Chemical Templating by AFM Tip-Directed Nano-Electrochemical Patterning

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Chemical Templating by AFM Tip-directed Nano-electrochemical Patterning

Kyle A. Nelson

A dissertation submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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December 2011

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ABSTRACT

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This work has examines the creation and use of chemical templates for nanocircuit and other nanodevice fabrication. Chemical templating can be useful in attachment, orientation and wiring of molecularly templated circuits. DNA origami provides a suitable method for creating molecularly templated circuits as DNA can be folded into complex shapes and functionalized with active circuit elements, such as semiconducting nanomaterials. Surface attachment of DNA origami structures can be accomplished by hybridization of dangling single-stranded DNA (ssDNA) on the origami structures with complementary surface-bound strands. Chemical templating provides a pathway for placing the patterned surface-bound attachment points needed for surface alignment of the molecular templates. Chemical templates can also be used to connect circuit elements on the surface by selectively metallizing the templates to form local wiring. AFM tip-directed nano-oxidation was selected as the method for patterning to create chemical templates. This project demonstrates new techniques for creating, continuous metallization of, and DNA attachment to nanochemical templates.

Selective-continuous metallization of nanochemical templates is needed for wiring of circuit templates. To improve the metallization density and enable the continuous nano-scale metallization of amine-coated surfaces, the treatment of amine-coated surfaces with a plating additive prior to metallization was studied. The additive treatment resulted in a 73% increase in seed material, enabling continuous nano-scale metallization. A new method was developed to create amine nanotemplates by selective attachment of a polymer to surface oxide patterns created by nano-oxidation. The treatment of the templates with the additive enabled a five-fold reduction in feasible width for continuous metallization. Nano-oxidation was also used in the nanometer-scale patterning of a thiol-coated surface. Metallization of the background thiols but not the oxidized patterns resulted in a metal film that was a negative of the patterns. The resulting metal film may be useful for nanometer-scale pattern transfer.

DNA-coated gold nanoparticles (AuNPs) were selectively attached to amine templates by an ionic interaction between the template and ssDNA attached to the particles. Only the ssDNA on the bottom of the AuNPs interacted with the template, leaving the top strands free to bind with complementary ssDNA. Attempts to attach origami structures to these particles were only marginally successful, and may have been hindered by the presence of complementary ssDNA in solution but not attached to the origami, or the by the low density of DNA-AuNPs attached to the templates. The formation of patterned binding sites by direct, covalent attachment of ssDNA to chemical templates was also explored. Initial results indicated that ssDNA was chemically bound to the templates and able to selectively bind to complementary strands; however, the observed attachment density was low and further optimization is required. Methods such as these are needed to enable nano-scale, site-specific alignment of nanomaterials.

Keywords: AFM tip-directed nano-oxidation, silane layers on silicon oxide, PAAm, palladium seeding, metallization additive, MPS, DNA origami
ACKNOWLEDGMENTS

I thank Dr. Harb, Dr. Wheeler, Dr. Davis, and other professors of the ASCENT group who provided constructive feedback and help with this project. I would also like to thank Dr. Solen and Dr. Hedengren for their timely editing of this dissertation. Support from the National Science Foundation (CBET-0708347) is also gratefully acknowledged.

I also want to thank my wife. Her constant support during the necessary long hours and help editing made possible the timely completion of this work.
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1 INTRODUCTION

1.1 Purpose

The ability to control the placement and orientation of nanometer-scale objects on a surface would enhance our ability to understand and use such objects, while providing a pathway for practical application. Directed surface alignment of nanometer-scale objects can be accomplished by surface patterning of chemical groups that bond specifically with those materials. Chemical patterns designed for specific attachment of nanomaterials to a surface will be referred to as chemical templates. While directed surface alignment of nanomaterials is the application of chemical templating with a high impact, applications of chemical templating include (but are not limited to) selective surface alignment of metals, semiconductors, or biological materials. Controlled positioning and alignment of these materials is useful in applications such as surface wire, transistor, and sensor fabrication. These materials can be combined for nanometer-scale transistor and circuit fabrication. Development of nanometer-scale chemical templating and its applications for nanocircuit fabrication are the focus of this work.

1.2 Justification

Figure 1.1 displays how nanomaterials could be used in circuit fabrication. An object designed to make use of molecular attachment to assemble circuit elements (a molecularly templated circuit) will have to be positioned and oriented correctly on a surface by chemical templating of functional groups that can attach to the molecularly templated circuit objects (see
Figure 1.1A and 1.1C). Direct wiring may also be accomplished by chemical templating of functional groups that can be selectively metallized (see Figure 1.1B and 1.1D).

Figure 1.1: Diagram of nanocircuit fabrication by chemical templating.

One nanometer-scale material that may be useful for surface attachment, alignment, and use as a circuit template is DNA. Metallization [1] of DNA and attachment of semiconducting nano-objects [2, 3] (to be used as circuit active elements) to DNA, in conjunction with the ability to form DNA nanostructures with complex shapes, make it a useful material for forming molecularly templated circuits. DNA strands have a unique ability to bond other DNA strands because of base pairing. Thus, DNA sequences can be designed for highly selective attachment to other DNA strands, forming programmable shapes for circuit templates. This would fill the need for a circuit template as illustrated in Figure 1.1A, while providing a pathway for
attachment and orientation of the circuit templates (as shown in Figure 1.1C). Dangling single strands on the circuit template could pair with the complementary single strands attached to the surface. Directed surface alignment of these DNA nanostructures would require attachment to the surface at multiple points, making orientation possible. Development of chemical templating methods will provide a pathway for surface patterning of chemical functionalities, leading to attachment and orientation of DNA nanostructures to surfaces.

Chemical templating will also be necessary for local wiring of the molecularly templated circuit (see Figure 1.1D). Direct wiring may be accomplished by selective metallization of chemical templates. This will require development of solution based surface metallization procedure to deposit continuous metal features on surfaces compatible with the previously mentioned DNA processes. New methods of chemical templating are developed to selectively position the chemical functionalities necessary for selective metallization. As amines and thiols are useful in the metallization of nonconductive surfaces, they are utilized in template chemistry for metallization. Development of procedures for metallization of amine- and thiol-coated surfaces will aid in creating continuous metal deposits on nanometer-scale amine and thiol based chemical templates.

1.3 Scope

Directed attachment and orientation of DNA nanostructures and nanowire patterning by chemical templating are methods of nanocircuit fabrication that are explored in this work. The following questions are answered. What factors control immobilization of DNA to multiple surface points, and how do they affect orientation? What are the mechanisms controlling metallization of chemical templates on the nanometer scale, and how can this knowledge be used
to create nanometer-scale wires? DNA nanostructures for this work are designed and produced with the help of collaborators in the Brigham Young University Department of Chemistry and Biochemistry. Development of chemical templating will lead to direct attachment and orientation of DNA nanostructures while providing a pathway for local wiring of these DNA-based molecular circuits.

The following tools and methods are used in this study in creating, imaging, and analyzing surfaces for chemical templating. Silicon oxide surface are coated with organosilanes of various function groups by liquid and vapor phase deposition. Metallization of surfaces and templates utilizes solution-based electroless metal deposition techniques. AFM (atomic force microscopy) is utilized as a tool for patterning to create and image nanometer-scale chemical templates. XPS (x-ray photoelectron spectroscopy) is used to analyze organosilane modified silicon oxide surfaces and subsequent treatments of those surfaces to determine their effects in the metallization of nanometer-scale chemical templates. SEM (scanning electron microscopy) is used to image and determine the results of the metallization of templated surfaces.

1.4 Outline

The remainder of this document is organized as follows.

*Background.* Chapter 2 is a brief survey of the literature with description of methods for surface functionalization, metallization, DNA attachment, and AFM-based surface patterning necessary for chemical templating. Advancement of current and the development of new techniques will lead to directed attachment of DNA and continuous nanometer-scale metal deposits on chemical templates.
Increased Metallization of Amine-coated Surfaces by MPS Treatment. Chapter 3 discusses the mechanism for and describes the role of MPS (mercaptopropylsulfonate) treatment in the increased metallization of palladium-seeded amine-coated surfaces. MPS treatment of amine-coated surfaces is found to increase the quantity of palladium seeding, leading to significantly increased subsequent copper metallization of the surface.

Nanometer-Scale Amine Templates by Polymer Attachment to Surface Pattern Created with AFM Tip-directed Nano-oxidation. Chapter 4 presents a new method of chemical templating of amines by the attachment of an amine functionalized polymer to oxide surface patterns created by AFM tip-directed nano-oxidation. The amine templates were used to demonstrate the increased metallization effects of MPS on nanometer-scale chemical templates. MPS treatment of amine templates reduced the practical feature width of continuous copper metallization from 500 nanometers to 80 nanometers.

Negative Patterning of a NiB film by AFM Tip-Directed Nano-oxidation of a Mercaptoproyl Silane Monolayer. Chapter 5 presents a new method for negative patterning of a NiB (Nickel-Boron) metal film with potential applications in parallel patterning. AFM tip-directed nano-oxidation of a thiol-coated surface with subsequent NiB metallization allows for patterning of the metal film with nanometer-scale resolution.

DNA Attachment to Surface Patterns Created by AFM Tip-directed Nano-oxidation. Chapter 6 presents methods developed for attachment of DNA to chemical templates and align DNA origami to surface pattern created with AFM tip-directed nano-oxidation. Definition of major roadblocks for the research lays the foundation for future work.
Conclusion. Chapter 7 presents the conclusions drawn from this work as well as direction for future work in the attachment and alignment of DNA origami to chemical templates.
2 BACKGROUND

2.1 Chemical Templating

A chemical template is a pattern created with localized chemistry on a surface. Unlike a stencil or overlay, a chemical template exploits local surface chemistry instead of a mechanical guide as its key patterning mechanism. Several methods of chemical templating have been demonstrated.

Surface patterning methods are generally divided into two categories, parallel and serial. Parallel methods modify a 2-dimensional area, while serial methods pattern line by line. Serial methods are considered slow and are usually more expensive than parallel methods. Examples of nanometer and micrometer scale chemical templating in parallel include photo patterning of silane monolayers [4-7] and micro-contact printing [8-10]. Serial methods of chemical templating have been demonstrated by applications of atomic force microscopy (AFM) [11-16] and electron-beam lithography [17-19]. AFM-based patterning methods were chosen for this study because they provide specific advantages in research applications. AFM-based patterning methods have been demonstrated at resolutions below 10 nm. Also, some AFM-based patterning methods have the potential for development as parallel patterning processes [20-24], and the use of AFM methods allows for nondestructive imaging of surfaces before and after patterning. An explanation of atomic force microscopy and a thorough examination of demonstrated AFM patterning techniques (on silicon oxide) are given later in Section 2.3. First background
information on silicon oxide surface properties and the modification of those properties is provided. A review of DNA attachment to and metallization of silicon oxide surfaces is also included as a foundation for the present work.

2.2 Surface Preparation and Characterization

For successful chemical templating, a surface is needed that will be modified locally by a patterning method of choice. If, for example, one wanted to use photo patterning, then a surface or surface chemistries that were reactive to light would be needed. Thus, surface modifications are designed to work with the desired patterning method. For circuit fabrication to be useful it must be demonstrated on or transferable to a potentially insulating substrate. Silicon oxide substrates provide a suitable surface for demonstration of chemical templating.

2.2.1 Silicon Oxide

Silicon oxide is widely known as an excellent insulator and dielectric material, and as the oxide becomes very thin it becomes susceptible to tunneling. An oxide any thicker than 5 nm would prevent substantial tunneling and provide a suitable surface for demonstration of chemical templating for circuit fabrication [25]. When silicon oxide is grown on silicon, divalent oxygen atoms readily find silicon atoms to bind with because there is little over-constraint, and uncompensated oxygen bonds are hydrogen terminated [26]. It stands to reason that the highest concentration of uncompensated oxygen bonds would be on the oxide surface. Surface silanols (Si-O-H groups) are acidic in neutral aqueous solutions [27], giving the surface a negative charge. The Si-O-H surface groups also allow for surface modification using organo silane molecules (silanes). While some patterning techniques require tunneling of electrons through the
oxide, complex processing of SOI (silicon on insulator, a substrate with a thin layer of semiconducting silicon on top of silicon oxide) provides a potential pathway to isolate nanocircuit features or convert the thin silicon layer to insulating oxide after nanocircuit fabrication.

2.2.2 Modification of Silicon Oxide

Because of the free hydroxyl groups on a silicon oxide surface, certain silanes are able to covalently bond to the surface via a Si-O-Si bond. Figure 2.1 displays how chlorosilanes and alkoxy silanes bond with silicon oxide surfaces. Silanes are available with a variety of different functionalities, and have been used for electrostatic [7, 28, 29] and covalent [30-33] surface attachment of single-stranded DNA (ssDNA) to silicon oxide. Surface functionalization with silanes are also used for metallization of silicon oxide [4, 6, 34-43]. Silane monolayers are often referred to as self assembled monolayers (SAMs) because given sufficient reaction time and conditions most silanes will form a complete monolayer on a silicon oxide surface.

![Figure 2.1: Reaction of a trimethoxy silane and a trichloro silane with a silicon oxide surface.](image-url)
2.2.3 Attachment of DNA to Silicon Oxide

One application of chemical templating to consider for nanocircuit fabrication is directed surface alignment of DNA nanostructures. There are two major reasons DNA is useful as a molecular circuit template. First is the capability for selective attachment of semiconducting nanomaterials (that could be used as circuit active elements) [2, 3]. Second, DNA can be used as a metallization template [1, 44-49]. Before these techniques can be applied for nanocircuit fabrication, surface attachment and orientation of DNA nanostructures has to be developed.

Attachment of DNA to silicon oxide has been accomplished by modifying SiO₂ surfaces with silanes. One silane that has been widely studied and used to functionalize silicon oxide surfaces with amine groups for electrostatic DNA attachment is APTES (3-aminopropyl triethoxy silane) [7, 28, 29]. The protonated surface amine groups are positively charged and attract the negatively charged DNA backbone (see Figure 2.2). Another method that exploits an electrostatic interaction for DNA attachment to silicon oxide is a magnesium bridge, where MgCl₂ aids attachment of DNA to silicon oxide[17, 18]. While electrostatic interactions have yielded positive results for DNA surface attachment, metallization of DNA templates also exploits charge interactions. With the metallization solution interacting with both the DNA and the surface, the link between the surface and the DNA may be weakened or shielded completely and specific positioning would be lost.
Covalent attachment of DNA strands to SiO$_2$ surfaces (DNA immobilization) has been demonstrated by bonding silanes and DNA strands (were each has a specific chemistry designed to bond with the other) [30-33]. Figure 2.3 is a chart of several methods that have been developed for immobilization of DNA on silicon oxide. The attachment of complementary strands to these surface bound single strands is called DNA hybridization [51, 52]. Another well known and reliable reaction that could be used to bond a DNA sequence to a silicon oxide surface is alkene-thiol click chemistry (see Figure 2.4). With the alkene bound to the surface the thiolated oligomer may be attached by photo initiation[53]. Aqueous attachment of aminated
DNA strands to surface bound carbocyclic acids provides another pathway for immobilization (see Figure 2.5) [54].

Figure 2.3: Demonstrated methods of covalent immobilization on silicon oxide of DNA using silanes (adapted from reference [31]).

Figure 2.4: Alkene thiol click chemistry (adapted from reference [53]).
DNA nanostructures called DNA origami can be designed with specific sticky ends for surface attachment. The formation of DNA origami is accomplished by taking a long single strand of DNA, called the scaffold strand, and adding several shorter staple strands to fold the scaffold strand into a designed shape. Figure 2.6 is a diagram of the concept. The long grey strand is the scaffold and the colored strands are the staple strands [55]. Using this technique, DNA can be used to form a wide variety of shapes. Some of the staple strands (such as the orange strand at the top of the design in Figure 2.6) may be designed with more bases than necessary at one end of the sequence. When the origami is formed these strands will extend beyond the designed shape. These dangling strands create sites for surface attachment, as the extended portion of the staple strand will be free to base pair with a surface bound complementary strand.
Figure 2.6: DNA origami concept, with a scaffold strand (the long blue strand) folded into a specified shape (in this case a rectangle) by staple strands (colored) (designed using cadnanoSQ).

Selective attachment of DNA origami structures to surfaces has been demonstrated by a few different methods. The first was on gold pads created by electron beam lithography. The gold pads were functionalized with 11-mercaptoundecanoic acid with the thiol end attaching to the gold. The acid functionality was used for origami attachment with the MgCl\(_2\) method described previously [19]. Also, small DNA origami “rafts” were selectively deposited on silicon oxide surfaces patterned with APTES [28]. Selective positioning and orientation of origami triangles has been demonstrated by electron-beam lithography of diamond like carbon (DLC) covered silicon oxide. The DLC surface prevents DNA deposition, and electron-beam lithography is used to pattern the surface in triangular shape revealing the oxide below. Again MgCl\(_2\) is used to attach the DNA to the patterns [18]. Also gold nanoparticles were attached to the vertices of the triangles to create nanoparticle arrays [17]. Each of these methods exploits an ionic interaction for attachment of DNA to patterned surface. Ionic interactions may not provide suitable surface attachment for using origami as the molecularly templates circuit because subsequent procedures would require solution based metallization, exposing the surface to highly ionic solutions and possibly allow the origami to shift or come off of the surface. Two studies
have demonstrated attachment of DNA nanostructures to gold features on silicon oxide. The first used a DNA structure with thiol groups at either end to suspend the structure between gold pads created by ebeam lithography [56]. The other presented attachment of thiolated DNA strands to an array of gold dot3 on a surface and suspended an origami structure with a dangling strand between the gold dots by hybridization of the dangling single strands with the thiolated strands [57]. This kind of approach with chemical attachment of DNA to a surface may prove to have advantages over ionic surface attachment of DNA nanostructures when treated with the aforementioned metallization solutions.

2.2.4 Metallization of Silicon Oxide

Selective attachment and orientation of DNA origami as molecular circuit templates must be complemented by a local wiring method for circuit fabrication. Local wiring of molecular templates may be accomplished by selective metallization of chemical templates. One way metallization of insulating substrates is accomplished is by templating of the seeding precursor, depositing a seed layer, and subsequently depositing metal by electroless plating. Metallization of chemical templates will provide a pathway for local wiring to connect the molecularly templated circuits.

2.2.4.1 Seeding of Insulating Surfaces

Seeding is the process by which a metal that will catalyze further metal deposition is initially placed on a nonmetallic surface. Seeding does not generally provide a conductive coating, but serves as a layer of initiation sights for subsequent metal deposition. The metal used to seed the surface is matched with a surface chemistry that will aid adsorption of that metal to
the surface. In chemical templating for wire patterning it is necessary for the template to aid seed adsorption while the background has no affinity for the seeds; creating the contrast of high seed density on a template, but very low seed density everywhere else on the surface. APTES has been used extensively to support palladium seed deposition [42, 43, 58]. This seeding approach has been studied and used frequently by researchers at the NRL, and they have demonstrated that the bond energy between amines and metallic palladium is weaker than covalent bonds and stronger than coulombic interactions. It is also noted that in acidic aqueous seeding solutions palladium exists as PdCl$_4^{2-}$, which would have a coulombic attraction to the protonated surface amines [4, 37, 38, 40, 59], but ultimately the Pd ion sheds its chlorine groups and chelates with the amines unpaired electrons [60]. Palladium is an excellent seed material because most metals can be electrolessly deposited on a palladium seed layer [61].

Recent work has also shown the advantages of using MPTES (3-Mercaptopropyltriethoxysilane) or AEPTMS (3-[2-(2-Aminoethylamino)ethylamino]propyltrimethoxysilane) monolayers as a surface for Pd seeding, to yield smaller seed size and greater seed density relative to APTES monolayers [43]. While seeding on APTES itself may not provide the necessary seed density, using AEPTMS or MPTES (see Figure 2.7) may help provide seeding dense enough to support nanometer-scale metal deposition.
2.2.4.2 Electroless Plating

Electroless plating is a simple method of metal deposition in which an external power supply is not required, making it ideal for metallization of isolated features on nonmetallic surfaces. Autocatalytic plating is a subset of electroless plating where metal ions are complexed in solution and a chemical reducing agent is employed to reduce metal ions. A metal (either surface or seed) is required to catalyze the reduction of metal ions from solution. As displayed in Figure 2.8, the reducing agent is oxidized at the metals surface, and electrons are transferred to reduce the metal ions. With the reduction from an ionic to a metallic state, metal is added to the
surface deposit. The metal deposited from the solution also catalyzes the reaction so that it can continue as long as there is a source of the required reactants [62]. This makes the seeding portion of the process previously mentioned very important as the seeds must support the necessary redox reactions and be large enough to allow nucleation of the metal from solution.

![Figure 2.8: Autocatalytic plating concept.](image)

### 2.2.4.3 Additive Effects

Additives are chemicals that can change the behavior of the plating solution. Additives are used to accelerate, smooth, and otherwise affect the metal plating. MPS (3-mercaptopropyl-1-sulfunonic acid) is an additive commonly used in copper electroplating, and has recently been studied along with PDS (1,3-propanedisulfonic acid) and PDT (1,3-propanedithiol) to determine the role of sulfonates and thiols in acceleration and inhibition of electroplating rates (Figure 2.9) [63].

Bird [64] discussed in his thesis the use of MPS and PDS as surface treatments to increase the plating density of an APTES treated silicon oxide surface. MPS treatment of APTES layers
before palladium seeding and PDS treatment after palladium seeding lead to much higher electroless palladium plating density when compared to seeded APTES layers that were not treated with an additive. In the case of metallization after MPS pre-seeding treatment and palladium post-seeding treatment, seeds were more uniformly dispersed on the surface with a smaller distribution of particle size compared to metallization of untreated surfaces. While the effects of using these surface treatments were noted, the mechanisms were not explored and plating of patterned surfaces was not attempted. Understanding the mechanism for these processes will help determine if and how the effect of additive treatments will be useful in enhancing the metallization of nanometer scale chemical templates to decrease the possible line width of continuous metallization. Understanding how these additive treatments affect the metallization processes will help in creating smaller wires by chemical templating.

Figure 2.9: Molecular diagrams of 3-mercaptopropyl-1-propylsulfonic acid sodium salt (MPS), and 1,3-propane disulfonic acid sodium salt (PDS).
2.3 AFM (Atomic Force Microscopy)

Having discussed surface attachment of DNA and surface metallization, an explanation of the basic concept of atomic force microscopy (AFM) is still needed before discussing AFM patterning methods. AFM is a probe microscopy technique where a surface may be imaged for topographical or chemical changes. Figure 2.10 displays the basic idea behind AFM. Data are obtained by the reflection of a laser from a cantilever to a detector that can measure the deflection or amplitude of oscillation of the cantilever. As AFM is a scanning method, the tip is swept back and forth over the surface, taking data at specified intervals. The lateral resolution of AFM imaging (i.e. parallel to the surface) is limited by the radius of curvature of the probe or tip. Generally, AFM tips have a radius of curvature around 5-15 nm, which depends on the materials they are made of and the production methods. It is important to understand and keep this in mind while creating or imaging nanometer-scale features [65]. Also of note, is that AFM imaging may be performed with the AFM tip submerged in liquid.

Two major types of AFM imaging are generally employed; tapping mode and contact mode, although other types continue to be developed and gain popularity. For contact mode the tip is brought to the surface and the deflection of the laser on the position sensitive detector is maintained at a constant deflection voltage and a topographical image is generated from the vertical adjustment of the instrument’s response to the changing deflection voltage. In tapping mode the tip is stimulated to vibrate at the cantilever’s resonance frequency and as the tip approaches the surface (within a few nanometers) the resonance frequency is affected by the interaction of the tip with the surface. The microscope maintains a constant amplitude of
oscillation by adjusting the distance of the tip from the surface, creating a topographical map in the process. While vertical resolution is only limited by noise and calibration when using either the tapping or contact modes, horizontal resolution becomes increasingly skewed as the size of features being imaged approaches the size of the AFM tip. Imaging a 10nm particle with a tip having a radius of curvature at 10 nm will add 5 nm to either side of the particle (see Figure 2.11). Also, imaging a hole on this same scale would result in a feature that looks like an inverted cone, not providing any indication of the true depth or shape of the hole. This information is important to keep in mind when imaging and analyzing nanometer-scale features. Several methods have been developed to exploit the capabilities of AFM for nanometer-scale patterning, as discussed in the next section.
2.4 Application of AFM in Chemical Templating

Because AFM tips have a radius of curvature in the 5-15 nm range, they can be used to not only probe a surface, but also to manipulate a surface. The three main types of AFM patterning that have been used to manipulate SiO₂ surfaces with the capability to create sub 50 nm patterns are dip-pen nanolithography, local tip-directed nano-oxidation, and nanoshaving/nanografting. The development and current state of each technique will be treated in turn. While each of these techniques has been developed for conducting and semiconducting substrates, the discussion will be limited to patterning on silicon oxide.

![AFM scanning profile of tip-scale surface features](adapted from reference [66]).

2.4.1 Dip-pen Nanolithography

In dip-pen nanolithography (DPN) an AFM tip is dipped in a chemical that is to be patterned onto a surface. One key to making DPN work is the formation of a water meniscus that connects the AFM tip to the substrate. The chemical in which the tip was dipped is shuttled down the tip and onto the surface via the meniscus. In this way the desired chemical is patterned only in the regions where the tip has passed. Patterning has been performed in both tapping and contact AFM modes. Figure 2.12 is a diagram of the concept. Usually a chemical interaction
between the patterning molecule and the surface is employed to keep the patterned molecules in patterned regions. The first work of DPN was that of Piner et al. using a thiol on a gold substrate. A line width of 30 nm was demonstrated [67]. In a theoretical study J. Jang et al. reported that the meniscus forms because of capillary condensation, and its size is relative to the sharpness of the AFM tip with a theoretical minimum width of 1.9 nm for an atomically sharp tip. As normal tips have a radius of curvature ranging from 10 to 25 nm, a 30 nm pattern is very close to the smallest possible line width that can be demonstrated by DPN [68].

![Figure 2.12: Dip-pen nanolithography concept (adapted from reference [11]).](image)

One of the major advantages of DPN is direct writing. The surface is only exposed to the patterning chemical in the regions of intentional templating. It is, however, limited in possible resolution. The resolution of DPN patterning is limited to the diameter of the water meniscus formed between the tip and the surface; clean silicon oxide wets completely, increasing the range
of the meniscus to deposit the templating material. A surface molecule binding interaction, either ionic or covalent, is also required so that spreading of the templating molecules is limited. Two papers recently reported the use of DPN on silicon oxide. The first is the direct writing of a protein on silicon oxide. Protein arrays were successfully patterned with a minimum feature size of 55 nm [69]. The protein arrays use charge interaction for maintained surface localization. The second is the patterning of an organosilane on silicon oxide for selective nanoparticle deposition. The covalent Si-O-Si bond of organosilanes with silicon oxide requires time or heat to form, allowing the silane to spread after patterning. While the minimum feature size demonstrated was 60nm, the lower limit for patterning silanes on silicon oxide can be estimated from the data given to be between 35 and 45 nm [70]. DPN also requires AFM tip speeds that are an order of magnitude slower than other AFM patterning methods. The limited resolution for patterning silicon oxide surfaces highlights the difficulty of using DPN as a method for patterning sub 25 nm features on silicon oxide.

### 2.4.2 AFM Tip-Directed Nano-oxidation and Nano-reduction

In nano-oxidation and reduction, a conductive AFM tip is used and a voltage difference is applied between the tip and the substrate. The tip is used to direct an electric field to a very small area on the surface. AFM nano-oxidation has been shown to modify silane monolayers. Sagiv’s group demonstrated use of nano-oxidation to pattern an NTS (18-nonadecenyltricloro-silane) monolayer on a native oxide silicon surface [16]. In that study, the terminal alkene was converted by electro-oxidation to a carboxylic acid which was then used to direct surface deposition of a second silane layer. Nanopatterning was demonstrated with a 9 nm feature width. In subsequent studies Sagiv’s group also demonstrated selective reduction of silver ions on a
thiolalkysilane monolayer [71] and selective deposition of gold nanoparticles via nano-oxidation of a nonodecylsilane monolayer [72]. The mechanism for monolayer oxidation is similar to the mechanism presented for selective oxidation of silicon. This can be explained through electrochemical oxidation of water molecules at the AFM tip that are then transported through a meniscus created by field induced condensation [73]. The final metallized pattern was preceded by complex procedures for organic modification of a silane bilayer deposited on the patterns. One other limit of this technique is oxide thickness; the mechanism requires tunneling of electrons through the oxide. In the formation of SiO₂ features when oxidizing a silicon surface, it has been demonstrated that features of only 7nm can be created at a potential of -10V (tip potential relative to a grounded substrate) [73]. Complete oxidation of an alkyl monolayer to produce a clean silicon oxide formation [74] has also been demonstrated with application of ionic DNA attachment [15].

AFM tip-directed nano-oxidation is a useful technique for chemical templating because of the capability for sustained patterning at the desired feature size, as tip wear was not mentioned as an issue in the work presented by Sagiv. No resolution limit other than the size of the tip has been determined as far as current work to date has shown. Though the necessity of a water meniscus similar to DPN could be a limiting factor, Sagiv has demonstrated pattern widths of 9nm with the final metal features ranging from 17 to 40 nm [16, 71, 72, 75-77]. While this technique has been used for creation of metal surface features (one aspect of the desire outcome), it has not been used to demonstrate the other desired outcome of this work, directed surface attachment of DNA. Also, recent advancements suggest the possibility that nano-oxidation can be performed in a parallel process [20-24]. The opportunity remains to oxidize surface moieties
other than alkyl chains and demonstrate DNA attachment to chemical templates created by AFM tip-direct nano-oxidation. This does introduce complex problems due to the limited surface chemistries available after oxidation; in the case of oxidizing alkyl monolayers on native silicon oxide, the only products left for use are carboxylic acids or silicon oxide.

2.4.3 Nanografting and Nanoshaving

Nanoshaving is the removal of materials from a surface by AFM on the nanometer-scale, and nanografting is the nanometer-scale removal of molecules or objects on a surface so that others may take their place. AFM nanografting was a concept first developed by Liu at Wayne University. Nanografting was demonstrated by using an AFM tip to scratch off a self assembled monolayer (or SAM) of alkane thiols on a gold surface and replace them with an alkyl thiol of a different length. Patterned surface attachment by nanografting thiolated DNA strands on gold surfaces has been demonstrated with features as small as 20 nm [78]. This work continues to be developed on conducting substrates.

Nanografting and shaving on silicon oxide has proven to be somewhat more difficult. In a study demonstrating nanografting of silane monolayers on silicon oxide the force required to remove the silane causes significant AFM tip wear. Nanometer-scale features were presented, but resolution was quickly lost and the features broaden as the radius of curvature of the tip increases. This is presumably due to the covalent bond between the silane and the surface. A force of 10 µN was required for patterning as opposed to the 5 µN required for nanografting thiol on gold. Features of 100 nm width were scribed. DNA localization to and metalization of patterns were demonstrated [29]. Despite the challenges, further development of AFM nano-
grafting of thin-film polymers on silicon oxide could provide a pathway for patterning of multiple chemistries on a single surface.

2.5 Conclusion

Advancement of current and the development of new techniques for surface treatment of silicon oxide can lead to directed attachment of DNA and continuous nanometer-scale metal deposits. Specifically, methods can be developed for use of AFM tip-directed nano-oxidation to create nanometer-scale chemical templates to demonstrate continuous nanometer scale metallization and DNA surface localization. These templates will allow directed surface alignment of DNA origami and selective metallization as enabling technologies for nanocircuit fabrication.
3 INCREASED METALLIZATION OF AMINE-COATED SURFACES BY MPS TREATMENT

3.1 Introduction

As selective continuous metallization of chemical templates is necessary for wiring of circuit templates, development of metallization procedures is needed to produce continuous metal deposits on surface features of nanometer-scale width. As discussed in Bird’s thesis [64], the seed density of a metallization procedure becomes a limiting factor in the metallization of nanometer-scale surface features. As displayed in Figure 3.1, the minimum size of the continuous metallized pattern that can be formed is directly related to the maximum distance between seeds. While seeds may not be evenly spaced in real world scenarios, the example in Figure 3.1 demonstrates the possibility that an increase in the density of seeds on a template would allow for metallization of continuous features with a smaller width. Bird demonstrated that if an APTES (3-aminopropyltrimethoxysilane) coated surface was treated with MPS (3-mercaptopropylsulfonate) before seeding with PdCl₂, the subsequent electroless palladium metallization resulted in a much higher plating density compared to metallization of an APTES-coated surface without MPS treatment. While the effect of increased metallization was shown, the mechanism remained undetermined. Also, the increased metallization was shown on APTES-coated surfaces and was not demonstrated on patterns or templates.
Bird’s results bring up a few questions about the possible use of MPS in increasing the density of metallization of amine-coated surfaces. Is the effect of increased metallization limited to the electroless deposition of palladium? How does MPS increase the density of metallization, and will the same effect be seen if applied to the metallization of nanometer-scale amine templates? To verify these statements, it was necessary to explore the increased metallization effect of MPS treatment with the electroless deposition of a metal other than palladium. Also, to determine if MPS treatment could possibly increase the density of metallization of nanometer-scale amine templates, it was important to understand how MPS treatment increased seeding and metallization density of amine-coated surfaces. This was accomplished by XPS (x-ray photo electron spectroscopy) analysis of APTES-coated surfaces after MPS treatment and palladium seeding.

In the present study, the increase in metallization density was demonstrated using electroless Cu metallization to establish that MPS treatment can be used to enhance palladium
seeding for the electroless deposition of metals other than palladium. XPS analysis of APTES-coated surfaces with MPS and/or palladium treatment revealed that MPS treatment increased the quantity of palladium adsorbed onto the surface during seeding. It was determined that MPS treatment increased the metallization of APTES-coated surfaces by attachment of the sulfonate functionality to the surface amines. With the sulfonate bound to the surface, the thiol group was free to aid in adsorption of palladium ions. As the thiol functionality of MPS was found to be important in enhancing the palladium seeding of the surface, electroless copper metallization of a palladium-seeded MPTES (3-mercaptopropyltriethoxysilane) coated surface was compared to metallization of an MPS-treated APTES-coated surface.

3.2 Experimental Procedures

3.2.1 APTES Surface Preparation

Substrates used in this aspect of the work were Si(100) wafers covered with a ca. 2 nm native oxide. Si(100) shards (~1cm²) were cleaned in a plasma reactor (Harrick Plasma, PDC-32G) on the high setting for 30 sec and then placed in a vacuum oven at -10 psig and 150°C. APTES (Aldrich 99%) was then injected into the oven yielding a vapor phase concentration of 1.2 x 10⁻⁴ mol/L. The samples were exposed to vapor phase APTES for 30 minutes to form an APTES layer on the surface. The resulting monolayer was 0.9 nm thick by spectroscopic ellipsometry (J.A. Woollam Co., Inc., Model M2000D) and had an advancing water contact angle of 55° (Ramé-Hart Inc., Model 100-00). These values are in reasonable agreement with literature values for APTES monolayers on silicon oxide surfaces and suggest a small amount of water was present in the deposition system [79-82]. The water only affected the system by
slightly increasing the thickness of the APTES coating and did not result in any inconsistency in film thickness or a change in the oxidation state of the primary amine.

### 3.2.2 Additive Treatment and Surface Analysis

After APTES deposition, samples were treated with MPS, PDS and/or the palladium solution and analyzed immediately. APTES-coated samples were treated with MPS or PDS by immersion in 0.1 M aqueous solution of the desired additive for one hour, rinsed with water for 5 sec, and dried with a clean nitrogen stream. Samples were analyzed for changes in surface chemistry by XPS (Surface Science SSX-100 instrument with a monochromatized Al Kα source and a hemispherical analyzer). All water used in this study was 18.2 MΩ resistivity deionized water obtained from a Millipore Milli-Q filter.

### 3.2.3 Metallization Procedures

Surfaces were seeded by immersion for 15 minutes in a PdCl₂ and HCl solution (0.15-0.2 g dm⁻³ PdCl₂, pH 3.5) [83], followed by a 30 sec dip in 0.1 M aqueous NaBH₄ [29]; samples were rinsed with water and dried in a nitrogen stream after each step. The surfaces were subsequently plated with copper by immersing them in an electroless copper plating solution (0.06 M CuSO₄; 0.5 M NaOH; 0.25 M Rochelle Salt; 0.12 M formaldehyde)[61], rinsed with water, and dried in a clean nitrogen stream (plating time is specified for each set of results).

### 3.3 Increase Copper Metallization by MPS Treatment

As the results for the increased metallization with MPS pretreatment were demonstrated using a palladium seeding/palladium plating system [64], electroless copper plating was used to
test if the increased metallization effects could be extended to other metals for which palladium acts as an appropriate seed. To demonstrate the effect of MPS treatment on palladium seeding for electroless copper plating, APTES layer were prepared and metallized with and without an MPS treatment prior to the seeding step. A comparison of metallized APTES-coated surfaces and APTES-coated surfaces that have additionally been treated with MPS shows that the addition of MPS resulted in a significant increase in the density of electroless copper metallization. These results are similar to those reported previously for the electroless deposition of Pd on Pd-seeded surfaces [64]. Figure 3.2 displays a side by side comparison of samples seeded with a PdCl$_2$ solution, reduced with NaBH$_4$, and immersed in an electroless copper bath for 20 seconds. The MPS treated surface is more densely metallized than the untreated surface, suggesting better dispersion of nucleation sites, smaller size distribution of seeds, and/or higher seed density.

![Figure 3.2: SEM images of (a) an APTES-coated surface and (b) an MPS-treated APTES-coated surface that have been seeded with Pd, reduced, and plated by electroless Cu deposition for 20 sec. The scale bar denotes 2 µm.](image-url)
impact of this additive on electroless copper deposition shows that the effects of MPS are not limited to electroless palladium metallization.

### 3.4 Determination of Mechanism for Enhanced Metallization with MPS Treatment

Experiments were performed to determine the mechanism by which the MPS led to an increase in plating density. X-ray photoelectron spectroscopy (XPS) was used to measure the quantity of nitrogen and palladium on APTES-coated surfaces that had been seeded with and without MPS treatment. PDS (1,3-propanedisulfonic acid disodium salt, \(\text{NaO}_3\text{SCH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}\)) was used as a comparison to MPS to help understand the specific role of the two functional groups of MPS in enhancing seeding. The structure of these two additives is similar except that MPS has a thiol group at one end and a sulfonic acid group at its other, while PDS has two sulfonic acid groups, one at either end of the molecule. The XPS results in Table 1 show that seeding of a surface that had been treated with MPS results in a 74% increase in the ratio of palladium to nitrogen (Pd/N ratio, atom%) relative to the Pd/N ratio of a seeded APTES surface that had no additive treatment. In contrast, treatment with PDS appeared to reduce the Pd/N ratio on the surface.

#### Table 3.1 Pd/N ratios obtained by XPS of seeded surfaces before the reduction step. Errors are standard deviations of XPS measurements and the number of replicates is 8.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Average Pd/N Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>APTES</td>
<td>0.42 ± 0.01</td>
</tr>
<tr>
<td>APTES + PDS</td>
<td>0.36 ± 0.03</td>
</tr>
<tr>
<td>APTES + MPS</td>
<td>0.73 ± 0.10</td>
</tr>
</tbody>
</table>
XPS was also used to characterize the chemical interactions of the additives with the APTES monolayer prior to exposure to the Pd solution. Nitrogen and sulfur peaks are relatively low-signal peaks, so significant and varying amounts of noise were present even after 3-5 hours of scan time. Despite the high level of noise, the desired data, namely peak positions, was discernable. Comparison of the results for MPS-treated surfaces with those treated with PDS permitted assessment of the effect of the two different chemical groups on seeding and metallization. XPS revealed that the nitrogen peak obtained from an APTES surface was present primarily as a single peak (chemical entity, Figure 3.3a), while the nitrogen peak of the MPS-treated APTES surfaces was split (Figure 3.3b). The same peak splitting was observed in the analysis of the PDS-treated APTES surface (Figure 3.3c). The peak splitting (the presence of more than one chemical state) is indicative of an interaction between the additives and the amine groups on the surface. As the interaction is similar for both additives, and the only groups present on the PDS for potential interaction with the surface are sulfonic acid groups, it follows that the interaction of the additive with the surface for both MPS and PDS is primarily through the sulfonic acid group. The most likely interaction is an ionic bond between the protonated amine and the deprotonated sulfonic acid. Thus, for MPS, the sulfonate binds ionically with the amine, and the thiol was free to bind PdCl$_4^{-2}$ ions. The 2 eV shift in the binding energy of the nitrogen causing the peak split is consistent with that expected for the proposed attachment mechanism [84]. In contrast, a larger shift would have been expected for a change in the oxidation state of the nitrogen (a minimum of 4 eV for oxidation of amines) [85].

The results for sulfur (Figure 3.4) showed two oxidation states for the MPS-treated surface (one for the sulfhydryl and one for the sulfonic acid in two peaks of ca. equal area), and
one oxidation state for the PDS-treated surface (corresponding to a sulfonic acid group). The sulfur to nitrogen (S/N) ratios from the XPS data for MPS and PDS were 1.9 and 0.3, respectively. The ratio for MPS (1.9) is consistent with high surface coverage and two sulfurs per amine, one sulfur associated with the sulfonic acid group that attaches to the amine, and the other with the thiol on the opposite end. While a palladium ion may interact with more than one amine on the surface [86], only one thiol is likely needed in order to bind a palladium ion [43]. It is also understood that PdCl$_4^{2-}$ ions bind the lone pair electrons of amines [60] and displace the hydrogen of thiols [87], shedding the chlorines in each case. Binding of metals to functional groups in this manner is often referred to as chelation. The low S/N ratio for PDS treated surface is believed to be the result of both ends of the molecule interacting with the amine functionalized surface, where each end bound to the surface provides one sulfur per amine. In addition, the PDS molecule blocks attachment sites as it lays on the surface, leading to the observed low S/N ratio of 0.3. The S/N ratios dropped to 0.6 (MPS) and 0.2 (PDS), respectively, when the surface was treated with the palladium seeding solution, indicating that palladium ions compete with the sulfonic acid groups for interaction with the amines. The presence of PDS on the surface led to a Pd/N ratio that was lower than that observed for APTES alone, as the sulfonic acid groups do not interact significantly with palladium ions in acidic HCl solutions [27]. The addition of MPS resulted in a significantly higher Pd/N ratio (0.73) relative to APTES, which resulted in an increase in copper plating density (as seen in Figure 3.2) and is expected to improve the nucleation density of nanopatterned surface features. The measured MPS S/N ratio of 0.6 after treatment in the palladium solution (approximately 1 MPS molecule to every 3 amines) indicates that both thiols and the amines could play a role in palladium ion adsorption.
Figure 3.3: Nitrogen 1s XPS spectra of differently treated APTES surfaces, (a) APTES without additive treatment, (b) MPS-treated APTES, and (c) PDS-treated APTES. The peak split is caused by the ionic bonding of sulfonic acid groups with the primary amines of the APTES monolayers.

A qualitative model was developed in order to understand how the palladium ions interact with the MPS treated surface as illustrated in Figure 3.5. Based on the XPS data taken, the model includes sulfonic acid attachment to the primary amines of the APTES monolayer. Palladium treated APTES coated surfaces, both with and without MPS or PDS treatment, are shown. Also presented in Figure 3.5 are the atomic ratios measured by XPS. The palladium binding capability of both the amine and the thiol groups are necessary to achieve the observed increase in palladium attached to the surface in the presence of MSPA. The model for each
scenario is in good general agreement with the XPS measurements, except in the case of the ratio of protonated to unprontonated amines. The amine-sulfonic acid interaction is the least understood of all the molecular interactions presented, and is shown to weaken with the addition of PdCl$_2$ solution as the S/N ratio decreases with palladium treatment of both PDS and MPS treated APTES layers. This is a possible explanation for the discrepancy in the atomic ratios of the model and the measurement.

Figure 3.4: Sulfur [2s] signal peaks of (a) MPS and (b) PDS treated APTES surfaces. As expected, the sulfur peak of the MPS treated surface was split (with the sulfhydryl at 228 eV and the sulfonic acid at 233 eV) and the sulfur peak of the PDS treated surface was present only in its more oxidized/higher binding energy state.
Figure 3.5: Model of palladium ion interaction with a) an APTES coated surface, b) an MPS treated APTES coated surface, and c) a PDS treated APTES coated surface with atomic ratios of the model and as measured by XPS.

3.5 Metallization of a Thiol-coated Surface.

Given the role of the thiol groups in this system in increasing the amount of Pd on the surface, one might legitimately wonder if the amine groups are really necessary, or if plating would be better served by a surface that contained just thiol groups. Such a surface would have the potential to chelate more palladium to the surface than the amine/thiol combination of the MPS-treated APTES surfaces. To determine if a mercapto silane layer would promote more uniform metallization of Cu on palladium seeds, an MPTES layer (3-mercaptopropyl...
triethoxysilane, Gelest 95%) was deposited on a clean silicon oxide surface by immersing the wafer in a 1% solution of the silane in toluene at 60°C for 10 minutes [42]. After 10 minutes the wafer was removed from the solution, rinsed with methanol, and dried with a clean nitrogen stream. The wafer was immediately seeded using the same procedure as used for the APTES-coated surfaces. The resulting surface was analyzed by XPS and found to have a Pd/S atomic ratio of 0.87, indicating more palladium seeding than even the MPS-treated APTES surface. An SEM image of the surface after subsequent copper metallization is presented in Figure 3.6. Despite having more palladium than an MPS-treated APTES coated surface, the resulting metallization is only as dense as the metallization of an untreated APTES-coated surface (Figure 4.1). An explanation for this may be found in capillarity theory of heterogeneous nucleation. Given the free energy of a metal deposition system, there is a corresponding critical seed size, and seeds smaller than the critical seed size are unlikely to form [26]. In autocatalytic metallization, if a seed is smaller than the critical seed size, it is unlikely to catalyze subsequent metallization. As reported, the size of palladium seeds on an MPTES-coated surface are smaller than the palladium seeds of an APTES-coated surface [43]. The smaller seed size may be explained by the comparative strength of amines and thiols in chelating palladium. A stronger palladium-thiol interaction will likely lead to higher dispersion of the Pd and a smaller seed size; in contrast, the weaker palladium-amine interaction would allow more mobility and aggregation of palladium ions to form a larger seed. The APTES/MPS system seems to combine the advantages of both the amine and thiol systems. The amines allow enough aggregation to form seeds that are sufficiently large for copper metallization, and the thiols provide increased dispersion over the APTES surface as well as an increase in the amount of Pd on the surface, enabling a more uniform copper deposit.
As MPS-treatment of APTES-coated surfaces was shown to increase density of metallization compared to metallization of both APTES- and MPTES-coated surface, it is important to note that the APTES/MPS combination will not always be better than the amine or thiol only surfaces. The MPTES-coated surface resulted in the most palladium attached during seeding, and an electroless bath that can catalyze the metallization of the smaller seeds of the MPTES-coated surface could produce continuous metallization at an even smaller length scale than demonstrated with the APTES/MPS system.

Figure 3.6: SEM image of palladium seeding and copper metallization of an MPTES layer. The copper deposition time was 2 minutes. The scale bar denote 2 microns
3.6 Summary

MPS was found to increase the plating density of copper on amine-functionalized surfaces by attaching to surface via the sulfonic acid group, leaving the thiol free to enhance surface adsorption of palladium ions from solution. The increase in metallization density was demonstrated with copper, indicating that the increase in metallization can also be extended to deposition of other metal that can be deposited on palladium seeds. The enhanced seeding was also found to require both the thiol groups from the MPS and the primary amines of the APTES layer. The increase in palladium in conjunction with the apparent enhanced dispersion of seeds of appropriate size, observed with metallization of MPS treated amine layers, means that MPS should be effective in enhancing the metallization of nanometer-scale amine templates.
4  NANOMETER-SCALE AMINE TEMPLATES BY POLYMER ATTACHMENT TO 
SURFACE OXIDE PATTERNS CREATED WITH AFM TIP-DIRECTED NANO-
OXIDATION

4.1  Introduction

As amine-coated surfaces have been used to demonstrate metallization of silicon oxide 
surfaces, it was necessary to create a chemical template of amines to demonstrate selective 
metallization for local wiring. Amines have proven to be a very useful chemical group for 
chemical templates. Patterned surface amines have been used for the selective attachment of gold 
nanoparticles [77], proteins [88], DNA [15, 28, 29, 88, 89], and palladium-catalyzed surface 
mellation [4, 29, 35, 36, 38]. In this study, amine templates will be created to demonstrate 
palladium-catalyzed metallization of nanometer-scale surface patterns.

For palladium-catalyzed metallization of insulating surfaces, amine containing silane 
monolayers can be used to prepare a surface for palladium attachment prior to electroless 
mellization of the surface [36, 42, 43]. Palladium is often used as a seed metal because of its 
ability to facilitate the electroless deposition of a variety of metals [61]. Chemical templating of 
amines for palladium-catalyzed metallization has been demonstrated with photolithographic 
alteration of silane monolayers [4, 36, 90] and nanografting of silane monolayers [29]. It appears, 
however, that both of these methods are limited to features greater than 200 nm. Amine 
templates with feature sizes less than 100 nm have been fabricated by modification of 
multilayered silanes [77] and the deposition of APTES (3-aminopropyl-triethoxysilane,
NH₂CH₂CH₂CH₂Si(OCH₂CH₃)₃ on surface patterns created by AFM tip-direct nano-oxidation [15], with applications of gold nanoparticle and DNA surface attachment respectively. These methods were not used to demonstrate palladium catalyzed metallization.

The present study examines the use of AFM tip-directed nano-oxidation to create finely patterned amine-templated surfaces, and the use of an MPS (mercaptoproylsulfonate) to enable continuous copper metallization of those templates. To create amine templates, a native oxide silicon surface was passivated against PAAm (polyallylamine, a polymer with a high density of amine functional groups) deposition by application of an OTS (n-octadecyltrichlorosilane) monolayer to the surface. The substrate was then oxidized by AFM tip-directed nano-oxidation and PAAm was deposited selectively on the oxidized surface patterns. This process yielded a nanotemplate of amine groups suitable for palladium-catalyzed electroless metallization and demonstration of the increased seeding and metallization effects of MPS treatment.

4.2 Experimental

4.2.1 Silane Monolayer Preparation

Si(100) surfaces were cleaned in a plasma reactor (Harrick PDC-32G) on the high setting for 30 sec and then twice immersed in a 5mM solution of OTS (octadecyltrichloro silane, Gelest, 95%) in dicyclohexyl (Aldrich, 99%) for 30 seconds and rinsed with toluene for thirty seconds[16]. The resulting monolayer was 1.3 nm thick by ellipsometery and had an advancing water contact angle of 100°, characteristic of a dense though not complete monolayer.
4.2.2 Procedures for AFM Tip-directed Nano-oxidation

AFM tip-directed nano-oxidation was performed using a Dimension V AFM (Veeco) and platinum-coated AFM tips (DPER 14, MikroMasch). Features were oxidized locally at an applied potential between -10 and -11 V at a tip speed of 5.0 to 5.1 μm/s.

4.2.3 Amine Functionalization of Oxide Patterns

Nano-oxidized surfaces were immersed in an aqueous solution of 1% APTES in toluene for 10 min at 80°C, and rinsed with methanol. 0.2 wt% PAAm (Sigma, 17000MW, 20% aq) and 15-20% CTAC (+, sigma, 25% aq) [88]. These surfaces were then treated with MPS and/or metallized as per the procedure given in Section 3.2.2.

4.3 Creation of an Amine Template

To create an amine template by deposition of APTES on oxide patterns, an OTS monolayer was deposited on a silicon wafer to passivate the surface against the deposition of APTES. The oxide pattern were created by AFM tip-directed nano-oxidation and the APTES deposition procedures were use to deposit APTES on the oxide patterns. While APTES has been used for creating amine templates on oxide surface patterns [15], palladium seeding and subsequent copper metallization resulted in a high level of nonselective background metallization (see Figure 4.1). As the purpose of this project is to template wires, it is necessary to have little or no metallization on the background and continuous metallization of the template. While Figure 4.1 does display metallization of the oxide pattern, the non-selective metallization of the background was unacceptable. PAAm (polyallylamine) was tested for select
metallization of OTS monolayers as a process that had been developed to deposit PAAm on micron scale oxide patterns while keeping it from sticking to a hydrophobic background [88].

It was necessary to first determine if PAAm would cause a significant level of background metallization on silicon wafers coated with OTS monolayers. Silicon surfaces were coated with an OTS monolayer and treated with CTAC (cetyltrimethylammonium chloride, the surfactant in the PAAm solution that prevents the deposition of PAAm on hydrophobic surfaces [88]), PAAm, and/or MPS, and subsequently metallized with the procedures given in Section (Figure 4.2). No significant metal deposition is observed on OTS monolayers that had been treated with a 15% aqueous CTAC solution (the PAAm solution without any PAAm, see Figure 4.2a). Surfaces treated with PAAm/CTAC before metal deposition (shown in Figure 4.2b) consistently displayed some metal deposition, indicating nonspecific adsorption of PAAm would be the main contributor to nonselective metallization on the surfaces. As MPS treatment enhanced the metallization of APTES coated surfaces, it would also enhance the metallization of nonspecifically adsorbed PAAm. To show that specific metallization of patterns would not occur without PAAm treatment, OTS monolayer-coated silicon surfaces were patterned by AFM tip-directed nano-oxidation and treated with a 15% aqueous CTAC solution or MPS before metallization (Figure 4.2). While a minor amount of specific metallization of patterns treated with MPS can be seen in Figure 4.3b, samples not treated with PAAm did not exhibit significant metallization.
Figure 4.1: SEM images of metalized APTES-treated surface patterns. The electroless deposition time was 2 minutes and the scale bar denotes 2 μm.

Having established that PAAm deposition provided acceptable selectivity in the metallization of the background monolayer, amine-functionalized templates were formed by the process illustrated in Figure 4.4. First, a silicon surface with a native oxide layer was passivated with an octadecyltrichlorosilane (OTS) monolayer. The passivated surface was then patterned by AFM tip-directed nano-oxidation to form a fresh raised oxide in the pattern of interest. Finally, an amine-functionalized polymer, PAAm, was selectively deposited on the patterned areas. PAAm was used because of a process that had been developed to deposit PAAm on oxide patterns while keeping it from sticking to a hydrophobic background [88].
Figure 4.2: SEM of OTS surfaces (a) treated with 15% aqueous CTAC, seeded, and plated (b) treated with PAAm, seeded, and plated, and (c) treated with PAAm, MPS, seeded, and plated. As no oxide formations are present, the data presented is only the metallization of the background surface. The electroless deposition time was 2 minutes, and the scale bar denotes 2 µm.

To demonstrate that PAAm would deposit on oxide patterns and provide the desired amine template, a silicon wafer coated with an OTS monolayer was pattern by AFM tip-directed nanoxidation, treated with PAAm, seeded, and reduced. AFM height measurements following oxidation, polymer deposition, and seeding and reduction with Pd are shown in Figure 4.5. The height increase of patterned regions after PAAm treatment was 4 Å. While this height is lower than the reported thickness of PAAm deposited on clean oxide for this PAAm/CTAT solution [88], it is reasonable to expect that PAAm may deposit differently on these patterns as nanoxidation may not provide a surface of the same quality. The measured height change was consistent for 60 patterned lines on two different surfaces, suggesting deposition of ca. a single monolayer of PAAm. In the PAAm/CTAC solution, CTAC significantly decreases the amount of PAAm that sticks to hydrophobic surfaces. While decreasing the percent CTAC in this solution may have allowed more PAAm to deposit on the oxide patterns, it would also have increased nonspecific adsorption of PAAm [88].
4.4 Effects of MPS Treatment on Metallization of Amine Templates

Having determined how the use of the additive MPS may enhance the metallization of nanometer scale amine templates in Chapter 1, nanometer scale amine templates were used to determine the effectiveness of using MPS to enhance the copper metallization of PAAm templates. Two OTS surfaces were prepared, patterned by AFM tip-directed nano-oxidation and treated with PAAm. Only one surface was treated with MPS and both seeded with palladium. Once seeded, samples were metallized by plating with electroless copper for 2 minutes. Figure

Figure 4.3: SEM images of (a) a patterned OTS surface treated 15% aqueous CTAC, seeded, and plated and (b) a patterned OTS surface treated with 15% aqueous CTAC, MPS, seeded, and plated. The electroless deposition time was 2 minutes, and the scale bar denotes 2 µm.

Figure 4.4: Schematic diagram of a stepwise process for selective surface patterning of PAAm on alkyl monolayers.
4.6 shows a comparison of metallization results for a series of lines of different widths, both with and without MPS treatment. Without MPS only sparse metallization was observed for line widths below 400 nm. In contrast, samples treated with MPS showed nearly continuous metallization for the entire range of line widths considered. The effect of MPS on increased metallization of the templates is clear. MPS treatment enabled metallization of surface patterns 5 times smaller than those patterned with PAAm alone.

A comparison of patterned lines smaller than 100 nm shows a distinct contrast in metallization with the use of MPS on nanometer scale amine templates (see Figure 4.7). Without MPS treatment, no appreciable metal deposition was observed. In contrast, continuous, selective metallization was observed for samples treated with MPS (Figure 4.7b). As discussed previously, both the amine and thiol groups have a role in the seeding process. In the discussion of Figure 4.5: AFM tapping mode height images of lines patterned after (a) AFM tip-directed nano-oxidation, (b) with attachment of PAAm, and (c) after Pd seeding of the lines. The scale bar denotes 1 µm., it is noted that even on the smallest patterns a height increase at each step indicates polymer deposition and palladium attachment. Therefore, the smallest patterns appear to have templated amines that are expected to attract palladium. However, without MPS treatment no notable electroless metallization was observed. It is possible that MPS was needed in order to attract enough palladium to reach the critical seed size needed for deposition.
Figure 4.5: AFM tapping mode height images of lines patterned after (a) AFM tip-directed nano-oxidation, (b) with attachment of PAAm, and (c) after Pd seeding of the lines. The scale bar denotes 1 µm.

Figure 4.6: SEM images of metalized, patterned PAAm nanotemplates showing varying line widths (a) without MPS treatment and (b) with MPS treatment. Line widths for a and b from top to bottom are 400, 300, 200, 100, and 80 nm (two lines). Each surface was immersed in an electroless copper plating bath for 2 min. The patterned lines are 5 µm long.
Figure 4.7: SEM images of metalized, patterned PAAm nanotemplates (a) without MPS treatment and (b) with MPS treatment. Pattern widths are all under 100 nm. Each surface was immersed in the electroless copper solution for 2 min. The patterned lines are 5 µm long.

Figure 4.8 depicts a model for the metallization of PAAm templates with and without MPS treatment. The positive impact of MPS treatment on nanometer-scale copper deposition is clearly evident in these results, especially for the smallest line sizes where no clear evidence of plating was observed without the additive. AFM tip direct nano-oxidation for creation of PAAm templates can be used not only for creating straight wires and curved lines, but also has the potential to be used for patterning of spots and pads. The method is also not limited to AFM based serial patterning methods, but as discussed in Section 2.4.2, nano-oxidation can also be performed in parallel patterning of larger areas. The PAAm templates demonstrated are also feasible for use in patterning of biological molecules. Patterning and MPS-enhanced metallization of alternate shapes, including curved and straight lines highlights some of the capabilities of the method (see Figure 4.9). Treatment of amine patterns with MPS resulted in a 80% reduction of the feasible pattern width for continuous metallization, demonstrating both
chemical templating of PAAm on nano-pattern oxide and the utility of MPS in reducing the feature width for practical metallization of those templates.

Figure 4.8: Stepwise metallization on templated PAAm with and without MPS treatment.
4.5 Summary

Amine-functionalized nanotemplates were made by selective deposition of PAAm onto surface patterns created by nano-oxidation of OTS-coated silicon substrates. Selective, continuous metallization was observed for MPS-treated nanotemplates. These results demonstrate the successful creation of flexible amine-functionalized nanotemplates, and the enabling influence of MPS for the metallization of nanometer scale features. In particular, MPS was found to enable a reduction in pattern width for feasible metallization from 500 nm to less than 100 nm. While the PAAm templates were used to demonstrate selective metallization, they have the potential for broad application in areas such as selective surface attachment of biomolecules to nanometer scale surface features.
NEGATIVE PATTERNING OF A MERCAPTOPROYL SILANE MONOLAYER BY AFM TIP-DIRECTED NANO-OXIDATION

5.1 Introduction

The last chapter included the description of a process for metallization of “positive patterns” where the metal is deposited on the patterned areas. In doing this, a new idea was generated for “negative patterning” of metals through a different application of AFM tip-directed nano-electrochemical modification (nano-oxidation or nano-reduction). With the positive patterning PAAm templating procedures, AFM tip-directed nano-oxidation was used to oxidize through the monolayer and oxidize the substrate. The new idea for “negative patterning” was based on finding a chemical functional group that facilitated metallization and could be electrochemically modified to a chemical group that would not metallize. The surface would then be patterned by AFM tip-directed nano-electrochemical modification (as shown in Figure 5.1), with oxidation or reduction of the patterns and no modification of the background surface. Upon patterning and subsequent metallization of the surface, the background would metallize as if no patterning had been performed. The areas of the surface patterned by AFM tip-directed nano-electrochemical modification would not metallize. The metallization of the background but not the patterns would create a metal negative of the pattern.
Figure 5.1: Concept of “negative patterning” by nano-electrochemical modification of a monolayer that can be metallized.

Ideally, a simple process could be developed where the local surface chemistry could be changed directly via AFM oxidation or reduction from a functional group that promotes metallization to one that does not, without the need to oxidize the underlying substrate. AFM tip-directed nano-oxidation could be performed to oxidize solely the organic monolayer and not the substrate as discussed in Section 2.4.2. The threshold for oxidation of an OTS (n-octadecyltrichlorosilane) monolayer has been established at about -8 V. When oxidizing alkyl chains at the minimum absolute tip potential to sustain oxidation, the chains were partially oxidized to yield carboxylic acid groups at the surface [16]. One advantage to this type of chemical templating is that there will be no issues with the nonselective deposition of the template chemistry, as the patterns are modified by the tip and do not require further chemical treatments to create the desired template. As AFM tip-directed nano-electrochemical
modification could be used to modify local surface chemistry, a suitable chemical functionality was still needed.

A search was implemented for a chemical functionality that supported metallization and could be oxidized to a form that did not support metallization. As palladium-based seeding was also desirable (for the advantages previously discussed in Section 2.2.4.1), thiol and amine groups (both being useful for aiding palladium seeding of surfaces) were initially considered as possible functional groups for this negative patterning concept. Upon a survey of the literature it was determined that thiols possessed each of the desired properties. Thiol-terminated silanes have been demonstrated for solution-based seeding (seeding by treating a surface with an ionic or colloidal solution of the desired metal) of palladium on silicon surfaces [43]. The threshold for oxidation of organo sulfurs is known to be lower than the threshold for oxidation of alkyl chains, and electrochemical oxidation of thiol groups has been shown to produce sulfonic acid groups[91]. AFM tip-directed nano-oxidation has been shown to oxidize thiols at a lower absolute tip potential than an OTS monolayer [92]. Lastly, thiols chelate palladium ions, while sulfonic acid groups (also referred to as sulfonate groups, R-SO$_3^-$, an oxidized form of organo sulfur) do not have a chelating interaction with palladium ions and should not support electroless metallization [93]. This means that nano-oxidation of a thiol-coated surface to produce patterns of sulfonates on a thiol background may produce the desired contrast in subsequent metallization of the surface. AFM dip-directed nano-oxidation of MPTES-coated surfaces has been demonstrated to produce disulfides (an oxidation state of organosulfurs between thiols and sulfonates) [92], and it has been suggested that oxidation of thiols by AFM tip-directed nano-oxidation may produce sulfonate groups [92, 94].
Based on the properties of thiol groups mentioned above, it appeared that the local oxidation of thiols may produce the desired contrast in metallization and, therefore, a chemical means of affecting the desired negative patterning. Consequently, the thiol-coated silicon oxide surface was tested to see if “negative patterning” by oxidation of surface-bound thiols could be performed. The surface was locally oxidized by AFM tip-directed nano-oxidation. After patterning, the surface was seeded with palladium and metallized by electroless NiB metallization. Both metallization results and chemical analysis of the surface were used to assess the feasibility of the proposed patterning and to provide a detailed explanation of its performance.

5.2 Experimental Procedures

5.2.1 Deposition, Characterization, and Nano-oxidation of a Mercapto Silane layer

A mercaptopropyl triethoxy silane (MPTES) layer was deposited by immersing a 1 cm\(^2\) Si(100) silicon substrate with a native oxide layer (cleaned in a Harrick Plasma, PDC-32G, plasma reactor on the high setting for 30 sec) in 0.2 wt. % MPTES in toluene at 120 °C for 10 minutes. This resulted in a 1.2 nm layer (as measured by spectroscopic ellipsometry, J.A. Woollam Co., Inc., Model M2000D) and a 65° advancing water contact angle (Ramé-Hart Inc., Model 100-00). As a monolayer thickness is noted at 0.8 nm [95] a 1.2 nm film thickness indicates greater than monolayer coverage. The 120 °C procedure was a modification of common procedures for deposition of triethoxy silanes in toluene, where concentration, time and temperature vary from 0.1–30 wt.%, two minutes to 24 hours, and room temperature to the reflux temperature of toluene (110 °C) respectively [42, 96-100]. Initially a procedure to deposit an
MPTES layer using 1 wt.% MPTES in toluene at 60 °C for ten minutes resulted in a silane multilayer of 3.2 nm that was scribed off of the surface by the AFM tip when imaged in contact mode with an AFM at the minimum possible deflection voltage (the lowest force that can be used to image a surface without the tip disengaging the surface) and no applied tip potential (see Figure 5.2). As discussed in Section 2.2.2, heat influences the dehydration reaction that binds the organo silanes to the surface silanols of silicon oxide by forming Si–O–Si bonds. The temperature was increased from 60 °C to 110 °C (the reflux temperature of toluene, or the hottest reasonable temperature for solution deposition of an MPTES layer in toluene) to promote the necessary dehydration processes needed to covalently bind the MPTES layer to the surface [101]. As previously tested procedures have shown suitable monolayer coverage at silane concentrations of around 0.1 wt.% in toluene [100], the concentration of the MTPES solution was decreased from 1 wt. % to 0.2 wt. % in an attempt to reduce the deposition to near but not below a single monolayer of MPTES molecules. Decreasing the concentration of silane and increasing the temperature of reaction resulted in a thinner layer that was not scribed off the surface when imaging by AFM in contact mode. While the MPTES-coating formed at 1% 60 °C MPTES layer (because it is polymerized but not bound well to the surface the MPTES layer was essentially a polymer layer) would provide a possible patterning method by scribing alone, the scribing of the polymer coatings has presented significant challenges in reproducibility, and polymer sticking to the tip has caused significant rapid broadening of AFM tip size [102].

AFM tip-directed nano-oxidation of MPTES-coated surfaces was performed with a Bruker NCHV-A tip on a Dimension V (Veeco) atomic force microscope.
5.2.2 Metallization of the Silane Monolayer

To create a “negative pattern” with nanometer-scale resolution, a metallization procedure was needed that would produce a continuous metal film. The density of seeds and the fraction of those seeds that nucleate subsequent electroless metallization are factors that control the possible resolution of metal patterns. The nucleation density directly affects how much electroless metal deposition is required for continuous metallization. For example, growth of nucleation sites by electroless metallization to a diameter of 10 nm would not produce a continuous film if the spacing between seeds were 20 nm. Figure 3.1 was used to illustrate how the nucleation density may limit the possible pattern width for positively patterned metal lines. For the creation of a negative pattern, the nucleation density must be sufficiently high so that the spacing between nucleation sites is smaller than the size of the patterned features. If this is not so, plating will occur over the patterned area, even if there is no metal nucleation on the pattern. Figure 5.3 displays how the particle size of continuous metallization impacts the possible resolution of a negative metal patterning process. If the particle size is larger than the patterns, then metallization will bridge the gap. This would mean that in creating a continuous metal layer, any
patterning would be covered by the electroless deposition on the seeds (see Figure 5.3d). If the particle size of continuous metallization is smaller than the patterning width, then, after metallization, the pattern will be evident in the metal layer. For patterning and subsequent metallization of the MPTES monolayer, a metallization process where the spacing between nucleation sites is 10 nm or less will be required to demonstrate a negative pattern with 20 nm gap. Electroless copper plating of an MPTES monolayer (Figure 3.6) showed a spacing of 300-400 nm between particles after 50 nm of growth by electroless deposition. These results indicate that the electroless copper metallization procedure on MPTES was not suitable for demonstration of negative patterning at the desired resolution. The literature was searched for an electroless bath that produced a continuous metal film with a particle size less than 10 nm on palladium-seeded MTPES-coated surfaces. An electroless NiB (nickel/boron) deposition solution was found that produced a continuous metal film of less than 10 nm particle size on a palladium-seeded MPTES-coated surface [43]. This particular NiB film has been used as barrier layer, and has been shown to readily catalyze electroless plating of other metals [97, 103].

MPTES-coated oxide surfaces were activated for metal deposition by immersion for 20 min in a PdCl₂ and HCl solution (0.15-0.2 g dm⁻¹ PdCl₂, pH 3.5) [42], and metallized by immersion in an electroless NiB plating solution (0.1M NiSO₄, 0.2M sodium citrate, 0.05M DMAB (dimethylamineborane), pH 10, 70 °C) for 35 seconds [97, 103]. This NiB bath is known to deposit a film with ~6.5% boron [97].
Figure 5.3: Comparison of metallization of a negative pattern with different nucleation density, relative to pattern size; a) patterned surface, b) particle size for continuous metallization relative to patterns, c) metallization of patterned surface with higher nucleation density (smaller particle size than the pattern), d) metallization of the patterns surface with lower nucleation density (larger particle size than pattern).

5.3 NiB Metallization of Thiol and Sulfonate Surface Coatings

The procedure described above was used to deposit a NiB film on an MPTES-coated silicon surface with a native oxide layer. The NiB film was analyzed for continuity and particle size as the MPTES deposition procedure had been modified from previous demonstration of
palladium seeded NiB metallization reported in the literature [42, 103] (see Section 5.2.1). The result was a metal film with continuous metallization and a particle size of less than 15 nm, suitable for demonstration of nanometer scale patterning (see Figure 5.4) and similar to NiB films produced on both APTES and MPTES (with the 1 wt.% toluene, 60 °C procedure) layers [42].

![Image of NiB film on Pd-activated MPTES-coated silicon oxide surface.](image)

*Figure 5.4: NiB film on Pd-activated MPTES-coated silicon oxide surface.*

The resulting NiB film was found to have a thickness of 14 nm (as will be discussed in the presentation of Figure 5.16), and a particle size less than 15 nm with continuous metallization (as determined by visual inspection of SEM images). As NiB metallization of the MPTES monolayer produced a metal film suitable for demonstration of nanometer-scale templating,
metallization of a sulfonic-acid-coated surface was attempted to confirm that the lack of palladium chelation by the sulfonate groups would prevent the electroless metallization of NiB, and to ascertain the contrast achievable by NiB metallization of nano-oxidative patterning on an MPTES-coated surface. A surface layer of sulfonates was prepared by immersing an APTES-coated silicon oxide surface in a 1% aqueous solution of PSS (polystyrenesulfonate). This resulted in a 2 nm polymer layer of PSS on the APTES-coated surface, blocking the amine functionality and producing a surface layer of sulfonate groups. For comparison, an MPTES-coated surface, an APTES-coated surface, and a PSS-treated APTES-coated surface were treated with the palladium seeding solution and analyzed by XPS (Figures 5.5). Important peaks from these spectra are the nitrogen 1s peak at 400 eV, the palladium 3d3 and 3d5 doublet at 340 eV, and the sulfur 2s peak at 228 eV. Other peaks noted on these spectra include the 535 eV oxygen 1s peak, the 284 eV carbon 1s peak, the 100 and 150 eV silicon 1s and 2p peaks, and the 200 and 271 eV chlorine 2p and 2s peaks. The APTES and PSS surfaces both display the expected nitrogen 1s peak at 400 eV, and the PSS and MPTES surface both present a sulfur 2s peak around 230. It is noted that the sulfur peak of the sulfonate-covered PSS-treated surface is present at 232 eV, a 4 eV shift from the 228 eV sulfur 2s peak of the thiol covered MPTES surface; indicating the expected difference in oxidation state of the organosulfur functionality of the thiol- and sulfonate-coated surfaces [104]. As expected, the spectra for both the MPTES and APTES surfaces display a strong palladium doublet at 340 eV, but the PSS-treated APTES-coated surface had very little palladium (10% of that measured on the APTES-coated surface). NiB metallization of a palladium-seeded PSS-treated surface is presented in Figure 5.8. The XPS and SEM data indicate that sulfonates do not chelate palladium or support electroless NiB metallization.
Figure 5.5: XPS survey spectra of a palladium-seeded MPTES-coated surface.

Figure 5.6: XPS survey spectra of a palladium-seeded APTES-coated surface.
Figure 5.7: XPS survey spectra of a palladium-seeded PSS treated APTES-coated surface.

Figure 5.8: SEM image of a PSS-treated APTES-coated surface after exposure to palladium seeding and NiB metallization procedures showing lack of NiB metallization on a sulfonate-coated surface.
5.4 Negative Patterning of a NiB Film

Having established and demonstrated suitable procedures for MPTES coating of a silicon oxide surface and for metallization of the coated surface, a procedure was developed to selectively oxidize the MPTES layer. The process is illustrated in Figure 5.9. An MPTES layer is patterned by AFM tip-directed nano-oxidation, activated with the PdCl₂ bath, and plated with the electroless NiB solution. As the sulfonates do not chelate palladium ions [93], selective oxidation should produce a negative pattern. With palladium activation of the background, but not the pattern, subsequent NiB metallization would result in a NiB film that is the negative of the oxidized pattern (i.e., metal deposits in the unpatterned areas).

![Diagram](image_url)

Figure 5.9: Process for “negative patterning” of a NiB film by Pd activated metallization of an MPTES film that had been patterned with AFM tip-directed nano-oxidation.
It was necessary to determine if there was a tip potential that would result in the oxidation of thiols to sulfonates. The tip potential was stepped from -1 V to -8 V (potential of tip relative to surface, which was grounded) in 1 V increments and the surface was metallized with the NiB procedures. This was a reasonable range of voltages given that OTS monolayers oxidize at -8 V [74], thiols have a lower oxidation potential than alkyl chains, and it is unknown at what tip potential a thiol may be oxidized to a sulfonate. The patterning was done in contact mode at the minimum deflection voltage necessary to keep the tip engaged with the surface (as operating at a lower deflection voltage will cause the tip to scan some distance above the surface) to ensure the effects of patterning were caused by the tip potential and not mechanical scribing (as too high a deflection voltage will cause the tip to exert a force larger than necessary on the surface and potentially scratch off the MPTES layer).

An MPTES-coated surface was patterned by AFM tip-directed nano-oxidation, activated with PdCl₂, and metallized with the NiB solution. Patterning at tip potentials of -1 V to -3 V resulted in no discernible change in the subsequent metallization, when imaged by SEM. SEM images of NiB metallization on an MPTES-coated surface that was patterned at -4 and -5V with a tip speed of 1µm/s are presented in Figure 5.10. The significant metallization of the patterns (or bridging of the metal film across the patterns) created at -4 V indicates incomplete oxidation of the surface thiols (Figure 5.10a), and clear separation of metallization at the patterns indicates acceptable oxidation of the thiols at -5 V (Figure 5.10b). The oxidation at -5 V and subsequent metallization resulted in a height differences between the top of the NiB film and the patterns, making the patterns appear darker than the metal film.
Figure 5.10: SEM image of NiB plating of an AFM tip-directed nano-oxidized MPTES-coated surface patterned with tip voltages of a) -4V and b) -5 V.

High resolution patterns were demonstrated at -5 V and a tip speed of 5 \( \mu \text{m/s} \) (see Figure 5.11). Though the patterns appear to be bridged in several places, the spacing of the gap in the metal film along the pattern was 25 nm (as measured by SEM). This demonstrates the possibility for very high resolution patterning. Further optimization of tip potential and tip speed, along with a sharper tip, may narrow the gap further. Figure 5.10 also demonstrates the possibility for high resolution patterning. Nano-oxidation of two lines close together, and metallizing the space between the patterned lines, created a continuous metal feature of 50 nm width (again measured by SEM, see the metallization between the top two oxidized lines of Figure 5.10b). This demonstrates the possibility of wire patterning with narrow line widths. This may not be the most efficient way to pattern metal lines or wires, but this result, along with the narrow gap, demonstrates that this method can be used to create a negative with a high level of detail.
One possible application of a “negative pattern” lies in pattern transfer. A negative can be useful in mask making, or as the metal film is conductive, the negative could be used as an electrode to transfer the negative to a second surface. Concentric circles were patterned at -5V and 1 µm/s, and, as expected, the isolated patterns retained good adhesion to the surface; given the thiol functionality chelating the seeds and the thin NiB film. Figure 5.12 shows two rings and a center disk which are attached to the surface while isolated from the bulk NiB film. This means that complex patterns of lines and shapes may be able to retain their shape well after metallization. Also of note in Figure 5.12 is that most of the rings are slightly darker than the background, indicating that they are electrically isolated from the background. As both the background and the isolated shapes are conductive and somewhat insulated from the substrate, both may retain some charge from the electron beam during scanning (which can cause a brightening of color). With the background film having more exposure to the electron beam, the
smaller patterns appear darker. At -5 V (Figure 5.12a) the outer ring is the same color as the background and, as indicated by the red circles, metallization has bridged the gap. At -6 V (Figure 5.12b) no bridging is seen and the whole feature appears to be electrically isolated from the bulk film.

![Figure 5.12 SEM image of NiB plating on an MPTES-coated surface patterned with concentric circles at a tip potential of a) -5 V and b) -6 V (tip relative to surface). The red circles indicate areas where the NiB metallization may have bridged the gap due to incomplete oxidation of the thiols in the patterned area.]

It has been shown that given a high enough potential, nano-oxidation will result in complete oxidation of an organic monolayer and oxidation of the silicon substrate [74]. To ensure that oxidation of the substrate did not occur, the potential was pushed to, but did not exceed, -8 V. Results for attempted patterning at -7 and -8 V can be seen in Figure 5.13. At -7 and -8 V the partial oxidation of a larger area around to the tip was observed (see Figure 5.13,
30–40 % relative humidity was noted during patterning). Figure 5.14 is an enlarged image of the edge of the halo and displays the decrease in metallization of the surface within the halo. To determine if humidity was a factor in the formation of the halo of sparse metallization a surface was pattern at 0 % humidity. Three spots were patterned at -8 V and increasing time steps 0.1 seconds, 0.5 seconds, and 1 second before the surface was metallized (see Figure 5.15). The results show an increase in diameter of the pattern with increasing pulse time and no halo is observed. Comparison of Figure 5.13 and Figure 5.15 indicate that humidity was a contributing factor in creating the observed halo. The light color of the halo is explained by edge effects in SEM imaging. Edges appear brighter in SEM images as it is easier for secondary electrons to escape a surface when the beam is imaging near an edge. In the bright halo, the decrease in metallization leads to an increase in exposed edges of metal particles. The effects of patterning in a humid environment can also be seen in Figure 5.11, where a slight halo appears after patterning in 30 % humidity. In comparison, Figures 5.10 and 5.12 show no such effect after patterning at less than 10 % relative humidity.

Patterning at -7 V was also used to determine the thickness of the NiB film. An MPTES coated surface was patterned at -7 V, metallized, and imaged with AFM. The result is presented in Figure 5.16. The NiB film was found to have a thickness of 14 nm. A four point probe was used to measure the sheet resistance, which was found to be about 570 Ω sq⁻¹ (or about one tenth the conductivity of bulk nickel).
Figure 5.13: SEM image of NiB metallization of nano-oxidized MPTES layer patterned at -7 and -8 V.

Figure 5.14: SEM image of edge of halo seen in Figure 5.13.
Figure 5.15: SEM image of NiB plating of an MPTES film with spots patterned by AFM tip-directed nano-oxidation at -8 V and 0 % humidity for a) 0.1 seconds, b) 0.5 seconds, and c) 1 second prior to metallization of the surface.

Figure 5.16: An AFM image (with an averaged profile) of a patterned NiB film, indicating a 14 nm NiB film thickness.

5.5 Large-scale Oxidation of an MPTES-coated Surface

While it was been shown that AFM tip-directed nano-oxidation resulted in successful patterning of the NiB film, the product that resulted from nano-oxidation of the MPTES layer
had not yet been explicitly determined. To oxidize a large enough area for XPS analysis, an MPTES-treated surface was contacted with a planar gold electrode and stepped from -5V until the area contacted by the electrode did not metallize. At -12 V (electrode relative to surface) the monolayer was oxidized by the applied potential and the oxidized area did not metallize (see Figure 5.17). The -12 V required for oxidation of the MPTES monolayer with the planar gold electrode is much greater than the -5 V necessary to oxidize the surface by AFM tip-directed nano-oxidation. In comparison, potentials for AFM tip-directed nano-oxidation of a C_{18} monolayer as demonstrated by Sagiv have a minimum oxidation threshold of around -8 V, and oxidation of the monolayer with a larger 2D electrode (in their case a TEM grid) was also observed at -12 V [105]. One explanation for this observation is the possibility of a larger potential barrier to produce the necessary water layer between the surface and the electrode for oxidation (compared to meniscus formation with AFM tip-directed nano-oxidation). This potential barrier for the formation of the necessary water layer would explain why both an MPTES and OTS monolayer require -12 V to be oxidized by a larger 2-dimensional electrode, but have differing oxidation thresholds when patterned by AFM tip-directed nano-oxidation. As neither the gold surface nor the silicon wafer is perfectly flat, it is possible that the observed result is the oxidation of a few contact points and the halo effect on the rest of the surface. SEM imaging of the surface will help better understand this result.
One advantage of AFM tip-directed nano-electrochemical surface modification is that it has been demonstrated as a parallel process (as discussed in Section 2.4.2) [20, 22-24], meaning that a process demonstrated using AFM tip-directed nano-electrochemical modification (a serial patterning method) could likely also be demonstrated in a parallel patterning process. Successful patterning of this large area demonstrates the capability to pattern these surfaces in a parallel process. As discussed in Section 2.1, serial patterning methods (i.e. AFM patterning) are limited to line-by-line patterning of surfaces, but parallel methods (i.e. photolithography) can pattern larger 2-dimensional patterns simultaneously. This means that this “negative patterning” technique may not be limited by the serial nature of the AFM tip-based patterning methods, and simultaneous surface oxidation of patterns of larger area by a single electrode should be possible. Also with the possibility of complex patterns maintaining their shape and positioning (see the discussion of Figure 5.12), it may be possible to use the negatively patterned metal surface as an
electrode to transfer the pattern to another surface or as a mask for other parallel patterning applications. One challenge in these parallel processing schemes is contact of surface with the electrode, as neither will be perfectly flat.

The oxidation of the MPTES layer with a planar electrode was used to determine the oxidation state of the patterned thiols. As the oxidized patterns were not metallized by palladium seeding it was believed that the thiols were oxidized past the disulfide oxidation state (which is known to allow metal chelation), and it was also possible that with enough oxidation the sulfur may be removed from the surface entirely. Confirmation of products of the oxidation reaction was obtained by XPS analysis of an MPTES surface that was oxidized with planar gold electrode at -12 V. This oxidation resulted in the emergence of a peak at 232 eV, a 4 eV shift from the 228 eV thiol peak, indicating that sulfonate groups were a product of the oxidation reaction. Figure 5.18 displays XPS sulfur 2s spectra, showing both the thiol and sulfonate peaks of the oxidized MPTES layer. XPS analysis of an MPTES-coated surface that had not been oxidized displayed no discernable peak at 232 eV. Comparison of the sulfur 1s spectra of the two surfaces revealed no substantial change in the quantity of sulfur on the surface, indicating that the oxidation did not result in the removal of sulfur from the surface. These results indicate that sufficient oxidation to prevent metallization of surface patterns resulted in the formation of sulfonic acid groups, though the presence of sulfurs in the thiol oxidation state was observed.
Figure 5.18: Sulfur 2s XPS spectra of MPTES surfaces oxidized with a planar gold electrode at -12 V with peak fits of the thiol (228 eV) and sulfonic acid (232 eV) oxidation states.

5.6 Summary

To produce a negative metal film with nanometer-scale resolution, AFM tip-directed nano-oxidation was used to selectively oxidize a MPTES layer. Subsequent metallization of NiB on the patterned surface resulted in a metal film with metallization of the background surface and not the oxidized patterns. Metallization gaps less than 30 nm and continuous metal lines less than 50 nm were demonstrated. These MPTES-coated surfaces can also be patterned by parallel methods. The negative patterning of a metal film also provides a pathway for pattern transfer by parallel nano-oxidation.
6 DNA ATTACHMENT TO SURFACE PATTERNS CREATED BY AFM TIP-DIRECTED NANO-OXIDATION.

6.1 Introduction

Having demonstrated continuous metal deposition on chemical templates, efforts turned to the use of such templates for attachment and alignment of DNA origami structures. The location-specific attachment and orientation of DNA origami structures on a surface is essential for use of these structures as feasible templates for nanodevices. My initial approach was to apply the methods demonstrated in Chapter 4 for template metallization to the attachment of DNA. Attachment of DNA to chemical templates was investigated by both ionic and covalent interactions. As shown in Figure 6.1, if either ionic or covalent interactions could be used to attach single-stranded DNA (the red strands) to a chemical template, the location of those surface-bound strands could then be used to orient a larger origami structure (the red rectangle). This orientation could be achieved by hybridization of the dangling strands (the blue strands attached to the origami structure) with the surface-bound strands. Attachment of DNA nanostructures to prepositioned gold particles arrays created by block-copolymers and e-beam patterning has demonstrated DNA origami surface attachment of this nature [56, 57]. In each case, the demonstrated attachment allowed for attachment of only one sequence or functionality to the gold particles, and a method was sought that would allow specific positioning and attachment of two or more single stranded sequences to the surface for more specific orientation of the DNA origami. Chemical templating would be used to specify the location and chemistry
for attachment of DNA strands, providing the necessary functionality and location for hybridization and thus, orientation of the origami structures.

Several methods for ionic and covalent attachment of single stranded DNA to surfaces have been demonstrated in the literature and were presented in the Background (Section 2.2.3). Each method provides possible solutions for the attachment and alignment of DNA origami. Ionic DNA attachment is discussed and presented first, followed by an examination of covalent surface attachment of DNA.

Figure 6.1: Attachment and orientation of a DNA origami structure (red rectangle) by hybridization of the dangling strands (blue strands) with surface strands (red strands) with a) side view and b) top view.
6.2 Alignment of DNA by Ionic Attachment

6.2.1 Introduction

Ionic attachment of DNA to surfaces is accomplished by the interaction of the negatively charged phosphate backbone of DNA with positive charges at the surface. Several methods of ionic surface attachment and positioning of DNA have been demonstrated by surface functionalization with amines \([15, 28, 29]\) and by using Mg\(^{2+}\) ions as a bridge to attach DNA to negatively charged silicon oxide surfaces \([7, 17, 19]\), as described in Section 2.2.3. However, attachment of single-stranded DNA to a chemical template cannot be used for hybridization because the full length of the single-stranded DNA interacts with the template \([15, 29]\). This means that even though charge interactions are useful in the attachment of single-stranded DNA to surfaces, such strands would not be useful for the subsequent attachment of DNA origami. One way to overcome this problem is to use DNA-coated gold nanoparticles. The DNA-coated gold nanoparticles will attach to a positively charged chemical template by the interaction of the negatively charged phosphate backbone of the DNA strands (attached to the gold nanoparticles) with the template. The DNA strands on the bottom of the particle will interact with the positive surface charge of the template, and the strands on top of the particle will have no interaction with the template and be free to hybridize with the dangling strand(s) of a DNA origami structure (see Figure 6.2).
To enable the use of DNA-coated gold nanoparticles for alignment of DNA origami structures a few conditions need to be met. The DNA-coated gold nanoparticles have to be functionalized with single-stranded DNA. The DNA-coated gold nanoparticles need to completely and selectively cover the positively charged template to prevent nonselective/unoriented attachment of DNA origami nanostructures to the templates. The single-stranded DNA on top of the gold nanoparticle needs to be able to hybridize the dangling strands of DNA origami structures. As attachment of DNA-coated gold nanoparticles to patterned surface charge has been demonstrated [106], and the creation of suitable DNA-coated gold nanoparticles has been documented [107, 108], attachment of DNA-coated gold nanoparticles to a positively charged chemical templates was attempted.

To selectively position DNA-coated gold nanoparticles, a template of positive charges was required. The PAAM templating procedure (as described in Section 4.2) was used to create an amine template (which is positively charged in neutral aqueous solution) for attachment of the gold nanoparticles (see Figure 6.3), as amine templates have been shown to selectively attach
single-stranded DNA. With DNA-coated gold nanoparticles templated on a surface, an attempt was made to align a DNA origami shape to the gold particles.

To demonstrate the alignment of DNA origami structures, DNA was folded into a shape that could be easily identified during imaging, with an easily discerned orientation. The green triangle in Figure 6.4 is just such a shape. With dangling strands at the vertices of the hypotenuse for hybridization with the single-stranded DNA on the gold nanoparticles, the triangle would be
aligned along the hypotenuse. It is also noted that the triangle could lie to either side of the line of patterned gold nanoparticles.

![Image of alignment of DNA origami by hybridization](image)

Figure 6.4: Alignment of DNA origami by hybridization of the dangling strands to the single-stranded DNA of a line of patterned DNA-coated gold nanoparticles.

6.2.2 Experimental Procedures

6.2.2.1 Surface Preparation

The OTS (octadecyltrichlorosilane) monolayer preparation was used in the study as described in Section 4.2.1.

6.2.2.2 Procedures for AFM Tip-Directed Nano-oxidation for PAAm Treatment

AFM tip-directed nano-oxidation of the OTS surfaces was performed with Bruker NCHV-A AFM tips on a Veeco Dimension V AFM in contact mode at the minimum deflection voltage necessary to maintain contact with the surface. The AFM tips mentioned here are
different than the tips used in Chapter 4, and the conductivities of the two tips are not the same. Therefore, the nano-oxidation procedures were optimized in order to account for the different conductivities of the tips used in this study. For patterning, a tip potential of -9 V (tip relative to the surface, which was grounded) and a tip speed of 3–5 microns per second were used. For clarification, the deflection voltage is a measure of the force the tip is exerting on the surface, and the tip potential is the electrical potential applied to the tip. The minimum deflection voltage was determined by reducing the deflection voltage until the tip disengaged from the surface and was used to ensure that no mechanical scribing of the surface with the tip was occurring. As expected, the exact value of the minimum deflection voltage varied from one experiment to the next as it depends on the mechanical properties of the tip and the initial position of the laser on the detector; the tip potential for oxidation did not vary from surface to surface. Contact mode scanning at this deflection voltage and a tip potential of 0V (tip and surface grounded) resulted in no discernible change to the surface, as was reflected in the measurement of surface height and/or friction.

6.2.2.3 PAAm Treatment

The procedure used for PAAm deposition was the same as that presented in Section 4.2.3, except that longer PAAm/CTAC treatment times were used to optimize DNA-coated gold nanoparticles.

6.2.2.4 Preparation of DNA-Coated Gold Nanoparticles

DNA-coated gold nanoparticles were prepared according to the procedure described in Ref. [107, 108], with the following modifications and details. The nanoparticles were 7.6 ± 0.8
nm in diameter, and the disulfide form of mercaptohexylpolyT (HS(CH$_2$)$_6$TTTTTTTTT) was used to coat the particles with polyT DNA sequences. Thiolated DNA was used without reducing the disulfide bond as we found the reaction worked either with or without reduction. The gold nanoparticles and thiolated DNA were combined in a 1:200 molar ratio and left to react at room temperature for at least 19 hours. The gold nanoparticle DNA conjugates were filtered using 30 kDa Amicon filters to remove the unbound thiolated DNA strands from the solution. Samples were rinsed twice during the filtration using 450–500 µL 0.5 X TBE buffer. About 30–35 mL were recovered, with Au NP concentrations around 1–3.5 mM. The DNA-coated gold nanoparticle solution was diluted to a final concentration of 0.2 µM for use in surface treatment.

6.2.2.5 Triangle-Shaped Origami

As it was desired to orient a DNA nanostructure, an origami shape was needed for which the orientation on the surface after attachment would be easily discernible by AFM imaging. A triangle shape was designed to have a hypotenuse length of 140 nm and a 70 nm height, as displayed in Figure 6.5 a-c. The shape was designed using cadnanoSQ, with m13mp18 DNA as the scaffold strand. A complete list of the required staple strands is provided in Appendix A. The design includes two polyA sequence dangling strands (8 base pairs each) at each of the vertices of the hypotenuse. The dangling strands were added so that the triangle had attachment points to anchor it to the functionalized gold nanoparticles. The shape was folded by mixing a 1:10 ratio of scaffold strands to staple strands in 1X TAE-Mg$^{2+}$ buffer (a biological buffer with 40mM tris(hydroxymethyl)-aminomethane, 20 mM acetic acid, 1 mM ethylene diamine tetraacetic acid, and 12.5 mM MgCl$_2$) for a final origami concentration of 2 nM. The solution was heated to 95 °C for 3 minutes and then slowly cooled to 4 °C over 14 hours. An initial temp of 95 °C was
used to ensure all of the DNA strands were solubilized and that the m13mp18 strand was separated from its complementary strand. The temperature ramp allows the staple strands time to move into place while increasing the stability of the staple strands that had already paired with the scaffold strand. A 14-hour cooling time was used as cooling times of 3 and 6 hours resulted in incomplete folding of the triangle. The result was the formation of the triangular origami shape displayed in Figure 6.5. Also presented in Figure 6.5 are details of the design including the staple strand scheme for the center seam and one of the vertices with dangling strands.

**Figure 6.5**: Design of triangle DNA origami with the a) scaffold, b) staple strand near the center seem, c) staple strands and dangling strands near the bottom left vertex, d) AFM image close-up of one triangle, and e) an AFM image of several triangles. The triangle is 140 nm along the hypotenuse and 70 nm tall. The scale bars denote 100 nm.
6.2.3 Ionic Attachment of DNA-coated Gold Nanoparticles to PAAm Templates

Before templating, a surface was required that would be passive against the adhesion of PAAm and DNA-coated gold nanoparticles. If PAAm or DNA-coated gold nanoparticles attach to the background surface, then attachment of these materials on surface patterns or templates would not be specific to the patterns and may not useful in aligning the DNA triangles. An OTS monolayer was prepared, as alkyl monolayers are known to prevent attachment of PAAm in the presence of CTAC. The surface was tested for nonspecific attachment of DNA-coated gold nanoparticles. A fresh OTS monolayer was treated with a 0.2 µM solution of DNA-coated gold nanoparticles for 30 minutes and rinsed with water. Figure 6.6 is an AFM image of the resulting surface; there was no discernible deposition of the DNA-coated gold nanoparticles on the surface.

Figure 6.6: AFM image of an OTS monolayer treated with a 0.2 µM solution of DNA-coated gold nanoparticles for 30 minutes.
Before the alignment of DNA origami to the surface patterns, DNA-coated gold nanoparticles were attached to the PAAm templates; this resulted in a pattern of gold nanoparticles coated with single-stranded DNA. A 2 µm x 2 µm square was patterned by AFM tip-directed nano-oxidation on an OTS passivated silicon surface. The surface was then treated with the PAAm/CTAT solution to deposit the PAAm on the oxide patterns. The resulting surface was treated with a 0.2 µM solution of DNA-coated gold nanoparticles for 30 minutes. An AFM image of the square is presented in Figure 6.7. The DNA-coated gold nanoparticles were selectively attached (though sparsely) to the PAAm template, with nonselective positioning of a few gold nanoparticles on the hydrophobic background monolayer.

The sparse attachment of DNA-coated gold nanoparticles to the PAAm templates is one issue that would limit the capability to align origami to the surface patterns. The PAAm and gold nanoparticle treatment times were varied to examine their impact on the density and selectivity of gold nanoparticle deposition. Comparison of Figure 6.7 to Figure 6.8, which displays a 2 µm x 2 µm square treated with PAAm for 2 hours and the DNA-coated gold nanoparticle solution for 60 minutes, clearly shows that the treatment time impacts the attachment of the gold nanoparticles to the template. Figure 6.8 also reveals that with a 60-minute treatment time, the DNA-coated gold nanoparticles begin to deposit on the hydrophobic background. Figure 6.9 displays an image of a 2 µm x 2 µm square treated with PAAm for 12 hours and the DNA-coated gold nanoparticle solution for 60 minutes. A comparison of Figure 6.8 and Figure 6.9 reveals that the longer PAAm treatment time resulted in a slight increase in density of gold nanoparticles attached to the template. Additionally, an increase of DNA-coated gold nanoparticle attachment to the background was noted. These images were analyzed using Gwyddion AFM image
processing software, and found that Figure 6.7 had about 600 gold nanoparticles on the patterned square, Figure 6.8 had about 1200, and that Figure 6.9 had about 1500. This indicates that the DNA-coated gold nanoparticle solution treatment time was an important factor in the attachment density of gold nanoparticles to the PAAm templates. The quantity of gold particles varies with both the gold nanoparticle treatment time and the PAAm treatment time, but the density does not appear to be high enough to completely cover the chemical template without creating problems with non-selective deposition.

![AFM height image of DNA-coated gold nanoparticles attached to a PAAm-functionalized 2 μm x 2 μm square created by AFM tip-directed nano-oxidation. The PAAm treatment time was 2 hours and the DNA-coated gold nanoparticle treatment time was 30 minutes.](image-url)

Figure 6.7: AFM height image of DNA-coated gold nanoparticles attached to a PAAm-functionalized 2 μm x 2 μm square created by AFM tip-directed nano-oxidation. The PAAm treatment time was 2 hours and the DNA-coated gold nanoparticle treatment time was 30 minutes.
As none of these results for the attachment of DNA-coated gold nanoparticles to PAAm templates resulted in an acceptable density of nanoparticles on surface patterns, an experiment was designed to determine the effectiveness of PAAm layers in attaching the DNA-coated gold nanoparticles. A clean silicon-oxide surface was treated in the PAAm solution for 30 min to deposit a PAAm layer on the surface. The surface was then treated with the solution of DNA-

![AFM height image of DNA-coated gold nanoparticles attached to a PAAm-functionalized 2 µm x 2 µm square created by AFM tip-directed nano-oxidation. The PAAm treatment time was 2 hours and the DNA-coated gold nanoparticle treatment time was 1 hour.](image)

Figure 6.8: AFM height image of DNA-coated gold nanoparticles attached to a PAAm-functionalized 2 µm x 2 µm square created by AFM tip-directed nano-oxidation. The PAAm treatment time was 2 hours and the DNA-coated gold nanoparticle treatment time was 1 hour.
coated gold nanoparticles. The result can be seen in Figure 6.10. The DNA-coated gold nanoparticles attached to this surface with a density that is about the same as on the patterned squares. Given these results, a switch to a new template functionality or longer treatment times with the DNA-coated gold nanoparticles may improve the attachment density of gold nanoparticles to the amine templates.

Figure 6.9: AFM height image of DNA-coated gold nanoparticles attached to a PAAm-functionalized 2 µm x 2 µm square created by AFM tip-directed nano-oxidation. The PAAm treatment time was 12 hours and the DNA-coated gold nanoparticle treatment time was 1 hour.
To determine whether or not DNA-coated gold nanoparticles would stick to oxide patterns, an OTS monolayer was prepared and a 2 µm x 2 µm square was patterned by AFM tip-directed nano-oxidation. The square was exposed to a 0.2 µM solution of DNA-coated gold nanoparticles for 90 minutes. The 90-minute treatment time was used to determine if any significant attachment of the DNA-coated nanoparticles to the patterns would occur without PAAm treatment. The result can be seen in Figure 6.11. Even with the 90-minute DNA-coated gold nanoparticle treatment time, no significant attachment of DNA-coated gold nanoparticles to the oxide pattern was observed. It is also noted that with the 90-minute treatment time, there are few gold nanoparticles on the background OTS monolayer. The PAAm treatment was necessary to provide the amine functionality to attach the DNA-coated gold nanoparticles to the oxide pattern.

Figure 6.10: AFM height image of a PAAm-coated silicon oxide surface treated for 30 minutes with the solution of DNA-coated gold nanoparticles.
6.2.4 Triangle Origami Structure Treatment of Patterned DNA-coated Gold Nanoparticles

Attachment of the DNA coated gold nanoparticles was demonstrated on templated PAAm lines of 60 nm width, as displayed in Figure 6.12. While the DNA-coated gold nanoparticles are attached to the PAAm templates, several can be seen on the background. From the image, it appears that the DNA-coated gold nanoparticles that are not attached to the lines in the image may have been attached and then moved off onto the background. If the nanoparticles come off of the PAAm templates easily, there are implications regarding the utility of the process as the nanoparticles may also be mobile once the surface is treated with origami. Despite all of these issues, attachment of a triangle origami structure to the patterned gold nanoparticles was attempted.
After attachment of the DNA-coated gold nanoparticles, the nano-oxidized and PAAm-functionalized surfaces were treated with a 2-nM solution of triangle origami structures. It was expected that the polyA dangling strands of the triangle origami structure would hybridize with the polyT sequences on the gold nanoparticles, attaching and aligning the triangles to the lines of gold nanoparticles on the surface. Figure 6.13 is an image of what appears to be one such attached and aligned origami structure (indicated by the red circle). The triangle laid between two gold nanoparticles that are 140 nm apart, exactly the length of the hypotenuse of the triangle.

While specific alignment of one DNA origami triangle was seen, on this sample it was the only aligned triangle found on 100 µm of lines (20 lines of 5 µm length) on the surface from which the image in Figure 6.13 was obtained. Also, several triangle origami structures are seen in Figure 6.13 that are not aligned with the gold nanoparticles on the patterned lines. Single-stranded DNA and DNA nanostructure attachment to amine templates and surfaces has been demonstrated repeatedly [15, 28, 29]. However, there does not appear to be a preference for the attachment of the origami to the PAAm template. The cause of this may be due to the nature of the PAAm template, or possibly to the single-stranded DNA in the origami solution.

A raised oxide feature demonstrated in this case for attachment of PAAm (2.5 nm above the background after PAAm treatment). Therefore, the patterned gold nanoparticles are a significant height (2.5–10 nm, height of the patterns and the gold nanoparticles) above the surface compared to the thickness of the origami triangles (~1nm). Origami structures are known to have a weak attraction with alkyl monolayers. Rather than sticking to the alkyl monolayer and becoming immobile, the origami structures move along such surfaces until they find binding sites [56]. The raised oxide features, despite being functionalized with PAAm and DNA-coated
gold nanoparticles, seem to present a barrier, preventing the interaction of the triangle with the DNA-coated gold nanoparticles.

Figure 6.12: AFM height image of select attachment of DNA-coated gold nanoparticles to 70-nm lines patterned by AFM tip-directed nano-oxidation and treated with a PAAm/CTAC solution.

The other issue that may prevent the origami from attaching to the DNA-coated gold nanoparticles and/or the PAAm templates is that the final origami solution used to treat the surface contained the mixture of unfolded staple strands. The DNA origami was folded in a solution of 10 times excess staple strands. This means that the final solution contained a large quantity of single-stranded DNA. Some of the single-stranded DNA was of the same sequence as the dangling strands, but had not been folded into an origami structure. These strands will
certainly take up many of the hybridization sites on the DNA-coated gold nanoparticles, as there are at least 36 times as many polyA strands in the solution as triangle origami structures.

Despite these issues, the triangle in Figure 6.13 may have been aligned to the two nanoparticles by the dangling strand hybridizing with the single strand of one of the nanoparticles while approaching the surface. With one vertex attached, the other could have migrated around until it was in close enough proximity to the second nanoparticle for the other dangling strand to hybridize with one of the second nanoparticle’s single strands.

![Figure 6.13: AFM height image of attachment and alignment of a triangle origami to patterned lines of DNA-coated gold nanoparticles.](image)

Attempts to filter the origami solutions (to remove the excess single-stranded DNA needed to fold the structure) using centrifuge filtration procedures resulted in unfolding of the triangular origami structure. Using a 50 kDa filter (Amicon), the origami solution was
centrifuged for 10 minutes at 13000 rpm. Two more cycles were used with the addition of 500 µL of the 1X TAE-Mg$^{2+}$ buffer solution as washing steps. The 1X TAE-Mg$^{2+}$ buffer was used as this concentration of Mg$^{2+}$ is known to help maintain the stability of DNA origami structures [55, 109, 110]. Figure 6.14 displays the result of this filtering procedure. Triangles were not identified on the surface, and only these 5-nm tall shapes were identified. In an attempt to filter and maintain the triangle shape, a 30 kDa filter was used with the same procedures as before. Figure 6.15 displays shapes of 1–2 nm height and about the right size for the DNA origami triangles, but no triangle shapes were observed. Reduction in the time and speed of the centrifuge cycles may help in obtaining a filtered solution of stable origami triangle structures.

Figure 6.14: AFM Height image of origami triangles filtered using the centrifuge filtration procedures and a 50 kDa filter.
6.2.5 Summary

Patterns of DNA-coated gold nanoparticles were created by ionic attachment of DNA-coated gold nanoparticles to PAAm templates. Alignment of triangular-shaped DNA origami was attempted by attachment of origami to lines of templated DNA-coated gold nanoparticles. The unfiltered origami solution had too many excess dangling strands, which may have blocked the origami triangles from hybridizing with the single-stranded DNA of the DNA-coated nanoparticles. A filtering procedure needs to be developed to separate the triangle origami shapes from the excess staple strands. Treatment of patterned DNA-coated gold nanoparticles on PAAm templates with a filtered triangle origami solution will help establish whether the height of the templates is a factor preventing alignment of origami triangles. Additionally, significant improvement of gold nanoparticle attachment to PAAm, or a change in template chemistry, will
be required to achieve the desired density of DNA-coated gold nanoparticles attached to the surface patterns.

6.3 DNA Alignment by Covalent Immobilization of Single-stranded DNA to Chemical Templates

6.3.1 Introduction

Alignment of DNA origami structures by immobilization of single-stranded DNA to chemical templates was also explored, in addition to the ionic attachment described previously in this chapter. Covalent attachment of single-stranded DNA, also referred to as immobilization, could potentially provide a method for surface attachment and orientation of DNA origami structures. Referring back to Figure 6.1, covalent binding of a DNA strand to a chemical template could also provide hybridization sites for the dangling strands of origami structures and may circumvent many of the issues presented in the ionic-attachment scheme. Covalently bound DNA strands are less likely to be removed from the template than a strand with an ionic interaction with the template. Another advantage of using DNA immobilization to create attachment sites is the possibility of patterning DNA strands of different sequence on the same surface. Chemical templating of two or three distinct functionalities on the same surface may allow immobilization of different DNA sequences to each template. If, for example, two different DNA sequences were patterned on the same surface and an origami structure were designed with complementary sticky ends, then the surface could be patterned to exactly specify the orientation of the origami structure. Figure 6.16 illustrates this concept using a “T”
shaped origami structure. To utilize the advantages of this patterning, first patterning and attachment using a single chemistry must be demonstrated.

Figure 6.16: Diagram displaying the advantage of having multiple attachment chemistries. “T” shaped origami structures with a) one attachment sequence, and b) two attachment sequences, with subsequent surface attachment.

To immobilize DNA strands on a chemical template, a template must be created with a chemistry that can react with one of the possible moieties that can be attached to the end of a DNA strand. As discussed in Section 2.2.3, there are a limited number of immobilization schemes that have been used reliably to immobilize DNA to silicon oxide surfaces. The limitation exists in the interaction of reactants and reaction conditions with DNA, as it is
undesirable to modify the DNA during the immobilization procedure. The immobilization scheme decided upon for this study was the amide linkage to carboxylic acids presented initially in Figure 2.5 and shown here for convenience (Figure 6.17). An aminated DNA strand (a strand of DNA terminated with a primary amine group) and a template of carboxylic acids are required for this immobilization scheme. A template of carboxylic acids can be patterned on a surface by controlled oxidation of an alkyl monolayer as discussed in Section 2.4.3. Binding the aminated DNA strand with the carboxylic acid template may potentially result in a DNA template suitable for hybridization with the dangling strands of a DNA origami structure, attaching and orienting the origami structure on the surface. Figure 6.18 is a diagram of the desired outcome of this portion of my work, namely, the selective alignment of DNA origami structures by hybridization of the dangling strands of origami structures to DNA strands immobilized on chemical templates.

Figure 6.17: Reprint of Figure 2.5, immobilization of a DNA strand to a carboxylic acid using EDC, NHS, and an aminated DNA strand (adapted from reference [54]).
Figure 6.18: Alignment of DNA origami by attachment to multiple surface sites. DNA strand A is immobilized on the chemical template and can be hybridized with the complementary strand A’ (the origami structure’s dangling strand).

6.3.2 Experimental Procedures

6.3.2.1 Surface Preparation

OTS monolayers were prepared for use in this portion of the study as described in Section 4.2.1.

An octyl silane monolayer (OMCS, octyldimethylchlorosilane, Gelest 98%) was also used in the covalent attachment scheme, and served the same purpose as the OTS monolayer. As the OMCS chain (C₈) is shorter, it was expected to oxidize at a lower tip potential than the OTS monolayer (C₁₈). To prepare an OMCS monolayer for nano-oxidation, native oxide silicon wafers were cleaned in a Harrick Plasma (PDC-32G) plasma reactor and immersed in neat OMCS at 80 °C for 15 minutes. This resulted in a monolayer with a thickness of 0.7 nm (as measured by spectroscopic ellipsometry, J.A. Woollam Co., Inc., Model M2000D) and an advancing water contact angle of 100° [102, 111, 112]. This monolayer was used as it was found to produce a clean-flat surface of alkyl chains during a long period of deposition problems with the OTS monolayer.
6.3.2.2 Procedures for AFM Tip-Directed Nano-oxidation for Amide Linkage

To prepare chemical templates for covalent DNA attachment, an OTS or OMCS surface was patterned at the minimum deflection voltage necessary to maintain contact with the surface and a tip potential of -7.2 V or -6 V (the minimum voltage found to sustain oxidation) of the OTS and OCMS monolayers respectively. The minimum tip potential for oxidation was used to ensure that the alkyl monolayer was only oxidized to a carboxylic acid and not completely removed from the surface [16, 74]. The result of oxidizing at this deflection voltage and tip potential is seen by a change in friction (meaning a change in the tip surface interaction) between the oxidized pattern and the alkyl monolayer, and minimal change in height from the background to the pattern [16, 74]. Friction imaging is an application of contact mode imaging. As the tip is scanned over the surface, a change in friction can be detected by the rotation of the cantilever. The rotation of the cantilever is caused by a change in the tip-surface interaction and causes a horizontal shift of the laser on the detector (see Figure 2.10). While a contrast in friction indicates a change in surface chemistry, quantifying the change is difficult as the values obtained vary from tip to tip. The minimum potential was found by stepping down the tip voltage until no height change was discernible after attempted patterning.

6.3.2.3 Carbodiimide DNA Immobilization Procedures

After patterning, the samples were immersed in deionized water for 30 minutes, then treated for 90 minutes in a 5 mM/5 mM EDC (N-(3-dimethylaminopropyl)-carbodiimide, 98%, Sigma)/NHS (N-hydroxysuccinimide, 98%, Sigma) solution at 15 °C and rinsed with water for five seconds. The reaction is diagrammed in Figure 6.19. The complexation of the carbodiimide with the carboxylic acid allows for the formation of a more stable NHS ester. The NHS ester
then reacts with the amine-terminated DNA strand to form the desired chemical bond, with the amide replacing the ester in an aqueous solution. If the carboxylic acid is not protected by the NHS ester, then the product of primary amines and carboxylic acids is proton exchange.

After reacting in the EDC/NHS solution, the surfaces were functionalized overnight with a 10 μM 5’aminohexylpolyA DNA (a DNA strand of sequence AAAAAAAA terminated with a six carbon chain and a primary amine). Because the interaction that binds the immobilized strands to the surface was a chemical bond (unlike the ionic effect that interacted with the phosphate backbone of the whole strand) the immobilized strands were free to base pair with a complementary strand. The desired result was surface patterns of DNA strands with a hydrophobic background. Figure 6.20 illustrates each step of the process to use DNA immobilization on a chemical template to patterned sites for hybridization of the dangling strands of DNA origami structures.

![Diagram of EDC/NHS reaction for amide linkage of DNA to carboxylic acids](image)

**Figure 6.19: Diagram of EDC/NHS reaction for amide linkage of DNA to carboxylic acids (adapted from reference [113]).**
Figure 6.20: Stepwise process to create surface patterns of DNA strands of a desired sequence. An alkyl monolayer is oxidized by AFM tip-directed nano-oxidation to create carboxylic acids on the surface, then treated with an EDC/NHS solution prior to functionalization in a solution of amine-terminated DNA strands.

6.3.2.4 Long Arm T Origami Structure

A long-arm T origami structure was acquired from collaborators and used as received. Figure 6.21 is a diagram and AFM image of the design and resulting shape [114]. The only modifications to the reported design were the addition of two dangling strands of sequence AAAAAAAA to each end of the long arm, and the concentration of staple strands to scaffold strands was reduced to 10:1. As this modification of the design has not been published, details of the design are available in Appendix A.
6.3.3 Hybridization of DNA Origami Structures to DNA Strands Immobilized on Chemical Templates

A 2 µm x 2 µm square was patterned by AFM tip-directed nano-oxidation to create a template of carboxylic acids. As discussed in the Background (Section 2.4.3), oxidation of alkyl monolayers on silicon surfaces at the minimum tip potential and residence time results in the formation of carboxylic acids [16, 74]. Figure 6.22 displays height and friction images of a 2 µm x 2 µm square patterned by AFM tip-directed nano-oxidation of an OTS monolayer. Height data is presented at the same data scale as Figure 6.7 to emphasize the contrast in height change. The minimal change in height upon oxidation indicates that oxidation of the monolayer and not the substrate has occurred. The friction change (Figure 6.22b) demonstrates a chemical contrast between the oxidized pattern and the original background monolayer.

Figure 6.21: AFM images of the long-arm T origami. These images were provided by Elisabeth Pound.
To determine if the OTS monolayer would remain unaffected by the EDC/NHS solution, an OTS monolayer was treated for 90 min in the EDC/NHS solution and then imaged by AFM. The result (see Figure 6.23) was some contamination of the monolayer.

Figure 6.22: AFM a) height and b) friction images of AFM tip-directed nano-oxidation on an OTS monolayer to produce a 2 µm x 2 µm square surface pattern of carboxylic acids.

Figure 6.23: AFM height image of an OTS surface treated for 90 minutes with the EDC/NHS solution.
After reacting a carboxylic acid template in the EDC/NHS solution, the surface was reacted overnight with aminated DNA. The surface was then exposed to a 2 nM solution of the long-arm T structure for 2 hours so the dangling strands on the long arm T structure could hybridize with the polyA immobilized on the surface patterns. Figure 6.24 displays an AFM image of a 2 µm x 2 µm square patterned and functionalized by the EDC/NHS amide linkage procedure and treated with the long arm T structure. A number of long-arm T structures are

Figure 6.24: “T” shape DNA Origami attached to a 2 µm x 2 µm square chemical template. The red circles identify five distinct individual T-shaped origami structures, though others can be seen in the image.
bound to the square. With the complex solutions and long treatment times that accompany treating the surface with the DNA origami, both of which could contribute to contamination of the surface, simplification of the initial problem was necessary. Instead of attaching the T structure to the surface it was decided to attach DNA-coated gold nanoparticles to a patterned area that had been functionalized with DNA via the EDC/NHS reaction, as solutions of DNA-coated gold nanoparticles have fewer components and require only 30 minute treatment times.

As the OTS monolayer did not deposit cleanly for a time, likely due to a humidity change in the lab, an OCMS monolayer was used. It was expected that the oxidation for the OMCS layer would occur at a lower tip potential than the tip potential required for the OTS monolayer, as the carbon chain of the OMCS (C₈) monolayer is shorter than that of the OTS monolayer (C₁₈). An OMCS surface was prepared, a 2 µm x 2 µm square was patterned by AFM tip-directed nano-oxidation to create a template of carboxylic acids (a tip potential of -6.3 V was found to reproducibly create the desired patterns), and the surface was reacted with EDC/NHS and an aminohexylpolyA (NH₂(CH₂)₆AAAAAAA) DNA strand. The surface was then treated with a solution of DNA-coated gold nanoparticles (for which the DNA sequence was TTTTTTTT). Figure 6.25 is an AFM image of the resulting surface. Although the density is low, selective attachment of DNA-coated gold nanoparticles to the patterned and functionalized areas was observed, despite the contamination film left by the EDC/NHS solution (similar to but more pronounced than the contamination left on the OTS monolayer). Rinsing procedures were implemented before the overnight aminated DNA treatment to remove the contamination film left by the EDC/NHS reaction. These rinsing procedures included longer water rinse times and sonication in acetone, methanol, and water. In each case, the more aggressive rinsing procedures
resulted in a significant decrease of attachment of DNA-coated gold nanoparticles to the patterned and functionalized area.

The result of the origami and gold dot attachment tests (Figure 6.24 Figure 6.25) show that the apparent density of immobilized aminated DNA strands was lower than desired and/or that surface contamination was blocking the dots from attaching to the area. These contamination problems arise in part in the interaction of the EDC/NHS solution with the surface. After a 90-minute treatment of an OMCS surface with the aqueous EDC/NHS solution, a film of 0.5 nm (as measured by spectroscopic ellipsometry) was deposited on the OCMS monolayer. Aggressive

![AFM height image of the attachment of polyT DNA-coated gold nanoparticles to a 2 μm x 2 μm square created by AFM tip-directed nano-oxidation and functionalized with polyA DNA.](image)
rinsing (longer rinsing times and sonication) with water, acetone and methanol were found to reduce the contamination, but also resulted in an even lower gold nanoparticle density as compared to the original rinsing procedure. One way this problem may be resolved is by using a different solvent and/or a different carbodiimide. Acetone, dichloromethane, and methanol (because they are relatively inert-polar solvents and we did not note the use of EDC in solvents other than water) were all tested as solvents for the EDC/NHS reaction; EDC did not dissolve in acetone or dichloromethane, and the EDC/NHS/methanol solution deposited a 2.5 nm contamination layer on an OMCS monolayer. DCC (dicyclohexylcarbodiimide) is a carbodiimide commonly used in organic solutions. The use of a DCC/NHS or EDC/NHS solution with a different solvent may resolve these contamination issues.

One other possible issue is the density of DNA attachment to carboxylic acids. In an attempt to determine the density of amide attachment, a carboxylic-acid-coated surface was prepared by depositing a layer of triethoxysilylpropyl succinic anhydride (TESPSA) on a silicon wafer [115]. XPS analysis confirmed that carbonyl carbons were present on the surface, indicating functionalization of the surface with carboxylic acids. The surface was reacted with the EDC/NHS solution for 90 minutes and overnight with an aminated DNA strand. XPS analysis of the surface confirmed the presence of phosphorus on the surface (see Figure 6.26). While this confirms the presence of DNA [116], the low signal to noise for both the phosphorus and carbonyl peaks does not allow for reasonable quantification of DNA attachment. Increasing the density of deposition of TESPSA and use of ToF-SIMS (time-of-flight secondary ion mass spectrometry) may enable quantification and optimizing of the EDC/NHS reaction procedures.
Also visible in Figure 6.25 is the apparent adsorption of the background contaminants to the patterned areas. EDC/NHS solutions have been used for amide linkage immobilization of DNA (and subsequently hybridization of DNA to the immobilized strands) to silica surfaces functionalized with a carboxylic-acid-terminated organic layer and did not result in the contamination of those surfaces [54]. This brings up the question of the density of carboxylic acids after AFM tip-directed nano-oxidation. If only a small portion of the carbon chains on the monolayer are converted to carboxylic acids, the result may be the same contamination as the background monolayer. Confirmation of the oxidation product would be useful in determining the quantity and functionality of the chains on the oxidized patterns. ToF-SIMS may be a useful tool in analyzing patterned areas for mass fragments that correspond to particular functionalities, and in analyzing the density of those fragments.

![Figure 6.26: XPS spectra of the phosphorus 1s peak (135 eV) of a EDC/NHS and aminated DNA treated TESPSA-coated surface.](image)
6.3.4 Summary

Selective attachment of DNA origami and DNA-coated gold nanoparticles to surface-patterned templates was demonstrated. Surface contamination by the EDC/NHS solution made it difficult to ascertain the degree of DNA attachment to the surface patterns. Further use of XPS and ToF-SIMS to analyze surface attachment of DNA by the EDC/NHS reaction and carboxylic acid density on oxidized patterns will lead to location specific attachment of DNA to surfaces patterned by AFM tip-directed nano-oxidation. Development of the AFM tip-directed nano-oxidation and EDC/NHS reaction and other immobilization chemistries may open a pathway for templating of multiple-different DNA sequences on the same surface, potentially adding to the ability to control surface alignment of DNA origami structures.
7 CONCLUSION AND FUTURE WORK

7.1 Conclusions

This work has examined the creation and use of chemical templates for nanocircuit and other nanodevice fabrication. Chemical templating can be useful in attachment, orientation and wiring of molecularly templated circuits. DNA origami provides a suitable method for creating molecularly templated circuits as DNA can be folded into complex shapes and functionalized with active circuit elements, such as semiconducting nanomaterials. DNA origami structures can be designed with dangling single-stranded DNA to be used for surface attachment by hybridization with complementary surface-bound strands. Chemical templating provides a pathway for placing the patterned surface-bound attachment points needed for surface alignment of the molecular templates. Chemical templates can also be used to connect circuit elements on the surface by selectively metallizing chemical templates to create local wiring. AFM tip-directed nano-oxidation was selected as the method for surface patterning to create chemical templates, as it has proven to be a flexible and reliable patterning tool. This project provides demonstration of new chemical templating techniques, continuous metallization of nanometer-scale chemical templates, and attachment of DNA to chemical templates.

As selective-continuous-nanometer-scale metallization of nanochemical templates is necessary for wiring of circuit templates, development of metallization procedures was needed to produce continuous metal deposits on chemical templates of nanometer-scale width. It was
discovered that MPS treatment led to a 74% increase in the quantity of palladium seeding on the surfaces. As local wiring may require the use of metals other than palladium, MPS treatment was tested to ascertain the possibility of enhancing the deposition of other metals. The increased metallization effect of MPS treatment was demonstrated with electroless copper metallization, indicating that increased metallization density by MPS treatment could be extended to other metals which deposit on palladium seeds. These results indicate that the MPS treatment of amine templates will result in an increase in palladium seeding, enabling the continuous metallization of nanometer-scale amine templates for local wiring of molecularly templated nanoelectronic devices.

Having studied the metallization enhancement of amine-coated surfaces by MPS treatment, a nanometer-scale-amine template was needed to test if MPS treatment would indeed enable the continuous metallization of nanometer-scale features. A new chemical templating procedure was demonstrated by selective attachment of PAAm to surface oxide features created by AFM tip-directed nano-oxidation. These amine-based chemical templates were used to test the effect of MPS treatment on the metallization nanometer-scale features. MPS treatment of the PAAm templates resulted in an increase in the metallization of the templates, making possible a reduction of the feasible width for continuous copper metallization from 500 to less than 100 nanometers. The PAAm templates, in conjunction with MPS treatment, enabled the creation of continuous nanometer-scale metal deposits that could be used for local wiring of molecularly templated circuits. These oxide patterns for PAAm templating are created not only by AFM tip-directed nano-oxidation, but also by parallel methods; making possible the simultaneous-high resolution patterning of larger 2-dimmensional areas.
The negative patterning of a metal film provides a pathway for parallel nano-oxidation. To produce a negative metal film with nanometer scale resolution, AFM tip-directed nano-oxidation was used to selectively oxidize a MPTES layer. Subsequent metallization of NiB on the patterned surface resulted in a metal film with metallization of the background surface and not the oxidized patterns. Metallization gaps less than 30 nm and continuous metal lines less than 50 nm were demonstrated. These MPTES-coated surfaces can also be patterned by parallel methods.

Ionic and covalent attachment of DNA to chemical templates was attempted for the surface alignment of DNA origami structures to enable their use as molecularly templated circuits. These template-bound strands would be used to position and orient origami structures by hybridization of surface-bound strands with the dangling strands of origami structures. Patterning of single-stranded DNA was attempted by ionic attachment of DNA-coated gold nanoparticles to PAAm templates, and resulted in a less than desirable density of DNA-coated gold nanoparticles to the PAAm template. The deposition time and concentration of the DNA-coated gold nanoparticle solution may have been limiting factors in the density of DNA-coated gold nanoparticles attached to the PAAm templates. Alignment of triangular-shaped DNA origami to the patterned surface was attempted by attachment of the origami structures to lines of templated DNA-coated gold nanoparticles. Attachment of the origami structures to the patterned DNA-coated gold nanoparticles may have been prevented by the low density of the DNA-coated gold particles on the templates, the height of the template above the background, and/or the excess staple strands in the DNA origami solution.

Selective attachment of DNA origami and DNA-coated gold nanoparticles to templates with covalently immobilized single-stranded DNA was also demonstrated. Surface contamination of the OTS layer and patterned areas by the EDC/NHS solution was reduced by
aggressive rinsing, but also made it difficult to ascertain the density of DNA attachment to the chemical templates. Selective attachment of DNA origami and DNA-coated gold nanoparticles to the DNA functionalized templates demonstrates the potential of using chemical templating for the directed alignment of DNA origami structures, enabling their use in the fabrication of nanoelectronic devices. These advances together demonstrate progress toward the realization of using chemical templating to position and connect functional devices that are fabricated by assembling molecularly templated components.

### 7.2 Future Work

The position specific attachment of nanomaterials was demonstrated by chemical templating utilizing AFM tip-directed nano-oxidation. The progression of this work for eventual demonstration of surface alignment of DNA origami structures, enabling their use in nanoelectronic device fabrication, lies in a three key areas; 1) the high density attachment of DNA-coated gold nanoparticles to chemical templates, 2) the immobilization of single-stranded DNA to chemical templates for patterning of multiple compatible chemistries, and 3) the development of the parallel nano-oxidation with the negatively patterned NiB films.

First, the density of attachment of DNA-coated gold nanoparticles to amine templates must be increased to create patterns of DNA-coated gold nanoparticles suitable for the attachment of DNA origami structures. An increase in the density of DNA-coated gold nanoparticles to templates may be accomplished by a change in template chemistry (use of another amine-based template or other positively charged species) and/or a change in the procedures for deposition of the DNA-coated gold nanoparticles on the PAAm templates (by increasing deposition time and
improving selectivity and/or rinsing). As the attachment of DNA-coated gold nanoparticles has very recently been demonstrated at a significantly higher density than that observed on the PAAm templates [106], the PAAm template may be fundamentally limiting in this application. If the PAAm system is eventually found to be limiting, a new template will need to be developed for attachment of the DNA-coated gold nanoparticles. Once a procedure for increasing the density of DNA-coated gold nanoparticle attachment to chemical templates has been established, the patterns of DNA-coated gold nanoparticles may be used to demonstrate and study the attachment of DNA origami.

Second, advancement in the immobilization of single-stranded DNA to chemical templates may allow for patterning of multiple different single-stranded DNA sequences to a surface. For the amide attachment specifically, greater understanding of both the nano-oxidized template and the attachment chemistry is needed. The density of aminated DNA strands that will attach the carboxylic-acid templates using the EDC/NHS system is currently unknown. Selective attachment of DNA nanostructures to templates was shown. Understanding and demonstrating the selective immobilization of multiple different sequences of single-stranded DNA to templates of different chemistry may produce DNA surface patterns for use in the attachment and orientation of more complex DNA origami structures.

Third, continued development of the negative patterning of NiB films may enable its use as parallel technique for making masks and for other applications. It remains to be determined if a nickel-boron electrode can be used for parallel nano-oxidation. In particular, the roughness of the film may be a factor in uniform pattern transfer. Deposition of a second metal may be necessary to smooth the layer and/or to create a suitable electrode for consistent, uniform, parallel nano-
oxidation. Deposition of a second metal may also be used to improve the conductivity of the deposited NiB layer. With a suitable, patterned metal film, it should be possible to pattern other surfaces at high resolution by parallel nano-oxidation using the methods demonstrated in this study.

The above extensions of the work described in this dissertation will permit chemical templating of multiple chemistries and open a pathway for DNA attachment to and the metallization of different chemical templates on a single surface. These combined capabilities will enable the surface alignment and local wiring of complex DNA origami structures as the basis for a new generation of nanocircuits, nanosensor arrays, and other nanodevices.
8 REFERENCES


APPENDIX : DNA ORIGAMI DESIGN

Triangle Origami Structure Design

Scaffold:

M13mp18, bases 7174,

Fold Time:

14 hour origami program. Cool from 95 °C to 4 °C.

Staple sequences:

AGTAACAGTGCCCGTATAAACAGTTAATGCC
CCCTGCCTATTTTCGGAGGGGTCAGTGCCCTTG
TTTGATGATACAGGAGTGACTGGTAACGTTCCAG
TTAACACCTATTATTCTGAAACATGAGGATTA
TAAGCGTCTTTAAAGCCAGAATGGAGGAGGTTG
GGATTAGCGGGGTCTGAATTACTAAGTT
GAGACTCCTCAAGAGAAAGTATTAAGAGGCT
TCACAAAACAATAAATCCTCAATACATGGCT
CAGTCTTTTGCTCAGTACCAGCGGGATGTACTCAG
GCCGTCGAGAGGTTGATATAA
AGGCAGGTACCAGAACCACCACCAGCACCAC
GAGGTAGTAGACGATGACAAAGCG
GTAGTGCCGCTCAGGACACCACCACCTCAT
CACCCTCAGAGCCACCACCCTCAGAACCAGC
AGCCGCCAGACGATTGCGTCCCGATAT
CCGCCGCCACCCTCAGAACCAGGCCACCGTAACAC
CCGCCACGAATAGGTGTATCACCAAGT
CGAACCACCTTGCATCTTTTCATAACCAATGA
TGAGTTTCGTCACCAGGAAACCAGAGGCCG
TTTCAGGGATAGCAAGCCCAAGGCCCCTCAGATAGTTAGGTATGGGA
ACTGATAGCGCCTTTTTCATCG
GCATTTTCGGTCATAGCAGTAGC
TTAGCGTCCTCCCTCAGAGCGCCGACCCTCAG
ATCACCAGTACAACATACACGCTTTTCAGCG
CCACAGACTAGGAAACCATGTACCCTCAGAA
CGATCTAAAGTTTGGTCGTCTT
GACAGAATGCCAATTGGGAATTAGTCAACCGA
AACCATCGAGTACCCATTACCTTTACCAG
GAGTGAGAATAGACGGAAACGTCATCAAA
TTTTGCTATCACGTTGAAATCTAACAGCTT
TCCAGACGTTAAAGGAGCCCTTTAATTGTA
TAAAGGGTGAATTATCAACGGAAATTATTCAT
GACCTGACAAGTTCCTGCTTACGTCAG
AAATCACCATAGCAGCACCCTGTAATCCCCCTTA
AAGGCAAGGAACAACTAAAGGAATTGACAAC
TAAATTTAACAACCTTTCAACAGGTCAGATT
AAGGCTCCAGTAATGAATTTTCTCGTAA
TTGAGGGATATAAAAGAAACGCAAGAAGGAA
CGCCAAAGAGTTTTTATTTGTACACAAAAAGTAA
ACCATCGCCCACGAATTCATATGGATTAGC
GATACCGAAGTTAAGGCGCTTTTAATACGTA
TCGGTTTATCAGCTTTTCTCAGCAGCAGAAGACTTTCATGA
ATTACGCAGTTAGTTAGCAAA
CGTAGAAAATACATAGAATACCC
TGGCAACAGGGGAAAGATATATTGCGTCACC
ACGGAATAAACAAGGGCGACATAGCCAGCA
TAGAACATAACGATATATTGGTCGTTAAACGA
TGCAGGGTAGTTGCCGCCAGACATGCGAATAA
CGTCACCCGAGGTGAATTTCTTACCCAAAAA
GGAACGAGGGTAGCAACGGC
AAAAGAACTAATATCGAGAGATATAACATAA
ACCGAGGAGTTAAGCCCCATAATAAAAAATGAA
GCAGATAAAAATAGCAATAGCTACAAAATAAG
AAGAGGCAAAGACCCCTTTTAAGATCAA
ATGCCACTATACCAAGCGCGAAACAGATGAA
GGAAGTTTTTGATATCAGCTGGGAACC
ACAGAGGCTTATCCGCACCTGCTCCATGT
CCCTGAACAAAGTCAGGAGAATTAACTGAAACA
TTGAGCGCTGGCATGATTAAAGACTCTCTT
GAATTGAAACGCAATAATAACGCATAAAAGG
AAACAATTTGCCGAAACAAAAGTTACCAAGACACC
CGAAGATACACTAAACACTCATCTGCTGCTGGCTG
CAGCGATTACGAGGCAACCAAACCCTGAGGCT
AACGGAGATCTCATTAAACGGGTAATGGGGGAT
GTGTCGAATGAGGACTAAAGACTTACATTC
AAACAGGGAGCTACAATTTTATCCCTTATCCG
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AGGAGCAGGGCGTACGAGGCTGTGGTAAAGAG
AAGTTGGGAGGAAGGAGAAGGGAGAAGTTGTAGC
AAACCGGCTCATAGACCTAAACTCGGCC
AAACCGGCTCATAGACCTAAACTCGGCC
Long Arm T Design with Dangling Strands

Scaffold:

M13mp18, bases 5734-1442, 2958 bp

Fold Time:

2 hour origami program. Cool from 95 °C to 4 °C.

Modified staple strands:

GCATCAATTCTACTAAATAAAAAAAA
GGTAGAAAGTCTATCAGAAAAAAAAAA
GGAAACACATTATTACAAAAAA
CATAACCGATTGAAAAGGTGAAAAAAAA

Regular staples:

AGATCGCACCAGTCGGG
TTCTGGTGACATTAATTGCAGTCTCACCTCTG
CGCCATTCAAGGCCTGGGTTGCTAATGAGTGA
CGATCGGTACACAAACATACGAGCCGGAAGCAT
GCTGGCGACCTGTGTGAAATTGTATCCGCTC
TAAGTTGGGCTCGAAATTCGTAATCATGGTCAT
CGACGTTCAGGCTCGACTCTAGAGGATCCCGG
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AGAGTCTGTCTGCCCAGTTTGAGGGGGCACCAGC
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