TUCKER, ERIC ZACHARY. Issues in Patterning Self-Assembled Monolayers by Molecular Replacement: Comparison of Adventitious and Directed Replacement of One Molecule in a SAM with another. (Under the direction of Christopher B. Gorman).

In this work the directed (replacement lithography) and non-directed replacement of Self-assembled monolayers (SAMs) of various binding groups and structures on different substrates was explored. First, the effect of order in alkanethiol SAMs on gold on the amount of replacement in replacement lithography was explored. It was shown that higher ordering in these SAMs resulted in less amounts of replacement. Attempts were made to explore the use of alkanethiol SAMs on GaAs in replacement lithography, but this was frustrated by difficulties characterizing the initial SAM formed and the stability of the SAM. In another case, non-directed (adventitious) replacement of SAMs comprised from \( n \)-alkane thiols and terminal alkynes on gold were explored. These SAMs were subjected to solutions containing ferrocene-terminated thiol, thioacetate and terminal alkyne, respectively. The rate and extent of chemical exchange was monitored by scanning tunneling microscopy (STM). In several cases, a rate constant for exchange could be obtained by fitting to a model for exchange. In each case where this could be accomplished, a different rate model gave the best fit to the data, suggesting that the mechanism of exchange depended on either or both the original SAM and the incoming molecule. In scenarios where the rate of exchange was slow, replacement lithography was accomplished. The extent of exchange by replacement lithography was independent of the ink molecule, suggesting that tip-induced desorption was the limiting factor in this process. Also, the adventitious replacement of SAMs comprised from \( n \)-alkane thiols and alkylisonitriles on platinum was explored. These SAMs were
subjected to solutions containing ferrocene-terminated thiol and ferrocene-terminated isonitrile. The rate and extent of chemical exchange was monitored by STM, but the rapid amount of replacement frustrated attempts to study the exchange of these films.
Issues in Patterning Self-Assembled Monolayers by Molecular Replacement: Comparison of Adventitious and Directed Replacement of One Molecule in a SAM with another

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DEDICATION

This work is dedicated to my parents, Michael and Diane Tucker, and the rest of my family who always believed in me, even during times when I struggled to believe in myself.

Thank you so much for your continued support, especially during difficult personal times.

You are always there to listen to me and offer guidance whenever it is needed. Words cannot express how much it has helped me, especially during more recent times.
BIOGRAPHY

Eric Tucker grew up in Valatie, NY where he attended Ichabod Crane high school, graduating in 2001. After, he attended Elmira College where he received a B.A. in chemistry in 2005. While at Elmira College he discovered an interest in chemistry, especially relating to nanoscience. In the Fall of 2005, he began his PhD work in the department of chemistry at North Carolina State University in Raleigh, NC. Under the guidance of Dr. Christopher B. Gorman, he studied the exchange of self-assembled monolayers with other molecules that have affinity for the substrate being employed.
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Chapter 1 - INTRODUCTION

1.1 Miniaturization of Electronics

As predicted by Gordon E. Moore in the mid 1960s there has been a continued demand to push electronic components to smaller dimensions to allow for increased functionality within a restricted amount of space.\(^1\) Moore predicted that the number of transitors in a circuit will double every 18 months. Figure 1.1 shows the original graph forecasting this trend. As shown in Figure 1.2, which is an updated version of this graph, this prediction has held true up until the present.\(^2\) Along with integrated circuits, there is a demand to fabricate nanostructures for a variety of applications.

It is generally accepted that photolithography, the main tool responsible for allowing the trend shown in Figure 1.1 to hold true, will have to be replaced by another technique for patterning surfaces due to various limitations.\(^2\)\(^-\)\(^5\) In photolithography, complex patterns are made to form the intricate network of transistors necessary to form an integrated circuit.\(^2\)\(^,\)\(^5\) A crucial step in forming this network of transistors involves directing light through a mask, which is patterned beforehand, to allow for one to project a desired pattern onto a photosensitive surface. One limitation of this process is that the minimum feature size that can be obtained is restricted by the diffraction of light as it passes through the mask. This has led to increased interest in other photolithographic and non-photolithographic techniques for patterning surfaces in the continued development of smaller features sizes in integrated circuits, but also for other applications where miniaturization is of interest, such as biosensing, microptics, microanalysis, etc.
As described above, much of the patterning done in the advancement of integrated circuits is done through photolithography, which is a “top down” method, but other “top-down” methods and “bottom-up” methods have been developed for making patterns at small length scales for various applications.\textsuperscript{2,3,5,6} A “top-down” method for making patterns on
surfaces can be defined as a method for creating patterns where one starts from a larger pattern and progressively decreases the dimensions of the pattern until features reach the desired size. Alternately, a “bottom-up” approach for patterning is a technique where one starts with small amounts of material and progressively adds more of the material in a controlled, confined manner. However, both “bottom-up” and “top-down” methods for patterning surfaces have been shown to have limitations.\textsuperscript{5} Many “bottom-up” approaches have yielded nanostructures with dimensions smaller than 10 nm with relative ease compared to most “top-down” approaches, which have pushed down to the nanometer length scale, but have become quite elaborate and expensive.\textsuperscript{2,5} So, it has been proposed that a “bottom-up” approach, using self-assembly, could be used as a means to organize molecules so they can function as a device.\textsuperscript{3} For instance, there has been extensive interest in using molecules with interesting electronic properties to act as various components in a nanoscale device, especially in integrated circuits.\textsuperscript{3,4,7} However, despite the relative ease at which one can make nanometer scale structures through some “bottom-up” approaches, making elaborate patterns using these methods and incorporating these methods to build structures for various applications has proven to be difficult.\textsuperscript{5}

It has been suggested by some that a combination of “top-down” and “bottom-up” approaches for patterning surfaces could overcome the limitations of these processes when used separately, especially for making smaller features in integrated circuits.\textsuperscript{8} For instance, Oda et al. used e-beam lithography, a “top-down” approach, to create nanoelectrodes on heavily doped silicon, which then templated assembly, a “bottom-up” approach, of silicon
nanodots of 4-8 nm in diameter onto the nanoelectrodes.\textsuperscript{8} It was suggested that this method could possibly be used to make silicon nanodot based transistors, providing more control could be established during silicon nanodot assembly. It is clear that the best approach for fabricating devices at the nanoscale will depend on the type of device desired and the function, so investigating new methods for patterning and controlling functionality across surfaces is highly desirable for the advancement of various technologies.\textsuperscript{2}

1.2 Scanning Probe Microscopy

Scanning probe microscopy (SPM) is a group of techniques that allows for one to image and manipulate matter at the nanoscale.\textsuperscript{9,10} In general, when imaging the morphology of a surface using SPM, the interaction (ideally a non-destructive interaction) of a sharp probe with the surface is being measured. The probe is raster scanned across the surface while being in close proximity to it. The probe is close enough to where the interaction with the surface is on the order of a few nanometers or less.

Atomic force microscopy (AFM) is one type of SPM technique where the morphology of a surface is measured by monitoring the attractive and repulsive forces between a probe and surface as the probe is being scanning across the surface.\textsuperscript{10,11} The probe being used in AFM is actually a sharp tip on the end of a cantilever. If the sharp tip is brought within a close enough distance to the surface, attractive and repulsive forces occur between the tip and surface. When scanning this tip across the surface, raised or lowered features repel or attract the tip. The tip movement is sensed by a laser reflected off the end of a cantilever and onto a photodiode as the tip is being raster scanned. A feedback mechanism
is used to modulate this interaction and keep the tip within close proximity to the surface during scanning. This feedback system applies a voltage to drive a piezo that controls the z-axis movement of the tip (e.g. height of the tip) relative to the surface. Another set of piezos drives the raster scanning process across the surface and defines the area to be scanned. The overall deflection of the tip and controlled raster scanning of the surface allows one to measure the morphology of the surface. This type of tip repulsion and attraction exist universally for all materials, so most types of samples can be imaged with AFM. Therefore, one can obtain very accurate height contrast data (the height difference between different points on a surface) regardless of the composition of the surface.

Scanning tunneling microscopy (STM) is a related SPM technique where imaging is accomplished through monitoring the tunneling current between the tip and sample. First demonstrated by Binning and Rohrer in 1982, STM is very similar to AFM in that topography is measured by raster scanning a tip over a surface while monitoring an interaction between the surface and tip through a feedback mechanism, except the interaction is a tunneling current. In STM, a sharp metal tip is brought into close proximity with the surface and a bias is applied across the tip-surface gap. When the tip is close enough to the surface a tunneling current is generated, which is very sensitive to the separation between the tip and sample (exponentially dependent). It is necessary for the surface being scanned to be conductive, which restricts use of this instrument to metals or semiconductors. In constant current mode, this tunneling current is held constant as the tip is raster scanned across the surface. When the tip encounters height change or conductivity change at the surface, the tip
height is adjusted through the help of a feedback mechanism to keep this current constant. In height mode the tip absolute height remains constant and the change in tunneling current is recorded as the tip encounters height changes across the surface (Figure 1.3). This tunneling current change can be translated to a height change. In either mode it can be said that “what is converted into an image in STM is either the spatial variation of the tunneling current or the spatial variation of the tip height.”

Imaging by STM is dependent on electronic tunneling, a quantum mechanical phenomenon, and a relatively simple quantum mechanical equation can be applied here. Classical theory describes electrons as finite particles where tunneling is forbidden, which fails to explain electronic tunneling in STM. However, in quantum theory, electrons behave more like waves and the wave function, \( \Psi \), can be used to more accurately describe the behavior of electrons. In this theory electrons are allowed to extend into areas that are forbidden by classical theory, so electronic tunneling can occur. Electronic tunneling can
occur from the overlap of the wave functions of two mechanically and electronically separated electrodes upon the application of a bias (Figure 1.4). The equation below (Equation 1.1) is a simplified quantum mechanical treatment describing electronic tunneling through a planar barrier. In this equation $\psi$ is defined as the tunneling barrier height (related to work function), $S$ is the tunneling barrier width, $J_T$ is the tunneling current, and $A=1.025 \text{A}^{-1} \text{eV}^{-1/2}$.

$$J_T \alpha e^{-A\psi S} ; A = (4\pi / h)2m^{1/2}$$

The equation above can be used to highlight the effect of certain variables on the tunneling current and can be used to explain the high resolution of STM. In this equation there is an exponential relationship between current ($J_T$) and $S$ (Tunneling barrier width). The variable $S$ is related to the distance between tip and surface, so tunneling current is exponentially dependent on tip-sample separation. The result is that small changes in tip-sample separation cause large changes in tunneling current, which allows one to monitor apparent height contrast very accurately across a surface. In addition, since the tunneling current is so sensitive to tip-sample separation, only atoms at the very end of the tip are involved in tunneling. If a very sharp tip is used with only a small number of atoms at the apex, then only a small number of atoms are involved in tunneling, which causes the electronic tunneling to be highly localized. This highly localized tunneling current allows for very accurate lateral resolution. The combination of good lateral and vertical resolution allows for atomic and molecular scale resolution in STM imaging.
Further analysis of Equation 1.1 shows that barrier height ($\psi$) affects the tunneling current, which implies that changes in barrier height (or type of material on the surface) can affect the tunneling current and cause inaccurate height contrast data.\textsuperscript{13} Barrier height is related to the work function of a material. If the composition of the surface is uniform, then the work function is uniform and accurate height contrast data can be collected. However, when the surface composition is not uniform, then the work function changes. Since tunneling current is also exponentially dependent on barrier height (as well as barrier width), small changes in the work function should cause large changes in the tunneling current, which will make collecting accurate height contrast data difficult. Surface topography can still be collected, but one has to keep in mind that the apparent height contrast data will reflect both changes in physical height and work function.\textsuperscript{10} Since few surfaces are perfectly uniform in composition and structure, STM height data is more accurately described as apparent height contrast data.

Figure 1.4. Diagram illustrating the concept of electronic tunneling in STM. Tunneling occurs across the gap between the tip and the sample surface, which is shown by the red arrow.
Since being invented, SPM techniques, especially STM and AFM, have allowed one to manipulate and study the properties of a variety of surfaces at the nanoscale.\textsuperscript{9,10} Part of what makes various STM and AFM techniques capable of resolving and manipulating structures at the atomic scale is their high resolution. Both STM and AFM achieve these tasks through sharp probes that interact with the surface via some sort of mechanism. Since, in these techniques the mechanism varies, this allows for a variety of methods to induce local surface modification at nanometer length scales.\textsuperscript{9,10}

1.3 Alkanethiol Self-assembled Monolayers on Gold

One common method for creating nanostructures is through self-assembly, especially via alkanethiol self-assembled monolayers (SAMs) on gold.\textsuperscript{2,7} Alkanethiol molecules have been shown to spontaneously bond to form single layer films of these molecules on various coinage metals, especially gold where highly ordered, compact, and relatively stable SAMs can be formed. These SAMs offer an easy method for controlling the interfacial properties of surfaces.\textsuperscript{2,7,15} For instance, through the adsorption of these films, SAMs can act as barriers towards oxidation of metals, as ultra-thin resist for applications where patterning is desired, means to facilitate protein adsorption for sensing applications, as electrically insulating layer for various applications, a means to change wetting of a surface, a means to change adhesion of a surface towards materials, etc. Because SAMs are able to afford control over the properties of various surfaces, there are a lot of potential applications in fields, such as sensing, electronics, and biology.\textsuperscript{7}
The formation and structure of alkanethiol SAMs on gold have been widely studied. However, there are many details about the binding and formation of these films that are still highly debated. 

It has generally been accepted that alkanethiols bind to gold as alkanethiolates (RS-) where sulfur binds to the surface and the hydrogen is lost. The bond that forms between the gold and sulfur is strong enough to persist in ambient conditions, but evidence has been found that under conditions of elevated temperature the thiolates covert to disulfides and desorb from the surface. At some point during adsorption of thiols onto gold, the hydrogen is lost, but the mechanism for this process and fate of the hydrogen has not been unambiguously determined. In one proposed mechanism, it was proposed that when the monolayer is vapor deposited in vacuum, the hydrogen is lost as H₂ gas (Figure 1.5). Alternately, it has been suggested that when the monolayer is formed in solution in ambient conditions, oxygen assists in oxidative conversion of hydrogen to water.

The formation of alkanethiol SAMs on gold is a complicated process where several intermediate steps have been argued to exist depending on the conditions. Deposition from either solution or gas phase is thought to be quite complicated, but solution phase deposition is particularly complicated due to the many interactions that can exist between adsorbent and solvent. Ultimately, similar structures are formed whether the monolayer is formed from
vapor or solution deposition.\textsuperscript{16} Several intermediate steps have been proposed, but generally deposition from both phases form SAMs in two steps.\textsuperscript{7,19-21} The first step involves the initial adsorption of the thiol onto the gold, which is thought to be the fast step.\textsuperscript{20,21} Some reports have attempted to model this step using a Langmuir isotherm kinetic model, but others have suggested that this first step is too complex to be described by such a simple model.\textsuperscript{7,22} Intermediate phases are difficult to identify when studying adsorption of these molecules from solution, but in the gas phase an intermediate lying down phase was found to exist upon initial adsorption. This phase was then found to be followed by a standing up phase as the surface coverage increases and reaches saturation.\textsuperscript{7} Contact angle measurements, which can provide a rough idea of surface coverage, were found to reach 80-90\% of their maximum value during this stage of adsorption.\textsuperscript{23} During the second, much slower step, contact angle measurements reach their final values as the SAM organizes to achieve a more energetically stable state.\textsuperscript{7,23} Also, ellipsometry measurements show that the final film thickness is reached during this phase. Through the course of this organization step the alkanethiol chains begin ordering to “maximize density and minimize defects.”\textsuperscript{7} In addition, contaminants still left on the surface are displaced, which are usually unavoidable when making SAMs in ambient conditions.\textsuperscript{7,23} It is thought that this organizing step is driven by van der Waal attraction between the alkyl chains where it has been calculated that for every methylene added to the chain, an additional ~1 kCal/mol of stability is incorporated into the system.\textsuperscript{7,17}
In general, more is known about the final structure of alkanethiol SAMs. When fully formed on gold, these films adopt an ordered structure described by $(\sqrt{3} \times \sqrt{3})R30$ unit cell. Each of the sulfur groups tend to bind to a three-fold hollow site, but some studies have suggested that binding can occur over a bridge site (in between two gold atoms). Figure 1.6 shows a representation of the $(\sqrt{3} \times \sqrt{3})R30$ structure of alkanethiols on gold with the yellow circles indicating the sulfur binding position to the gold atoms (white circles) at the three-fold hollow site. These alkanethiol molecules tilt $30^\circ$ from the surface normal to maximize van der Waals interactions between the alkyl chains (Figure 1.7).
However, it has been strongly suggested that alkanethiol SAMs on gold have more complicated ordering.\textsuperscript{7,24} For instance, recently it has been argued that alkanethiol SAMs on gold preferentially form a orthorhombic $c(4 \times 2)$ secondary superlattice structure, but the exact structure of this phase has been debated.\textsuperscript{7,16,18,24-26} It is suggested that the ($\sqrt{3} \times \sqrt{3}$)R30 unit cell can be used to describe the position of the sulfur groups, but the orientation of the alkanethiol chains are different.\textsuperscript{7,16,18,24-26} The $c(4 \times 2)$ phase can also be described as a $2\sqrt{3}a \times 3a$ unit cell (where $a$ equals the gold lattice constant). The differing chain orientations that characterize the $c(4 \times 2)$ phase is best illustrated in Figure 1.8 where wedges indicate the tilt direction of the alkyl chains and dark colored circles indicate the sulfur atoms. The chains still have the same tilt angle but prefer to have different chain tilt directions (chains are not tilted facing the same direction within a domain), which is shown by the orientation of the wedges in Figure 1.8. Alternately, it is thought that this model might involve a reconstruction of the underlying gold substrate.\textsuperscript{26,27} It is still unclear whether this structure is the dominant structure when alkanethiol SAMs on gold are formed and it may depend on several factors including preparation conditions.\textsuperscript{7,16,18} Although, studies have shown that this $c(4 \times 2)$ phase is energetically more favorable than a ($\sqrt{3} \times \sqrt{3}$)R30 structure because of increased van der Waals interactions between the chains.\textsuperscript{7,26} However, diffraction studies and molecular dynamics calculations illustrate that these confirmations differ only slightly in energy.\textsuperscript{2,16} It is thought that the $c(4 \times 2)$ phase is favored at near 100% surface coverage of alkanethiols on gold, but that many other phases, including the ($\sqrt{3} \times \sqrt{3}$)R30 structure, can be dominant at lower surface coverage.
As mentioned above, the final structure of a SAM can depend a lot on the preparation condition, which may need to be considered when probing certain properties. For instance, structure can be affected by the choice of solvent,\textsuperscript{7,23} chain length of the adsorbent,\textsuperscript{7,23,28} purity of adsorbate,\textsuperscript{7,23} contamination on "bare" surface,\textsuperscript{7,23} immersion time,\textsuperscript{7,23} concentration of adsorbent,\textsuperscript{7,23,29} bulkiness of tailgroup,\textsuperscript{7,23} flatness of the underlying substrate,\textsuperscript{30} and temperature used during deposition.\textsuperscript{7,31} Different measurement techniques have different sensitivities to local and the average structure of alkanethiol SAMs deposited across a gold surface. For many types of measurements, most preparation conditions yield reproducible data that implies SAMs of near identical structure and integrity. For example, contact angle measurements of SAMs deposited from various solvents yield nearly identical contact angle values.\textsuperscript{23} When employing techniques more sensitive towards organization and defects,
however, it has been found that the type of solvent and many other conditions have an effect on the final structure. For example, when employing STM to probe the effect of the underlying substrate flatness on structure of the resulting SAM, it was discovered that rough surfaces yield SAMs with multiple phases, but flatter surfaces tend to yield monolayers with only the c(4 × 2) phase. The effects of some of other variables on defects will be elaborated on later in this document.

Since the interaction between the sulfur and gold is fairly strong, alkanethiol SAMs on gold have greater stability compared to many other types of SAMs on surfaces, although the stability is still highly debated in the literature. This stability is improved when longer chain length alkanethiol molecules are employed as implied above and these SAMs have been found to be more stable than SAMs, such as alkylamines on chromium, but less stable than alkylsilanes on oxidized surfaces. Regardless, it has been found that alkanethiol SAMs on gold are stable for up to one month, but this is highly dependent on the conditions the film is exposed to. According to water contact angle and ellipsometry measurements, these SAMs show very little deterioration after one month when exposed to water, air, ethanol, or basic conditions, but in acidic conditions these films deteriorate to a far greater extent in the same period of time. Since contact angle and ellipsometry measures an average of large areas of the surface, it is difficult to determine from these analytical tools what sort of structural changes have occurred throughout specific areas of the film. The definition of stability also requires specification of temperature. At elevated temperatures, these SAMs have even less stability where on average desorption of a typical alkanethiolate SAM on gold
occurs near 70 °C. In general, however, alkanethiolate SAMs on gold have a relatively high
degree of order and, with the caveats expressed above, are reasonably stable.

1.4 Scanning Probe Lithography

Various SPM techniques have been employed to create nanostructures on surfaces
coated with SAMs.\textsuperscript{12,15,32} As mentioned previously, SPM techniques utilize probes that
extend down to the nanometer scale, providing a means to measure topography and
manipulate the surface at this length scale. This type of lithography is called scanning probe
lithography (SPL) and most often initiates the creation of patterns on surfaces via a
mechanical interaction, electrochemical reaction, or through high electric fields. In addition
to SAMs being a useful way to change the functionality across a surface, these films are
amenable to having their functionality changed locally through the use of SPL.\textsuperscript{15} Through
the use of this type of lithography, patterns can be formed on surfaces where one can vary the
tail group of the molecules being added or removed to locally control the functionality of the
surface. The use of both self-assembly to make the monolayers and SPL to locally modify
the film can be considered a combination of both bottom-up and top-down approaches for
 patterning surfaces.

AFM has frequently been used as a SPL technique, especially in dip-pen-
nanolithography (DPN), which was developed by Mirkin et al. in 1999.\textsuperscript{15,32,33} To make
nanostructures DPN uses the well established concept of dip-pen-technology. In DPN, a tip
was first briefly “dipped” into a well containing a solution of an ink, which has some affinity
for the substrate. Then, the tip was contacted with a substrate surface, which resulted in
diffusion of the ink onto the substrate. Initially, this group focused on illustrating DPN with octadecanethiol (C\textsubscript{18}SH) on gold (Figure 1.9).

The versatility of DPN has been demonstrated by extending this SPL technique to other systems, such as different substrates\textsuperscript{33,34}. For example, DPN has been extended to use on oxidized GaAs and silicon with hexamethyldisilazane (HMDS) as the ink where patterns with 100 nm dimensions were made. The silazane end unit in the HMDS reacted preferentially with the oxide surface forming trimethylsilyl group on the surface and releasing NH\textsubscript{3} in the process. HMDS was used because trichlorosilanes and trialkoxysilanes are incompatible with water and will tend to polymerize, but its use in the semiconductor industry as an adhesion promoter makes the choice of this ink more useful and interesting.

Furthermore, the versatility of DPN was further demonstrated by its conversion into a parallel technique to allow for higher throughput\textsuperscript{35}. As with all SPL techniques, DPN is a serial technique for patterning surfaces, so it faces the limitation that it is slow and has low throughput. In an attempt to add more throughput and overcome this limitation, Mirkin et al. utilized an array of cantilever mounted together and controlled by one feedback system to
pattern the surface simultaneously. Employing one feedback loop to control the array of tips allowed this technique to remain relatively simple. Since one feedback system was used, the force applied by each cantilever varied significantly. However, similar line widths and quality lines were created despite the differences in force applied by the cantilevers.

STM offers an alternate SPL method for patterning surfaces that relies on different interactions with the surface to initiate patterning compared to SPL patterning techniques that rely on AFM. STM has often been applied to pattern alkanethiol SAMs on gold, but many other surfaces have been patterned as well with this technique.

Many of these SPL methods relying on STM are based on elimination lithography where desorption of material is the primary means for creating patterns. Here, SAMs, especially alkanethiol SAMs on gold, have often been the material being removed. This desorption was initiated by employing different scanning conditions to the surface.

Bard and Kim showed one of the first illustrations of using STM to locally desorb regions from a C18SH SAM on gold. Here, different scanning conditions were employed to initiate desorption via different mechanisms. Initially, when scanning a C18SH SAM by STM at 1 V and 1 nA, pits were rearranged and merged together to form bigger pits (Figure 1.10a). It was thought that very slight tip-surface interaction was initiated under these conditions, which yielded insignificant surface modification.
However, more extensive modification was observed when the bias was decreased to 10 mV and the tunneling current increased to 10 nA. Under these conditions material was removed and depressions with dimensions as small as 10 nm were formed. When scanning under these conditions, which should bring the tip closer to the surface, debris was found around the edges of the depressions. Figure 1.10b shows four depressions made by these conditions, which are within the square drawn in the middle of the image. It was claimed that these scanning conditions yielded “significant tip/surface interactions.” The authors argued that under these scanning conditions, the force applied to the surface by the tip was greater than the force applied by an AFM tip during normal contact mode AFM operation (10-17 N). Thus, the STM tip was contacting the surface under these conditions. Coupled with the observation of debris at the edge of the depressions, these observations support the presence of a mechanical mechanism for this desorption and this type of lithography.

Also, desorption was initiated through elevated biases with the tip further away from the surface. When applying a bias of 3 V and a tunneling current of 1 nA to the surface,
depressions were observed that were similar to ones made under mechanical desorption. Figure 1.11 shows a depression made while exposing a confined area to 3 V (labeled A). When elevating the bias, the STM current becomes less a tunneling current and more a field emission current. It was argued that his behavior allows for molecules to be ionized and ejected from the surface. Consequently, a field ionization mechanism was proposed, but it is difficult to rule out any other mechanism for desorption because no evidence was shown to support these claims.

Crooks et al. initiated depression in C_{18}SH SAMs by STM under similar conditions of low bias and elevated bias. Both sets of scanning conditions formed depressions and similar mechanisms seemed to be responsible for forming these features. As was the case above, this report used STM to provide insight into the mechanisms responsible for forming depressions in these SAMs on gold.
First, depressions were formed in the C\textsubscript{18}SH SAM under conditions of relatively low bias and high current similar to what was employed by Kim and Bard above\textsuperscript{42,43}. Under these scanning conditions of 300 mV and 0.1 nA, depressions were formed in the surface with debris present along the outside of the patterned areas (Figure 1.12a and b).\textsuperscript{42} It was observed that additional scanning over the patterned area tended to remove the debris. Additional observations were made that supported a mechanical desorption mechanism. For instance, the apparent height contrast between the removed monolayer area and the monolayer was around 0.71 nm, which is significantly shorter than the actual height of these C\textsubscript{18}SH SAMs measured by ellipsometry and Fourier transform infrared spectroscopy (FTIR) (2.2 nm to 2.8 nm).\textsuperscript{23} Electrochemical blocking data suggested that these depressions were void of material.\textsuperscript{42} In order to account for the much smaller than expected height contrast value, it was concluded that the tip must be penetrating the monolayer during scanning. Later results by other researchers support this claim that the tip is in the C\textsubscript{18}SH monolayer by showing that the same SAM could be scanned without modification at lower tunneling currents and higher biases.\textsuperscript{45,46} As with the similar conditions employed above by Bard and Kim, it was argued that, under these conditions, the depressions were induced by mechanical contact of the tip with the monolayer.
Also, Crook et al. used relatively high biases, similar to what Bard and Kim used, to induce desorption in localized areas in a C_{18}SH SAM. When employing a bias of 3 V and a set point current of 0.15 nA depressions were observed that were found to be dependent on relative humidity (Figure 1.13). More specifically, it was observed that desorption of the C_{18}SH only occurred at elevated biases and relative humidity levels above 70%. Since water was found to play a significant role in desorption of the SAM and these biases should bring
the tip away from the surface, it was concluded that an electrochemical mechanism, strongly
influenced by the presence of water was responsible for the desorption behaviors observed.

Figure 1.13. STM images (300 x 300 nm) of octadecanethiol SAMs after patterning a roughly 50 x 50 nm
feature. (a) Image after scanning a 50 x 50 nm area at lower biases and 75% relative humidity (RH),
which shows no discernable difference in the topography. (b) Image after scanning a 50 x 50 nm area at
3 V and 6.6% RH. (c) Image after scanning a 50 x 50 nm area at 3 V and 75% RH, showing a depression
of 0.29 nm in depth. All images were captured with a grey scale of 2 nm, a bias of 0.3 V and a set point
current of 150 pA.43

Gorman et al. extended desorption lithography by using elevated biases to remove
local areas of a SAM, then filling in the vacated regions with another molecule, which they
called replacement lithography.38,39,41,44 The replacing molecule was usually dissolved in
dodecane and the solution was in contact with the sample. When elevated biases were
applied by the tip to remove the SAM, the replacing molecule filled in the vacated area and
patterns with dimensions as small as 10 nm have been made.
Initially, Gorman et al. employed this technique with alkanethiol of varying chain length as the ink where the apparent height varied according to the length of the ink in relation to the background. In one case, a 3.8 V bias was used to remove regions of a decanethiol SAM, which allowed dodecanethiol ink dissolved in a dodecane solution exposed to the surface to fill these vacated areas. Figure 1.14a shows an example of when this occurred. In these STM images, the area that was replaced, which is composed of alkanethiol molecules with a longer chain length, is shown as having a lower height contrast.
compared to the background SAM. An area of lower apparent height results due to the
decreased tunneling probability associated with this region of greater film thickness. In
another case, a 3.6 V bias was used to remove regions of a dodecanethiol SAM, which
allowed decanethiol ink molecules to fill these vacated areas. Figure 1.14b is a STM image
showing this replacement where an ink of shorter chain length was replaced into a SAM
composed of molecules with a longer chain length. The patterned regions appear as areas
that are brighter and of higher apparent height because of the increased tunneling probability
associated with this region of smaller thickness. When scanning these same lines in air (after
removal of the ink solution), a reversal of the height contrast was observed where the
patterned area had a shorter apparent height compared to the background SAM. This
observation helped confirm the contents of these patterned areas.

Gorman et al. claimed that replacement lithography was most influenced by the
desorption step and that this step followed an electrochemical mechanism.\textsuperscript{39} Specifically,
replacement occurred more readily at higher relative humidity values. Even though,
dodecane covered these SAMs during replacement lithography, the authors claimed that a
thin water layer could exist in between the SAM-dodecane interface at elevated relative
humidity. Thus, they claimed that an electrochemical mechanism was responsible for this
process, which was strongly influenced by the presence of water. The proposed
electrochemical mechanism is consistent with what was reported by Crook et al.\textsuperscript{39,43}

The versatility of replacement lithography was illustrated by incorporating other
molecules with different tail groups as the ink, such as 11-ferrocenylundecanethioacetate
(FcC$_{11}$SAc), which offered a means to construct nanopatterns with interesting electronic properties and limit unwanted spontaneous replacement.$^{38,41}$ When employing FcC$_{11}$SAc as the ink molecule, the replaced areas had an increased apparent height compared to the background because of the greater conductivity of regions composed of this ink. This higher apparent height of the replaced regions provided better distinction between the background SAM and patterned areas. Also, it was shown that this ink molecule with a thioacetate head group could be used in replacement lithography in place of an alkanethiol and it displayed less spontaneous, unwanted replacement. It was speculated that some of the thioacetate could deprotect in situ to form a thiolate, which can then bind to gold, but a significant amount of the ink molecule remained as the thioacetate and this limited the amount of adventitious replacement. A more recent study by Lee et al. showed that alkanethiocetates form SAMs on gold, but at a relatively slower rate compared to the corresponding alkanethiol.$^{47}$ It was suggested, especially through X-ray photoelectron spectroscopy (XPS), that the binding species is still the thiolate, but that the thioacetate protecting group hindered the formation of this species.

In one report, the effect of scanning parameters, such as scan rate and writing bias on the replacement during replacement lithography was explored qualitatively by making gradients with FcC$_{11}$SAc as the ink.$^{38}$ These gradients were made by incrementally decreasing or increasing these variables while scanning across a given area of a dodecanethiol SAM in the presence of FcC$_{11}$SAc. The amount of replacement across the scanned area was compared and the effect of these parameters on the amount of replacement
was observed. It was shown that as lithographic scan rate was increased, the amount of replacement decreased (Figure 1.15). In contrast, if bias was incrementally increased, the amount of replacement increased.

Figure 1.15. STM images of FcC_{11}S-SAM mesoscale chemical gradients fabricated in a dodecanethiol SAM by systematically varying replacement bias (A), or lithographic scan rate (B), while maintaining all other STM parameters constant. Replacement condition limits are annotated in images. The averaged section analysis is shown to the right of each gradient structure. All images were captured after the gradients were formed with a z-scale of 5 nm, bias of 1 V, set point current of 8-10 pA, and scan rate of 1 Hz.38

In later reports, this same FcC_{11}SAc ink was used to probe the effect of the SAM-substrate composition on the amount of replacement provided by replacement lithography.41,44 Instead of exploring the amount of replacement using gradient structures, a series of lines were written at incrementally higher biases and the amount of replacement at these biases was measured. One could then compare the amount of replacement at these biases between two different assemblies. Analyzing the amount of replacement through this method allowed one to explore the effect of different conditions on replacement more quantitatively.
In one case, the above method was used to explore the effect of the background SAM on the amount of replacement. In this report, replacement lithography lines of FeC$_{11}$SAc were written into different SAMs and the amount of replacement was determined versus a theoretical maximum. In one instance, the amount of replacement was compared between SAMs consisting of octanethiol, decanethiol, dodecanethiol, and tetradecanethiol (Figure 1.16). Predictably, all the different SAMs replaced at high enough biases, but at lower biases the shorter chain length SAMs had more replacement. In the same report, the amount of replacement was also compared between SAMs with different tail groups. SAMs terminated with a carboxylic acid group were shown to yield more replacement compared to those with less bulky tail groups. SAMs with bulkier tail groups and shorter alkyl chain length were
found to have less order by STM. As a consequence, the authors argued that SAMs with more order in their structure were less prone to being replaced.

In another report, Gorman et al. probed the effect of substrate on the amount of replacement. As before, a series of lines were written in a SAM at incrementally higher biases and the amount of replacement was compared between different assemblies. Here, the amount of replacement was compared between dodecanethiol SAMs on gold, palladium, and platinum. Replacement of these SAMs on gold occurred at lower biases than on palladium or platinum.

There are some limitations using replacement lithography to pattern surfaces. As a means to pattern surfaces, replacement lithography is like most “writing techniques” because each feature has to be written independently, so this process is serial and relatively slow. Despite efforts to make SPL techniques into a more parallel technique, it has been shown that it will be difficult for any of these techniques to rival the output of photolithography for making patterns. As a consequence, it is unlikely that replacement lithography will be suitable for applications where high throughput is necessary.

However, replacement lithography does have some advantages over many parallel techniques for creating patterns. Replacement lithography, which employs STM, has advantages over many other lithographic techniques because it can simultaneously pattern and image features at the nanoscale. More specifically, as described above, one can probe the effect of various SAM structures on the efficiency of replacement lithography. Above, the effect of chain length of the SAM, tail group in the SAM, and substrate were explored.
One can envision repeating this experiment for other systems where the ink has a different binding group or for other substrates besides gold, palladium, and platinum, then studying the effect of these different systems on replacement lithography. Also, replacement lithography can be used to remove areas of an alkanethiol SAM and insert molecules with interesting properties. Since, replacement lithography employs STM, electronic properties and structure can be probed simultaneously following the formation of these nanostructures. Presently, this ability is not available for most methods that have been used to create nanostructures, including many other SPL methods.
1.5 References


Chapter 2 - EFFECT OF DEFECTS ON REPLACEMENT LITHOGRAPHY

2.1 Introduction: Types of Defects in Alkanethiol SAMs on Gold

As described earlier, alkanethiol molecules exposed to a gold surface spontaneously form SAMs with a high degree of order. Despite their high degree of order, many defects in these films exist that can affect their properties.\(^1\) One example where defects can be important is when SAMs are employed as electrochemical blocking layers. Here, the presence of defective sites in the film can provide a pathway for species to come into close proximity with the surface where they can be oxidized or reduced.\(^2\)

Some of the most common defects in alkanethiol SAMs on gold are pin hole defects, monoatomic steps, domain boundaries, and vacancy islands (pits).\(^1\) Pin hole defects, which are usually present in very small quantity, are areas of the SAM that are missing alkanethiol molecules.\(^3\) Monoatomic steps are areas of the SAM where the underlying gold layer changes in height equal to the diameter of one gold atom, which translates to an overall height change in the film equal to this value. Consequently, this defect is heavily influenced by the flatness of the gold surface and, in general, it can be said that the morphology of the underlying gold surface is translated into the morphology of the film. Domain boundaries are borders that separate near perfectly ordered domains or regions of the SAM.\(^4,5\) In general, it is thought that these boundaries are formed because of a mismatch in orientation of different domains or ordered areas of the SAM. This results in different types of domain boundaries, which are characterized by different structures and thicknesses. The density of alkanethiol molecules is lower in these regions, which results in an overall lower packing
density and order. Domain boundaries typically link pits together, which are defects that are present as circular depressions in a SAM.

There has been a great deal of interest in pits, especially in defining the structure of these features, but a number of studies have concurred that these defects are due to depressions in the underlying gold.\textsuperscript{6-10} It has been debated whether pits are defects caused by missing alkanethiol molecules (pin holes) or removed gold atoms, equal in depth to the height change of monoatomic steps. One group explored these defects in hexanethiol (C\textsubscript{6}SH) and docosanethiol (C\textsubscript{22}SH) SAMs with STM.\textsuperscript{7} These molecules have drastically different lengths, so SAMs composed of these molecules should have significantly different thicknesses. If the pits in SAMs made from these two molecules are due to missing alkanethiol molecules, the depths of the pits should be significantly different and should correspond roughly to the known thickness of the SAMs. When imaging the C\textsubscript{22}SH SAM on gold, the authors identified regions that had measured depths of roughly 25 Å, which corresponded well to the length of a C\textsubscript{22}SH molecule. However, these features, which were identified as pin hole defects, were distinctly different in appearance compared to pits and were of much less abundance. The pit defects in both SAMs had comparable depths and did not match the expected thickness of either the C\textsubscript{6}SH or C\textsubscript{22}SH SAM. These depths were found to be equal in value to the diameter of a gold atom or a value divisible by the diameter of a gold atom, so it was concluded that the pits were caused by depressions in the gold surface. Other researchers confirmed these results by showing that SAMs composed of various alkanethiol chain lengths all had pit depth of nearly equal value and in many cases
these depths tended to correspond closely with the diameter of a gold atom. As with many other studies, Schönenberger et al used STM to confirm these results. In addition, these authors used STM to preferentially image either the gold or SAM lattice by changing the resistance (or bias) during scanning. When preferentially imaging the gold surface, depressions could be seen in the surface. More significantly, when imaging the SAM, the authors were able to resolve the SAM structure within the pits, which suggest that these depressions contain alkanethiol molecules and are not equivalent to pin hole defects. Others have been able to resolve the SAM structure within these pits and have confirmed this result. As a result, it has been generally accepted that the pits contain alkanethiol molecules and are depression in the gold, but this still raises questions about how this defect and others form.

The formation of defects in alkanethiol SAMs on gold are caused by both external and internal factors. Many of these defects seem to be influenced by conditions present during formation of these SAMs while other defects are present due to the complex intrinsic behavior of these molecules when adsorbed onto gold.

As mentioned in the previous chapter, preparation conditions can have an effect on the final structure of alkanethiol SAMs on gold, especially on the number and type of defects. By properly adjusting the preparation conditions, some defects can be removed, but others can only be reduced. Some parameters that have been shown to affect defect density are concentration, temperature, chain length of the adsorbent, phase of adsorbent (vapor or liquid), flatness/quality of the substrate, amount of contaminants, adsorption time, choice of solvent, and nature of the tail group. A few of these parameters have been shown
to affect pit density in particular. If pit density in alkanethiol SAMs can be reduced or completely removed, then, presumably, more ordered SAMs could be made.³

Since many processes are defect mediated, it became of interests to probe the effect of defect density and overall order on replacement lithography. STM allows one to investigate defects and order in SAMs while also allowing one to perform replacement lithography. Experiments were performed where the defect density in dodecanethiol SAMs on gold was modulated by varying preparation conditions and the effect of the resulting structure on replacement lithography was explored.

2.2 Reducing Defects in SAMs by Vapor Deposition

2.2.1 Literature Precedent

Touzov and Gorman published a report where they claimed that “defect free” alkanethiol SAMs “on the 100 nm length scale” could be produced by vapor deposition of decanethiol on gold peeled from mica.¹¹ Other references have shown that alkanethiol SAMs on gold can be made by vapor deposition as mentioned earlier, but defect density was found to be fairly high.¹² In many of these reports the top side of gold on mica was selected as the substrate. It was argued in the report by Touzov and Gorman that preparation of the gold surface is as important as the conditions employed during deposition when one is concerned about defect density.¹¹ The procedure followed differed slightly from most reports as they used the underside of gold peeled from mica. First, gold was carefully peeled from the mica. Then, the underside of the gold was exposed to vapor of decanethiol under reduced pressures. Figure 2.1 shows a STM image of the resulting SAM where no pits can be seen. In contrast,
this SAM deposited on this same surface from solution yielded a significant number of pits. Also, if this vapor deposition procedure was applied to electrochemically polished gold or gold on the front side of mica, then high pit density was observed.

Figure 2.1. STM image (400 x 400 nm) of a decanethiol vapor deposited SAM on the backside of gold peeled from mica. Images were collected at a scan rate of 2.3 Hz, 1 V bias, and 1 pA tunneling current. Inset in the bottom right shows a 10 x 10 nm molecular scale image of the SAM.11

Although the above method formed SAMs having less pits compared to SAMs on annealed gold, it should be noted that Figure 2.1 shows that there was a higher density of step edges than what is observed when other procedures are followed.11 For instance, when forming alkanethiol SAM on annealed gold beads, large terraces composed of alkanethiol void of any step edges can be observed.3,13-15 In contrast, Figure 2.1 shows a SAM surface with a much greater density of step edges.11 As was discussed earlier, these step edge defects are very similar to pits as they are both defects in the gold surface that disrupt the order of the alkanethiol SAM by causing a height change equal to the diameter of a gold atom. Therefore, it can be argued that having more step edge defects at the expense of pit defects will not create a film with significantly more order or significantly greater quality.
Consequently, it was of interest to apply this vapor deposition method for forming high alkanethiol SAMs with less pit density to an annealed gold bead or gold on mica surface, which has less step edge density. Thus, the above method developed by Touzov and Gorman was applied to more flat gold surfaces to determine if both pit density and step edge density could simultaneously be reduced by vapor deposition.

2.2.2 Results and Discussion

The procedure developed by Touzov and Gorman was followed but annealed gold beads or annealed gold on mica were used as the substrate in place of gold stripped from mica. This was done by annealing either a gold bead or gold on mica (see experimental section). These samples were placed in a ca. 100 mL glass jar with a lid modified to contain a septum. Then, deposition was performed via the method reported by Touzov and Gorman.

When annealed gold on mica or an annealed gold bead was used, a high density of pits was consistently observed. Figure 2.2 shows a STM image of the resulting surface that was created when annealed gold on mica was used. One can see that the pit density is much higher than what is observed in Figure 2.1. Likewise, when an annealed gold bead was used, a lower density of step edges was observed, but a pit density was present that was similar to what was observed in Figure 2.2. Thus, this method was not successful in making SAMs with a low density of both pits and step edges.
As mentioned above, in the report by Touzov and Gorman it was claimed that the type of substrate was an important factor in creating pit free decanethiol SAMs.\textsuperscript{11} It is possible that this method can only be successful for creating pit free alkanethiol SAMs on a gold surface peeled from mica. However, this substrate is undesirable as the number of step edge defects in the SAM will be relatively high (Figure 2.1). In addition, in order to compare the effect of structure on replacement lithography according to previously described methods,\textsuperscript{3,13-15} one has to measure percent replacement of lines drawn in the SAM. Measuring percent replacement is usually done by thresholding the data where points above a certain height value are measured. If the lines run through areas of different heights, then it becomes difficult to measure the area of the replacement lithography lines. Since the
literature describes other conditions that can modulate pit density, this attempt to follow the Touzov preparation closely was abandoned and other procedures for creating lower defect density alkanethiol SAMs were explored.

2.3 Reducing Defects in SAMs by Thermal Annealing in Air

2.3.1 Literature Precedent

Heating an alkanethiol SAM in air has been found to be another way to modulate defect density, especially pit density. Several reports utilize this treatment to remove pits in alkanethiol SAMs and show evidence that this treatment does not initiate the formation of other defects.\textsuperscript{6,8,16}

McCarley et al. showed that the pit density in hexadecanethiol and C\textsubscript{18}SH SAMs can be decreased by heating these structures to 100°C for 2 h.\textsuperscript{8} In this report it was claimed that when heating these alkanethiol SAMs, no other defects were formed. In particular, the surface showed no signs of any of the molecules being desorbed. To support this conclusion, the voltammetric response of 16-[(ferrocenecarbonyl)oxy]hexadecane-1-thiol (FcCO\textsubscript{2}C\textsubscript{16}SH) on gold was recorded before and after annealing. It was found that there was no significant change in the voltammetric response before and after this treatment. If substantial monolayer removal occurred during this treatment, a significant decrease in the voltammetric response would have been observed. STM images of the alkanethiol SAMs after annealing supported this data, but no molecular scale images were presented.

Kern et al. also showed that heating an alkanethiol SAM in air can remove pits.\textsuperscript{6} More specifically, these authors heated a hexanethiol SAM to various temperatures and
imaged the resulting surface with STM. At elevated temperatures, between 72-75°C, merging of pits occurred. Figure 2.3 is a reported STM image of a hexanethiol SAM on gold where a decrease in the density of pits was observed following this treatment. As with the previous study, it was claimed that pit density could be significantly reduced without creating other defects, but no molecular resolution STM images were presented to support this claim.

![STM image of hexanethiol SAM on gold](image)

Figure 2.3. STM images of hexanethiol SAM on gold formed by immersing gold in 1 mM of the thiol in ethanol for 7 min. The resulting SAM was then heated to 345 K and this image was captured at 300 K. The image was scanned at a bias of 50 mV, scan size 400 x 400 nm, and set point of 1 nA.16

In a third report, Cavalleri et al. showed that annealing SAMs could result in decreased pit density.16 These authors heated a decanethiol SAM on gold from 77°C to 97°C while scanning the surface with STM. It was claimed that molecular scale STM images (not shown in the report) of these annealed SAMs showed “well-ordered alkanethiolate surfaces.”16
2.3.2 Results and Discussion

A set of experiments were conducted to determine the veracity of the claims above. Alkanethiol SAMs were annealed under various conditions similar to what these authors employed. First, dodecanethiol SAMs were made from 1 mM ethanolic solution (see experimental section), then annealed in air without much temperature control. STM images of these surfaces showed near complete removal of the pits (Figure 4a). It was discovered, however, that upon imaging the surface with molecule resolution, that the removal of the pits occurred in tandem with the appearance of molecular scale stripes (Figure 4b). Additional experiments confirmed that removing pits through excessive annealing of these alkanethiol SAMs lead to the appearance of these features across all areas of the SAM.

Figure 2.4. Images of a dodecanethiol SAM formed on gold by refluxing a gold substrate in 1 mM of the alkanethiol solution in ethanol and then annealing for 2 h at elevated temperatures. (a) A 500 x 500 nm image showing that the surface is free of pits. (b) A 40 x 40 nm image showing molecular scale stripes covering the surface. Both images were captured at 1 V scanning bias and 10 pA set point current.

Thus, experiments were done to limit the appearance of the striped phases by controlling temperature more carefully. It was postulated that by maintaining stricter control over temperature, the appearance of these molecular scale stripes described above could be
avoided. Dodecanethiol SAMs were made from a 1 mM ethanolic solution (see experimental section), then annealed in air at controlled temperatures (below 110°C). When temperatures below 100°C were employed, no significant changes in pit density were observed. When heating these dodecanethiol SAMs at temperatures between 100-110°C, the number of pits was reduced (Figure 2.5). However, in these images very thick lines could be seen at much larger scales than the molecular scale stripes observed above. Also, these lines were found randomly across the surface. Despite efforts to avoid the appearance of these features by modulating the annealing temperature, these structures were consistently seen whenever temperatures high enough to reduce pit density were used.

Figure 2.5. STM image of an annealed dodecanethiol SAM on gold showing mesoscale lines. SAM was fabricated by heating a gold substrate in a 1 mM solution of the alkanethiol in ethanol. Then, this sample was annealed in an oil bath at 110°C for four hours. Image was captured at a bias of 1 V, set point of 10 pA, and a scan size of 250 x 250 nm. The more narrow, parallel lines in the image running diagonally are artifacts from the STM and are not real surface features.
Ultimately, it was found that pits in a dodecanethiol SAM on gold could be completely removed upon annealing in air, but not without creating mesoscale or molecular scale stripes. Some literature sources have claimed that annealing alkanethiol SAMs reduces pit density without introducing other defects.\textsuperscript{6,8,16} In contrast, other reports have shown that annealing these SAMs introduces striped defects, which they argue are unavoidable and are an integral part of eliminating pits.\textsuperscript{17,18} In these studies, these striped phases were seen and two different explanations were given regarding their formation. One study by Delmarche et al. probed the formation of these striped phases in a dodecanethiol SAM by STM when the surface was exposed to temperatures around 100°C.\textsuperscript{17} These researchers argued that the formation of these striped phases occurred in two steps. First, upon annealing the SAM, the domain boundaries reorder to create large domains, which allows the SAM to pack more efficiently and leaves areas void of alkanethiol. In response, rows of alkanethiol molecules tilt to cover these areas void of any adsorbent (Figure 2.6). It has been argued by other sources that domain boundaries in alkanethiol SAMs that have not been annealed form due to similar reasons.\textsuperscript{11,19} It is claimed that these features consist of a low density of alkanethiol where the molecules present tilt over to compensate for the areas void of this adsorbent. In another study, Palmer et al. formed these striped lines by slowly increasing temperature from
27°C to above 91°C. These authors observed by STM that these features had a depth roughly equal to the diameter of a gold atom. Thus, they concluded that these features must form due to a reconstruction of the underlying gold surface. Both these studies concur that these striped phases are unavoidable when annealing an alkanethiol SAMs on gold to remove pits. When experiments were done to probe whether pits could be removed without introducing any other defects, it was found either molecular or mesoscale stripes were formed. Since annealing alkanethiol SAMs on gold seems to introduce other defects despite removing pits, it became of interest to explore other methods for reducing pit density.

2.4 Reducing Defects in SAMs by Lower Adsorbent Concentration

2.4.1 Literature Precedent

Another parameter that has been claimed to have an effect on pit density is concentration of the adsorbent. In general, preparation methods for forming alkanethiol SAMs on gold vary greatly through the literature. However, a typical alkanethiol SAM can be formed by immersing a gold substrate in a 1 mM solution of the adsorbent for 1 h under reflux. An alkanethiol SAM formed under these conditions yields an abundance of pit defects, which can be observed by STM. It was of interest to probe the effect of alkanethiol concentration used to form the SAM on pit density in the resulting SAM.

2.4.2 Results and Discussion

Before concentration effects were tested systematically, SAMs were fabricated in neat dodecanethiol at elevated temperatures and room temperature. Neat dodecanethiol has a higher boiling point than dilute solutions of dodecanethiol in ethanol. When these SAMs
were made under elevated temperatures, the temperature was much higher than the boiling point of ethanol, but below the boiling point of neat dodecanethiol. Thus, this experiment tested mainly the effect of temperature on the formation of dodecanethiol SAMs on gold made from neat dodecanethiol. More specifically, in one set of experiments, the gold surface was placed in neat dodecanethiol and this solution was heated to temperatures exceeding 100°C for various amounts of time. In another set of experiments, the gold surface was placed in neat dodecanethiol and left at room temperature for 24 h. Figure 2.7a is a STM image representative of what was observed when SAMs were made by immersing a gold surface into neat dodecanethiol at temperatures above 100°C. Figure 2.7b shows a STM image representative of what was observed when SAMs were made in neat dodecanethiol at room temperature. In Figure 2.7a, fewer pits are observed compared to Figure 2.7b, but when zooming in to obtain molecular scale images of these areas, molecular scale stripes were observed (not shown). The pit density in Figure 2.7a is comparable to what was observed when annealing SAMs in air. In contrast, even though striped phases were absent in dodecanethiol SAMs made in neat dodecanethiol at room temperature, a very high pit density was observed (Figure 2.7b).
Figure 2.7. STM image of a dodecanethiol SAM made by immersing a gold bead in neat dodecanethiol (a) heated for 1 h at temperatures exceeding 100°C and (b) maintained at room temperature for 24 h.

Other experiments were done to probe the effect of concentration on the formation of a dodecanethiol SAM on gold. Contrary to some reports, it has been suggested that lower concentrations initiate less pit density and higher concentrations yield SAMs containing more pits. To probe the effect of lower concentrations, SAMs were fabricated by immersing annealed gold beads in solutions of dodecanethiol in ethanol at concentrations ranging from 1 µM to 100 µM under reflux for 1 h. Then, the sample was removed and put in a 1 mM solution of dodecanethiol in ethanol at room temperature for 15 min. These SAMs were briefly exposed to an elevated concentration of the adsorbent in order to ensure near complete surface coverage of the alkanethiol on the substrate. Figure 2.8a and b show STM images representative of what was observed when fabricating dodecanethiol SAMs with 0.01 mM and 1 mM concentrations of the adsorbent. As can be seen in these STM images, alkanethiol SAMs made from 0.01 mM concentrations of dodecanethiol yielded surfaces
with less pit density compared to when 1 mM concentrations of the adsorbent were employed.

Figure 2.8. STM images of dodecanethiol SAMs fabricated by refluxing gold bead substrates in (a) 1 mM and (b) 0.01 mM concentrations of the adsorbent in ethanol. After formation of both dodecanethiol SAMs, samples were immersed in a 1 mM solution of dodecanethiol in ethanol at room temperature. Images were captured at a bias of 1 V, a set point of 10 pA, and a z-range of 3 nm.

Figure 2.9. STM image of lines composed of FeC_{11}SAc written into a dodecanethiol SAM made from 0.01 mM solutions of the adsorbent in ethanol. The image was captured at a bias of 1.5 V and 10 pA.

Next, the effect of different pit densities on replacement lithography was explored using the dodecanethiol SAMs made above using 0.01 mM and 1 mM concentrations of the adsorbent. As was described above, 1 mM and 0.01 mM concentrations of dodecanethiol in
ethanol produced SAMs with significantly different pit densities. So, experiments were done where dodecanethiol SAMs were fabricated from both these concentrations according to the procedure outlined above. Before initiating replacement, relative humidity was set at 55% ± 2% and 4 µM of 11-ferrocenylundecanethioacetate (FeC₁₁SAc) in dodecane was exposed to the substrate. Replacement lithography was performed on these SAMs by writing nine lines at biases from 2.5 V to 3.3 V (where the bias used to write each line was incrementally increased by 100 mV). After replacement lithography was done, STM images of these lines were captured at a scanning bias 1.5 V. Percent replacement was determined versus a theoretical maximum according to procedure outlined in the experimental section. Figure 2.9 shows a STM image representative of what was observed when making a series of replacement lithography lines composed of FeC₁₁SAc in a dodecanethiol SAM made from a 0.01 mM solution of the adsorbent. Similar lines were observed in dodecanethiol SAMs made from a 1 mM solution of the adsorbent. Figure 2.10 shows a graph of percent replacement versus bias used to make each line. In the graph it is shown that dodecanethiol SAMs made from 0.01 mM and 1 mM concentrations of the adsorbent yield similar percent replacement at lower biases. In addition, the onset of replacement for a dodecanethiol SAMs made from 0.01 mM and 1 mM concentrations of the absorbent occurs at the similar biases. However, SAMs made from 0.01 mM concentrations of the adsorbent show less percent replacement at higher biases compared to these SAMs made from 1 mM concentrations. As mentioned previously, dodecanethiol SAMs made from the lower concentration of the
adsorbent yield SAMs with less pit density. Thus, it is concluded that an alkanethiol SAM on gold with lower pit density is more stable towards replacement lithography.

![Graph of percent replacement versus bias used to make the replacement lithography lines composed FeC_{11}SAc. Percent replacement is shown at biases 2.6 V to 3.3 V.]

2.5 Reducing Defects in SAMs Via an Alternate Vapor Deposition Procedure

In the above experiment, dodecanethiol SAMs with lower pit densities compared to typically prepared dodecanethiol SAMs were successfully made and it was shown that these SAMs were replaced using replacement lithography less easily compared to SAMs with higher pit density. However, it was still of interest to make a dodecanethiol SAM without any pits and explore the effect on replacement lithography. It was hypothesized that a dodecanethiol SAM with no pits would replace a lot less easily compared to the SAMs made from 0.01 mM and 1 mM of the adsorbent in ethanol, which still have a significant number of pits per unit area.
Bumm et al. developed a method to deposit decanethiol SAMs on gold by vapor deposition. These researchers made these high quality SAMs by putting a gold substrate in a perfluoroalkoxy (PFA) inert vial with a few microliters of decanethiol, then sealing the sample in the vial and putting it in an oven set at 100°C for 12 h. It was claimed that the resulting SAMs were completely pit free.

Thus, experiments were done to explore what pit density could be created in decanethiol SAMs on gold beads and annealed gold on mica made following the above procedure. The above method was used to make decanethiol SAMs without pits, but it was hypothesized that similar results could be obtained later with SAMs composed of alkanethiols having different chain lengths, especially dodecanethiol. First, decanethiol SAMs were made following closely the above method developed by Bumm et al. In these experiments, the substrate used was a gold bead or annealed gold on mica, which was the only modification of this method. Figure 2.11 shows a STM image of the resulting decanethiol SAM that was created on a gold bead. It can be seen here that the SAM has a lower pit density than any of the methods explored so far, but there are still an abundance of pits.
Next, experiments were done to try and modulate the pit density by changing various parameters during deposition. The volume of the container the sample was placed in, the temperature, the amount of decanethiol, and the time of deposition that was employed to make these SAMs on gold were all varied. As was the case in previous experiments, pit density could be decreased further, but other defects tended to appear. Figure 2.12 is a 250 x 250 nm STM image of a decanethiol SAM made following the method developed by Bumm et al. except the deposition time was increased to 18 days. Here, it can be seen that the pit density was significantly reduced, but striped phases appeared in the surface. Many of these other parameters tended to not improve pit density significantly compared to when the method developed by Bumm et al. was followed closely or when they did, other kinds of defects were observed.
2.6 Conclusions

When investigating methods for reducing pit density, either pit density was not significantly reduced or other types of defects were found in greater abundance. However, by using lower concentrations of alkanethiol in ethanol compared to what is typically employed during solution deposition to make alkanethiol SAMs, the pit density could be reduced without creating other defects and the effect of pit/defect density on replacement lithography was explored. It was observed that less replacement occurred with the dodecanethiol SAMs made from 0.01 mM concentrations of the adsorbent. It can be said that SAMs with less pits have a higher degree of order. Thus, the difference in the amount of replacement suggests that the degree of order and defects influences replacement lithography. Also, these results suggested that these SAMs having less pit density and more order are of greater stability (e.g. more difficult to desorb). Additional experiments were performed to
decrease the pit density further or remove the pits completely by following a vapor deposition method developed by Bumm et al. These experiments did yield slightly less pit densities in decanethiol SAMs on gold, but the pit density wasn’t significantly different compared to when 0.01 mM concentrations of alkanethiol were employed.

2.7 Experimental Section

**General Considerations**

Dodecanethiol and decanethiol were purchased from Alfa Aesar. Dodecane was purchased from Aldrich. Gold wire of 99.999% purity and 0.5 mm diameter was purchased from Alfa Aesar. PFA vials were purchased from Jensen Inert Products. Absolute ethanol was used as a solvent and was used without further purification. Gold on mica was purchased from Novascan. FcC₁₁SAc was synthesized in our laboratory following previously documented procedures.²² All water used was purified by reverse osmosis.

**Preparation of Gold Surfaces**

Gold on mica was treated as follows. First, the gold on mica substrate was placed on a quartz surface. Then, a H₂ flame about 4 cm long was brought within close proximity to the surface and continually moved over the surface to heat the surface enough to turn the gold a dim orange color. Care was taken not to overheat the surface. Gold bead substrates were prepared by annealing gold wire with a H₂ flame to form a gold bead, which upon further heating formed atomically flat facets suitable for the formation of monolayers. These substrates were often used again after being cleaned with “piranha” solution (3:1 H₂SO₄/H₂O₂), washed with water and reannealed under the H₂ flame to reform the facets.
Caution! “Piranha” solution should be handled carefully because of its violent reactivity with organic molecules.

Standard Solution Preparation of Dodecanethiol SAMs

SAMs of dodecanethiol were deposited by refluxing a freshly annealed gold bead in a 1 mM ethanol solution of the alkanethiol for 1 h followed by cooling of the solution to room temperature for 15 min. Then, the samples were rinsed with ethanol immediately after removing from the solution and dried under a stream of nitrogen.

Characterization

Scanning tunneling microscopy images were taken with a Nanoscope III (Digital instruments) after fixing the samples in a sample holder. These sample holders allowed one to scan with the sample submerged in a liquid solution of an ink. In experiments where pit density was explored, STM images were taken at 1.0 V scanning bias, 10 pA set point, and a scanning rate of 1 Hz. During experiments exploring percent replacement, images were taken at a capture bias of 1.5 V, 10 pA set point, and a scanning rate of 1 Hz.

Replacement Lithography

When relative humidity needed to be elevated, this was done by bubbling nitrogen through 18 MΩ·cm reverse osmosis water. Relative humidity was measured using a digital thermohydrometer.

Measuring Percent Replacement

To determine the extent of replacement for a given bias, STM images containing lines drawn by replacement lithography were manipulated in imaging software (Scion Image
Release alpha 4.0.3.2.). First, the x and y dimensions of the image were converted from pixels to nanometers. The percent replacement for each line was then determined by the following method. First, a threshold value, which highlights points in an image that are greater than a specified height, was chosen that selected for heights corresponding roughly to the apparent height of the lines. The widest point of any of the eight lines in a given image was determined. This widest point was multiplied by the length of the line drawn (which was defined as 100 nm in the nanoscript macro used to write the lines) to determine the maximum replacement area. The area of each line was then calculated using the Scion Image software and was the total area of each line containing all the points not excluded when thresholding the image. This area for each line was individually divided by the theoretical maximum area to define the percentage of replacement for that trial.
2.8 References


Chapter 3 - GaAs AS A SUBSTRATE FOR REPLACEMENT LITHOGRAPHY

3.1 Introduction: Alkanethiol SAMs on GaAs

Gallium Arsenide (GaAs) has been commonly used in research and industry for applications in electronics and optoelectronics because of the interesting electronic properties of this substrate.\textsuperscript{1} In particular, this material has high electron mobilities. In addition, many reports have shown this material can act as a substrate for the formation of self-assembled monolayers (SAMs).\textsuperscript{1-5} SAMs, especially patterned SAMs, offer a convenient way to functionalize surfaces and could be employed to add useful functionality to GaAs. As mentioned in previous chapters, the functionalization of substrates with interesting properties is important for many applications, such as construction of biosensors, solar cells, chemical sensors, etc.\textsuperscript{1,2,4}

3.2 GaAs Surfaces Etched with HCl

3.2.1 Literature Precedent

Like many other semiconductor materials, GaAs is prone to forming an oxide layer upon exposure to air.\textsuperscript{1-5} Consequently, if one desires to work with an oxide free surface on this substrate, GaAs has to be treated with an etchant to remove the oxide layer. Most preparation conditions use an acid as the etchant, especially concentrated HCl, but bases have also been used. This process precedes formation of any type of SAM that is intended to bind to GaAs (as opposed to an oxide of this material).

Allara et al. in 1992 were one of the first to report the formation of alkanethiol SAMs on GaAs. In this report, the authors used concentrated HCl to etch n-type GaAs(100), which they argued created a surface mostly covered with arsenic. After etching, this substrate was
immersed in a solution of an alkanethiol at 100°C for 5 h to form the SAM. SAMs of HSC_{n}H_{2n+1}, where n ranged from 12 to 22, were made on these surfaces. Also, SAMs composed of HSC_{15}X, where X was either a carboxylic acid (-CO_{2}H) or carboxylic acid methyl ester (-CO_{2}CH_{3}) were formed. The formation of the monolayer was confirmed using water contact angles and FTIR measurements. These techniques indicated the presence of a high surface coverage and densely packed SAM. The mechanics of the etching processes and amount of defects in the film were not elaborated on in this report, although later studies probed this more extensively.

One study employed AFM to probe the structure of freshly etched GaAs and alkanethiol SAMs on GaAs.\textsuperscript{1} As mentioned previously, AFM and many SPM techniques are useful techniques for investigating defects and order at surfaces, especially in SAMs. Since the roughness of a surface affects the resulting order and amount of defects, surface roughness obtained by AFM was used to probe the quality of the resulting surface.\textsuperscript{1} Specifically, the root mean squared (RMS) surface roughness of GaAs surfaces was investigated before etching, after etching, and after subsequent SAM deposition. Prior to forming SAMs on GaAs, the substrate was always treated with concentrated HCl to remove the oxide layer. Following etching, SAMs of C_{18}SH, a methyl terminated SAM, and 11-mercaptoundecanol (HOC_{10}SH), an alcohol terminated SAM, were deposited on this surface by submerging the samples in a solution of the thiols in ethanol (EtOH) at room temperature for 12 h. Through the use of AFM, surface roughness was determined following etching of the surface under various conditions and an optimal procedure to minimize this
roughness during the etching of GaAs was devised. In addition, surface roughness was determined after deposition of the thiol SAMs on these surfaces to determine the quality of the films on GaAs treated with this optimal etching procedure. Using AFM, force-distance curves were taken on both the methyl terminated and alcohol terminated SAMs. The force-distance curves showed that the methyl terminated SAMs were, as expected, hydrophobic, and the alcohol terminated SAMs were hydrophilic. This observation helped confirm the presence of these SAMs and implied that they were of relatively high quality. However, all of the surface roughness and force curve measurements taken with AFM probed the surface at roughly the micrometer scale, so these measurements do not judge the ordering or surface roughness at the molecular scale.

The above report and others have investigated the mechanism of HCl etching and thiol SAM formation on GaAs.\(^1\) As mentioned above, Allara et al. proposed that the surface predominately consisted of arsenic upon HCl etching, but offered little support towards this claim.\(^5\) In the AFM study above, the authors proposed a more detailed mechanism, suggesting HCl reacts readily with gallium, which causes it to be removed from the surface.\(^1,5\) In addition, H\(^+\), provided by HCl, oxidizes the arsenide, but As\(^+\) remains present on the surface (Figure 3.1).\(^1\) It has been argued that the As\(^+\) has a high affinity for alkanethiol and this affinity is important for SAM formation. Some studies attempted to employ X-ray photoelectron spectroscopy (XPS) to characterize the bond formed between these two species, but these attempts were frustrated by the overlap of the sulfur 2p peak overlap with the gallium 3s peak.\(^1,3,5\) Other researchers have even suggested that bonding
occurs between gallium and the thiol. As a result, details about the bond that is formed between GaAs and the thiol as well as the mechanism of etching remain highly debated.

\[
\text{As} + \text{H}^+ \rightarrow \text{As}^+ + \frac{1}{2} \text{H}_2
\]

**Figure 3.1. Proposed reaction for the etching of GaAs with HCl.**

Many of the reports mentioned above show strong evidence that high quality SAMs can be made using HCl to remove the native oxide layer prior to monolayer deposition. Since the techniques used in most of these reports to characterize these SAMs on GaAs measure an average of large areas of the surface, questions remain concerning the nanometer scale surface roughness of the substrate and the degree of crystallinity in these SAMs. Despite these concerns, it was desired to make alkanethiol SAMs on GaAs following treatment of the surface with HCl and apply replacement lithography to these surfaces.

### 3.2.2 Results and Discussion

First, experiments were performed to determine the stability of these dodecanethiol monolayers on GaAs towards ambient conditions and STM scanning conditions. GaAs was etched with concentrated HCl for 1-2 min, then these freshly etched surfaces were submerged in purged 1 mM dodecanethiol in EtOH at room temperature for at least 2 h. Figure 3.2a shows an initial STM image of a sample made by etching the GaAs surface in concentrated HCl for 1 min, then submerging this sample in 1 mM dodecanethiol in EtOH for 1 hr at room temperature. It was observed that when scanning with STM in one area of the surface at 1 V and 150 pA (in air), the surface morphology changed considerably and surface roughness increased drastically (Figure 3.2b). When moving this scan area, the image would improve,
but after the first few scans, similar changes in the surface were observed. It was observed that areas of the surface not scanned with the STM showed morphology and surface roughness that remained relatively constant. Specifically, these areas were stable towards ambient conditions for greater than 3 days, although only stable towards the above scanning conditions for 1-2 images. When increasing the bias (positive or negative) or set point current, the scanning conditions seemed to cause greater changes in morphology and surface roughness. Thus, it can be said these SAMs are stable towards ambient conditions for a considerable length of time, but are not stable towards typical scanning conditions used for imaging SAMs on other surfaces such as gold.

Figure 3.2. Consecutive STM images of the same scan area of a dodecanethiol SAM on GaAs (a) Initial scan of the area. (b) Image of this same area after the completion of the first scan. The z range is set at 10 nm where greater heights are shown as lighter areas and smaller heights are shown as darker areas of the image. Images were scanned with a bias of 1 V and set point current of 150 pA.

Following this result, other conditions were employed to determine whether these dodecanethiol SAMs on GaAs could be stably scanned with STM. First, dodecanethiol
SAMs on these surfaces were made by etching the substrate in 2:1 HCl (concentrated)/water for 1 min, then submerging in purged 1 mM solutions of dodecanethiol in EtOH for at least 2 h. Along with the scanning conditions, it was speculated that the presence of oxygen could be contributing to the surface modifications observed above. So, in order to minimize the effect of oxygen towards the stability of the surface upon scanning with STM, the atmosphere exposed to the sample was continually purged with nitrogen. Also, the scanning conditions were adjusted to a scanning bias of -1 V and set points lower than 30 pA as it was speculated that the higher tunneling currents used previously could have contributed to the unstable imaging of these surfaces. Figure 3.3 shows a STM image representative of what was observed after consecutively scanning a confined area of a dodecanethiol SAM made following the procedure outlined above. More specifically, the GaAs was etched in 2:1 HCl (concentrated)/water for 1 min, and then the SAM was formed by submerging this substrate in a purged 1 mM solution of dodecanethiol in EtOH for 1 hr at room temperature. Here, the scanning was done under a scanning bias of -1 V and a set point of 30 pA. In comparison to what was observed above, the surface morphology and roughness remained stable under these conditions. So, when oxygen was minimized and the scanning conditions were adjusted properly, it appears that dodecanethiol SAMs on GaAs made following the procedure above can be stably scanned.
Figure 3.3. STM image of a dodecanethiol SAM on GaAs scanned under a scanning bias of -1 V and set point current of 30 pA with the sample area purged with nitrogen.

However, as shown in Figure 3.3, these dodecanethiol SAMs on GaAs contain a much greater surface roughness and disorder compared to alkanethiol SAMs on gold substrates. It was desirable to obtain ordered monolayers on GaAs, which is most easily done on surfaces that have large areas that are atomically flat. If smoother GaAs could be made with large atomically flat regions, then this surface might facilitate the formation of more ordered SAMs on this substrate.

Experiments were done to investigate whether the above etching procedure could be further optimized to obtain flatter GaAs to facilitate more order SAM formation on this surface. This was done by etching GaAs in various concentrations of the etchant in EtOH and water. In addition, the time of the etching process was varied between 30 seconds and 3 min. To characterize the effect of these etching conditions, the bare GaAs surface was scanned with STM and the RMS value was obtained. The bare GaAs was scanned without
passivation with a SAM. Although this surface is prone to oxidation, they were stable within the time scale of the experiment. Figure 3.4a is a STM image representative of what was observed when scanning bare GaAs after employing the most optimal etching conditions. More specifically, this surface was treated with a 4:1 concentrated HCl/EtOH, which yielded RMS values of approximately 0.25 nm. It can be seen in Figure 3.4a that these surfaces still do not have a comparable surface roughness to annealed gold or gold on mica. Despite efforts to minimize the surface roughness further and obtain regions that were atomically flat, all other conditions employed yielded surfaces with similar roughnesses.

Even though atomically flat regions could not be obtained when etching GaAs under all the conditions employed above, attempts were made to apply a dodecanethiol SAM to
GaAs treated with the most optimal etching procedure determined above to see whether an ordered SAM could still be made. This was done by etching GaAs in 80% concentrated HCl in EtOH. Then, deposition was done by immersing this surface in a purged 1 mM solution of dodecanethiol in EtOH. Figure 3.4b is a STM image consistent with what was observed when a SAM was deposited on GaAs treated in such a manner. In the image it can be seen that a monolayer formed on these etched surfaces using these optimal conditions had little order. Even when scanning under smaller scan sizes to probe the surface more closely, it was not possible to observe any sort of ordering in the SAM. As a result, it was not possible to differentiate between areas of the surface that are covered with dodecanethiol and not covered with this molecule. So, it remained unclear how well this system would accommodate replacement lithography.

3.3 Lithography on GaAs etched with NH₄OH

3.3.1 Literature Precedent

In addition to employing HCl as the etchant, much of the initial work with alkanethiol SAMs on GaAs employed a base, ammonium hydroxide (NH₄OH), as the etchant and other studies utilized this etchant during deposition to suppress oxide formation.²⁻⁴ In one report, NH₄OH was utilized during both the etching and deposition steps.³ Various agents were explored for optimizing the quality of the alkanethiol SAMs on GaAs, but when NH₄OH was employed during etching and SAM deposition, the best results were found. The resulting SAMs were characterized by a number of complementary techniques where, in summary, contact angle, FTIR, and single wave ellipsometry (SWE) measurements indicated a high
surface coverage, organized SAM with film thickness values consistent with a monolayer of molecules. Tilt angles of ~18° from the surface normal were calculated from FTIR data. These values were suggestive of improved surface coverage compared to the much larger tilt angles of ~57° found in most other reports. Furthermore, the appearance of a sulfur 2p peak in the XPS spectrum, which could be resolved from the gallium 3s peak, indicated the presence of sulfur from the alkanethiol. However, as with previous studies, no bonding information could be extracted because of significant overlap between the sulfur 2p and the gallium 3s peaks. Thermal stability experiments suggested that the monolayer was completely stable up to 100°C, which is comparable to the stability of alkanethiols on gold. Overall, it was claimed by the authors that the resulting alkanethiol SAMs on GaAs were comparable in quality to ones formed on gold surfaces. One experiment showed spontaneous (adventitious) replacement by as much as 30% of deuterated alkanethiols in the original SAM with unlabeled alkanethiol exposed to the surface via a solution. Here, exchange was followed with FTIR by monitoring the decrease in intensity of the C-D stretching modes along with the increase in intensity of the C-H stretching modes. This type of spontaneous replacement has been observed with alkanethiol SAMs on gold and this suggests that directed replacement via replacement lithography could be employed with these structures.

Given the convincing evidence concerning the quality of alkanethiol SAMs on GaAs made by the procedure above, SAMs were made following this protocol, roughness/order was assessed using STM, and some preliminary scanning probe lithography experiments were attempted. It was hypothesized that these structures would provide a more stable
surface for the controlled removal of alkanethiol SAM. In addition, since SAMs on GaAs made by this method appear to be of better quality, characterization of the initial surface could be permitted by imaging order in these monolayers.

3.3.2 Results and Discussion

Experiments were performed where GaAs was etched in concentrated NH₄OH (30%), then a SAM of dodecanethiol was formed on this substrate and initial replacement attempts were made with this SAM. This was done by etching the GaAs in 30% NH₄OH for 1 min. Then, the SAM was deposited by immersing the substrate in 10 mM NH₄OH and 3 mM dodecanethiol in EtOH for greater than 20 h. Figure 3.5a is a STM image representative of what was observed following the above treatment. The resulting surface had a surface roughness comparable to what was observed when SAMs were made with HCl as the etchant and no apparent ordering could be observed. As mentioned previously, surfaces without any distinct structure or order are difficult to characterize with STM and thus the quality of these SAMs was questionable. Next, replacement of this SAM with a different molecule was attempted. This was done by exposing this surface to 4 µM of FcC₁₁SAc in dodecane and raising the humidity to ~45%. To initiate replacement, nine lines were written at incrementally higher biases ranging from 2.5 to 3.3 V and the resulting modification was imaged with STM. Figure 3.5b is a STM image representative of what was observed when replacement lithography was attempted on this surface. It can be seen from the image that a dramatic, uncontrollable change occurred upon attempting replacement lithography and it
was difficult to determine the reason for this uncontrolled modification or the nature of the features made.

Figure 3.5. STM images of a dodecanethiol SAMs on GaAs (a) before and (b) after replacement lithography was attempted. The SAM was made using 30% NH$_4$OH to etch the GaAs, followed by deposition in a mixture of NH$_4$OH and dodecanethiol in EtOH for greater than 20 h. Replacement lithography was attempted with FeC$_{11}$SAc in dodecane as the replacing solution where 9 lines were written at incrementally higher biases ranging from 2.5 to 3.3 V.

To promote ordering of these monolayers and easier characterization of the initial SAM, the etching procedure employed above was adjusted to provide optimal conditions to minimize surface roughness. This was done by varying the etching times when employing 30% NH$_4$OH as the etchant and characterizing the resulting surface roughness using STM. More specifically, RMS surface roughness was calculated and the general surface morphology was explored. Then, surfaces with different treatments were compared. Figure 3.6a is a STM image of bare GaAs that is representative of what was observed when etching times were kept below 2 min, which yielded optimal surface roughnesses. Specifically, the GaAs surface in this image was etching for 45 seconds in the NH$_4$OH solution. As with the
previous GaAs surfaces etched with HCl and NH₄OH, these surfaces were still atomically rough and had a RMS surface roughness of 0.2-0.3 nm, which is comparable to the best surface roughness observed before.

Surfaces prepared with these optimal etching conditions were then used to make dodecanethiol SAMs, which it was hoped would have more order. This was done by etching the GaAs in 30% NH₄OH for under 2 min and then exposing this surface to a solution of 10 mM NH₄OH and 3 mM dodecanethiol in ethanol for ~24 h. Figure 3.6b shows a STM image representative of what was observed following this treatment. No ordering could be observed in these surfaces when scanning with STM at smaller scan sizes.

Despite the lack of order and questionable quality of the SAMs produced on these surfaces, previous reports imply that scanning probe lithography on SAMs lacking any
apparent order is still feasible. There are various reports where scanning probe lithography (SPL) is initiated on SAMs on other substrates where there appears to be no apparent order in the monolayer.\textsuperscript{9,10} In these reports, little characterization of the initial SAM was reported, but attempts to initiate patterning through SPL were successful. In addition, the resulting patterns were well characterized. These previous results imply that replacement lithography on the dodecanethiol SAMs on GaAs made following the procedure above could be employed successfully. In addition, it was hypothesized that uncontrolled modification, similar to what was observed previously, could be avoided by limiting the presence of oxygen.

Thus, replacement lithography was attempted with dodecanethiol SAMs on GaAs made from the above procedure without concern over the order and initial state of the SAM. This was done by etching GaAs in 30\% NH\textsubscript{4}OH for 1 min, then immersing the substrate in a solution of 3 mM dodecanethiol and 10 mM NH\textsubscript{4}OH in ethanol for \sim24 \text{ h}. The resulting surface was then scanned with STM under a bias of -1 V and set point current of 10 pA. In addition, the scanning was done under nitrogen. The sample was found to be stable to these scanning conditions. To initiate replacement lithography, the sample was exposed to micromolar amounts of 6-ferrocenylhexanethiol (FcC\textsubscript{6}SH) in dodecane. Upon exposure to FeC\textsubscript{6}SH, the imaging conditions altered the surface. Figure 3.7 shows a STM image representative of what was observed when the surface was exposed to conditions of scanning bias of -1 V and a set point of 10 pA. In the center of the image a 500 x 500 nm box was created by previous scanning in that area at those dimensions. Other experiments initiated
similar lithography. Even though the patterning was more controlled compared to previous attempts, it was difficult to confirm the presence of the FcC₆SH in the patterned areas or determine what the patterned area consisted of. Also, large height changes greater than the expected thickness of the monolayer were observed in and around the pattern. In these experiments it was noticed that all modifications did not seem to damage the tip, so it is speculated that the mechanism was not mechanical in nature.

Figure 3.7. STM image of a dodecanethiol SAM on GaAs scanned at 10 pA and -1 V where the box pattern in the middle of the image was formed previously by scanning under the same conditions, except at a scan size of 500 x 500 nm (half the scan size). The sample was prepared using NH₄OH to etch the GaAs and during deposition of the SAM.

3.4 Conclusions

Many reports in the literature show that alkanethiol SAMs on GaAs of relatively high quality can be formed. However, much ambiguity remains as to the most effective method for removing oxide from the GaAs surface and forming nearly atomically flat terraces that can accommodate high levels of crystallinity in the SAM. Despite this ambiguity, it was
hypothesized that replacement or desorption lithography could be applied to SAMs on this surface. This hypothesis was tested through various experiments. First, experiments were done to devise an optimal etching procedure for allowing the formation of highly crystalline alkanethiol SAMs on GaAs. When methods were employed that utilized HCl as the etchant, surfaces that were atomically rough and SAMs with no apparent order were observed. As a result, another method for making dodecanethiol SAMs was pursued where NH₄OH was employed during both the etching process and SAM formation. Even after optimizing the etching procedure to obtain smoother surfaces for the deposition of a dodecanethiol monolayer, order was still not observed. Lithography experiments were attempted on dodecanethiol SAMs on GaAs made from this method. The results indicated that both standard scanning conditions and scanning under elevated biases resulted in relatively controlled modification of the surface, but the height changes within and around the patterned area were highly irregular. The features made consisted of both raised areas and depressions where height change often were significantly greater than the expected thickness of the dodecanethiol SAM. Thus, it was difficult to determine the nature of these patterns. Moreover, the mechanism for these modifications is unknown. The lack of apparent order in the background monolayer throughout all these experiments made it difficult to characterize the initial alkanethiol SAM on these surfaces as well as the patterns created. Therefore, it became of interest to explore replacement lithography with other substrates, which could be made atomically flat more easily, and facilitate more order in SAMs deposited on these surfaces.
3.5 Experimental Section

**General Considerations**

P-type GaAs (doped with zinc) was purchased from Institute of Electronic Materials Technology. Dodecanethiol was purchased from Alfa Aesar. NH₄OH and HCl were purchased from Fisher Scientific. Dodecane was purchased from Aldrich. Absolute ethanol was used as a solvent. All these chemicals were used without further purification. FcC₁₁SAc and FcC₆SH was synthesized in our laboratory following previously documented procedures. All water used was purified by reverse osmosis.

**Preparation of GaAs**

GaAs was etched with either HCl or NH₄OH as described throughout the chapter.

**Preparation of Dodecanethiol SAMs**

SAMs of dodecanethiol were deposited on GaAs following procedures described throughout the chapter. The samples were rinsed with ethanol immediately after removing from the deposition solution and dried under a stream of nitrogen. Then, the samples were fixed to a metal disk with silver paste before scanning with STM.

**Characterization**

Scanning tunneling microscopy (STM) images were taken with a Nanoscope III (Digital instruments) after fixing the samples to the metal disk. Scanning conditions varied between experiments. In order to reduce the presence of oxygen during scanning with STM, the instrument was covered with a metal can and nitrogen was continuously flowed into the can.
3.6 References


Chapter 4 – ADVENTITIOUS REPLACEMENT OF ONE MOLECULE IN A SAM ON GOLD FOR ANOTHER FOLLOWED BY STM

4.1 Introduction: Terminal Alkynes SAM on Gold

Self-assembled monolayers (SAMs) of alkanethiols on gold provide a convenient way to add functionality across a surface or in selected areas via various scanning probe lithography (SPL) techniques as was described earlier.\(^1\) Other types of SAMs on gold and other substrates have been explored and well documented.\(^2\) However, these systems do not rival alkanethiol SAMs on gold for most studies and applications because alkanethiol SAMs are simple to form and are relatively more stable. However, SAMs of alkanethiols on gold do have some limitations. Thiols desorb from gold at elevated temperatures of approximately 80-100°C.\(^3\) Also, for electronic applications, a linker with π-type character may facilitate greater orbital overlap and thus greater electronic coupling between the molecule and the metal substrate.\(^4\) Thus, it has become of interest to explore other binding group SAMs on gold where there could be improved stability and better electronic coupling.

One system that has begun to show promise in forming high quality SAMs is terminal alkynes on gold. A theoretical study has shown that binding of ethynylbenzene molecules to gold is energetically favorable.\(^5\) In addition, another study investigated diethynylbenzene on gold nanoparticles by surface-enhanced Raman scattering (SERS), and the results supported a near vertical configuration of the molecule.\(^6\) Another report gave evidence of the presence of alkynes on relatively large, flat gold surfaces where the presence of a densely packed film was indicated by large water drop contact angles, ellipsometry, electrochemical blocking, and infrared spectroscopy (IR).\(^7\)
4.2 Adventitious Replacement into Alkyne and thiol SAMs on Gold

This work was the subject of a publication, Tucker, E. Z.; Gorman, C. B., “Terminal Alkynes as an Ink or Background SAM in Replacement Lithography: Adventitious versus Directed Replacement” *Langmuir*, **2010**, 26 (18), 15027-15034

4.2.1 Literature Precedent

It has been shown previously that when a SAM is exposed to a solution containing another thiol, spontaneous (adventitious) replacement can occur. Richardson et al. reported the adventitious replacement of a \( n \)-octanethiol SAM on gold by a semifluorinated \( n \)-octanethiol that was exposed to this surface via a solution.\(^8\) In addition, the reverse process was explored where a semifluorinated \( n \)-octanethiol SAM on gold was adventitiously replaced by \( n \)-octanethiol exposed to the surface. Both exchange processes were followed by photoelastic modulation infrared reflection adsorption spectroscopy (PM-IRRAS) and STM. It was found that the \( n \)-octanethiol SAM was replaced by semifluorinated \( n \)-octanethiol through domain boundaries while the reverse process was found to occur more homogenously. Moreover, the adventitious replacement of adamantanethiol SAMs on gold by dodecanethiol has been followed via various techniques.\(^9-12\) The bulky molecules in this SAM are easily displaced, and the mechanism and the kinetics of this exchange process have been very thoroughly investigated. In summary, it was found that the adamantanethiol SAM was replaced by dodecanethiol at defect sites, such as substrate step edges and substrate vacancy islands. In addition, others have shown that thiol SAMs can be replaced by other SAM forming molecules and probed the mechanism of these replacement processes.\(^{13,14}\) As mentioned in Chapter 1, when a background alkanethiol SAM is exposed to solutions
containing 11-ferrocenylundecanethiol or 11-ferrocenylundecanethioacetate during replacement lithography experiments, adventitious replacement is observed.\textsuperscript{15}

Therefore, experiments were done where terminal alkynes were used as the replacing molecule or background SAM in adventitious replacement. More specifically, the propensity of adventitious replacement of both dodecyne (C\textsubscript{10}≡) and dodecanethiol (C\textsubscript{12}SH) SAMs on gold is explored.

4.2.2 Results and Discussion

The relative reactivity of a terminal alkyne SAM and an alkanethiol SAM toward adventitious replacement was probed with STM. In previous work, we have shown that, at slightly elevated biases (ca. 1 V), alkanethiol SAMs containing ferrocenyl head groups display enhanced tunneling compared to methyl-terminated alkanethiols when bound to gold.\textsuperscript{16} This enhancement may be due to resonant tunneling between the tip and ferrocenyl head group,\textsuperscript{17,18} although other explanations have been offered.\textsuperscript{19,20} In any event, the higher rate of tunneling manifests itself as an increase in the apparent height of the ferrocenyl-terminated SAM compared to the methyl-terminated SAM regions. This height contrast allows one to distinguish the ferrocenyl-containing molecules from methyl-terminated regions of the SAM. In addition, as mentioned above, it has been shown that alkanethiol and alkanethioacetate molecules in a solution covering an alkanethiol SAM can adventitiously replace into the SAM.\textsuperscript{15,16} By using an ink containing a binding group with an affinity for gold and ferrocene tail groups that cause increased height contrast, adventitious replacement could be monitored by STM. The relative rates and extent of
replacement give an idea of the relative stability of a C\textsubscript{12}SH and C\textsubscript{10}≡ SAM. It was expected that adventitious replacement would occur to a greater extent in the SAM with more defects and/or a lower thermodynamic stability.

Adventitious replacement experiments were performed as follows. SAMs of either C\textsubscript{12}SH or C\textsubscript{10}≡ on gold were imaged in air. Then, in separate experiments, solutions of 11-ferrocenylundecanethiol (FeC\textsubscript{11}SH), 11-ferrocenylundecanethioacetate (FeC\textsubscript{11}SAc), and FeC\textsubscript{11}≡ were placed onto the C\textsubscript{12}SH and C\textsubscript{10}≡ SAMs, covering the surface and tip. After adjusting the relative humidity to ca. 47%, imaging was continued in dodecane to monitor the amount of adventitious replacement of the molecule in solution into the initial SAM. When lower concentrations of the replacing molecule were used, a solution of the replacing molecule was slowly pumped over the sample to ensure that its concentration remained constant during experiments (e.g., the replacement did not deplete the molecule in solution).

Figure 4.1 shows a series of STM images that follow the replacement process. Panels A and B are STM images of SAMs of C\textsubscript{12}SH and C\textsubscript{10}≡ before the solution of the replacing molecule was added. Pits (vacancy islands) were present in both C\textsubscript{12}SH and C\textsubscript{10}≡ SAMs. The remaining panels in Figure 4.1 are images that were taken after a 50 μM solution of FeC\textsubscript{11}SAc in dodecane was exposed to these samples for 20 min (Figure 4.1C and D) and 60 min (Figure 4.1E and F).
Figure 4.1. A series of STM images comparing the process of adventitious replacement of FeC_{11}SAC into a C_{10}≡SAM (top, panels A, C, and E) and a C_{12}SH SAM (bottom, panels B, D, and F). Images were taken before FeC_{11}SAC was added (A, B), 20 min (C, D), and 60 min after addition of FeC_{11}SAC (E, F).

The rate and extent of replacement were obtained quantitatively by taking STM images collected at different replacement times and calculating the percent of the area occupied by the replacing molecule. Histograms of the height values were constructed and fit to a sum of two Gaussian functions (Figure 4.2B). The Gaussian curve with the lower apparent height was assigned to the background, and the curve with the higher apparent height was assigned to the replaced area. In this process, regions containing pits and step edges were avoided. However, to the extent that they existed, they were counted as
unreplaced regions as shown by the annotations in Figure 4.2B. Thus, the extent of replacement is systematically underestimated by this error which is estimated at <5%.

Figure 4.2. Schematic showing process used to quantify the amount of adventitious replacement for each STM image collected: (A) raw image; (B) fit to a sum of two Gaussians.

The amount of adventitious replacement was calculated from the images in Figure 4.1 along with images collected at different time points and from additional trials. These data allowed the adventitious replacement of FcC11SAc into C12SH and C10≡SAMs to be compared. Figure 4.3 shows a plot of the area adventitiously replaced versus time when a 50 µM solution of FcC11SAc was exposed to a C12SH and C10≡SAM. FcC11SAc replaced far less into the C12SH SAM than into the C10≡SAM. Within ca. 80 min, FcC11SAc had replaced to an extent of ca. 90% into the C10≡SAM and to ~40% into the C12SH SAM.
Figure 4.3. Comparison of adventitious replacement with 50 µM of FeC_{11}SAc into C_{10}≡ (black squares) and C_{12}SH (red circles) SAMs. Error bars are 90% confidence intervals derived from multiple trials.

The experiment above was repeated using FeC_{11}SH in place of FeC_{11}SAc. Figure 4.4 shows a plot of the area adventitiously replaced versus time when 10 µM of FeC_{11}SH was exposed to a C_{12}SH and C_{10}≡ SAM. FeC_{11}SH replaced more slowly into the C_{12}SH SAM than into the C_{10}≡ SAM. In contrast to what was observed with FeC_{11}SAc, replacement of both the C_{10}≡ and C_{12}SH SAMs by FeC_{11}SH approached 100% within 2 h.
Figure 4.4. Comparison of adventitious replacement with 10 µM of FeC_{11}SH into C_{10}= (black squares) and C_{12}SH (red circles) SAMs with error bars at each point representing 90% confidence intervals derived from multiple trials.

The observation that FeC_{11}SH and FeC_{11}SAc replaced more slowly into the C_{12}SH SAM than into the C_{10}= SAM is consistent with the hypothesis that the alkanethiol SAM is more stable than the alkyne SAM. In the following experiments, various replacing molecules were exposed to either a C_{12}SH or C_{10}= SAM at various concentrations. The kinetics of the replacement were modeled when possible and used to probe these replacement processes more thoroughly.

In one case, a comparison was made between the adventitious replacement of FeC_{11}SAc, FeC_{11}SH, and FeC_{11}= into a C_{10}= SAM. First, replacement of FeC_{11}SAc into a C_{10}= SAM was explored. The adventitious replacement was investigated at 5, 25, 50, and 100 µM concentrations of FeC_{11}SAc to explore the effect of concentrations of the replacing...
molecule on the rate and extent of replacement. Figure 4.1A, C, and E shows representative images of what was collected during this experiment.

![Graph showing time dependence of the average fractional surface coverage of FcC11SAc as it replaced into a C10≡SAM by 5 µM (blue stars), 25 µM (orange triangles), 50 µM (black squares), and 100 µM (red circles) concentrations of the replacing molecule with error bars at each point representing 90% confidence intervals derived from multiple trials. The red lines are a best fit of a first-order Langmuir equation to the points. Note that the values in Table 4.1 are the average of fits of individual trials where these are fits of the average values of all the trials.]

Figure 4.5 shows a plot of the adventitious replacement (as fractional surface coverage of FcC11SAc) at these concentrations versus time where each curve represents an average of several trials. As concentration FcC11SAc increased, the extent of replacement increased. The individual trials were fit using a first order Langmuir equation of the form
\[ \theta(t) = A_1 - A_2 e^{-kt} \]

Where \( A_1 \) was allowed to vary to account for less than 100% replacement as time approached infinity (\( t \to \infty \)) and \( A_1-A_2 \) is an error that reflects the apparent amount of replacement at time \( t = 0 \). Values for \( k \), \( A_1 \), and \( A_2 \) were determined for each trial at each concentration, and then values for a given concentration were averaged together to give the data shown in Table 4.1. For all concentrations of \( \text{FcC}_{11}\text{SAc} \), the values of \( k \) were similar. The lack of dependence of rate on concentration of \( \text{FcC}_{11}\text{SAc} \) suggests a dissociative mechanism rather than an associative mechanism. Specifically, the unimolecular dissociation of the alkyne would be rate determining in this case. One interesting trend is the tendency for the extent of replacement (\( A_1 \)) to decrease with decreasing concentration. Thus, this process involves some type of equilibrium that limits the extent of replacement. It has been speculated previously that \( \text{FcC}_{11}\text{SAc} \) can become deprotected in situ to ferrocenylundecanethiolate, which can then bind to gold.\(^{13} \) Depending on the equilibrium for the reaction, this deprotection reaction could limit the amount of thiolate available to adventitiously replace into the background SAM, causing a lower extent of replacement at lower concentrations. So, in the time scale of the experiment, the thiolate replacing molecule could effectively be depleted, and this could account for the lower extent of replacement when lower concentrations of the replacing molecule were used.
Table 4.1. Rate Constants, $A_1$, and $A_2$ Values Obtained from Fitting Each Individual Trial for the Replacement of a C$_{10}$≡ SAM with FcC$_{11}$SAc with a Modified First Order Langmuir Equation$^a$

<table>
<thead>
<tr>
<th>concn (µM)</th>
<th>$k$ (s$^{-1}$)</th>
<th>$A_1$</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.039 ± 0.019</td>
<td>0.46 ± 0.20</td>
<td>0.24 ± 0.15</td>
</tr>
<tr>
<td>25</td>
<td>0.042 ± 0.015</td>
<td>0.61 ± 0.14</td>
<td>0.44 ± 0.09</td>
</tr>
<tr>
<td>50</td>
<td>0.048 ± 0.010</td>
<td>0.90 ± 0.11</td>
<td>0.65 ± 0.15</td>
</tr>
<tr>
<td>100</td>
<td>0.043 ± 0.025</td>
<td>0.84 ± 0.07</td>
<td>0.60 ± 0.07</td>
</tr>
</tbody>
</table>

$^a$The error for these values is represented as 90% confidence intervals derived from multiple trials.

Above, a thioacetate was used instead of a thiol as the replacing molecule. Thioacetates were preferred because they showed lesser/slower adventitious replacement than thiols when exposed to a preformed SAM, making it easier to characterize the replacement process. However, as the relative rate and extent of spontaneous replacement are being characterized here, it begs the question as to how a thiol behaves as a spontaneous replacement molecule compared to an analogous thioacetate. Thus, the experiments described above were repeated using FcC$_{11}$SH in place of FcC$_{11}$SAc. At 50 µM concentrations of FcC$_{11}$SH, replacement into the C$_{10}$≡ SAMs was too rapid to characterize by STM. Thus, replacement with FcC$_{11}$SH was studied at concentrations of 1 and 10 µM.

After exposure of the C$_{10}$≡ SAM to FcC$_{11}$SH, STM images similar to what was observed in the experiments with FcC$_{11}$SAc were collected. As was done with FcC$_{11}$SAc, the amount of replacement of C$_{10}$≡ SAM by FcC$_{11}$SH was determined from the STM images collected during the experiment, and individual trials were fit with an equation to describe the kinetics of the replacement process. This replacement process was found to fit best with the Johnson, Mehl, Avrami, and Kolmogorov (JMAK) model, which has previously been used to describe exchange of 1-adamantanethiolate monolayers with C$_{12}$SH.$^{10}$ This model
had been used to effectively model nucleation and island growth kinetics of various systems.

The JMAK2 model is of the form

\[ \theta(t) = A_1 - A_2 e^{-(kt)^2} \]

where, as with the equation above, \( A_1 \) was allowed to vary to account for less than 100% replacement as time approached infinity \( (t \rightarrow \infty) \) and \( A_1 - A_2 \) is an error that reflects the apparent amount of replacement at time \( t = 0 \). Table 4.2 shows values for \( k, A_1, \) and \( A_2 \) obtained from the fit of JMAK2 equation to the data from FcC_{11}SH replacing into C_{10}≡SAM.

Table 4.2. Rate constants, \( A_1, \) and \( A_2 \) Obtained from Fitting the Replacement of C_{10}≡SAM with FcC_{11}SH with JMAK2^a

<table>
<thead>
<tr>
<th>concn (μM)</th>
<th>( k ) (s(^{-1}))</th>
<th>( A_1 )</th>
<th>( A_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.162 ± 0.093</td>
<td>0.895 ± 0.078</td>
<td>0.710 ± 0.067</td>
</tr>
<tr>
<td>10</td>
<td>0.214 ± 0.148</td>
<td>0.917 ± 0.075</td>
<td>0.797 ± 0.175</td>
</tr>
</tbody>
</table>

^a The error for these values is represented as 90% confidence intervals derived from multiple trials.

Several observations can be made from these fits. First, the values of \( k \) at each concentration are similar within experimental error. This observation suggests that replacement with FcC_{11}SH also follows a dissociative mechanism although the relatively large error in these values (mostly due to the speed of replacement) makes this conclusion tenuous. In addition, the value of \( A_1 \) is close to unity. The STM images show that the spontaneous replacement with this replacing molecule approaches 100%. This suggests that the concentrations of FcC_{11}SH used provided enough replacing molecule to drive the replacement to completion during the time scale of the experiment. The JMAK2 model
fitting this data the best seems to suggest that this exchange process followed a nucleation and growth mechanism. However, it was difficult to determine whether this model was consistent with what was observed in the STM images because replacement happened so rapidly. So, the nucleation and growth process could not be discerned from the STM images.

To compare with the above experiments and to explore the effect of another replacing molecule with a different binding group, the replacement of a C₁₀≡ SAM with FcC₁₁≡ was explored. Several concentrations of FcC₁₁≡ in dodecane were exposed to C₁₀≡ SAMs. The adventitious replacement was monitored as described previously. After exposure of the C₁₀≡ SAM to FcC₁₁≡, STM images similar to what was observed when exposing this SAM to FcC₁₁SAc and FcC₁₁SH were observed. Replacement into the C₁₀≡ SAM appeared to occur homogenously across the surface. Figure 4.6 shows a graph of this replacement as fractional surface coverage of FcC₁₁≡ into a C₁₀≡ SAM. At all concentrations of FcC₁₁≡, the amount of replacement seemed to reach a maximum quickly. Thus, it appears that exchange did occur within ca. 10-20 min after exposure of the SAM to FcC₁₁≡ but quickly stopped. There may be a small decrease in replacement beyond this time interval, but the magnitude of this decrease is arguably within experimental error. If FcC₁₁≡ is desorbing from the surface, these experiments unfortunately provide no way to tell whether FcC₁₁≡ is being replaced by something or whether it is leaving behind a vacant spot on the surface. In the absence of this information, any quantitative model for this process is not meaningful, so no attempts were made to model these replacement kinetics.
Next, a comparison was made of the adventitious replacement of FcC\textsubscript{11}SAc, FcC\textsubscript{11}SH, and FcC\textsubscript{11}= into a C\textsubscript{12}SH SAM. Upon exposure of a C\textsubscript{12}SH SAM to FcC\textsubscript{11}SAc, STM images showed that replacement proceeded primarily through defect sites (Figure 4.1B, D, and F). As with all other forms of replacement, attempts were made to quantify the replacement versus time. However, it can be seen from Figure 4.3 that substantial variability in the amount of adventitious replacement existed when FcC\textsubscript{11}SAc was exposed to a C\textsubscript{12}SH SAM. This variability made it too difficult to effectively model the adventitious replacement.
of C$_{12}$SH SAM by FeC$_{11}$SAc. Thus, no efforts were made to model this data or repeat this experiment at different concentrations.

The adventitious replacement of a C$_{12}$SH SAM by FeC$_{11}$SH at concentrations of 1, 10, and 100 µM was investigated. STM images were collected before and after exposure of the C$_{12}$SH SAM to FeC$_{11}$SH. From these images, it was observed that the adventitious replacement of the C$_{12}$SH SAM proceeded primarily through defect sites. As can be seen in Figure 4.4, the variability in amount of replacement of the C$_{12}$SH SAM by FeC$_{11}$SH was less than that of FeC$_{11}$SAc (Figure 4.3), so individual trials could more easily be fit to equations describing the kinetics of this replacement process. Thus, the STM images were converted to an amount of replacement versus time and modeled. FeC$_{11}$SH replacing into a C$_{12}$SH SAM was found to fit best with a second-order Langmuir fit of the form

\[ \theta(t) = 1 - \frac{1}{1 + kt} \]

Table 4.3 shows values of $k$ obtained from the fit of the second-order Langmuir equation shown above to the data obtained from the replacement of FeC$_{11}$SH into a C$_{12}$SH SAM. The utility of this fit is discussed below. Here the rate constant varied slightly but not more than within experimental error, supporting the idea that the rate is independent of the concentration of FeC$_{11}$SH and follows a dissociative-type mechanism. Additionally, this model assumes that replacement approaches 100%, and the satisfactory fitting of this model to this data suggests that the amount of adventitious replacement tends to approach 100%, which is consistent with what was observed in the STM images.
Table 4.3. Rate Constants Obtained by Fitting Data of the Replacement of C₁₂SH SAM with FeC₁₁SH with a Second-Order Langmuir Equation

<table>
<thead>
<tr>
<th>concn (μM)</th>
<th>k (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0832 ± 0.0561</td>
</tr>
<tr>
<td>10</td>
<td>0.0488 ± 0.0087</td>
</tr>
<tr>
<td>100</td>
<td>0.0655 ± 0.0322</td>
</tr>
</tbody>
</table>

*The error for these values is represented as 90% confidence intervals derived from multiple trials.

As mentioned previously, the adventitious replacement of a thiol SAM by another thiol molecule has been studied, albeit by different characterization methods. Various models have been used to describe this type of replacement. Weiss et al. found that replacement of 1-adamantane-thiol SAMs by dodecanethiol fit best with JMAK2, although the 1-adamantane-thiol SAMs were very labile and had a different lattice constant on gold compared to alkanethiol SAMs.¹⁰ A second-order Langmuir fit is consistent with a second-order reaction that is dependent on the square of the concentration of one reactant. In two cases, second-order Langmuir equations were used to model the adventitious replacement of thiol SAMs by another thiol molecule. In one case, Schlenoff et al. found that adventitious replacement of octadecanethiol molecules into octadecanethiol SAMs on gold could be fit reasonably well with a second-order Langmuir equation, although first-order kinetics yielded a better correlation.¹³ However, both reactions they proposed to explain the first- and second-order Langmuir equation fits were based on the formation of a disulfide from thiolates on the surface. To justify the use of the first-order Langmuir fit, they proposed a unimolecular reaction of the form

\[ \text{RSSRAu}_2(s) \rightarrow \text{RSSR} + 2\text{Au}(s) \]
rate (monolayers\(^{-1}\)) = k[RSSRAu\(_2\)(s)]

To justify the use of the second-order Langmuir fit, they proposed a bimolecular reaction of the form

\[
2RSAu(s) \rightarrow RSSR+2Au(s)
\]

rate (monolayers\(^{-1}\)) = k[RSAu(s)]^2

In another case, a second-order Langmuir model similar to the one above was used to describe the adventitious replacement of dodecanethiol into decanethiol-capped gold nanoparticles. However, the model was a diffusion-limited kinetic model, which was also expected to be independent of the concentration of the incoming thiol.\(^{21}\) Clearly these different fits fail to support an unambiguous mechanism for the different types of replacement. However, it is evident that adventitious replacement of a thiolate in a SAM by another is not general for all types of thiols and substrates.

Next, experiments were done to probe the replacement of FcC\(_{11}\equiv\) into a C\(_{12}\)SH SAM. Concentrations of 10 µM, 100 µM, and 1 mM of FcC\(_{11}\equiv\) in dodecane were employed. As before, STM images were collected before and after exposure of the SAM to a solution of the replacing molecule. It was observed from these images that the replacement occurred exclusively at defect sites and did not proceed into domains. The amount of replacement was determined and Figure 4.7 is a graph showing the amount of replacement versus time. Consistent with what was seen in the STM images, replacement was minimal throughout the experiment, even at relatively high concentrations. Also, it can be seen in the graph that the
extent of replacement was similar at all concentrations of the replacing molecule. Efforts to model this replacement process were frustrated by the low amount of replacement. However, the observation that FcC11≡ replaced only at defect sites, while FcC11SH tended to initiate complete replacement seems to suggest that the replacing molecule does have some influence on the amount of replacement. Likewise, the rate of reaction seems to be governed by the nature of the background SAM as well as the nature of the replacing molecule but is independent of the concentration of the replacing molecule.

![Graph showing the average adventitious replacement as fractional surface coverage of FcC11≡ at concentrations of 10 µM (black), 100 µM (red), and 1 mM (blue) replacing into a C12SH SAM versus time with error bars at each point representing 90% confidence intervals derived from multiple trials.](image)

4.3 Conclusions

The differences in adventitious replacement observed above suggest there is a significant difference in the stability of C12SH and C10≡ SAMs. When appropriate models were fit to the replacement of C12SH and C10≡ SAMs by FcC11SAc, FcC11SH, and FcC11≡, it was shown that a different mechanism of exchange was in operation although all appeared to
be dissociative in nature (within our ability to probe them). Thus, in all cases, the rate of adventitious replacement was not affected by the concentration of the replacing molecule and was limited by the type of SAM. The difference in size between the methyl tail group of the original SAM and the ferrocenyl tail group of the replacing molecules should also be considered as a factor governing rate. The results from adventitious replacement experiments suggested that the type of replacing molecule affected the extent of replacement as well as the rate.

4.4 Experimental Section

**General Considerations**

1-Dodecanethiol was purchased from Alfa Aesar. 1-Dodecyne (99%) was purchased from GFS chemicals. Dodecane was purchased from Aldrich. Absolute ethanol was used as a solvent. All these chemicals were used without further purification. 11−Ferrocenylundecanethioacetate and 11−ferrocenylundecanethiol was synthesized in our laboratory following previously documented procedures.22 FcC$_{11}$≡ was prepared in our laboratory following previously documented procedures and a newly devised synthetic methodology. Gold wire of 99.999% purity and 0.5 mm diameter was purchased from Alfa Aesar. Absolute ethanol was used as a solvent for formation of the SAMs. All water used was purified by reverse osmosis. All other chemicals were used without further purification.

**Preparation of Gold Surfaces**

Gold substrates for the deposition of a C$_{12}$SH and C$_{10}$≡ SAM were prepared by annealing gold to form a gold bead with a H$_2$ flame, which upon further heating formed
atomically flat facets suitable for the formation of the monolayers. These substrates were often used again after being cleaned with “piranha” solution (3:1 H$_2$SO$_4$/H$_2$O$_2$), washed with water and reannealed under a H$_2$ flame to reform the facets. Caution! “Piranha” solution should be handled carefully because of its violent reactivity with organic molecules.

**Preparation of Dodecanethiol and Dodecyne SAMs**

SAMs of dodecanethiol were deposited by refluxing a freshly annealed gold bead in a 1 mM ethanol solution of the alkanethiol for 1 h followed by cooling of the solution to room temperature for 15 min. Then, the samples were rinsed with ethanol immediately after removing from the solution and dried under a stream of nitrogen. SAMs of dodecyne were deposited by submerging a freshly annealed gold bead in 10 mM dodecyne in ethanol for 48 h at room temperature. The samples were rinsed with ethanol immediately after removing from the deposition solution and dried under a stream of nitrogen. Both these samples were imaged immediately following preparation.

**Characterization**

Scanning tunneling microscopy (STM) images were taken with a Nanoscope III (Digital instruments) after fixing the samples in a sample holder. These sample holders allowed one to scan with the sample submerged in a liquid solution of an ink. All experiments were performed with the tip and substrate immersed in dodecane solutions. STM Images were taken at 1.6 V scanning bias, 10 pA set point, and a scanning rate of 2 Hz (2000 nm/s for the 500 × 500 nm images collected with a frame time of 8 min and 32 seconds). The tip was within tunneling range of the sample surface as adventitious
replacement was monitored. This geometry invites several possible concerns. The tip in close proximity could affect the mass transport, potentially decreasing the rate of replacement. However, the residence time of the tip over a small region of the sample is short. The tip also could, to some extent, perturb the SAM, potentially increasing the rate of replacement. These concerns were ruled out by moving the tip to different regions and capturing only one image at each location. Under these conditions, the rate of replacement was similar to those in which the tip was constantly scanning the same area. However, this experiment was significantly more tedious, so continuous scanning in the same area was preferred.

Use of Peristaltic Pump during Adventitious Replacement Experiments

Use of a peristaltic pump allowed for lower concentrations of the replacing molecule to be employed while still providing a quantity of replacing molecule that was at least two orders of magnitude greater than that needed to form a full monolayer on these substrates. The homemade STM sample holder used could only hold ca 500 µL of solution containing the replacing molecule. Rough calculations suggested that a ca 0.4 µM concentration of replacing molecule is needed to form a full monolayer with this sample holder volume. This was adequate for experiments where 10 µM or more concentrations of replacing molecule were employed. However, using a peristaltic pump to flow the replacing solution through the cell and some length of tubing allowed for increased volumes of replacing molecule solution to be used. Increasing the volume exposed to the sample allowed for lower concentrations to be used. So, for all experiments where ca 1 µM or lower concentrations of the replacing
molecule were used, the peristaltic pump was used to allow for an appropriate volume of replacing solution.

**Procedure for Measuring Adventitious Replacement**

Adventitious replacement was measured by importing images as ASCII files into Origin version 7.5 and putting all points in the images into histograms according to their height value. The bin size was adjusted to 0.002 nm and bin range was adjusted to 1 nm to -1 nm in apparent height. Then, the total count in each bin was plotted versus apparent height. Two Gaussian curves were fit to this plot with one Gaussian curves assigned to the background and one to the replaced areas.
4.5 References


Chapter 5 - REPLACEMENT LITHOGRAPHY USING TERMINAL ALKYNES

This work was the subject of a publication, Tucker, E. Z.; Gorman, C. B., “Terminal Alkynes as an Ink or Background SAM in Replacement Lithography: Adventitious versus Directed Replacement” *Langmuir*, 2010, 26 (18), 15027-15034

5.1 Introduction: Employing other Types of SAMs and Substrates Towards Replacement Lithography

When exploring new types of self-assembled monolayers (SAMs), one question of interest is how they can be patterned using various lithography methods, such as replacement lithography. The basic methodology of replacement lithography has been outlined in Chapter 1 and is illustrated in Figure 5.1. Briefly, a scanning tunneling microscope (STM) is used to desorb alkanethiol from a SAM by applying an elevated bias between the tip and sample. This desorption occurs in the presence of another molecule, which can bind to the exposed gold surface. This additional thiol acts as an ink that fills these vacated areas. One key advantage of this technique is it can be applied to other substrates or SAMs containing other binding groups. For example, this technique has been extended to platinum and palladium.¹ In addition, it has been shown that by comparing the amount of replacement induced at a series of different biases between different SAMs on metals one can probe the ease at which one SAM is replaced relative to another slightly different SAM. This process gives an idea of the relative stability of the two systems towards replacement lithography.¹²

As mentioned previously, terminal alkyne SAMs on gold have been explored as an alternative to alkanethiol SAMs on this surface.³⁻⁵ In the development of replacement lithography, it is of interest to incorporate molecules containing other binding groups (here,
the terminal alkyne group) using this technique as components of either the initial or replacement SAMs.

Figure 5.1. Schematic representing the process of replacement lithography. The white bars represent the background SAM, and the red bars represent the ink.

Therefore, experiments were done where a terminal alkyne was used as the ink or background SAM in replacement lithography (directed approached) and compared to a thioacetate as the ink. The molecule Fe-C≡C-p-C_{6}H_{4}-C≡C was incorporated as an ink and compared to analogous incorporation of Fe-C≡C-p-C_{6}H_{4}-S-Ac in the experiments described below.

5.2 Comparison of Percent Replacement between Inks of Different Binding Groups into a Thiol SAM

Here, the effect of the replacing molecule on replacement lithography is explored. These experiments compliment the adventitious replacement experiments from the previous chapter and probe the difference between use of a terminal alkyne and thioacetate binding
group as an ink in replacement lithography. Conjugated phenylethynyl ferrocenyl inks designated **Ink 1** and **Ink 2** were used.

![Chemical structures](image)

**Ink 1**, $X = S\text{CH}_3$

**Ink 2**, $X = C\equiv CH$

Lines were drawn using this directed technique at a range of biases, and the resulting percent replacement was compared. First, attempts were made to do this with C$_{12}$SH SAMs on gold by exposing these SAMs to 6 µM concentrations of either Fc-C≡C-p-C$_6$H$_4$S-Ac (**Ink 1**) or Fc-C≡C-p-C$_6$H$_4$C≡C (**Ink 2**) in dodecane (see experimental section). Under these conditions, adventitious replacement was insignificant over the course of 1-2 h and allowed ample time for replacement lithography lines to be written and captured using STM.

Figure 5.2 is a STM image showing a representative set of replacement lithography lines written with **Ink 2** into a C$_{12}$SH SAM where lines in the image were always written from lower biases on the left to higher biases on the right. The percentage of replacement was determined for each line in the set using procedures previously described (see experimental). As is shown in Figure 5.2, more replacement was seen at higher biases, whereas at insufficiently low biases, no replacement was seen. In addition, 100% replacement never occurred.
Many sets of lines (in addition to the data above) were combined and the average percent replacement at each bias was determined. Figure 5.3 shows a graph of bias used to write the lines versus average percent replacement. At higher biases, the average percentage of replacement was around 50%. Also, over the range of biases used to write the lines, the amount of replacement was similar using both these inks. The inks have different binding groups but identical backbone chains. Thus, it was concluded that the binding group of the ink molecule has little effect on the amount of replacement during replacement lithography.
5.3 Difficulties with Directed Replacement into an Alkyne SAM

The results of the adventitious replacement experiments in the previous chapter show that FeC11SAc, FeC11SH, and FeC11≡ exposed to a C10≡ SAM resulted in rapid, adventitious replacement. Replacement lithography into this type of SAM is frustrated by this rapid adventitious replacement. An attempt was made to do replacement lithography into a dodecyne SAM using Ink 2. However, significant adventitious replacement occurred during the course of the experiment, making it impossible to characterize the replacement process.
5.4 Comparison of Height Contrast between Inks of Different Binding Groups in a Thiol SAM

5.4.1 Literature Precedent

Conductivity through molecules in a monolayer on a substrate are modulated by different binding groups and composition of the chain.\textsuperscript{6,7} In one case, Weiss et al. investigated the isolated contact conductance between alkaneselenol and alkanethiol SAMs on gold.\textsuperscript{7} It was found that alkanethiol SAMs on gold have a lower barrier towards tunneling and thus, a higher conductance compared to alkaneselenol SAMs of the same chain length. This results in a higher apparent height of regions composed of alkanethiol compared to alkaneselenol when mixed SAMs of these species are deposited on gold (Figure 5.4). In a related study, Weiss et al. investigated the conductance of alkanethiols of different chain lengths on gold.\textsuperscript{6} Here, mixed SAMs of decanethiol and dodecanethiol were made, and then the difference in apparent height was probed with STM. It was shown that the longer chain length alkanethiol SAM on gold, as expected, had a higher apparent height compared to the shorter chain length alkanethiol SAM on this surface. However, this apparent height difference was much smaller than the expected height difference, which was attributed to the lower transconductance of regions composed of the longer alkanethiol molecule. Thus, it was concluded that longer chain length SAMs on gold have a lower conductance compared to shorter chain length alkanethiol SAMs. It was of interest to explore apparent height contrast between lines made by replacement lithography that were composed of different inks. It was hypothesized that replacement lithography lines of greater height contrast could be attributed to having higher conductance.
Figure 5.4. (A) STM image (55 x 55 nm) of a mixed SAM of dodecanethiol and dodecaneselenol on gold prepared from a 4:1 solution of the selenol to the thiol. Inset is a 20 x 20 nm image. The blue circle highlights an area of dodecanethiolate, which is of a higher apparent height compared to the surrounding dodecaneselenol. All images were collected at -1 V and 1.0 pA tunneling current. (B) Scan profile drawn through an area composed of both molecules showing the difference in apparent height between these two SAM forming molecules.7

5.4.2 Results and Discussion

To probe the difference in conductivity of replacement lithography lines composed of molecules with a terminal alkyne binding group and thioacetate binding group, the apparent height contrast of lines composed of **Ink 1** and **Ink 2** were compared while imaging at a range of different biases. This was done by making a C_{12}SH SAM (see experimental
section), then exposing this film to 6 µM concentrations of each of the molecules in dodecane by covering the surface with the solution. The relative humidity was increased to ca. 55% and replacement lithography lines were written at a bias of 3.2 V. Then, these lines were scanned at a range of different biases and an image of the lines was captured once at each bias (capture bias). Figure 5.5 is a representative STM image obtained when a set of replacement lithography lines was drawn with \textbf{Ink 2} into a C\textsubscript{12}SH SAM. All the lines in the image were written at a bias of 3.2 V, and the image was captured at a bias of 2 V. Similar STM images were collected at a range of different biases with \textbf{Ink 1} and \textbf{Ink 2} as the ink. The apparent height contrast of these lines captured at these different biases was then determined. Then, the apparent height contrast was compared between replacement lithography lines composed of both these ink molecules (see experimental section). Figure 5.6 shows a plot of height contrast versus capture bias for \textbf{Ink 1} and \textbf{Ink 2}.

![Figure 5.5](image.png)

\textbf{Figure 5.5.} A representative STM image of a set of lines written with replacement lithography where Fc-C≡C-p-C\textsubscript{6}H\textsubscript{4}-C≡C (Ink 2) was replaced into a C\textsubscript{12}SH SAM. A set of seven lines were written at a bias of 3.2 V (from left to right). These lines were captured at a bias of 2 V, although other images were taken of these lines at other biases.

It is shown in Figure 5.6 that the conjugated thioacetate (\textbf{Ink 1}) and the conjugated terminal alkyne (\textbf{Ink 2}) have equal apparent heights within experimental error at most of the
capture biases shown. This suggests that replacement lithography lines composed of these two inks have similar conductances despite the difference in binding group.

![Graph showing height contrast versus bias used to capture lines composed of Ink 1 (red circles) and Ink 2 (black squares) made from replacement lithography. Error bars indicate 90% confidence intervals from the average values obtained from multiple trials.](image)

Figure 5.6. Graph showing height contrast versus bias used to capture lines composed of Ink 1 (red circles) and Ink 2 (black squares) made from replacement lithography. Error bars indicate 90% confidence intervals from the average values obtained from multiple trials.

5.5 Conclusion

Terminal alkynes were successfully used in replacement lithography as inks. First, it was shown that there was little difference in the amount of replacement during replacement lithography when a terminal alkyne and thioacetate were employed as the inks. Also, it was shown that replacement lithography lines composed of a thioacetate and terminal alkyne had similar apparent heights at various capture biases, which implies that these features have similar conductances. Attempts were made to fabricate replacement lithography lines composed of molecules with these two binding groups into a terminal alkyne SAM, but it was found that adventitious replacement was too rapid, obscuring the patterns.
5.6 Experimental Section

**General Considerations**

1-Dodecanethiol was purchased from Alfa Aesar. 1-Dodecyne (99%) was purchased from GFS chemicals. Dodecane was purchased from Aldrich. Absolute ethanol was used as a solvent. All these chemicals were used without further purification. Fe-C≡C-p-C₆H₄-S-Ac and Fe-C≡C-p-C₆H₄-C≡C were synthesized previously in our laboratory following reported procedures.⁸⁹ Gold wire of 99.999% purity and 0.5 mm diameter was purchased from Alfa Aesar. Absolute ethanol was used as a solvent for formation of the SAMs. All water used was purified by reverse osmosis. All other chemicals were used without further purification.

**Preparation of Gold Surfaces**

Gold substrates for the deposition of a C₁₂SH and C₁₀≡ SAM were prepared by annealing gold to form a gold bead with a H₂ flame, which upon further heating formed atomically flat facets suitable for the formation of the monolayers. These substrates were often used again after being cleaned with “piranha” solution (3:1 H₂SO₄/H₂O₂), washed with water and reannealed under a H₂ flame to reform the facets. **Caution!** “Piranha” solution should be handled carefully because of its violent reactivity with organic molecules.

**Preparation of Dodecanethiol and Dodecyne SAMs**

SAMs of dodecanethiol were deposited by refluxing a freshly annealed gold bead in a 1 mM ethanol solution of the alkanethiol for 1 h followed by cooling of the solution to room temperature for 15 min. The samples were then rinsed with ethanol immediately after removing from the solution and dried under a stream of nitrogen. SAMs of dodecyne were
deposited by submerging a freshly annealed gold bead in 10 mM dodecyne in ethanol for 48 h at room temperature. The samples were rinsed with ethanol immediately after removing from the deposition solution and dried under a stream of nitrogen. Both these samples were imaged immediately following preparation.

**Characterization**

Scanning tunneling microscopy (STM) images were taken with a Nanoscope III (Digital instruments) after fixing the samples in a sample holder. These sample holders allowed one to scan with the sample submerged in a liquid solution of an ink. During experiments exploring percent replacement, STM Images were taken at a capture bias of 1.5 V, 10 pA set point, and a scanning rate of 1 Hz (1000 nm/s for the 500 × 250 nm images collected with a frame time of 4 min and 16 seconds). During experiments exploring height contrast, STM images were taken at a range of capture biases, 10 pA set point, and a scanning rate of 1 Hz (1000 nm/s for the 500 × 250 nm images collected with a frame time of 4 min and 16 seconds). All experiments were performed with the tip and substrate immersed in dodecane solutions.

**Procedure for Replacement Lithography**

When relative humidity needed to be elevated, this was by bubbling nitrogen through 18 MΩ·cm water. Relative humidity was measured using a digital thermohydrometer. For experiments where percent replacement was investigated, replacement lithography was performed by exposing 6 µM dodecane solutions of either Fc-C≡C-p-C₆H₄-S-Ac or Fc-C≡C-p-C₆H₄-C≡C to the SAM, then a series of nine lines were written at biases 2.6 to 3.3 V under
a relative humidity of 55 ± 1% (where each line was incrementally increased by 100 mV).

After replacement lithography was done, STM images of these lines were captured at a
scanning bias 1.5 V. For experiments investigating height contrast, replacement lithography
was performed by exposing 6 µM concentrations of either Fc-C≡C-p-C₆H₄-S-Ac or Fc-C≡C-
p-C₆H₄-C≡C in dodecane to the surface. The relative humidity was increased to ca. 55% and
seven replacement lithography lines were written at a bias of 3.2 V. Then, these lines were
scanned at 1 V, 1.25 V, 1.5 V, 1.75 V, and 2 V where images of the lines were captured once
at each bias (capture bias). A second capture of the lines was done at a capture bias of 2 V to
confirm that these lines were not disturbed or removed under any of the scanning biases.

**Measuring Percent Replacement**

To determine the extent of replacement for a given bias, STM images containing lines
drawn by replacement lithography were manipulated in imaging software (Scion Image
Release alpha 4.0.3.2.). First, the x and y dimensions of the image were converted from
pixels to nanometers. The percent replacement for each line was then determined by the
following method. First, a threshold value, which highlights points in an image that are
greater than a specified height, was chosen that selected for heights corresponding roughly to
the apparent height of the lines. The widest point of any of the eight lines in a given image
was determined. This widest point was multiplied by the length of the line drawn (which
was defined as 100 nm in the nanoscript macro used to write the lines) to determine the
maximum replacement area. The area of each line was then calculated using the Scion Image
software and was the total area of each line containing all the points not excluded when
thresholding the image. This area for each line was individually divided by the theoretical maximum area to define the percentage of replacement for that trial.

**Procedure for Measuring Height Contrast**

Images containing replacement lithography lines were converted to an ASCII file and imported into Origin Lab V7.5 as a matrix, which was displayed as an image. A region around a line was selected and a histogram was created from this selected area. There were peaks in the resulting histogram that corresponded to the background SAM and the replaced area. These peaks were fit with Gaussian plots and difference between the center of the two peaks corresponded to the apparent height contrast. This procedure was repeated for all the other lines in the same image and in other trials. The average height contrast was then calculated and compared between lines imaged at different biases.
5.7 References


Chapter 6 - ADVENTITIOUS REPLACEMENT OF ONE MOLECULE IN A SAM ON PLATINUM FOR ANOTHER FOLLOWED BY STM

6.1 Introduction: Isonitriles and Thiols on Platinum

Alkanethiol self-assembled monolayers (SAMs) on gold are well studied, but have some limitations, which have lead to many efforts to discover other types of binding group SAMs on various surfaces.\(^1\)\(^-\)\(^\text{13}\) For example, in Chapter 3 studies were described showing that relatively high quality alkanethiol SAMs on gallium arsenide (GaAs) could be formed. The potential of these SAMs to be applied to replacement lithography was investigated. In Chapter 4, various studies were described that indicated the ability of terminal alkynes to make high quality SAMs. In Chapter 4 and Chapter 5, the directed (replacement lithography) and non-directed exchange of these molecules with other terminal alkynes and thiols was investigated. Others have investigated many other types of self-assembled monolayers on various surfaces and there exist various reviews summarizing these results.\(^{14}\)\(^-\)\(^\text{16}\)

One other type of SAM that has been investigated is alkanethiols and isonitriles on platinum. In one early study, Whitesides et al investigated the selectivity of isonitriles and thiols for gold and platinum.\(^1\) More specifically, solutions of different ratios of a redox active isonitrile incorporating an alkylferrocene group and a redox active thiol incorporating an acylferrocene group were exposed to both gold and platinum. The two different tail groups attached to the thiol and isonitrile molecules had redox potentials well separated from one another, which allowed the researchers to identify the species that was bound to the surface by cyclic voltammetry (CV). Here, the isonitrile was preferentially adsorbed onto platinum over the thiol. In another study, SAMs of alkylisonitrile and alkanethiol on
platinum were studied using x-ray photoelectron spectroscopy, contact angle, ellipsometry, and CV. Specifically, octadecylisonitrile and octadecanethiol SAMs were formed on polycrystalline platinum, which resulted in films that were slightly less ordered than alkanethiol SAMs on gold as indicated by the difference in advancing and receding water contact angle measurements. However, it was found that both these SAMs formed relatively high quality SAMs. Also, as mentioned in Chapter 1, the amount of replacement of alkanethiol SAMs on platinum, palladium, and gold by a thiol using replacing lithography was compared. Here, it was found that replacement of alkanethiol SAMs on gold and palladium occurred at lower biases compared to these SAMs on platinum.

To further probe the relatively stability of isonitrile SAMs and to determine whether they could be effective participants in replacement lithography, experiments were done where isonitriles were used as the replacing molecule or background SAM in adventitious replacement where platinum was used as the substrate. More specifically, the propensity of adventitious replacement of both dodecylisonitrile (C$_{12}$NC) and dodecanethiol (C$_{12}$SH) SAMs on platinum were explored.

6.2 Adventitious Replacement into isonitrile and thiol SAMs on Platinum

The relative reactivity of an alkylisonitrile SAM and an alkanethiol SAM toward adventitious replacement was probed with scanning tunneling microscopy (STM). In previous chapters, we have shown that, at slightly elevated biases (ca. 1 V), areas of a SAM containing ferrocenyl head groups show an increase in apparent height compared to the methyl-terminated SAM regions. This height contrast allows one to distinguish the
ferrocenyl-containing molecules from methyl-terminated regions of the SAM. In addition, it was shown that various molecules containing a binding group with an affinity for gold and a ferrocene tail group that causes increased height contrast can adventitiously replace into a SAM, which can be monitored by STM. The relative rates and extent of replacement give an idea of the relative stability of C_{12}SH and C_{12}NC SAMs. As before, it was expected that adventitious replacement would occur to a greater extent in the SAM with more defects and/or a lower thermodynamic stability.

Adventitious replacement experiments were performed as follows. First, platinum beads were formed by flame annealing a platinum wire (see experimental section). The platinum was meticulously protected from oxide formation throughout the experiment until a SAM was fully formed on the surface (see experimental section). Once SAMs of either C_{12}SH or C_{12}NC on platinum were formed, these samples were removed from the glove box and imaged by STM in air. Then, in separate experiments, solutions of either 11-ferrocenylundecanethiol (FcC_{11}SH) or (11-isocyanododecyl)ferrocene (FcC_{12}NC) were placed onto C_{12}SH or C_{12}NC SAMs, covering the surface and tip. After adjusting the relative humidity to ca. 47%, imaging was continued in dodecane to monitor the amount of adventitious replacement of the molecule in solution into the initial SAM. Since, relatively low concentrations of the replacing molecule were used, a solution of the replacing molecule was slowly pumped over the sample to ensure that its concentration remained constant during experiments (see experimental section).
In order to probe the effect of the background SAM on adventitious replacement by FeC_{11}SH, the adventitious replacement of FeC_{11}SH into a C_{12}SH and C_{12}NC SAM was compared. Figure 6.1 shows a series of STM images that followed this replacement process. Panels A and B are STM images of SAMs of C_{12}SH and C_{12}NC before the solution of the replacing molecule was added. Pits (vacancy islands) were present in both C_{12}SH and C_{12}NC SAMs on platinum. The remaining panels in Figure 6.1 are images that were taken after a 0.5 µM solution of FeC_{11}SH in dodecane was exposed to these samples for 5 min (Figure 6.1C and D) and 60 min (Figure 6.1E and F).

![Figure 6.1. A series of STM images comparing the process of adventitious replacement of FeC_{11}SH into a C_{12}SH SAM (top, panels A, C, and E) and a C_{12}NC SAM (bottom, panels B, D, and F) on Platinum. Images were taken before FeC_{11}SH was added (A, B), 5 min (C, D), and 60 min after addition of FeC_{11}SH (E, F).](image-url)
The rate and extent of replacement were obtained quantitatively by taking STM images collected at different replacement times and calculating the percent of the area occupied by the replacing molecule following the procedure used in Chapter 4 (see experimental section). The amount of adventitious replacement was calculated from the images in Figure 6.1 along with images collected at different time points and from additional trials. These data allowed the adventitious replacement of FeC_{11}SH into C_{12}SH and C_{12}NC SAMs to be compared. Figure 6.2 shows a plot of the area adventitiously replaced versus time when a 0.5 µM solution of FeC_{11}SH was exposed to a C_{12}SH and C_{12}NC SAM. FeC_{11}SH replaced similarly into both the C_{12}SH and C_{12}NC SAM. Within ca. 10 min, FeC_{11}SH replaced to an extent of ca. 90% into both SAMs. However, the error in these experiments made it difficult to model these replacement processes. As a result, no effort was made to fit any of these data.
Next, it was of interest to explore the effect of concentration of the replacing molecule on adventitious replacement into these SAMs on platinum and to explore the mechanism of replacement by modeling these processes. Initially, the adventitious replacement of a C_{12}NC SAM by FcC_{12}NC at different concentrations was explored. The adventitious replacement was explored at 1 and 10 µM of FcC_{12}NC to explore the effect of concentration of the replacing molecule on the rate and extent of total replacement.

Figure 6.3 shows a plot of the adventitious replacement of (as fractional surface coverage of FcC_{12}NC) at these concentrations versus time where each curve represents an average of several trials. Within ca. 10 min, FcC_{12}NC replaced to an extent of ca. 90% into the C_{12}NC SAM at both concentrations. Here, the error in the adventitious replacement is much smaller than what was seen above. However, along with all the other adventitious replacement explored using FcC_{11}SH or FcC_{12}NC as the replacing molecule and C_{12}SH or C_{12}NC as the background SAM on platinum, adventitious replacement was generally very rapid and difficult to model. As a result, no attempts were made to model any of these replacement processes on platinum.
6.3 Conclusion

FcC_{11}SH seemed to adventitiously replace similarly into both the C_{12}SH and C_{12}NC SAM, but this conclusion is somewhat tenuous due to significant error in the data. Attempts to model these exchange processes were frustrated by this error, so no information about the mechanism of these exchange processes could be gathered. When the effect of concentration of FcC_{12}NC on the adventitious replacement of a C_{12}NC SAM was explored, the error was considerably less. However, along with much of the other adventitious replacement explored, the adventitious replacement was rapid and few points could be obtained before replacement reached a steady state. Thus, attempts to model this exchange process were frustrated by the rate of these exchange processes. Future work is in progress where cyclic voltammetry is being used to explore the adventitious replacement of C_{12}SH and C_{12}NC
SAMs by FeC\textsubscript{12}NC and FeC\textsubscript{11}SH, which it is hypothesized, will allow for these rapid exchange processes to be followed more accurately.

6.4 Experimental Section

**General Considerations**

1-Dodecanethiol was purchased from Alfa Aesar. Dodecane was purchased from Aldrich. Absolute ethanol was used as a solvent. All these chemicals were used without further purification. (11-isocyanododecyl)ferrocene was prepared in our laboratory following previously documented procedures and a newly devised synthetic methodology. 11-ferrocenylundecanethiol was synthesized in our laboratory following previously documented procedures.\textsuperscript{17} Platinum wire of 99.95% purity and 0.5 mm diameter was purchased from Alfa Aesar. Absolute ethanol was used as a solvent for formation of the SAMs. All water used was purified by reverse osmosis. All other chemicals were used without further purification.

**Synthesis of Dodecylisonitrile**

The synthesis of dodecylisonitrile was performed based on a method described in the literature, but with some subtle modifications.\textsuperscript{18} Briefly, 1 g of dodecylamine was added to a dried round bottom flask, then under nitrogen 15.4 mL of ethylformate was added to the same flask and the mixture was heated to reflux. After 24 h the reaction contents were purified using column chromatography with various mixtures of ethyl acetate and hexane, which yielded a white solid (1.02 g, 89.0% yield). This white solid was identified as 1-formamidyldodecane by proton-NMR (See Appendix 1).
1-formamidyldodecane. White solid: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.81 (t, 3H, CH$_3$), 1.19 (s, 18H, CH$_2$), 1.43 (m, 2H, CH$_2$), 3.14 (q, 2H, CH$_2$), 3.24 (q, 1H, NH), 8.103 (s, 1H, COH).

Then, 0.5 g of 1-formamidyldodecane was added to a dried round bottom flask along with 5 mL of tetrahydrofuran (THF) and 1.63 mL of triethylamine. The contents of the round bottom flask were placed under nitrogen and cooled to 0°C. Then, using an addition funnel, 0.240 mL of phosphorous oxychloride (POCl$_3$) in 5 mL of THF was added drop wise over the course of 30 min. The reaction contents were left under stirring for 2 h at 0°C. The reaction contents were poured into 10 mL of water and extracted with ethyl acetate (EA) twice. The EA layer was washed with brine solution twice, then the organic layer was dried with sodium sulfate in an Erlenmeyer flask. The organic layer was removed using a rotator evaporator and purified using column chromatography with 100% hexanes, which yielded a light yellow oil (0.257 g). This yellow oil was identified as dodecylisonitrile by proton-NMR (See Appendix 1).

1-Dodecylisonitrile. Yellow oil: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.82 (t, 3H, CH$_3$), 1.20 (m, 16H, CH$_2$), 1.35 (m, 2H, CH$_2$), 1.60 (m, 2H, CH$_2$), 3.30 (m, 2H, CH$_2$).

Preparation of Platinum Surfaces

Platinum substrates used for the deposition of C$_{12}$SH and C$_{12}$NC SAMs were prepared by annealing platinum wire with a H$_2$/O$_2$ flame to form a bead, which upon further heating formed atomically flat facets suitable for the formation of the monolayers. While still at elevated temperatures, the platinum beads were quenched in H$_2$O that had been purged
with H₂ and N₂ for at least 15 min. Immediately after quenching, these substrates were immersed in ethanol that had been purged with N₂ for at least 15 min and brought into a glove box under a N₂ atmosphere. These substrates were often used again after being cleaned with sulfuric acid (H₂SO₄), washed with water and reannealed under a H₂/O₂ flame to reform the facets.

**Preparation of Dodecanethiol and Dodecylisonitrile SAMs**

SAMs of dodecanethiol and dodecylisonitrile were deposited by immersing a freshly annealed platinum bead in a 1 mM ethanol solution of the SAM forming molecule for 24 h at room temperature in a glove box with a nitrogen atmosphere. Then, the samples were removed from the glove box and deposition solution. The samples were rinsed with ethanol immediately after removing from the deposition solution and dried under a stream of nitrogen. Both these samples were imaged immediately following preparation.

**Characterization**

Scanning tunneling microscopy (STM) images were taken with a Nanoscope III (Digital instruments) after fixing the samples in a sample holder. These sample holders allowed one to scan with the sample submerged in a liquid solution of an ink. All experiments were performed with the tip and substrate immersed in dodecane solutions. STM Images were taken at 1 V scanning bias, 10 pA set point, and a scanning rate of 2 Hz (2000 nm/s for the 500 × 500 nm images collected with a frame time of 8 min and 32 seconds).
Use of Peristaltic Pump during Adventitious Replacement Experiments

Use of a peristaltic pump allowed for lower concentrations of the replacing molecule to be employed while still providing a quantity of replacing molecule that was at least two orders of magnitude greater than that needed to form a full monolayer on these substrates. The homemade STM sample holder used could only hold ca 500 µL of solution containing the replacing molecule. Rough calculations suggested that a ca 0.4 µM concentration of replacing molecule is needed to form a full monolayer with this sample holder volume. This was adequate for experiments where 10 µM or more concentrations of replacing molecule were employed. However, using a peristaltic pump to flow the replacing solution through the cell and some length of tubing allowed for increased volumes of replacing molecule solution to be used. Increasing the volume exposed to the sample allowed for lower concentrations to be used. So, for all experiments where ca 1 µM or lower concentrations of the replacing molecule were used, the peristaltic pump was used to allow for an appropriate volume of replacing solution.

Procedure for Measuring Adventitious Replacement

Adventitious replacement was measured by importing images as ASCII files into Origin version 7.5 and putting all points in the images into histograms according to their height value. The bin size was adjusted to 0.002 nm and bin range was adjusted to 1 nm to -1 nm in apparent height. Then, the total count in each bin was plotted versus apparent height. Two Gaussian curves were fit to this plot with one Gaussian curves assigned to the background and one to the replaced areas.
6.5 References


APPENDICES
Appendix 1 - $^1$H NMR Spectra

1-Formaidylododecane
Dodecylisonitrile