoresist 3012 is spin coated on the cantilever. The photoresist is exposed using a contact aligner and developed in CD26 to form an undercut profile. b) Silver metal is evaporated into the gap. c) The photoresist in dissolved in acetone and LOR in CD26 and the excess metal is removed, leaving the silver structure. d) Optical image of the cantilever tip after the lift-off process with four silver posts, e) one rectangular post, f) one circular post. (Scale bar=35 μm)
4.4.3 Force measurement set-up

The measurements using the modified AFM cantilever posses a challenge due to the small size and fragility of the tip. The silicon chip, to which the cantilever is attached, is first removed from the silicon wafer by dissolving the wax in acetone. Next the silicon chip is mounted on a circular washer as shown in Figure 4.13a. The washer attaches magnetically on to the endcap which is part of the AlphaSNOM WITec instrument. (Figure 4.13b) A wet-cell endcap is used which allows measurements to be taken when the cantilever is immersed in the fuel solution. The wet-cell endcap is similar in construction to the standard endcap except for the Ge crystal placed in the laser pathway to tailor the refractive index so that the laser is reflected from liquid medium. (Figure 4.13c) The end of the cantilever containing the catalytic post is submerged in a pool of ~1μL of fuel solution. The change in cantilever properties such as resonance frequency, deflection and quality factor are detected using a laser and a split photodiode setup shown in Figure 4.14.
Fig. 4.13: a) Image of the part of the AFM instrument containing the endcap with the washer magnetically mounted on the end. The cantilever is attached to the washer. (From Witec.com) b) Blown up illustration of the washer. The silicon chip with the 6 cantilevers is attached to the washer. One of the cantilevers has the silver post. c) Blown up illustration of the wet cell endcap, showing the path of the laser light. The laser passes through the Ge crystal and through a pool of fuel solution and falls on the cantilever. Also shown are the washer and the cantilever.
4.4.4 Calibration of the photodiode

The deflection of the cantilever is detected using a laser which is reflected off of the back of the cantilever. The reflected laser falls on a split photodiode with operates as a position sensitive detector. (Figure 4.14) The T-B (Top-Bottom) value represents the amount of deflection (in voltage) of the laser spot due to cantilever displacement in the vertical direction. Calibration of the photodiode allows the voltage to be converted to actual displacement of the tip. Calibration measurements to determine the sensitivity of the photodiode is essential to get an accurate value of the force. This is carried out by physically bending the cantilever a known amount and comparing this displacement with the change in voltage due to corresponding deflection of the laser spot on the photodiode.

Firstly, the cantilever is brought in contact with the z-stage of the AFM. This is the same as the first step of doing a contact force measurement. Next the cantilever and the stage are decoupled by cutting the feedback to the cantilever. This allows the cantilever and stage to be operated independent of each other. The exact location of the tip with respect to the stage is known i.e. the tip is at the near-contact position, ~5 μm from the stage surface and the stage is fully retracted. The stage is then carefully manually moved up till it comes in contact with the tip. At this point the T-B value increases because the cantilever bends upwards due to coming in contact with the stage. The stage is displaced upwards in fixed steps (microns) bending the cantilever as it moves. The T-B voltage is noted down for different displacements of the stage. This allows us to compare the T-B voltage readings of the photodiode to the actual z distance transversed by the cantilever
(stage) and to calculate the calibration constant. The WITec instrument used in the experiment had a photodiode which showed a calibration value of 205 nm/V.

4.4.5 Calibration of spring constant

Accurate measurement of the spring constant of the cantilever is an essential step towards meaningful force calculations. Spring constant ($k_c$) is a material and physical property of the cantilever which depends on the Youngs Modulus ($E$) and cantilever dimensions ($width w_t, thickness t$, and length $L$) (Eq. 4.7)
However many external factors influence the spring constant of the cantilever and need to be taken into account for accurate force measurements. These include the damping by the surrounding medium, additional mass added on the cantilever and the point of loading of the mass. In particular for the modified cantilever system, effect of the viscosity of the hydrogen peroxide, the effect of the mass and placement of the catalytic post and the effect of the force itself on the spring constants need to be considered.

Many methods have been explored in literature to accurately measure the spring constant of a microfabricated cantilever beam in a direct, non-destructive and reproducible manner.

Static methods: In these methods a constant force $F$ is applied to the cantilever, the deflection $Z_c$ is detected and the spring constant calculated using Eq. 4.8. Various techniques to apply the constant force are by adding a mass at the end of the cantilever, [30] gravitational forces, hydrodynamic forces etc.

$$k_c = \frac{Ewt_c^3}{2L}$$  \hfill (Eq. 4.7)

$$k_c = \frac{F}{Z_c}$$  \hfill (Eq. 4.8)

Dynamic methods: In this method resonant frequency of the cantilever is used to calculate the spring constant.
Sader et al. [31] proposed a method for measurement of spring constant from its unloaded resonant frequency which only requires prior knowledge of density ($\rho$), thickness ($t$), width ($w$) and resonance frequency ($\omega$) in vacuum. (Eq. 4.9) When using this method $M_e$ (normalized effective mass) is calculated numerically using finite element methods and depends on the aspect ratio of the cantilever. For a cantilever with length 90 $\mu$m and width 35 $\mu$m and poisons ratio 0.25 the $M_e$ value is given by 0.241.

$$k = M_e \rho_c wtL \omega^2_{vac} \quad \text{(Eq. 4.9)}$$

This equation is valid only for resonance frequencies measured in vacuum. The influence of density of the surrounding medium can be corrected using equation Eq. 4.10,

$$\frac{\omega_d}{\omega_o} = \sqrt{1 - \frac{1}{4Q^2}} \quad \text{(Eq. 4.10)}$$

which is valid for fluid with $Re<<1$. Here $\omega_d$ is resonance frequency as measured in the fluid, $\omega_o$ is the resonance frequency in vacuum and $Q$ is the quality factor. However this correction, as is stated in the reference, is almost an order of magnitude less than the normal 2% shift in frequency between air and vacuum.

The larger shifts in frequency experienced by the cantilever in liquid, as is the case for the catalytic force sensor, clearly cannot be accounted for in this method. Also the density of the cantilever is required which is difficult because of the cr/au coating on the cantilever. Accurate determination of spring constant using Sader method though straightforward is not suitable to be used for the catalytic force sensor.
Cleveland et al. [32] proposed a widely used dynamic method in which the resonant frequency is compared before and after the addition of a small end mass to the cantilever. (Eq. 4.11)

\[ k = (2\pi)^2 \frac{M_1}{(1/v_1^2) - (1/v_0^2)} \]  

(Eq. 4.11)

\( M_1 \) is the mass added and \( v_1 \) and \( v_0 \) are resonant frequencies of the cantilever before and after the addition of the mass.

This method can be conveniently extended to the modified cantilever system where the silver posts can be treated as the addition mass. The system used for measurement of catalytic forces is the cantilever with one silver post, 15 \( \mu \)m in diameter and 100 nm thick, fabricated at the tip. The one post model was used as opposed to the 4 posts or rectangular post model because the symmetry of the one post system helped reduce the frequencies at the higher modes. Figure 4.15a shows the amplitude vs. frequency data for cantilever with 4 posts in three different environments; air, water and 1\% hydrogen peroxide. The cantilever resonance in liquid has very low quality factor and higher resonance mode peaks are visible. It is believed that this is the result of the asymmetry in the system caused due to the off-center spatial positioning of the four posts. To overcome this problem cantilevers modified with one-post were used to make the force measurements. The resonance curves of the one post system shown in Figure 4.15b have higher quality factor and distinct zeroeth order resonance peak. The higher modes of vibrations have much smaller amplitude as compared to the resonant peak.
Fig. 4.15: Amplitude vs frequency curves for cantilevers having a) four post b) one post. Data is taken in air, water and hydrogen peroxide.
Using the Cleveland method and considering the post as the additional mass, the resonance frequencies were determined for the cantilevers with and without the post and also in air and in water. The resonance frequency values are given in Table 4-2.

Table 4-2: Experimentally determined resonance frequency in Hz

<table>
<thead>
<tr>
<th>Medium</th>
<th>Unmodified Cantilever</th>
<th>One-post Cantilever</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>193325.6</td>
<td>171499.8</td>
</tr>
<tr>
<td>Water</td>
<td>119290.1</td>
<td>71959.5</td>
</tr>
</tbody>
</table>

Inserting these values in Eq. 4.11 the spring constant values obtained were as 0.1079 N/m for air and 0.0064 N/m for water. The value of $k$ calculated in water is much less than that calculated in air. The response of the cantilever in liquid is much less than in air or vacuum. As all force calculations are done in liquid environment (dilute solution of hydrogen peroxide) the lower value of $k$ is considered for further calculations. The viscosity of the hydrogen peroxide solution is assumed to be similar to that of water. The value of $M_1$ (mass of the silver post) was calculated to 7.82E-13 kg taking the density of silver as 10490 Kg/m$^3$ and chromium as 7140 kg/m$^3$. The mass of the post was small so assumed to have negligible effect on the spring constant of the cantilever.

The value of $k$ is further corrected for the off-end loading using Eq. 4.12

$$k = k_e \left[ \frac{L}{L - \Delta l} \right]^3$$  \hspace{1cm} (Eq. 4.12)

where $k_e$ is the spring constant calculated assuming end loading, $L=90$ μm is the length of the cantilever and $\Delta l=5.5$ μm is the distance of the silver post from the edge of the
cantilever. The final value of $k$ used in the force calculation is 0.0077 N/m. The catalytic force is assumed to be small enough not to change cantilever properties.

4.4.6 Results and discussion

4.4.6.1 Static measurement

In the static deflection method the catalytic force is calculated using Eq. 4.8. Displacement $Z_c$ is measured as the T-B change in the photodiode due to deflection of the cantilever by the catalytic force. This value is converted to actual displacement using the calibration factor of 205 nm/V. The spring constant $k$ of the cantilever calculated using the Cleveland method is taken to be 0.0077 N/m.

The experiment is conducted by mounting the modified cantilever, using a wet cell end-cap, onto a Witec AFM instrument and submerging the cantilever tip in 1 μL of water. Care is taken that the water wets the bottom end of the endcap. The laser is turned on and reflected from the back of the cantilever. The T-B deflection value in volts is noted. In the beginning of the experiment this value is set close to 0 V. This means that the laser is close to the centre of the four quadrants of the split photodiode and this position of the laser is used as a reference point for measuring displacement.

Now known concentration and volume of hydrogen peroxide solution is added to the water. The liquids are allowed to mix and the system allowed to stabilize. The force causes the cantilever to bend and the laser spot to be displaced. The new T-B value is
noted down. As the concentration of hydrogen peroxide is slowly increased the downward force on the tip increases causing the laser to be further displaced. Care is taken through the experiment not to physically change the position of the laser and to make sure that the tip is always submerged in liquid. The T-B reading is noted down for every increase in concentration and the net displacement $Z_c$ calculated (taking as reference the T-B value for water). Table 4-3 shows the values of the T-B measured and the forces calculated for 0 to 1.8% concentration of hydrogen peroxide. Figure 4.16 shows the force vs. concentration graph.

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>T-B(V)</th>
<th>Displacement(m)</th>
<th>F(catalytic, pN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.109</td>
<td>2.2345E-08</td>
<td>0.00</td>
</tr>
<tr>
<td>1.01</td>
<td>0.085</td>
<td>1.7425E-08</td>
<td>37.84</td>
</tr>
<tr>
<td>1.52</td>
<td>0.070</td>
<td>1.4350E-08</td>
<td>61.48</td>
</tr>
<tr>
<td>1.79</td>
<td>0.059</td>
<td>1.2095E-08</td>
<td>78.82</td>
</tr>
</tbody>
</table>

Fig. 4.16: Force vs. concentration curve measured using static displacement method
The graph shows a linear increase in force with concentration. Higher concentration of hydrogen peroxide could not be used because of formation of bubbles on the cantilever. The error in reading the T-B value is ±0.01 V. The error is due to the noises such as thermal, environmental which do not allow the tip to stabilize and also influence its displacement.

4.4.6.2 Resonance method

The AFM cantilever can be driven at its resonant frequency using the piezoelectric resonator housed in the endcap. The resonant frequency is given by Eq. 4.13

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m^*}} \]  

(Eq. 4.13)

where \( k \) is the spring constant and \( m^* = 0.24m \) is the effective mass of the system (\( m \) = mass of cantilever). The resonance frequency of a cantilever is influenced by the surrounding medium as seen in Figure 4.15 which shows the resonance frequency of one and four post cantilevers in air and liquid. The change is more clearly seen in the one post system where the resonance frequency decreases from 171600 Hz in air to 74200 Hz (amplitude 0.212 V) in water. A decrease in quality factor and increase of higher modes of vibration is also seen.

Further decrease in resonant frequency and amplitude of resonance is observed on submerging the cantilever in hydrogen peroxide. At 1% hydrogen peroxide the resonant frequency of the cantilever is 71200 Hz with vibration amplitude of 0.202 V and at 2%
hydrogen peroxide 70000 Hz with vibration amplitude of 0.183 V. A corresponding increase in quality factor of the resonance peak from 6.67 in water to 10.76 in 1% hydrogen peroxide and 11.23 in 2% hydrogen peroxide is observed. Thus the catalytic force acting down on the tip of the cantilever has the effect of decreasing resonant frequency and amplitude and increasing quality factor. Similar effect was observed by Cleveland et al. [32] on attaching tungsten spheres of increasing mass \( M \) to the tip of the cantilever. A linear relationship was established between the added mass \( M \) and \( \nu^2 \) (inverse square of resonant frequency) given by Eq. 4.14 a,b

\[
\nu = \frac{1}{2\pi} \sqrt{\frac{k}{M + m^*}} \quad \text{(Eq. 4.14a)}
\]

\[
M = k(2\pi\nu)^{-2} - m^* \quad \text{(Eq. 4.16b)}
\]

In the resonance method for measuring catalytic force, the force is assumed to be an additional mass \( M \) added to the cantilever, analogous to the mass added in the Cleveland experiment. The mass \( M \), in this case, increases with increasing concentrations of hydrogen peroxide.

Specifically the measurements are taken by submerging the one post cantilever in water and then different concentrations of hydrogen peroxide. (Table 4-4) A resonance frequency decrease of 4 kHz is observed for a concentration range of 0-4% hydrogen peroxide. The resonance frequency in water represents the case when the added mass \( M(\text{catalytic}) = 0 \). Substituting this in Eq. 4.14b gives the value of \( m^* \) (Eq. 4.15)

\[
k(2\pi\nu_0)^{-2} = m^* \quad \text{(Eq. 4.15)}
\]
where $v_0$ is the resonance frequency of one post cantilever in water. Mass $M(catalytic)$ due to the catalytic force is calculated by substituting the measured resonance frequencies (Table 4-4) in Eq. 4.14b. It should be noted here that the spring constant value used is the same as that calculated using the Cleveland method with the cantilever submerged in water. It is assumed here that the viscosity of hydrogen peroxide is same as water and that the force produced is small enough not to change the spring constant $a$ of the cantilever.

Table 4-4 lists the calculated value of the additional mass $M(catalytic)$ and the force for various concentrations of hydrogen peroxide. The force vs. concentration values are plotted in Figure 4.17. Here the force is seen to increase linearly with concentration for dilute hydrogen peroxide ($<1\%$). The force begins to level off for concentration of hydrogen peroxide above 1\%. Similar effect of leveling of speed and directionality of gold/platinum nanorods with increasing concentration of hydrogen peroxide has been observed by Paxton et al.[7] In this case, the velocity of the nanorods saturated between 3.3\% and 5\% concentration of hydrogen peroxide. The leveling of the catalytic forces is perhaps because the silver reaches its maximum reaction rate and no further increase in electric field is possible. This further confirms the assumption of the electrochemical model that the reaction at the silver is rate limited. The magnitude of force produced can be increased by increasing the surface area of silver which allows the use of lower concentration of peroxide solution and thus less possibility of bubble formation.
Table 4-4: Table showing the resonance frequency of one post cantilever in different concentrations of hydrogen peroxide, the additional mass $M$ experienced by the cantilever due to the catalytic force and the force $F$ in pN calculated using the resonance method.

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Frequency (Hz)</th>
<th>$M$ (catalytic)</th>
<th>$F$ (catalytic, pN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71960</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.35</td>
<td>71499</td>
<td>1.92124E-14</td>
<td>0.19</td>
</tr>
<tr>
<td>0.4</td>
<td>71020</td>
<td>3.95726E-14</td>
<td>0.39</td>
</tr>
<tr>
<td>0.5</td>
<td>70680</td>
<td>5.42763E-14</td>
<td>0.53</td>
</tr>
<tr>
<td>1</td>
<td>69000</td>
<td>1.30149E-13</td>
<td>1.28</td>
</tr>
<tr>
<td>2</td>
<td>68520</td>
<td>1.52859E-13</td>
<td>1.50</td>
</tr>
<tr>
<td>3</td>
<td>68319</td>
<td>1.62511E-13</td>
<td>1.59</td>
</tr>
<tr>
<td>4</td>
<td>68000</td>
<td>1.78006E-13</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Fig. 4.17: Graph of the catalytic force in pN vs. concentration of hydrogen peroxide solution calculated using shift in resonance frequency.
The force calculated by the resonance method is one order of magnitude smaller than the static method. This could be because of the error while measuring the displacement of the static cantilever due to the thermal and surrounding mechanical noises. The measurements done using the resonance method is less influenced by these external noises as the cantilever is driven at a fixed voltage using the piezo. Also measurements at higher concentrations are possible using the second method because the constant vibration of the cantilever prevents bubble formation.

Force calculated using the cantilever based forces sensor predict values in the range of 0.1-1 pN. This is similar to the theoretical prediction of 0.1 pN for the nanorods. The cantilever has a silver surface area ~150 times the surface area of the platinum segment of the nanorods. Also the gold surface area of the cantilever is almost infinite while compared to the silver post, while the nanorod has comparable gold surface area. The larger surface area of the silver on the cantilever would warrant a larger force. This is not the case. This may be accounted for by the different mechanism models used in the two calculations. Also in the cantilever force sensor, drag force acting on the post is not considered which is taken into account for the nanorods.

4.4.7 Application to drug delivery

There is a lot of research being carried to build biosensors for glucose sensing and drug delivery vehicles. Glucose (D- β-oxidaseglucose:oxygen 1-oxidoreductase), is known to catalyze the oxidation of glucose into gluconic acid and H$_2$O$_2$ in the presence of molecular oxygen. (Figure 4.18) A cantilever based force sensor containing an active
catalytic site can be modified to be used as drug delivery device which is powered by catalytic force. (Figure 4.19) Glucose oxidase is immobilized on the cantilever and placed in a glucose containing fluid such as blood. Some of the methods to immobilize glucose oxidase by self-assembly are studied in reference [33]. The glucose oxidase oxidizes the glucose into hydrogen peroxide which triggers a catalytic reaction on the platinum and causes the cantilever to move upwards releasing the insulin contained in the device into system. The magnitude of displacement of the cantilever is directly related to the force produced which is proportional to the hydrogen peroxide produced due to reduction of glucose. Thus the amount of insulin that enters the fluid is controlled by the amount glucose present.
Fig. 4.18: Reaction showing the catalytic decomposition of glucose by glucose oxidase to produce hydrogen peroxide

\[
\beta\text{-D-glucose} + O_2 \xrightarrow{\text{glucose oxidase}} \text{D-glucono-1,5-lactone} + H_2O_2
\]

Fig. 4.19: Proposed insulin drug delivery device with glucose oxidase immobilized on one end and a catalytic active site on the other end of a cantilever
4.5 Summary

This chapter introduces the concepts related to the catalytic powered devices. Application of the catalytic power for rotational motion has been demonstrated by fabrication of gold microgears with platinum patterned on the spokes. The gears were seen to rotate at a speed of 1 rotation/second. Further the role of hydrophobicity in the movement of the gears was studied and explained with relation to the interfacial tension model via a series of contact angle measurement.

The electrochemical model was analyzed in the context of the inverted nanorod system. For this photolithographically patterned silver discs on a gold covered surface were fabricated. Positively charged tracers were observed to be swept up to the metal junction and negatively charged spacers accumulated to form a ring. A systematic study of the ring diameter under varying conditions showed that an increases with increasing concentration of hydrogen peroxide and increasing silver disc diameter. These observations points to a rate limited decomposition on the silver disc.

Also in this chapter a method to build force sensor that successfully operates on catalytic forces produced by the nanorod system and which has capabilities to measure quantitatively the catalytic forces was designed and demonstrated. Resonance frequency shifts of the cantilever were used to measure the force as a function of hydrogen peroxide concentration. The force produced by a 15 μm diameter silver post in 3% hydrogen peroxide solution was calculated to be ~1.6 pN. This is similar to the forces theoretically calculated for the gold/platinum nanorods. More accurate spring constant determination
of the modified cantilever needs to be performed. An also novel process for reproducible
lift-off of silver post on the cantilever needs to be developed. Nevertheless, a
photolithographically modified AFM cantilever was shown to be an effective and
sensitive set-up for measuring catalytic forces.


4.6 References


Chapter 5

Self-assembled monolayers for surface engineering: Control of catalytically induced fluid flow

The key to engineering catalytically powered nano and micron scale devices such as fluidic pumps, particle sorting devices, sensors and roaming vehicles lies in the effective spatial and temporal control of the magnitude and direction of forces resulting from the catalytically produced gradients. In this chapter control of direction of motion of catalytically powered devices is demonstrated via novel device design and by surface engineering techniques.

5.1 Control of catalytic forces by device design

Control over resultant direction of motion via novel device design was achieved by positioning the bimetallic junctions in spatially defined regions such that the forces generated would align to achieve controlled rotation. In particular, gold gear-like structures [1] with platinum deposited on the tooth region were fabricated using conventional microfabrication processes and sustained rotational motion of these objects in a solution of hydrogen peroxide was achieved.

5.1.1 Experimental section: microgears

The fabrication process for the catalytically powered microgears consisted of the following steps. A quarter micron of silicon dioxide was grown on a n+ silicon (3 inch
thick) wafer. A seed metal layer consisting of 25 nm of chrome and 75 nm of gold was evaporated onto the oxide surface. Shipley 1827 positive photoresist was spun on the surface at 4000 rpm for 40 s, soft baked for 90 s at 110 °C and exposed through a mask for 3.5 s using a mercury lamp ultraviolet source calibrated to an exposure output of 12 mW/cm² on a Karl Zuss MA-6 optical contact aligner. The gear pattern was developed in 1:1 Tetra-Methyl Ammonium Hydroxide (TMAH): DI water for 90 s, and the wafer was rinsed and dried. The resist was hard baked at 90 °C for 5 minutes. The gear structures were then plated in the resist pattern to a height of 1.4 μm in gold plating solution (8oz) (Cyanide-free Techni Gold 25E from Techni Inc) for 3.5 minutes. The wafer was constantly moved in a pendulum like motion during the plating process to produce a smooth, uniform film. The wafer was rinsed and the photo resist was stripped in acetone and rinsed again in 2-propanol (IPA) and DI water. The chrome/gold seed metal was stripped by submerging the wafer in Gold Etch TFA, which is an aqueous solution of iodine complex and potassium iodide, for 60 s. A second lithography step was performed to define the catalytic platinum regions via a bi-layer lift-off process. 0.25 μm of MicroChem lift-off resist (LOR) 5A was spun onto the surface at 4000 rpm for 40 s then baked at 190 °C for 10 minutes providing a dissolving rate of 60 nm/minutes when exposed to the 1:1 TMAH:DI water development solution. Shipley 1813 positive photoresist was spun on at 4000 rpm for 40 s, soft baked for 90 s at 110 °C and exposed through a second aligned mask for 6 s. The pattern in the Shipley 1813 photoresist and the underlying LOR was developed in 1:1 TMAH: DI water for 70 s, and the wafer was rinsed and dried. During the development the underlying LOR layer is removed causing the 1813 resist to extend over the LOR by about 0.4 μm, resulting in a reproducible, high
yield lift off. 75 nm of platinum was evaporated onto the patterned surface and the platinum was lifted off by submerging the wafer into acetone for 5 minutes, followed by an IPA and DI water rinse. The LOR was stripped by submerging the wafer into 1:1 TMAH: DI water for 5 minutes and rinsed in DI water. The individual gears were released into solution by removing the sacrificial silicon dioxide layer through a 20 minutes soak in 1:1 HF: DI water. The gears were removed from solution and rinsed several times in DI water.

5.1.2 Results and discussion: microgears

Figure 5.1 depicts a sample of a gold gear structure measuring 150 μm in diameter fabricated using conventional microfabrication processes (see Experimental section). The gear in the Figure 5.1 has not yet been released and is shown on top of a silicon dioxide layer grown on a silicon wafer. The inset of the Figure 5.1 depicts the geometry of the platinum metal on the gear tooth. The interface region shown in the inset of the Figure 5.1 is where the gradient is formed which propels the device.
Gears fabricated and released using the above process were suspended in a few milliliters of hydrogen peroxide: deionized (DI) water (1:100). This concentration of hydrogen peroxide produced significant catalytic activity and bubbles of oxygen were clearly observed under an optical microscope emanating from the platinum sites. The formation and release of bubbles produces an intermittent uncontrolled burst-like movement of the structures, with little rotational component. Over 20-30 minutes, decrease in hydrogen peroxide concentration through its decomposition decreases the catalytic activity and the formation of visible bubbles ceases.

Figure 5.2a-d are stills taken from a movie showing rotational movement of a gear-like structure identical to the one depicted in Figure 5.1 except this structure has a hole located through its center. Figure 5.2a-d depict the structure at 0, 90, 180, and 270 degrees rotation. The structures are shown on top of a Silicon wafer with ~3 micron deep, ~20 μm diameter posts (measured at the base of the post; the post narrows toward its top...
surface) spaced at 132 μm etched into the surface. The initial solution consisted of peroxymonosulfuric acid: hydrogen peroxide: sulfuric acid : DI water (approximately 0.1:1:2:100) but images were taken after waiting 20-30 minutes for bubble formation to cease as described above. The gears float in few milliliters of the above solution and do not at any point come in contact with the posts. The posts were fabricated for pinning down the gears to the surface as a part of the next experimental step. The gears are positioned catalytic side down and are rotating in a clockwise motion toward the platinum coated side of the gear tooth in agreement with prior observations involving nanorod structures.[2] These structures are rotating at approximately 1 rotation per second, which, at the midpoint of the catalytic site, represents a speed of approximately 390 μm/second. This is approximately 100 times faster than the speed of the nanorods examined previously. [3]

The platinum area is approximately 400 times greater for the gear structures when compared to the nanorod structures. The increased micro-roughness of the evaporated platinum further increases the surface area available for catalytic activity. The increased speed is mainly related to this increase in the surface area of the platinum metal; however other parameters are expected to play a role.
Another method for achieving control over the direction of movement of the nanorods has been demonstrated by Kline et al.[4] by use of an external magnetic field. Here the nanorods were fabricated with platinum-nickel-gold segments. While the platinum and gold segments generated the catalytic force, the ferromagnetic nickel segments were magnetized by the external field and caused the nanorods to align perpendicular to the field lines, thus improving directionality of movement of the nanorods in solution.

Fig. 5.2: Photographs of a gold gear-like object with Platinum on the tooth region (as shown in the inset of figure 2). The object is positioned platinum side down on top of a silicon wafer with ~3 μm deep, ~20 μm diameter posts spaced at 132 μm etched into the surface and suspended in a solution of peroxymonosulfuric acid: hydrogen peroxide: sulfuric acid: DI water (approximately 0.1:1:2:100) for approximately 30 minutes. The object is rotating at a speed of approximately 1 rotation/second and is shown at a) 0 degrees, b) 90 degrees, c) 180 degrees and d) 270 degrees.
5.2 Control of fluid flow in the catalytic pumps by zeta-potential engineering using SAMs

Control over direction of fluid flow at the micro and nanoscale has been achieved in the past by use of external fields such as applied pressure and electric voltage.[5-7] Kline et al. [8] demonstrated temporal control over fluid flow in a system similar to the catalytic micropumps (Section 4.3.2) by using UV light to turn on and off the pattern formation around a silver disc. However in this case the photolytic decomposition of silver was considered to be the cause of pattern formation and not the catalytic decomposition of hydrogen peroxide. Directional control over the fluid flow produced by the catalytically generated ion gradient is important for the advancement of the applications of catalytically power to practical systems including channeless fluid pumping and has not been previously demonstrated. In this section a novel method for controlling the direction of fluid flow in catalytic micropumps is demonstrated via surface engineering without requiring any external power source.[9]

Micropumps, as described in Figure 4.5, are the inverted form of the nanorods. Here the catalytic metals are immobilized on a substrate and the influence of the ion gradient generated by the bimetallic system in the presence of hydrogen peroxide on the surrounding fluid is examined with the help of tracer particles. Surface properties of the metals play an important role in the functioning of the micropumps. The disproportional decomposition of hydrogen peroxide, formation of ion gradient and generation of electroosmotic fluid flow of ions in the double layer all occur on the surface of the metals. As explained in Section 4.3.2 and Eq. 4.4, the zeta potential of the surface determines the direction of electroosmosis. Systems studied to date have employed bare
gold surface which exhibits a negative zeta potential of -20 mV. As a result an inward flow of fluid towards the silver discs has been observed at all times. The direction of the electroosmotic fluid flow can be reversed by modifying the gold surface to have a positive zeta potential. Tailoring the magnitude and type of charge on the gold surface has been achieved by use of organosulfur self-assembled monolayers (SAMs). SAMs can be designed to have end groups of different functionalities and hence provide a simple and effective way to control the surface properties. Two kinds of SAMs, containing carboxylic acid and amine end-groups, have been used to vary the zeta potential of the gold surface from -60 mV to 50 mV, while the silver surface properties are kept constant. Monolayer formation on the silver is prevented by using a photolithographically patterned resist that protects the silver surface and remains inert during monolayer deposition. IR and XPS analysis of the surface show that the photolithographic process does not impact the SAMs and also that the SAMs retain their properties in the presence of dilute hydrogen peroxide.

Values of the zeta potential of the carboxylic acid and amine terminated SAMs were obtained from reference [10]. In this paper the zeta potential measurements were conducted using an electrophoretic light scattering spectrometer under varying pH conditions and the reported values of carboxylic acid terminated SAMs were ~-60 mV and amine terminated SAMs were ~+50 mV, both measured at a pH of 5.5 which is similar to the pH of the hydrogen peroxide solution. Motion of 2μm diameter polystyrene spheres having two kinds of functionalization: carboxyl terminated with positive charge of 40 mV, and amidine terminated with negative charge of -60 mV, is examined and is
consistent with the prediction of a zeta potential associated change in the direction of electroosmotic fluid flow.

5.2.1 Experimental section: micropumps

Test structures consisting of 50 \( \mu \)m diameter silver discs on gold coated silicon surfaces were fabricated using standard ultraviolet photolithography techniques. First, a silicon wafer was evaporated with 80 Å chromium and 500 Å gold using vapor phase deposition. Chromium was used for better adhesion of the gold to the silicon substrate. The silver metal dots were patterned on the gold layer using a bi-layer lift off process. In this process a non-photosensitive sacrificial layer LOR 5A (MicroChem Corp.), of thickness 4000 Å, is first spin coated at 4000 rpm for 40 s on the gold coated silicon wafer. The wafer is then baked at 190 °C for 10 minutes. Then a photoresist SPR 1813 (MicroChem Corp.) is spin coated at the same speeds on the sacrificial layer and baked at 110 °C for 90 s. The photoresist is exposed using a Karl Zuss MA6 contact aligner with an unfiltered mercury lamp UV source of output power 12 mW/cm\(^2\) for 6 s. It is then developed in CD26 (0.1N solution of Tetra Methyl Ammonium Hydroxy in water) for 1 minute 30 s. CD26 dissolves the exposed portions of the photoresist and the underlying LOR to form an undercut profile as shown in Figure 5.3a. The silver metal was deposited in the gaps and on the bi-layer resist structure. The excess metal was removed by dissolving the photoresist in acetone and the sacrificial layer in CD26 resulting in patterned metal features. Sonication of the sample in CD26 facilitated the easy and fast removal of the excess metal and sacrificial LOR layer.
Fig. 5.3: Photolithography based fabrication method for patterning and protecting of the silver discs on a gold coated silicon surface. Step a: The silver is patterned on a gold surface using lift-off method using sacrificial resist LOR 5A. Step b: LOR 2A is spin coated and pattern preferentially on top of the silver. Step c: SAM is deposited on the gold after removal of the top layer photoresist. Step d: The LOR 2A is stripped.
After fabrication of the silver disc the gold is now modified using organosulfur SAMs. However thiol terminated molecules form SAMs on gold and silver surfaces in a similar manner.[11, 12] It was found experimentally that formation of SAM on the silver inhibits catalytic reaction i.e. no bubble formation is observed in presence of hydrogen peroxide solution. This could be because of the structural differences in SAM on the gold and silver surface. It has been reported that the thiol molecules on silver are more perpendicular to the surface with lower intermolecular distance as compared to the SAMs formed on gold. Moreover it has also been observed that the ionic nature of the Ag-S bond leads to the transformation of the underlying Ag lattice and to the formation of a layer of Ag₂S on the surface upon long exposure to the thiol solution. The denser nature of the SAM and the change in silver properties could be the reason why catalytic activity is not seen when the SAMs are allowed to grow both on the silver and the gold. To prevent the formation of the monolayer on silver a method has been developed to preferentially assemble thiol molecules on the gold surface by protecting the silver surface. This was accomplished by patterning the silver surface with a thin layer of the non-photosensitive polymer LOR 2A (lift-off resist). LOR 2A belongs to the same family of non-photosensitive resists used in the bi-layer lift-off process. LOR was patterned because previous studies have shown that LOR is not dissolved in ethanol solutions used for SAM deposition.[13] In addition, both CD-26 and hydrogen peroxide do not remove the SAM from the surface of the gold, nor do they impact the end group functionality. Figure 5.4 depicts FTIR spectra of three gold samples with solution-deposited 16-mercaptophexadecanoic acid SAM. The first sample is untreated SAM. The second sample has been placed in a solution of 0.1N TMAH (CD26) for 10 minutes and the third sample
has been placed in a 1% hydrogen peroxide solution in water for 25 minutes. The $d^+$ and $d^-$ identified as the symmetrical and asymmetrical stretching modes of C-H are at 1852 and 1817 cm$^{-1}$ respectively. The $d^+$ and $d^-$ modes indicate the presence of SAMs on all the three substrates. Similar profile shapes and intensities indicate that the SAM structure and uniformity was unaffected by the solutions.[14]

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**Fig. 5.4:** FTIR spectra of three gold samples with solution-deposited 16-mercaptohexadecanoic acid SAM. The first sample is an unmodified SAM. The second sample has been placed in a solution of 0.1N TMAH (CD26) for 10 minutes and the third sample has been placed in a 1% hydrogen peroxide solution in water for 25 minutes. The $d^+$ and $d^-$ identified as the symmetrical and asymmetrical stretching modes of C-H are at 1852 and 1817 cm$^{-1}$ respectively. The $d^+$ and $d^-$ modes indicate the presence of SAMs on all the three substrates. Similar profile shapes and intensities indicate that the SAM structure and uniformity was unaffected by the solutions.
The gold surface containing the silver dots was spin coated at 4000 rpm for 40 s with a thin layer of LOR 2A. The wafer was baked at 150 °C for 5 minutes. The lower bake temperature and time facilitated the easier removal of LOR in the subsequent steps. Photoresist SPR 1813 was coated and exposed as discussed above for the bi-layer process Figure 5.3b. The mask used here was such that after development the LOR and photoresist was left behind only on the silver dots as seen in Figure 5.3c. The photoresist was stripped in acetone, LOR in CD26 and any excess LOR on the gold was removed in reactive ion plasma consisting of 20 sccm of O₂ and 7 sccm of Ar at 20 mtorr and 200 W. A thin layer of inert LOR 2A was left behind on the silver which prevented the SAM from forming on the silver.

Once the silver was protected, the sample was cleaned by rinsing in acetone, 2-propanol and ethanol. The sample was immersed in the 1 mM SAM solution in ethanol for approximately 12 hours, which caused a 2 nm thick single monolayer of the SAM to be deposited on the gold. (Figure 5.3d) Throughout this process the LOR did not react with the ethanol and the SAM molecule. The sample was removed, rinsed in ethanol and water and dried in nitrogen. LOR was stripped by placing in a bath of CD26 for 10 minutes. The CD26 used did not alter the properties of the SAM formed on the gold surface as described above. This SAM modified gold surface with silver dots was used as the test structure for observing the effect of SAM end-group functionality on the change in direction of fluid flow on the gold surface.
5.2.2 Results and discussion: micropumps

Table 5-1 lists the different kinds of SAMs and tracers used in the experiments. The movement of two kinds of tracers, carboxyl and amidine terminated tracers, on gold surface modified using two kinds of self-assembled monolayer, carboxylic acid terminated thiol and amine terminated thiol molecule, of comparable lengths were observed. The tracers were 2 μm diameter polystyrene spheres. The tracer solution was prepared by adding 1-2 drops of the tracers as-bought to 1 ml of DI water. This dilute tracer solution was mixed with 1% dilute hydrogen peroxide solution in equal ratios. A drop of this solution (~ 1 μL) was placed on the sample surface and viewed with a bright field microscope with a red filter The filter blocks the UV component of the light that might decompose the hydrogen peroxide. Movies were taken using a USB microscope and imaging software. The observations were taken 5-10 minutes after placing the tracer solution on the sample to allow the bubble formed due to the catalytic activity to subside.
Table 5-1: Summary of properties of tracers and SAMs.

<table>
<thead>
<tr>
<th>Gold Surface modified using</th>
<th>Terminology</th>
<th>Zeta potential in pH 5.5</th>
<th>Company</th>
<th>Processed</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS(CH2)15CO2H, 16-Mercaptohexadecanoic acid</td>
<td>-COOH surface, carboxyl terminated SAM</td>
<td>-60mV</td>
<td>Sigma Aldrich</td>
<td>As bought, 1mM solution in Ethanol</td>
</tr>
<tr>
<td></td>
<td>-60mV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-NH2 surface, amine terminated SAM</td>
<td>50mV</td>
<td>Dojindo Molecular Technologies, Inc.</td>
<td>As bought, 1mM solution in Ethanol</td>
</tr>
<tr>
<td>Tracers (2 μm diameter latex spheres)</td>
<td>Terminology</td>
<td>Zeta potential in pH 5.5</td>
<td>Company</td>
<td>Processed</td>
</tr>
<tr>
<td>carboxyl charge-stabilized hydrophobic polystyrene</td>
<td>Carboxyl tracers</td>
<td>-60mv</td>
<td>Interfacial Dynamics</td>
<td>As bought, Diluted with DI water</td>
</tr>
<tr>
<td>amidinated positively-charged hydrophobic latex</td>
<td>Amidine tracers</td>
<td>40mV</td>
<td>Interfacial Dynamics</td>
<td>As bought, Diluted with DI water</td>
</tr>
</tbody>
</table>
The effect of hydrogen peroxide on the SAM properties was studied using X-ray photon spectroscopy. Figure 5.5 shows results of a high resolution scan of the carbon C 1s and sulfur S 2p peaks of two samples. The first sample consisted of a 16-mercaptohexadecanoic acid on gold and the second sample was a similar SAM sample but immersed in hydrogen peroxide for 10 minutes. Qualitative and quantitative comparison of the two peaks shows very little change in monolayer property and coverage. FTIR studies confirm to above conclusion as can be seen by the presence of C-H symmetric and asymmetric modes in Figure 5.4 (last graph).

We have studied the movement and behavior of two kinds of tracers, carboxyl and amidine terminated latex spheres, on gold surface modified using two kinds of self-assembled monolayers, carboxylic acid terminated thiol molecule and amine terminated SAMs.

![Fig. 5.5: Hi-resolution XPS scans of two regions showing the C 1s and S 2p binding energies. The units of the x-axis are binding energy in keV and y-axis is in arbitrary units of intensity. The two samples used are gold with solution deposited mercaptohexadecanoic acid and a gold sample with the same SAM treated in dilute hydrogen peroxide for 10 minutes. The similarity in peaks suggests that the SAM was not affected by the peroxide treatment.](image)
thiol molecule of comparable lengths. All observation was taken using a dilute solution of tracers and 0.5% hydrogen peroxide solution. The observations were taken 5-10 minutes after placing the tracer solution on the sample to allow bubble formation due to the catalytic activity to subside. The catalytic dots used were 50 μm in diameter with a spacing of 500 μm.

5.2.2.1 Gold surface modified using amine terminated SAMs

Gold surface modified using mercaptohexadeconoic acid, also referred to as –COOH surface, has a measured surface zeta potential of -60 mV at the pH of 5.5. In the presence of the self-generated electric field, the ions in the double layer of gold move inwards towards the silver edge. The ions drag along with them the surrounding water molecules and causes an inwards fluid flow towards the feature edge. The tracers present in the fluid are also swept along with the fluid and migrate towards the silver, radially, from all directions. The crossed arrows in Figure 5.6a show the direction of electroosmotic fluid velocity on a –COOH modified surface. The optical microscope image shown in Figure 5.6a was taken 5 minutes after placing a 0.5% solution of hydrogen peroxide containing carboxyl terminated tracers on the sample. The electroosmotic fluid flow is experienced by the particles even as far as 500 μm away from the silver edge.[15] As the tracers move closer to the silver they also experience an electrophoretic velocity. As the tracer particle is negatively charged this velocity is directed outwards, opposite to the fluid flow (illustrated by the dotted arrow in Figure 5.6a). At a certain distance from the edge the two velocities cancel each other and
the tracers come to rest. This tracers begin to accumulation at this distance to form a ring like structure as seen in Figure 5.6a. The ring diameter is measured to be ~114 μm. This is in agreement with the ring formation on a bare gold surface which also has a negative zeta potential.[16]

In case of the tracer having positive charge, like with the amidine spheres with +40 mV, both the electroosmotic fluid flow and electrophoretic velocity experienced by the particle are in the same direction, as illustrated by the crossed and dotted arrows in Figure 5.6b. In this case all the tracers rush in towards the silver and are observed to stick to the silver surface. However some of the tracers that rush towards the silver feature are also swept upwards with the fluid. The fluid is assumed to move inward and upward to maintain fluid continuity.[17] The attachment of the tracers to the silver could be the result of weak electrostatic attraction between the negatively charge silver surface (due to the oxide) and the positive tracer. With time the silver disc gets covered with the tracers as seen in Figure 5.6b, where the silver is black in color, because of the accumulation of the tracers. No ring formation is seen in this system in agreement with studies done on bare negative gold surface.
Fig. 5.6: Fig 5: Matrix showing effect of tracer zeta potential (columns) and surface zeta potential (rows) on tracer behavior. The silver disc is seen as a circle in the optical images and as the black block in the illustrations. Top figures a and b have –COOH terminated SAM (negative charged) on the gold hence electroosmosis is inwards. The carboxyl tracers form a ring and amidine rush in towards the silver. The bottom figures c and d have amine terminated SAM (positively charged) on the gold hence electroosmotic velocity is outwards. The carboxyl spheres are pushed away and amidine tracers form a ring.
5.2.2.2 Gold surface modified using amine terminated SAMs

Gold surface modified using 11-amine-undecanethiol SAM, also referred to as amine terminated gold surface or \( \text{–NH}_2 \) surface, have a positive zeta potential of +50 mV at pH of 5.5. The ions in the double layer of gold migrate away from the silver edge in response to the self-generated electric field. This causes the fluid near the surface to flow away from the silver edge as indicated by the crossed arrows in Figure 5.6c, d.

Figure 5.6c illustrates the case of a charged carboxyl placed on the \( \text{–NH}_2 \) surface. As the tracer is negative, the electrophoretic velocity experienced by it will be in the outward direction aligned to the electroosmotic fluid velocity. (Crossed and Dashed arrows face the same way). The optical image shows two distinct regions surrounding the silver disc. Region 1 immediately adjacent to the disc is depleted of tracers and region 2 extends beyond the depletion region and has a uniform distribution of tracers. The first region is formed because both the forces acting on the tracer are aligned outwards and act simultaneously to push the tracers outwards, forming a region of no tracers upto a distance of 200 \( \mu \text{m} \). This is almost the double the ring diameter of Figure 5.6a as both the velocities are aligned in the same direction and act simultaneously on the particle. Beyond this depletion region the tracers are distributed evenly and are either stationary or continue to move slowly outwards [18] because of the electroosmotic flow of fluid and fluid continuity requirements that cause the fluid to continue to flow. Two distinct features in this case are no ring (high density of sphere in a given region) formation and absence of fluid flow inwards.
When an amidine tracer solution is placed on a –NH$_2$ surface the positive charge results in an electrophoretic velocity inwards towards the silver edge. The electroosmotic and electrophoretic flow are now in the opposite direction. The tracer particle comes to rest and accumulates to form a ring at a point where both the velocities cancel each other. This is similar to Figure 5.6a though velocity directions have been reversed. Given the similar magnitude of surface charge of the –COOH and –NH$_2$ SAM it is not surprising that the rings formed in both cases are at approximately the same distance from the silver edge. However the main difference is the absence of inward tracer movement in the –NH$_2$ terminated sample as is seen clearly in the –COOH terminated sample. In the amine sample the ring forms immediately and not much of fluid and tracers movement is observed with time. In fact the tracers seem to settle to the surface and stick to it, perhaps due to the interaction of the SAM and the tracer surfactant. (Figure 5.6d)

5.2.2.3 Conclusions: micropumps

The difference in behavior of tracers when using –COOH and –NH$_2$ SAMs is mainly due to the reverse in the direction of the electroosmotic velocity brought about by the change in surface zeta potential of the gold surface. Tracers form a ring when the electroosmotic flow is opposite to the electrophoretic velocity. When the two velocities are aligned in the same direction the tracers do not form a ring but instead are pushed away or pushed towards the silver edge. The difference in behavior of tracers in the presence of opposing fluid flow and aligned fluid flow is clearly seen on comparing Figure 5.6a,d with Figure 5.6b,c. While the former two have a distinct region of high
density of tracers in solution such a ring of tracers is absent in the latter. Also the inward flow of fluid and tracers, present even at long distances from the silver edge, observed when using –COOH SAM (Figure 5.6a,b) is not observed in –NH₂ SAM. These observations demonstrate the reversed flow of fluid due to electroosmosis bought about by change in surface charge of the gold. Further control of the on and off states of the catalytic pumps can be achieved by SAMs whose properties can be altered or switched dynamically by external stimuli like electrical potential.[19] Also as the charge of the SAMs are pH dependent flow direction can be reversed by using a fuel solution with a pH that switches the surface charge.

In conclusion, control over the direction of pumping by the catalytic micropumps has been successfully achieved by tailoring the surface charge using self-assembled monolayers with different end-group functionality. The SAM was successfully patterned preferentially on the gold surface by protecting the silver with an inert LOR layer. The robustness of the SAM during the patterning of the inert LOR layer and to the catalytic fuel solution has also been demonstrated. Directing the fluid flow using zeta-potential engineering allows for direct in-built control over microscopic regions on a wafer-scale without any additional external device. This provides an effective way to control the direction of the catalytic pumps for applications such as microfluidic devices, sorting devices and biological devices.
5.3 Patterning SAMs for achieving spatial control of fluid flow

The catalytic micropump design tested in the previous section and shown in Figure 5.3 is not ideal for meaningful and controlled pumping of the fluid. No net displacement or transportation of material is achieved because of the isotropic and symmetric nature of the force created. The force causes the fluid to be pumped either towards or away from the silver disc, with the action being localized to within a few hundred microns of the silver. Some of the new design architectures being tested include: circular rings, semicircular rings, triangular channels, rectangular lines as shown in Figure 5.7. The aim of these structures is to pump fluid or tracer particles from position A to position B as indicated by the arrows. For example in the triangular feature the electrophoretic forces in between the two structures is assumed to be asymmetric along the x axis due to the slant in the feature edges. It was expected that tracers in-between the features would move outwards in the direction indicated by the arrows. Also for the rectangular lines fluid flow was expected either in the x or y direction because of the interplay of electroosmotic flows in-between the lines. However the tracers did not move as expected. In most of the cases the structures behaved as one unit forming a larger ring structure surrounding the entire structure and following its contours. The forces were not distinguishable in-between the lines and dots due to their close proximity.
Fig. 5.7: Optical images of the different geometries being tested. All features are made of silver on a gold surface. A dilute solution of tracers and hydrogen peroxide is placed on the feature. Directional asymmetric fluid movement is expected in the direction shown by the arrows.
Another way to move fluid in an asymmetric, unidirectional manner for meaningful pumping, that is being studied, is by combining the appropriate pump geometry with surface engineering methods that have been shown to provide directionality. As was demonstrated in the last section, end-group functionality of the SAM determines the direction of electroosmotic flow of the fluid. A carboxylic acid terminated SAM with a negative zeta potential causes the fluid to flow towards the silver disc. An amine terminated SAM with a positive zeta potential causes fluid movement away from the disc. The key to creating practical pumps for microfluidic applications lies in introducing directionality to the pumping action by tailoring the surface of the gold adjacent to the silver in an asymmetric manner. For example if different functionality SAMs were placed on either side of the silver structure then the catalytic forces produced can be made to be asymmetric and point in the same direction. This idea was tested by combining the design structure shown in Figure 5.7f with self-assembled monolayer patterning towards making pumps that function in the x or y direction.

SAMs having different end-groups were patterned on either side of the silver as illustrated by the green and orange sections in Figure 5.8 (see experimental section for patterning details). The silver feature was protected throughout the self-assembly process using LOR in a similar manner described in Section 5.2.1. The right hand side of the silver was patterned with amine terminated SAM and the left hand side was patterned with carboxylic acid terminated SAM. The expected movement of the fluid due to catalytic induced electroosmosis is shown by the green/blue arrows in Figure 5.8a. The orange section is the –COOH terminated SAM and here the fluid moves towards the silver as shown by orange arrows. The green section is the –NH2 SAM and the fluid is
pumped away from the silver as shown by the green arrow. Both the SAMs working together result in the fluid being pumped from the left to the right. (red arrow) The direction of pumping can be changed by switching the position of the SAMs as shown in Figure 5.8b.

Fig. 5.8: Directional pumping in the x-direction using catalytic power a) the pumping is from left to right b) switching the SAM causes movement from right to left
5.3.1 Experimental section: patterning SAMs using ebeam and photolithography

In literature, patterning of self-assembled monolayers has been carried out using various methods including microcontact printing [20] scanning probe microscopy techniques such as nanografting, nanoshaving and dip-pen lithography [21]. However these methods suffer from either low resolution or low throughput. Wafer-level patterning of binary SAM has been achieved by photo-patterning of the monolayers using a photomask with UV light of different wavelengths such as 220nm and 365nm [22] and 193nm.[23] The exposed SAM regions are oxidized by the UV light and easily displaced in solution to be replaced by a SAM with different functionality. Gas and liquid phase deposition of SAM into electron-beam lithography defined opening has been demonstrated in reference [24]. This lithography based method is advantageous as it combines high resolution patterning and placement capabilities of ebeam lithography and also offers chemical versatility in the kinds of SAMs that can be assembled.

Photolithography and electron beam lithography were combined to pattern and overlay the self-assembled monolayers around the silver lines as shown in Figure 5.8. The silver features were patterned on gold coated silicon wafer using standard lift-off methods. The lines are 0.5 mm long, 10-50 μm wide and 100 nm thick. After patterning, the metal lines are protected using LOR 2A as described in Section 5.2.1.

The patterning of the SAM was accomplished by using ebeam lithography to open areas in a layer of polymethyl methacrylate (PMMA) (MicroChem Corp.) an ebeam resist.[24] PMMA is used because it has development and removal chemistries orthogonal to LOR2A and hence can be used without interference with the protective
LOR layer. A layer of PMMA of molecular weight 950 K and 3% dilution in anisole is spun on at 5000 rpm for 40 s and then baked for 180 s at 180 °C. A rectangular pattern, aligned adjacent to the silver feature is exposed using electron beam lithography at 100 KeV and at a dose of 800 µC/cm². The resist is developed is a solution of methyl isobutyl ketone (MIBK) diluted in 2-proponol (IPA) in the ratio of 1:3 for 90 s and rinsed in a bath of IPA for 60 s. This causes the exposed parts of the resist to be removed and the gold underneath to be exposed. The width of the exposed pattern is equal to half the line spacing between the silver features. (Fig. 5.9)

Fig. 5.9: Fabrication steps involved in the patterning of the SAMs on the gold. a) The initial structure consists of silver lines patterned on a gold coated silicon wafer, and protected using a layer of LOR 2A. b) PMMA is spin coated, exposed and developed to open patches of gold adjacent to the silver feature. SAM 1 is assembled on these open areas. c) The PMMA is dissolved in acetone and SAM 2 is assembled in the corresponding gold areas exposed. d) LOR is removed by dissolution in CD26.
Now this sample is immersed in a bath of 0.1 mM SAM solution in ethanol for ~12 hours. The SAM is deposited in the exposed areas only. The sample is then rinsed in acetone to remove the PMMA and then immersed in a bath of the second kind of SAM. As both the SAMs are of comparable length and are similar in structure and property except for the end group, the first SAM is not displaced by the second solution. The second SAM is formed in the areas uncovered by removal of the PMMA resist. The LOR layer is removed by dissolution in CD26 for 5 minutes. The resultant structure consists of silver lines with the SAM 1 on the right hand side and SAM 2 on the left hand side. (Figure Fig. 5.9)

5.3.2 Results and discussion

Catalytic pumps were fabricated using the SAM patterning method described above. Amine terminated SAM was placed on the right hand side (RHS) of the silver and carboxylic acid terminated SAM was placed in the remaining areas. A 1 μL solution of tracers of 2 μm diameter polystyrene spheres, negatively charged, in a solution of 0.5% hydrogen peroxide was placed on these catalytic pumps. Images of the tracer patterns are shown in Figure 5.10. Flow of the tracers was seen to be along the y-axis of the structures contrary to the expected x-direction pumping shown in Figure 5.8a.
The tracers used were negatively charged carboxyl spheres. On the side of the amine SAM (RHS) both the velocities were directed outwards and the tracers pushed away from the silver line edge. For carboxylic acid SAM (LHS) both the velocities balanced and the tracers accumulated at a certain distance from the silver edge. Both these effects when combined gave a tracer pattern shown in Figure 5.10. Here the tracers accumulate to the LHS of the silver line and formed depletion zone on RHS. Though the tracers were swept by electroosmotic velocity the fluid from the left to the right side, nearer to the silver edge the tracer movement was governed by the more dominant electrophoretic velocity. So instead of flowing with the fluid they accumulated in

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**Fig. 5.10**: Optical image of 2 set of silver lines. The lines are 5 μm wide and 50 μm in length. The top row lines are spaced 20 μm apart and bottom row lines are spaced 30 μm apart. RHS of every silver line is patterned with NH$_2$ SAM. The rest of the gold is covered with COOH SAM. The asymmetric pattern formation seen is due to the effect of electroosmotic fluid flow and electrophoretic forces acting on the tracers are seen as the large depletion zone on the RHS.
between LHS of the line. The tracers are trapped in the middle of the two silver lines and are not able to flow in the x direction.

The interaction of opposing electrophoretic forces pushing against the tracers accumulated in between the lines cause the tracers to escape the region. While some of them move upwards into the solution, the rest are pushed along the surface in the y-direction. They move away from the silver edge using the shortest possible route either upwards or downwards as indicated by the arrows in Figure 5.10. The actual movement of the fluid is not visible due to the effect of charge of tracers. Use of neutral tracers or dyes will help observe the movement of the fluid.

By this experiment directionality attributed by the SAMs to the flow of fluid is demonstrated by the asymmetry in the tracer pattern formed in-between the lines. It indicates that both the electroosmotic and electrophoretic velocities are acting on the tracers though closer to the silver edge electrophoresis dominates. Better understanding of the force magnitude and distribution profile of the electrophoretic and electroosmotic forces will aid in design of functional catalytic pumps placed at optimum distances to balance the effect of tracer charge and surface charge. Also the design of pumps for charged particles will need to take into account the charge of the particle. Hence it can be concluded that catalytically induced fluid flow combined with surface engineering techniques has the potential to create micropumps operating without any external stimuli for channeless transportation of fluid and tracer particle.
5.4 Summary

Control over the direction of movement is the key to making practical devices using catalytically generated forces. Photolithography was used to fabricate novel gear-like structures with platinum patterned on their spokes. The position of the platinum and the bimetallic junction was designed to align the catalytic forces through the centre of the gear and cause it to rotate. Sustained and continuous rotation of the gears at speeds of 1 rotation/sec was achieved in a solution of 0.5% hydrogen peroxide. Surface engineering methods were employed to control the direction of electroosmotic fluid flow in the micropumps. Self-assembled monolayers with different end groups and hence different zeta potentials were patterned preferentially on the gold. A zeta-potential controlled fluid flow was established.
5.5 References


Chapter 6

Conclusion and future work

New methods for scaling down devices beyond the limits of photolithography and supplying them with self-generated self-directed power are two of the greatest challenges remaining for making nanotechnology a reality. This thesis explores the application of self-assembled monolayers in these two contexts; as a tool for improving resolution of existing lithography techniques towards building sub-50nm features and as a tool to tailor the surface zeta potential of surfaces to control the direction of fluid flow in catalytically powered devices. Also discussed in this work are various novel nano and micro fabrication techniques that push the limits and extend functionality of the available resist chemistries and lithography tools.

The first part of the thesis describes the molecular ruler lithography process using sacrificial host structures. Here the original molecular ruler process was modified so as to isolate the final structures by patterning a sacrificial resist underneath the parent metal. This helped improve the reproducibly of the lift-off by decoupling the functions performed by the molecular resist. Now the molecular resist was used only to scale down the gaps between the parent hosts while the sacrificial host structure aided in the preferential lift-off of the parent. The parent structures were fabricated using contact lithography, deep-UV stepper lithography and electron beam (ebeam) lithography. Isolated 40 nm wide metal lines were fabricated using this method. This result demonstrated the feasibility of a novel hybrid nanolithography process that combines the
conventional top-down tools and fabrication expertise with inexpensive chemical self-assembly techniques to improve the achievable resolution without need for any new instrumentation or investment.

As molecular resists increase in thickness in order to reduce features sizes, issues of contamination of the SAM solutions during deposition became prominent. The clumping of the rulers, visible after assembly of 7 or more layers, is considered to be one of the main reasons for the nanoscale roughness visible in the final scaled down feature. Also the longer times required to build thicker resists seemed impractical for any large scale application. Therefore various methods were developed for reducing line edge roughness, reducing number of process steps, shortening process time and improving overall manufacturability and reproducibility of the molecular resist deposition process.

Possible use of longer molecules such has dendrimers was thoroughly investigated and the appropriate precursors consisting of high molecular weight dendrimers identified. However the high costs of the raw material precluded the testing of this method. Next step was to try to replace the solution phase deposition of molecular resist with vapor phase molecular layer deposition. To this end, a rudimentary organic vapor phase deposition system was built in the lab. In this system the appropriate precursor was heated using heating filament and the corresponding vapors carried into a vacuum chamber using nitrogen as a carrier gas. Vapor phase deposition of SAMs and atomic layer deposition of copper has been examined separately in the past. The key to the success of this process was the deposition of copper on the carboxylic end group functionalized SAM. The attachment of copper to the SAM was tested by heating the precursor solid (copper bis(6,6,7,7,8,8,8-Heptafluoro-2,2-dimethyl-3,5-octanedionate))
onto a SAM covered substrate. IR analysis of the sample showed that the copper formed a metal-ligand like complex with the carboxylic end group of the SAM. This process was successful in forming the metal-SAM linkage. This was perhaps the first time atomic deposition of copper on a SAM via vapor phase was shown to be feasible. These results opened new avenues for further optimization of the molecular ruler process and possible testing of new molecules through use of vapor phase deposition. Also this route can be easily scaled-up for incorporation into mainstream manufacturing environment as opposed to solution deposition method.

During the design and development of the molecular ruler process using sacrificial host structures it was found that the non-photosensitive PMGI-based lift-off resist (LOR), traditionally used as a sacrificial layer in the bi-layer lift-off processes to pattern metals, can also be used to pattern SAMs. It was experimentally discovered that LOR remains robust and inert towards self-assembly processes and conditions. Also a combination of wet and dry etch chemistries was developed and perfected that ensured controlled undercut of ~50 nm for a thick (~10000 Å) LOR layer useful for making high aspect ratio features. Also the patterning of the sacrificial host features using electron beam entailed consecutive lift-off steps i.e. lift-off of metal needed to be carried out over a LOR layer. This was made possible by using ebeam resist pair of PMMA/MMA, as the two resists (PMMA/MMA and LOR) had orthogonal development and removal chemistries. This was perhaps the first time ebeam lithography was carried out over an underlying LOR layer. This process sequence has potential applications in designing photolithography and electron beam lithography defined structures with controlled overlay and spacing.
Some of the issues concerning the molecular ruler lithography using sacrificial multilayer resists process not addressed in this thesis include improving the roughness in the final feature because of the parents, ability to create high density isolated lines and methods for accurate overlay of the final features as needed in the semiconductor processing environment. Also the effect of diffusion of gold and copper into the underlying silicon was not examined. This is extremely important if the molecular ruler process is to be incorporated into semiconductor manufacturing as both gold and copper have detrimental effects on the electrical properties of silicon. Detailed exploration of application of the process towards making a 40 nm wide MOSFET and for making nanogaps for plasmon sensor is described in Chapter 2. However considerably more design and experiments need to be conducted to build an operational device. This thesis focuses on applying molecular ruler lithography using sacrificial hosts towards building scaled down isolated lines with improved reproducibility, high yield, reduced roughness and shortened process time.

The following were accomplished in the first section:

1. Development of the molecular ruler lithography process using sacrificial host structures which successfully address the issue of preferential removal of the parent structure and improves overall reproducibility of the lift-off process.[1]

2. Demonstrated compatibility of the modified process with contact lithography. [1]
3. Demonstrated compatibility of the modified process with electron beam lithography and successfully fabricated 40 nm wide metal lines from 100 nm spaced parent hosts.[2]

4. Demonstrated compatibility of the modified process using stepper lithography by incorporating the barrier layer.[3]

5. Developed the vapor phase molecular layer deposition method and showed preliminary results of vapor phase deposition of the copper linker over the SAM.[4]

Some of the application and future work identified in this section are

1. Use of the modified molecular ruler process to build MOS devices by employing the daughter metal feature as a mask to define the gate.[5]

2. Use of the molecular ruler process to control the gap between metal structures for application in plasmon sensors.

3. Use of modified molecular ruler process for building high aspect ratio features by use of a thicker sacrificial layer.[2]

4. Reducing the number of process steps required for ruler assembly via use of larger molecules such as dendrimers.[6]

The second half of the thesis demonstrates application of self-assembled monolayers to control direction of movement in catalytically powered nano and micro scale systems. Though this is a totally different area of research than that described so far, the knowledge and expertise of nanofabrication and self-assembly techniques gained from the first part of the thesis was carried over to this project. Designing methods for making smaller functional nanodevices is obviously difficult but another equally
important challenge is developing methods to supply these miniature devices with power. Catalytic motors are an attempt to design a new class of nano and micro engines that operate on self-generated catalytic power. Work done so far in this field has shown that objects with bimetallic junctions when placed in a solution of hydrogen peroxide cause catalytic decomposition of the peroxide to generate a gradient in solution. The gradient autonomously propels the objects and cause fluid flow on the surface of the objects. This work describes two schemes for achieving directional control of catalytically powered devices.

The first method uses conventional lithography techniques to pattern catalytically active bimetallic junctions on the spokes of a gear-like structure such that the forces produced were perpendicular to the spokes and caused rotational motion. This was the first step taken towards building functional and practical micro and nanoscale devices operated on catalytically generated power initially observed only in nanorods. The microgears were fabricated on a silicon substrate such that they could be released from the surface by dissolving the underlying silicon dioxide layer. The gears were suspended in a dilute solution of hydrogen peroxide and were shown to rotate in a dilute hydrogen peroxide solution at speeds of 400 μm/sec. The larger surface area of the metallic junctions resulted in a much higher speed of the gears than that seen in nanorods. The gear design demonstrated the ability to scale up the catalytically produced energy to power MEMS like systems.

Another set-up examined in this thesis is the microfabricated AFM force sensor for quantitative measurement of the surface forces produced along a nanorod-like system. AFM cantilevers were chosen for force sensing because they are readily available and are
known to be sensitive to piconewton range of forces. A gold/silver junction was fabricated using the lift-off method on the tip an AFM cantilever. The tip was submerged in a pool of hydrogen peroxide solution. Catalytic force was produced at the metal junction on the tip of the cantilever. The magnitude of force was calculated using change in cantilever resonance frequency. For hydrogen peroxide solution having concentration between 1-4% the force was seen to be between 0.5-2 pN. This was the first attempt made to experimentally determine the magnitude of the catalytic force produced by the catalytic motors as a function of hydrogen peroxide concentration. The microcantilever based force sensor though not very straightforward to build reproducibly, offers accuracy in measurement and flexibly to test different structures and different metals. One possible application of such an AFM force sensor for drug-delivery is also designed and discussed. Further process development to allow for easy and reproducible fabrication of the force sensor is needed.

The idea for the second scheme for achieving directional control of catalytically powered devices originated from the electrochemical model that describes the role of surface charge in catalytic pump systems. The knowledge of SAM patterning was extended to tailor the surface charge of gold employed in the catalytic pumps. This work is one of the first to introduce directionality in catalytic induced fluid flow.

Catalytic pumps are bimetallic junctions immobilized on the surface. When placed in a solution of hydrogen peroxide the metals cause disproportional decomposition of the peroxide resulting in a proton gradient generated electric field in the solution. The ions in the double layer of gold respond to this electric filed and cause electroosmotic fluid flow along the surface. Analysis of the electrochemical model shows that the
direction of electroosmotic fluid flow depends on the charge of the surface of the gold metal. This means that the fluid flow could be controlled by tailoring the surface charge. SAMs having different end-groups hence different surface charge were deposited on the sample. However it was experimentally found out that SAMs formed simultaneously on the silver features and gold surface. The SAMs on the silver inhibited catalytic activity. SAM formation on the silver metal was prevented by protecting the surface with a thin layer of LOR, which was known from previous experiments to be inert to SAM deposition conditions. Further detailed study using IR and XPS analysis of the SAM proved the robustness of the SAM to exposure to dilute hydrogen peroxide solution used as a fuel and also to the CD26 solution used to remove the protective LOR layer during processing. The easy removal of the LOR was facilitated by use of lower molecular weight PMGI resist to pattern very thin layers and by lowering the baking temperature of the LOR. Though intuitively SAM formation on gold should also inhibit catalytic activity, however this was not the case. Perhaps one reason was the structural differences of the SAMs formed on silver and gold. Looking into literature it can be surmised that SAMs changed the surface property of the silver metal to form a layer of silver sulfide on the surface. Also it is known that SAMs on gold were not as dense and have defects in the layer. Perhaps the catalytic activity occurring in the exposed gold portions were enough to sustain the gradient in solution. Detailed study on the mechanism of interaction and penetration of hydrogen peroxide solution through the SAM to the underlying gold is needed to understand the phenomena.

The LOR patterning steps ensured that the silver was protected during solution-phase deposition of SAMs on the gold surface and that the LOR was removed after SAM
formation. Two kinds of SAM were chosen such that they were oppositely charged, had similar magnitude of charge and had similar thickness. Carboxylic acid terminated 16 carbon chain SAM with charge of -60 mV and amine terminated 11 carbon chain SAM with +50 mV charge were employed. The flow of fluid on the surface of the gold occurred in opposite directions in the two cases. This was observed by analyzing the behavior of tracers in the solution. The inwards flow of fluid and tracers seen on a negatively charged bare gold or carboxylic acid SAM covered gold surface was clearly absent when using amine terminated SAM. This was the first time when outward movement of fluid was demonstrated. This analysis took into account the tracer charge and the corresponding influence of the electric field on the tracer velocity.

The concept of SAM enforced directionality was extended to build structures having fluid flow aligned in the same direction to achieve practical transportation of fluid and tracers. This was attempted by patterning SAMs asymmetrically about a silver line and thus breaking the symmetry of the flow. The patterning of the SAMs was successfully achieved by combining and overlaying photolithography and electron beam lithography features. This method combined the advantage of nanoscale accuracy of ebeam patterning techniques with the flexibility of chemical assembly techniques to deposit any kind of SAM. However these systems did not behave in the manner expected because of the influence of the tracer charge which cause the electrophoretic component to become more prominent near the silver features.

Extensive theoretical modeling of the forces and gradients created in the solution and experimental studies using various surface areas of the metals and various combination of metals is needed to better understand the distribution of the catalytic
forces along different length scales. For example answers to questions such as how far vertically into the solution does the electric field extend, how far horizontally along the gold surface does the fluid experience the electroosmotic surface current, is the electric field constant or does it depend on the distribution of ions, is the proton gradient linear, is the reaction limited by the silver surface area or the gold surface area etc will help design structures with the right dimensions and surface properties to enable uniform fluid flow on the surface. This work however clearly demonstrates that one possible way to introduce asymmetry and directionality into the catalytic pump system and to control the flow of fluid is by patterning of SAMs to tailor surface properties.

The following were achieved in the second section:

1. Fabricated micron sized gold gears with platinum patterned on the spokes using conventional lithography techniques. Demonstrated catalytically powered rotation of the gears in a solution of hydrogen peroxide.\[7\] \[8\]
2. Demonstrated control over direction of catalytically generated electroosmotic fluid flow by employing SAM based surface engineering.\[9\]
3. Studied the dependence of diameter of ring formed using carboxyl spheres on the diameter of the silver disc used and the concentration of hydrogen peroxide.
4. Fabricated catalytically driven fluid pumps by patterning different end-group SAMs adjacent to silver features.
5. Designed and fabricated a microcantilever based force sensor which is powered using catalytic reactions taking place on the tip. Measured catalytic
force produced at a gold/silver junction as a function of concentration of hydrogen peroxide employed.

Some of the application and future work identified in this section are

1. Design of catalytically powered pumps for channeless microfluidics.
2. Use of the force sensor as a glucose drug delivery device.

Overall this thesis examines possible areas for applications of SAMs when combined with existing lithography methods. It demonstrates that SAMs are robust entities that can be employed in non-conventional ways to build new devices and improve functionality of existing devices. All future work is motivated by the idea of using these novel processes and methods developed in this thesis to build practical devices such as the CMOS where the gate is defined using the molecular ruler process, plasmon sensors with nanoscale gaps defined my rulers, channeless pumps using SAM directed catalytic fluid flow and drug delivery devices using catalytic powered force sensors. Definitely SAMs hold the potential of making applications of nanotechnology more available and realizable in the near future.


6.1 References


Appendix

Non Technical Abstract

This thesis explores in detail two nanotechnology-related applications of self-assembled monolayers. Self-assembled monolayers (SAM) are a single layer of molecules formed spontaneously on a solid substrate when the substrate is exposed to liquid or vapor containing the molecules. The molecule is made of three parts. The head group that adsorbs onto the substrate, a backbone made of carbon atoms and an end group. All these parts can be tailored individually using synthetic chemistry.

SAMs are a few nanometers thick, they are easy and quick to deposit, and they are robust and uniform. These properties combined with the flexibility to easily tailor the end-groups of the SAMs, have made them technologically attractive as a tool to enable nanotechnology related applications. Broadly their usefulness can be viewed from two aspects. Firstly as a building block to construct larger molecular assemblies and secondly for modification of surface properties, such as wettability, etch resistance and electrical charge.

The first part of this thesis applies SAMs as a building block, specifically to build a molecular film. A process called molecular ruler lithography using sacrificial host structures is developed. Scaling down features to below 50 nm is becoming increasing difficult, and available photolithography based technologies are being stretched to their limits. Molecular ruler lithography using sacrificial hosts is a hybrid nanolithography process that combines conventionally available lithography tools with a chemical assembly based processes to improve resolution. This is accomplished by
patterning functional host structures whose dimensions can be tailored by systematically assembling engineered organic molecules of precise length (SAMs) on their surface, creating a template for producing features with reduced dimensions. This thesis develops engineering solutions to improve reproducibility and yield, reducing roughness, reducing process steps and time and thus improving overall manufacturability of this method. Application of this method to build sub-50 nm channel width CMOS devices and plasmon sensors are also introduced.

The second half of the thesis applies SAMs to tailor surface properties of metal substrates, specifically the surface charge or zeta potential. Previous work has shown that catalytic reactions taking place on surface of metal junctions, for example silver and gold, placed in a solution of hydrogen peroxide can be used to convert chemical energy to mechanical energy. Such in-situ power generation methods are useful for powering nanoscale machinery, which are difficult to operate using external mechanisms. These chemical motors produce catalytic forces which cause surface confined fluid flow in the vicinity of the metal junctions. Thus a microscale fluid pump is realized which operates on catalytic power. The direction of movement of the fluid depends on the charge on the surface of the metals. SAMs have been employed to alter the surface charge of the metals to control direction of fluid flow. Using metals surfaces covered with SAMs having positive charged end-groups causes the fluid to flow radially inwards towards the metal junctions and using SAMS with negatively charged end-groups causes the fluid to flow radially outwards. Possible application to catalytically powered channeless micropumps is demonstrated. Also described in this thesis are
methods for building of a force sensor that detects and measures the catalytic forces and designing catalytically powered gears that rotate in solution of hydrogen peroxide.

Overall this thesis examines applications of SAMs in nanolithography and for control of direction of catalytically produced fluid flow. The work demonstrates that SAMs are robust entities that can be employed in non-conventional ways to build new devices and improve functionality of existing devices and thus SAMs have the potential of making applications of nanotechnology more available and realizable in the near future.
VITA

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Shyamala Subramanian was born in the small town of Coonoor, Tamil Nadu, India on July 9, 1980. She graduated from Little Flower School, Jamshedpur, India in 1998 after which she enrolled in the Metallurgical Engineering program at Indian Institute of Technology at Madras. She received her Bachelor of Technology degree in May of 2002. Next, Shyamala started her graduate studies at the Department of Engineering Science and Mechanics at Pennsylvania State University in August of 2002, working under the guidance of Dr. Jeffrey Catchmark. She has held a research assistantship position from 2002-2007. Her current research interests are in the area of micro and nanotechnology related to chemical assembly methods, semiconductor device fabrication and MEMS.