ABSTRACT

CHARACTERIZATION OF SILICON AND GOLD SURFACES MODIFIED BY NEW METHODOLOGIES

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With technology advancing at an incredible rate, especially in the microelectronics industry, there has been continuous research into finding new and ever more efficient ways to modify solid surfaces. The interaction of sulfur with metal surfaces has also been intensively studied owing to a direct impact on important areas such as environmental chemistry, fabrication of nanodevices, catalyst poisoning and corrosion. In my Ph. D. studies a new method for the modification of Si(111) surfaces without the use of heat, irradiation, or UHV conditions has been examined along with a new means of modifying Au(111) by a series of new sulfur source compounds in organic solvents. Modified surfaces were characterized by atomic force microscopy (AFM), cyclic voltammetry (CV), Fourier transform infrared spectroscopy (FTIR), scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS).

In an effort to explore a new and efficient means of modifying silicon, whose modification plays a vital role in electronic computer chips, freshly prepared Si(111)-H surfaces were used as the starting points. Our procedure is based on an electron transfer reaction from a good electron donor, ferrocene, to a good electron acceptor, N-bromosuccinimide (NBS) and N-bromophthalimide (NBP) that does not require the use of heat or irradiation. Characterization of the surface by XPS indicated the presence of the imidyl/phthalimidyl groups as well as bromine. Another signal which was detected
was that of iron. This is important as it indicates that ferrocene is being incorporated onto the surface and ferrocene groups on modified silicon have been previously cited as potential computer memory storage devices. Nucleophilic substitution was successfully performed on the modified surfaces using succinimide, phthalimide, and pentachlorophenol anions. FTIR spectroscopy on the modified surfaces gave strong signals for a carbonyl stretch. AFM studies indicated the presence of multilayers on the silicon surfaces.

Sulfur-gold interactions form the basis of what is probably the most studied self-assembled monolayer (SAM) system, organosulfur compounds and gold. SAMs have been cited for use in areas of study such as photoelectric catalysis, environmental chemistry and corrosion. By studying sulfur, which can be regarded as the shortest SAM, deposition in an organic solvent, new insights may be gained into the structure and dynamics of this phenomenon. Both polycrystalline gold and Au(111) were used to study the interaction of sulfur on gold surfaces using a series of new compounds (thiobisphthalimide, dithiobisphthalimide, p-iodobenzenesulfonyl phthalimide, p-methoxybenzenesulfonyl phthalimide, p-fluorobenzenesulfonyl phthalimide, thiobis(hexamethyldisilazane) and hexamethyldisilathiane) in various organic solvents. CV studies were used to assess the rate at which sulfur was deposited on a gold electrode. XPS data for all compounds showed signals consistent with sulfur deposition. Imaging of the sample surfaces with STM showed several instances of new pattern formations and moving rectangles, the latter of which provides an answer to a long standing debate in the literature as to what the nature of the rectangular structures observed at high coverage is.
Dedicated to

My Family:

Mom, Dad, Kelly, Elisa, Darlene, Lina, Fiorine, Lucky & Figgy
Acknowledgements

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<tbody>
<tr>
<td>ACS</td>
<td>American Chemical Society</td>
</tr>
<tr>
<td>AES</td>
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<td>FWHM</td>
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<td>SERS</td>
<td>Surface enhanced Raman spectroscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td>TBAHFP</td>
<td>Tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>TDS</td>
<td>Thermal desorption spectroscopy</td>
</tr>
<tr>
<td>TED</td>
<td>Transmission electron diffraction</td>
</tr>
<tr>
<td>μCP</td>
<td>Micro-contact printing</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>W</td>
<td>Spectrometer work function</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
List of Symbols

Å  Angstrom

°C  degrees Celsius

+  diffuse \( s \)- and \( p \)-type functions on heavy atoms

++  diffuse \( s \)-type functions on hydrogen

H  Hamiltonian operator

\( \pi \)  \( \pi \)

\( \sigma \)  \( \sigma \)

\( \Psi \)  Wavefunction
Preamble

As silicon approaches the fundamental limits of the size of devices which can be packed in a given area on its surface, finding new means of efficiently modifying silicon has initiated much research in the field. The modification of silicon is particularly interesting due to the ability of having direct electrical contact between an organic layer and a semi-conducting substrate. For example, biosensors can be fabricated directly on an oxide free silicon substrate for purposes of detecting specific proteins. Finding a robust method of modifying silicon in which different groups can be deposited on the surface may help in eventually leading to new multipurpose devices.

Gold has also been used for the fabrication of devices. The interaction of sulfur with metal surfaces has been intensively studied owing to a direct impact on important areas such as catalyst poisoning and SAM formation. Gold has been commonly used as a substrate due to high quality surfaces being available in a number of forms and gold shows excellent resistance to corrosion and oxidation which enables it to be handled in atmospheric conditions without adversely affecting the surface. Previously, several different sulfur sources have been used in S/Au studies, such as Na₂S and H₂S in electrolytic solutions and S₂ and SO₂ in the gas phase. By studying sulfur/gold interactions using new sulfur precursors in organic solvents, a more direct comparison to organosulfur SAMs on gold can be made. This may elucidate new details that could help understand some fundamental issues with SAMs including the adsorption mechanism, adsorption site determination and the movement of molecules on a surface.

There are several goals of this thesis. One is to investigate and evaluate a new method of modifying Si(111) using a combination of a good electron donor and a good electron
acceptor. Another is to modify both polycrystalline and Au(111) surfaces in organic solvents, with a series of new sulfur source compounds, some of which are chemically very different from one another. A third is to characterize the modified gold by a variety of techniques to see what species and patterns may or may not be present on the surfaces. A fourth goal is to resolve a highly debated question from the literature which is do the rectangular structures formed at high sulfur coverages correspond to a complex AuS phase, or to sulfur adlayers on gold?

An important note is that part of the XPS data, FTIR data, and AFM data from Chapter 3 as well as part of the STM images from Chapter 4 were collected by previous group members. In Chapter 3, Dr. M’hamed Chahma ran XPS studies on surfaces I, II, III and NBP/Fc modified silicon as well as collected FTIR data on surfaces I, II and III. Dr. Emad Hamed collected AFM images of surface I and NBP/Fc modified silicon. I confirmed the XPS results of surface I and did the deconvolution of all of the XPS signals. In Chapter 4, Dr. Md. Golam Moula collected the STM images from the dithiobisphthalimide modification of Au(111) on mica.

Also, portions of the results from Chapter 5 and Chapter 6 have been published in the following articles:


Chapter 1: Introduction

1.1 Surface Modification:

The modification of solid surfaces is a central objective in many commercial and research areas including passivation, microelectronics, corrosion prevention, and fabrication of nanodevices. These surfaces may be porous, polycrystalline or single crystal in nature. Titanium dioxide for example has been applied to glass surfaces to act as an antimicrobial agent. Solid surfaces may be of an insulating (ex. mica), semiconducting (ex. germanium) or conducting (ex. copper) nature. There are several techniques that have been used for modifying these surfaces including self-assembly, thermal means, UV radiation, and electrochemistry. Self-assembly is likely the most widely utilized technique owing to its accessibility in most laboratories. Ideally all that is needed is a beaker, substrate, solvent and the modification compound. No matter the method of modification, there are many techniques available to analyze the resulting surfaces. These include Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) for elemental/characteristic group identification as well as scanning probe techniques of atomic force microscopy (AFM) and scanning tunneling microscopy (STM) for visualizing the sample surfaces.

Passivation of single crystal silicon from oxide reformation can be achieved by the direct attachment of alkyl chains if an oxide-free surface is required. Silicon’s semiconducting properties are very important in its use in transistors for computer chips, the application of a certain voltage will change its conduction ability. Gold has excellent corrosion resistance properties which can make it an ideal candidate for
protecting metal surfaces from atmospheric exposure which can lead to oxidation and rust.\textsuperscript{12} The fabrication of nanodevices is an extensively studied area, with alkenes on oxide-free silicon\textsuperscript{13} and alkane thiols on gold being two of the most popular starting points.\textsuperscript{14}

\textbf{1.2 Modification of Silicon Surfaces:}

The immobilization of organic, bioorganic, and inorganic molecules on solid surfaces is important as they provide a direct route to biofunctionality for the adsorption of specific proteins, catalytically active surfaces, chemical and biochemical sensors and molecular based electronics.\textsuperscript{15-20} Silicon is interesting because its modification provides a pathway towards tunable thin films and solid state semiconductor devices that can have a direct impact on the rapidly miniaturizing microelectronic industry, particularly with work on the Si(100) surface.\textsuperscript{21,22} Silicon based nanowires have shown promise as nanosensors and field effect transistors.\textsuperscript{4,23} Essentially atomically flat Si(111)-H surfaces are ideal starting points towards patterning by lithography, for example Pd catalytic stamp lithography of terminal alkenes.\textsuperscript{24} Self-assembled monolayers (SAMs) covalently attached to Si(111)-H surfaces have also been successfully patterned by local oxidation lithography with a conductive atomic force microscopy (AFM) probe.\textsuperscript{25}

\textbf{1.2.1 Porous Silicon:}

In addition to flat silicon surfaces, porous silicon has also received a lot of attention in the literature.\textsuperscript{26-31} Silicon itself has an indirect band-gap of 1.1 eV,\textsuperscript{32} which means that there is no chance of light emission from silicon due to the lack of recombination of
optical states in the bulk structure. A major breakthrough occurred when Canham discovered that porous silicon can emit visible photoluminescence at room temperature which initiated numerous research efforts in this area. Luminescence results from a material absorbing energy in the form of a chemical reaction, electron beam, or radiation which does not occur at elevated temperatures. The atoms are promoted to an excited electronic state, but will not remain there indefinitely. When they relax back to their ground-state configuration, they release energy in the form of molecular motion or light.

The band-gap luminescence observed was assigned to a quantum confinement effect for three reasons: 1) band-gap luminescence was seen for all types of freshly anodized silicon ($n^+$, $n^-$, $p^+$, and $p^-$), provided the silicon wasn’t completely amorphous and the porosity was high enough, 2) luminescence was observed to increase during chemical dissolution in aqueous HF, 3) the half width of the luminescence band has the potential to be narrower than polysilane alloys and device quality $a$-Si:H. Quantum confinement refers to having excitons (electron-hole pairs) occupy a smaller volume in a film or particle than they would in the bulk material. A radiative recombination of these excitons with diameters of $\sim 2$ nm, is an accepted reason for the luminescence observed from porous silicon.

Porous silicon can be prepared from oxide covered Si(100) through a chemical, photochemical or electrochemical etching process with aqueous HF. The electrochemical method is the most popular and is usually accomplished with a combination of ethanol and HF. Ethanol is usually present as it has been found to remove hydrogen bubbles from the surface and helps to improve porosity size and distribution consistency. The mechanism of the etching of silicon has been thoroughly investigated and an outline is
shown in Figure 1-1\textsuperscript{35} and a SEM image of a freshly prepared porous silicon sample is shown in Figure 1-2.\textsuperscript{36}

\begin{center}
\begin{tabular}{c}
\includegraphics[width=\textwidth]{diagram.png}
\end{tabular}
\end{center}

\textbf{Figure 1-1.} Proposed etching mechanism for the anodic dissolution of Si(100)-H\textsubscript{2} to form a porous silicon surface.\textsuperscript{35}

\begin{center}
\includegraphics[width=\textwidth]{image.png}
\end{center}

\textbf{Figure 1-2.} Top-down SEM view of a freshly prepared porous silicon surface made with 12.5 \% HF, 47 x 35\textmu m\textsuperscript{2}.\textsuperscript{36} (Reprinted with permission from Elsevier, Copyright 2004)

Upon completion of the etching process, the exposed silicon surface, both the outer surface and inside the pores will contain a mixture of Si-H, Si-H\textsubscript{2} and Si-H\textsubscript{3} linkages.\textsuperscript{37} Due to this surface being metastable (oxidation will occur after short time periods), porous surfaces are usually prepared just prior to experimentation/derivatization.
This surface has been extensively used for purposes of sensing or biosensing applications. The work of Sailor’s group demonstrated that porous silicon could be used as a sensor in air for volatile compounds such as heptane and isopropyl alcohol by measuring the wavelength shift of photonic resonance.\textsuperscript{38} Fresh hydride terminated surfaces were also further derivatized by thermal oxidation of oxygen, ozone oxidation, electrochemical methylation, thermal acetylation (485°C), and hydrosilation. The surfaces containing Si-O-Si linkages and Si-C linkages from acetylation were found to show the most promise for operating in an atmospheric environment.

In regards to biosensing, work has been done in modifying the outer surface and inside of the pores with different functionalities towards cell adhesion studies, Figure 1-3.\textsuperscript{39} This was accomplished by taking advantage of first attaching a hydrophobic monolayer of 10-

\textbf{Figure 1-3.} Example of bi-functionally modified porous silicon for cell adhesion studies.\textsuperscript{39}
succinimidylundecenoate. The external surface was then modified with the peptide GRDGS in a slightly warmed aqueous solution and the internal surface was further modified with hexa(ethylene glycol) amine in acetonitrile.

Hydrosilylation reactions on porous silicon can also be promoted by white light,\textsuperscript{40} which has also been shown for alkenes and alkynes on Si(100)-H\textsubscript{2} and Si(111)-H.\textsuperscript{41} The use of a mask and moderate white light source has enabled patterning on porous silicon surfaces with various alkene and alkyne derivatives. Photoluminescence quenching agents such as decamethylruthenocene or ferrocene inhibit white light hydrosilylation. For this reaction to be successful, red light emission must be observed when the porous silicon is exposed to UV irradiation. The doping or morphology of the silicon is not

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{hydrosilylation.png}
\caption{White light induced hydrosilylation of an alkene to form a Si-C bond on a porous silicon substrate.\textsuperscript{40}}
\end{figure}
deemed a factor. A proposed mechanism, outlined in Figure 1-4, suggested that the first step in the reaction is the in situ generation of excitons which are also responsible for the luminescence.\textsuperscript{40} A surface localized hole forms a complex with the alkene. The alkene may then nucleophilically attack the electrophilic silicon forming a Si-C bond and the resulting carbocation is then stabilized by the $\beta$-silyl group. A hydride can then be abstracted forming a stable C-H and completing the hydrosilation.

1.3 From Sand to Semiconductor Grade Si Wafers:

Preparation of semi-conductor grade silicon from silicon dioxide, sand, is done in several steps. Silicon dioxide is first reduced by carbon, typically in the form of wood, charcoal and coal in a furnace at temperatures over 1900°C to form silicon, equation 1.1.\textsuperscript{12} The liquid silicon is then collected and cooled. This silicon is metallurgical grade silicon and is 98% pure. To get semi-conductor grade material, the Si is then reacted with HCl in a fluid bed reactor to produce trichlorosilane, HSiCl\textsubscript{3}, equation 1.2.

$$\text{SiO}_2(s) + C(s) \rightarrow \text{Si}(l) + 2 \text{CO}(g) \quad 1.1$$

$$\text{Si} + 3 \text{HCl} \rightarrow \text{HSiCl}_3 + \text{H}_2 \quad 1.2$$

Since trichlorosilane is quite volatile with a boiling point of 31.8 °C, it can be easily distilled, and several distillation steps are often undertaken to purify the material. The next step is the Siemen’s process\textsuperscript{42} which is a form of chemical vapour deposition. Trichlorosilane is exposed to high purity silicon seed rods along with high purity
hydrogen at about 1100°C. The heat causes the trichlorosilane to decompose and deposit ultra-pure silicon onto the seed rods which then can grow in size. The by-products from the decomposition of trichlorosilane include HCl and SiH₄, the latter of which can be recycled into trichlorosilane.

Silicon surfaces for imaging are made from semi-conductor grade silicon by the Czochralski process. The Czochralski process involves melting the silicon in a crucible typically made of quartz followed by the insertion of a seed crystal on a rod of well-defined geometry. The rod is then rotated and raised at a certain rate to obtain a large crystal called an ingot. The ingot can then be manipulated into other forms such as wafers or slabs. This process is typically done in an inert atmosphere for silicon to avoid oxide formation which is a disadvantage of silicon versus gold. Care must be taken to ensure an inert atmosphere environment when preparing silicon samples.

1.3.1 Si(100) and Si(111) in Ultra High Vacuum:

Silicon treated under ultra-high vacuum conditions can display significantly different properties than its wet chemical treated counterparts. Two very popular orientations to study under UHV conditions are Si(100) and Si(111). Both surfaces provide excellent platforms to study the adsorption of molecules directly onto bare silicon surfaces. When treated thermally at very high temperatures in conjunction with Ar⁺ sputtering, complex reconstructions can occur. Starting with the Si(100) surface, high temperatures and argon will remove the native oxide layer and produce a complex, but stable 2×1 reconstruction pattern. This was first proposed on the basis of low-energy electron diffraction (LEED) results and suggested that each silicon atom on the surface
Figure 1-5. High resolution STM images of a clean Si(100) surface exhibiting the 2 x 1 reconstruction with parallel rows of dimers showing (a) occupied states, -2 V bias and (b) unoccupied states, 2.3 V bias, 2.3 x 3.9 nm².⁴⁵,⁴⁷ (Reprinted with permissions from the ACS, Copyright 1995 and 1996)

was bonded to a neighbour, in effect resulting in rows of dimers.⁴⁶ STM observations of a clean Si(100) 2x1 surface, Figure 1-5,⁴⁵,⁴⁷ confirmed this, though there is not absolute certainty as to the exact nature of the bond between the two silicon neighbours.

The nature of the bond between the silicon dimers on the 2x1 surface is still a matter of debate.⁴⁸ Three possibilities which exist, Figure 1-6, are the silicon atoms are connected by a weak π bond and a σ sigma bond making them essentially a double bond analogous to an alkene, a diradical due to the low π bond strength, or an asymmetric dimer with one atom slightly higher than the other giving an overall zwitterionic character.⁴⁹ There has been experimental evidence which shows the dimers are tilted on the surface, but regardless of the orientation of the dimers, they present a very reactive surface with which to form well-ordered organic monolayers.⁴⁸
There have been many studies of attaching organic and inorganic compounds to the clean Si(100) 2x1 surface. These include dative bonding, dissociative addition and a whole series of addition type reactions. Dative bonding is a covalent bond that is formed as the result of one molecule donating both electrons needed to form a bond. A well-known example of this is the ammonia/boron trifluoride complex in which ammonia donates both of its lone pair of electrons to the electron deficient BF$_3$. A similar system of Me$_3$N/BF$_3$ was reacted on Si(100) to form a donor/acceptor complex of TMA-Si-Si-BF$_3$. When boron trifluoride was introduced to the clean surface, dissociation took place with Si-F and Si-BF$_2$ bonds forming. However, the authors found that if the one of the silicon atoms in a dimer first forms a dative bond with trimethyl amine, BF$_3$ will adsorb intact. An example of dissociative addition on Si(100) was seen with iodomethane. At submonolayer coverages, the authors postulated that the C-I bond is dissociated upon

---

**Figure 1-6.** Possible dimer structures on the clean Si(100) 2x1 reconstructed surface showing (a) symmetric dimers, (b) diradical dimers and (c) asymmetric dimers.
adsorption based on high-resolution electron energy loss (HREEL) experiments which did not reveal a loss feature for $\nu$(C-I) at 525 cm$^{-1}$.

Pericyclic reactions are popular in organic chemistry and pericyclic-like reactions have been used in many reactions with the Si(100) 2x1 surface. Examples of addition-like reactions which have been studied on Si(100) include: [1 + 1] TEMPO,$^{54}$ [1 + 2] tert-butyl isonitrile,$^{55}$ [1 + 3] nitroethane,$^{56}$ [1 + 2 + 1] norbornadiene,$^{57}$ [4 + 2] pyridine,$^{58}$ [1 + 6 + 1] perylene,$^{59}$ and [2 + 6] 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hhfac).$^{60}$ An example of a [2 + 2] cycloaddition like reaction is H$_2$C=CH$_2$ with the silicon dimer, as shown in Figure 1-7. This mechanism was proposed even though classic organic chemistry would suggest a concerted reaction, as based on the Woodward-Hoffman rules which use orbital symmetry to predict the stereochemistry of pericyclic reactions. Evidence for the proposed pathway came from Fourier transform infrared spectroscopy (FTIR) and density functional theory calculations of cis and trans-1,2-dideuterioethylene for the asymmetric $\nu$(C-H) and the symmetric $\nu$(C-H) stretching which indicated that symmetry of the original reactant is retained for the adsorbed product.$^{61}$ Addition of the cis product resulted in a (R,S) or (S,R) product while the trans product resulted in a (R,R).

**Figure 1-7.** Proposed reaction mechanism for the addition of ethylene to a clean Si(100) 2x1 surface via a step-wise pathway.$^{61}$
or (S,S) product. This in effect suggested that a concerted mechanism was not taking place, but more likely a step-wise one was. STM observations made by Wolkow’s group also arrived at a similar conclusion when studying the adsorption of *cis* and *trans*-2-butene. Their reasoning was based on counting the approximate number of molecules in a certain area and finding that the observed level of *trans* and *cis* isomers in the *cis* and *trans* samples were consistent with known impurity levels in the gas meaning that isomerization did not take place to any large degree and the stereochemistry of the reactants was the same as the adsorbed products.

Si(111) is another intensely studied surface for modification under UHV conditions. Low energy electron diffraction (LEED) studies on clean Si(111) indicated a 7 x 7 reconstruction, which was achieved after a combination of argon ion and high temperature treatment of the silicon surface. The surface structure was widely debated until a thorough investigation by transmission electron diffraction (TED) of the

Figure 1-8. Dimer adatom stacking fault model of the 7x7 reconstructed Si(111) surface.
reconstructed surface was published in 1985. This method, TED, has an important advantage over HREEL and LEED in that reflections of scattering vectors nearly parallel or parallel to the surface, which are very sensitive to surface-parallel atom positions, can be readily observed. The resulting, and very complex, DAS model (dimer adatom stacking) fault model, Figure 1-8, put forth by the authors consists of 12 adatoms sitting on top of a rest atom layer, which sits on top of a dimer layer, which in turn sits on top of a base layer. Due to a stacking fault in the unit cell, all of the adatoms are not electronically equivalent. Consequently, the unit cell is commonly said to contain a faulted and unfaulted sub-unit. When STM images of the clean Si(111) 7x7 reconstructed surface, for example in Figure 1-9(a) and Figure 1.9(b), started to be routinely produced, they gave further support for the DAS model of the surface. An important note is that on this reconstructed surface, the reactive sites are between an adatom and an adjacent rest

Figure 1-9. A 7 x 7 reconstruction on a clean Si(111) surface after thermal annealing under vacuum showing (a) unoccupied states, 7 x 7 nm$^2$ and (b) occupied states, 10.3 x 9.7 nm$^2$. (Reprinted with permission from the ACS, Copyright 1995)
atom, and that only the corner hole atoms, rest atoms and adatoms have dangling bonds.\textsuperscript{44}

Organic modification on clean Si(111) 7x7 reconstructed surfaces has also received a fair amount of attention. Addition-like reactions which have been studied include: [1 + 1] 2,2,6,6-tetramethyl-1-piperidinyloxy,\textsuperscript{64} [1 + 2] acetonitrile,\textsuperscript{65} and [4 + 2] aniline.\textsuperscript{66} Dissociative additions, for example with trichloroethylene,\textsuperscript{67} and dative bonding with pyridine,\textsuperscript{68} have also been explored. One compound whose addition on 7x7 reconstructed Si(111) has been heavily studied is benzene.\textsuperscript{69-71} Benzene adsorption has been investigated by HREELS, thermal desorption spectroscopy (TDS) and STM. Dosing of a clean substrate took place at 110 K, and then the temperature was raised to 300 K to remove all of the physisorbed benzene. The authors proposed that the chemisorbed benzene is adsorbed onto the surface by way of a [4 + 2] like cycloaddition resulting in a di-\(\sigma\) adsorption with a 1,4-cyclohexadiene type structure bond to the silicon.\textsuperscript{72} Evidence to support this from TDS showed a single desorption peak at 341 K at low dosings, 0.05 L, and a second peak at 363 K when the dosing was increased to 0.3 L. When the desorption energies were calculated and compared to a STM study by Wolkow’s group,\textsuperscript{73} benzene was indicated to be adsorbed at both corner and center adatom sites. HREELS experiments provided several key pieces of information and were studied without and with annealing. The results were compared to liquid phase benzene and liquid phase 1,4-cyclohexadiene. There was no observation of a peak at \(\sim 2055\) cm\(^{-1}\), attributed to a Si-H stretch, which means that benzene is adsorbed as a molecule. A Si-C stretch was seen at 540 cm\(^{-1}\) giving an indication of chemisorbed benzene. Signals were also present at 3025 cm\(^{-1}\) and 2920 cm\(^{-1}\) and are indicative of sp\(^2\) and sp\(^3\) hybridized carbon C-H stretches. On the basis of these results, a [4 + 2] pericyclic type reaction was proposed as
Simple inorganic compounds have also been explored on silicon, for example ammonia, and its behavior is different from surface to surface. On a clean Si(100) 2x1, ammonia dissociates into H and NH₂ at room temperature. If the temperature is increased to greater than 500 K, =N-H starts to form from -NH₂ as suggested by FTIR experiments. With ammonia adsorption on Si(111) a different situation occurs. At temperatures below 120 K, NH₃ can adsorb molecularly from high-resolution core level photoemission studies, but over a range of 70 K to 300 K, dissociation of the NH₃ to NH and NH₂ was also observed. Although UHV equipment can provide clean surfaces of Si(100) and Si(111), from which important technological and fundamental studies can be made, the major drawback is these surfaces are only available under UHV conditions. UHV equipment in and of itself is expensive and the upkeep is very costly. Wet chemically modified flat silicon surfaces can therefore be an attractive alternative, especially since the vast majority of technological devices operate in an atmospheric environment.
1.4 Wet-Chemical Modified Flat Silicon:

Wet-chemical methods have the accessibility advantage over UHV systems in that they can be prepared without the need for the vacuum. A common starting point for the organic modification of silicon is the silicon-carbon bond which forms densely packed monolayers, mainly from alkenes or alkynes.\(^{75-77}\) This allows for the direct electrical contact between the organic layer and silicon substrate. Before direct contact can be made, the native oxide layer must first be removed. This has been explored by several methods including water, alkaline solutions (KOH, tetramethylammonium hydroxide) and fluoride based solutions.\(^{78}\) When using water as an etchant for the oxide layer, the overall reaction can be expressed as two molecules of water react with a molecule of SiO\(_2\), equation 1.3.

\[
\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4 \tag{1.3}
\]

There are three steps which take place in order to break the Si-O bond. They are adsorption, followed by the formation of an activated complex, followed by hydrolysis. Of the species present in water, H\(_3\)O\(^+\), H\(^+\) and OH\(^-\), H\(_2\)O disrupts the silicon oxide network the least, but will break it given enough time. A possible pathway to breaking the Si-O bonds is shown in Figure 1-11. Studies conducted by water etching

\[\text{Figure 1-11. Si-O bond breaking from interaction with H}_2\text{O}\text{.}\]
of Si(100) were carried out at room temperature by Hines’s group. They found that deoxygenated water could etch the oxide layer away, but substantial time periods of approximately 12 hours were required. FTIR analysis indicated a rather homogeneous hydrogen terminated surface, but STM imaging revealed that the surface was very heterogeneous with many hills and valleys.

Alkaline based solutions have also been used for etching away the naturally occurring silicon oxide layers. Hydroxide ions cannot penetrate silica layer on their own to attack the silicon atoms because they are shielded by highly polarized oxygen atoms. Water can hydrogen bond to the oxygens of the silica layer, equation 1.4, which causes a charge transfer towards the water, weakens an Si-O bond, and allows an OH⁻ ion to attack the silicon, equation 1.5.

\[
\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2\cdot2\text{H}_2\text{O} \quad 1.4
\]

\[
\text{SiO}_2\cdot2\text{H}_2\text{O} + 2\text{OH}^- \rightarrow \text{Si(OH)}_6^{2-} \quad 1.5
\]

The use of hydrogen fluoride, HF, based solutions for etching oxide covered Si(100) and Si(111) surfaces is the most popular method. Though dilute solutions of HF on Si(100) and 40 % NH₄F on Si(111) produce excellent results, the precise chemical reactions taking place are still not understood. The pure fluoride ion, F⁻, will etch the silica layer very slowly. Previous research showed that the rate of oxide etching in a 1 M KF solution was 0.001 Å/s, which is much slower than the equivalent concentration using HF. An overall reaction, equation 1.6, has H₂SiF₆ (aq) as a final product, but it is quite
likely that other products are formed as well during the etching process. The addition of
H\(^+\) is known to increase the rate of the etching.\(^82\) This can be due to hydrogen bonding to
the oxygens of the silica network, which causes a charge transfer towards the hydrogen,
weakens the Si-O bonds and allows hydrogen fluoride to etch away the oxide layer more
rapidly. Possible reactions taking place during the etching are shown in Figure 1-12.\(^83\)

Figure 1-12. Possible etching pathways during silicon oxide dissolution.\(^83\)
In general dilute solutions of HF are used in the etching of Si(100). The pH of the HF was found to play a crucial role in the surface morphology as concentrated HF produced a very rough surface, but a buffered HF solution of pH=5, gave more promising results. An ideal hydrogen passivated Si(100) surface under wet chemical conditions would produce SiH$_2$ linkages, but quite often monohydride and trihydride bonded silicon is also observed. Silicon(111), on the other hand, can be etched with 40% NH$_4$F to reproducibly produce high quality, nearly defect free Si(111)-H. The fact that hydrogen-terminated surfaces are produced is interesting because even though Si-F bonds are extremely strong, they are also very polarized (Si$^{5+}$-F$^{5-}$), indicating that kinetics plays an important role in determining the final structure on the surface. Two very popular orientations for single crystal silicon wafers are Si(100), which ideally forms a dihydride surface and Si(111) which ideally forms a monohydride surface upon treatment with dilute HF / NH$_4$F, Figure 1-13. The hydride terminated Si(100) surface is usually less homogeneous than its Si(111)-H counter-part. Organic modification of these surfaces tends to be favoured for the Si(111)-H surface because it is essentially atomically flat and can form densely packed and well-ordered monolayers. This is important in regards to resistance to re-oxidation of the Si surface.

![Diagram of Si(100)-H2 and Si(111)-H](image)

**Figure 1-13.** Ideal hydrogen terminated Si(100) and Si(111) surfaces.
Organic modification of silicon involving radical reactions usually starts from the Si(111)-H surface. For modification involving nucleophilic substitution, for example from Grignard and organolithium reagents, the Si(111)-Cl and Si(111)-Br surfaces have been used as starting points.48 Chlorine terminated Si(111) surfaces can be produced by reacting a freshly prepared Si(111)-H, using chlorine gas with thermal or UV initiation and with phosphorus pentachloride/benzoyl peroxide.87 Similarly the bromine terminated surface has been prepared by treating Si(111)-H with bromotrichloromethane under thermal or UV means, or by the reaction of Si(111)-H with N-bromosuccinimide in dimethylformamide at 60°C using benzoyl peroxide as a radical initiator.88 Different methods for thin film deposition on Si(111) have been successfully utilized including thermal (diacyl peroxides),89 photochemical (alkenes),90 chemomechanical (aldehydes),91 and electrochemical means (aryl diazonium salts).92

1.4.1 Wet Chemical Modification of Si(111)-H:

Work has been done on adsorption of alkenes, alkynes and aromatic compounds on silicon due to the fact that silicon is a semi-conductor which could lead to interesting possibilities for future electronics.21 There have been several different types of reactions leading to the organic modification of oxide-free Si(111). These include 1) radical initiated hydrosilylation, 2) thermally induced hydrosilylation, 3) photochemically induced hydrosilylation, 4) lewis acid-catalysed hydrosilylation, 5) alkyl/aryl carbanion reactions with hydride- and halide-terminated surfaces, 6) chemomechanical modification of oxide or oxide-free silicon and 7) electrografting.
Initially, radical initiated hydrosilylation was achieved through covalently bonded Si(111)-C surfaces on oxide-free silicon, first prepared by diacetyl peroxide.\textsuperscript{89} The mechanism for these radical reactions are (equations 1.7, 1.8 and 1.9):

\[
[\text{RC(O)O}]_2 \rightarrow 2\text{RC(O)O}^* \quad 1.7
\]

\[
\text{RC(O)O}^* \rightarrow \text{R}^* + \text{CO}_2 \quad 1.8
\]

\[
\text{R}^* + \text{H-Si}(111) \rightarrow \text{RH} + \cdot\text{Si}(111) \quad 1.9
\]

The acyloxy radicals can be generated by heating, though extreme caution should be exercised when handling acyl peroxides as they are known to be contact explosives. Decarboxylation may then occur to give an alkyl radical and carbon dioxide. The radical alkyl group will then abstract a hydrogen atom from the Si(111) surface. The \( \cdot\text{Si}(111) \) can then react with either the acyloxy radical or the alkyl radical which forms Si(111)-R and Si(111)-O-CO-R linkages. Stability tests in boiling chloroform and boiling water showed \( \sim 30\% \) of the monolayer was removed and this was attributed to cleavage of the acyloxy group.\textsuperscript{89} The resulting Si-C bond is stable and has a bond dissociation energy of \( \sim 369 \text{ kJ/mol} \).\textsuperscript{48}

Thermally induced hydrosilylation of alkenes has been shown to attach them directly to a Si(111)-H surface without using a radical initiator, by heating the hydrogen-terminated silicon surface at temperature of up to 200\(^\circ\text{C} \), equations 1.10 and 1.11.\textsuperscript{7}
The radical generated on the attached molecule may then abstract a hydrogen atom from an adjacent Si(111)-H resulting in another silicon radical which can then be reacted with another alkene.

Ultraviolet light has also been utilized to generate a radical directly on the hydrogen terminated Si(111) surface, Figure 1-14.\(^{93}\) This can be followed by formation of a Si-C bond in the presence of an alkene. The radical on the $\beta$ carbon may abstract a hydrogen atom from an adjacent silicon, completing formation of an alkyl group and making a new silicon radical. The process could theoretically continue until a saturation coverage is reached. This view of the mechanism has been accepted for many years; however, recent experimental evidence from near-edge X-ray absorption fine structure (NEXAFS)
spectroscopy using synchrotron radiation has suggested this may not be entirely true.\textsuperscript{94} If the sample contains saturated carbons, there should not be a peak about 285 eV which is assigned to a $1s \rightarrow \pi^*$ transition for unsaturated carbon. The authors did see peaks which correspond to unsaturated carbons on three different samples: thermal hydrosilylation on rough silicon, thermal hydrosilylation on smooth silicon and chemomechanical modification. As a result of these studies, a new mechanism was proposed for alkene modification of Si(111)-H to account for the apparent presence of unsaturated carbon after modification was complete.\textsuperscript{94} The details of this mechanism are outlined in Figure 1.15.

**Figure 1-15.** New mechanism proposed for the alkene modification of Si(111)-H which accounts for carbon unsaturation in the final structure.\textsuperscript{94}

Lewis acid-catalyzed hydrosilylation has also been studied towards modifying Si(111)-H surfaces, though the conditions required for the reaction to proceed are much harsher than for porous silicon. For example, using ethylaluminum dichloride, EtAlCl\textsubscript{2}, as a catalyst, reaction of decene with Si(111)-H took place at 100°C for 18 hours leading
to a moderate surface coverage. Modification of porous silicon on the other hand using the same catalyst and a variety of alkenes and alkynes proceeded quite readily at room temperature for 1 hour. Though coverage was incomplete for both groups from Si-H stretches observed in transmission FTIR, the stability was noted to be excellent as the samples withstood boiling in basic solutions for 1 hour.

In the reactions of carbanions with oxide-free silicon surfaces, a chlorine terminated Si(111) surface was initially used in place of the hydrogen-terminated one. Chlorination of the Si(111) was accomplished through the aforementioned PCl₅/benzoyl peroxide route. Both Grignard reagents, R-MgX, and alkyl lithium reagents were successfully used to form Si-C linkages directly on the silicon surface, but extended time periods were required depending on the group attached, and an elevated temperature of 80°C was used. A few years later, lithiated thiophenes were covalently attached to a Si(111)-Br surface, with modification times ranging from several hours to two days at 60°C. Thermal modification at 85°C for 16 hours was utilized when decylmagnesium bromide was shown to attach directly to a Si(111)-H surface. Carbon-hydrogen stretches from FTIR and C (1s) / Si (2p) ratios from XPS confirmed the modified surface.

Chemomechanical modification of silicon is a method which can be used to modify oxygen passivated silicon without first removing the oxide layer. A cleaned Si(111) shard is placed into a solution containing the compound of interest (ex. alkynes, alkyl halides), passivated side up. A diamond tipped scribing pen can be drawn across the surface, Figure 1-16, removing the oxide layer and near instantly modifying the exposed silicon surface. This method is very versatile for the modification of Si(111) and recent
studies with alkenes have also provided new mechanistic information, similar to what was seen for thermal/UV modification, Figure 1-17.94

**Figure 1-16.** Chemomechanical scribing of oxide passivated Si(111) with an alkyl halide.

**Figure 1-17.** Possible mechanism for the modification of Si(111)-H with an alkene by chemomechanical scribing.94

Electrografting modification of Si(111)-H has also been previously studied using the aforementioned diazonium salts.92 A gallium-indium eutectic was used to provide electrical contact to the Si(111)-H surface. Aryl radicals are generated through the reduction of the diazonium salts which can then abstract a hydrogen from the silicon and allow the modification to proceed, equations 1.12 - 1.14.
Diazonium salts are a particularly interesting class of compounds as organic modification precursors. This has been demonstrated in the covalent modification of carbon (Highly ordered pyrolytic graphite, HOPG, glass carbon, GC, and carbon fibres) and semi-conducting surfaces such as GaAs, Ge, and Si.\textsuperscript{97-102} In general there is a wide

\begin{align*}
\text{Ar-N}_2^+ + \text{1 e}^- & \rightarrow \text{Ar}^\bullet + \text{N}_2 \quad 1.12 \\
\text{Si(111)-H} + \text{•Ar} & \rightarrow \text{Si(111)•} + \text{Ar-H} \quad 1.13 \\
\text{Si(111)•} + \text{•Ar} & \rightarrow \text{Si(111)-Ar} \quad 1.14
\end{align*}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure18.png}
\caption{Reduction of an aryl diazonium salt, substrate modification, followed by multilayer formation.\textsuperscript{98,103}}
\end{figure}
variety of diazonium salts that are readily available. Due to diazonium salts being easily reduced to radicals, the initial surface modification of carbon and silicon is usually very quickly followed by hydrogen abstractions from surface bound species and the subsequent formation of multilayers from electrochemistry or from solution, Figure 1-18.\textsuperscript{98,103} A mechanism has been proposed for the formation of multilayers and the attachment of the azo groups.\textsuperscript{104,105} In all cases, the stability of the surface towards oxide reformation is paramount as this can adversely affect the properties of the thin film.

Many modifications of oxide-free silicon begin with a derivative of an alkene or alkyne and very commonly require heat, as in the diacetyl example, or ultra-violet radiation for the initial attachment step. In this thesis, a new and efficient method for the organic modification of Si(111)-H which does not require heat, irradiation, or UHV conditions will be presented. The details of this work are outlined in Chapter 3.

1.5 Organic Modification of Gold:

The interaction of sulfur on metal surfaces has been studied extensively in recent years due to significance in many areas of research and commercial interest including catalyst poisoning, corrosion, surface passivation and the fabrication of nanodevices.\textsuperscript{14,106-109} Gold is commonly used as a substrate due the ease at which sulfur can adsorb from solution (alkane/aryl thiols\textsuperscript{14,110,111}, sulfenyl chlorides,\textsuperscript{112} thiocyanates\textsuperscript{113,114}), gaseous phase (SO\textsubscript{2}\textsuperscript{115,116}, S\textsubscript{2}\textsuperscript{117}), or electrochemical deposition (sodium sulfide).\textsuperscript{118,119} The relatively inert nature of gold is important because it can be handled in air without adversely affecting the surface. Essentially atomically flat Au(111) surfaces, Figure 1-19, can take a number of forms including gold beads,\textsuperscript{120} Au/Cr on glass,\textsuperscript{121} and gold on mica.\textsuperscript{122}
1.6 Organosulfur Self-Assembled Monolayers (SAMs):

The study of self-assembled monolayers (SAMs) is important as SAMs can play important roles in biological sensing,\textsuperscript{123} chemical sensing,\textsuperscript{124} study of electron transfer in DNA,\textsuperscript{125} lithography through micro-contact printing (\textmu cp),\textsuperscript{126} and in molecular electronics.\textsuperscript{127} There are three main components of the adsorbate which are critical in SAMs: the head group, the main chain and the terminal group, Figure 1-20.\textsuperscript{14} The head group is responsible for linking the substrate to the surface. Typically, thiols are used for gold and other class b metals (metals which form soft acids), Table 1.1, as these tend to form strong covalent bonds. The backbone is typically an alkane, therefore, van der Waal’s interactions are of great importance to the packing of SAMs. The SAMs must preferentially pack in an ordered and regularly oriented array with few defects.\textsuperscript{128} The terminal group can be used to tune the properties of the surface either by facilitating interactions with hydrophobic or hydrophilic molecules, biomolecules, or nanoparticles.
with various functional groups. For example, CF$_3$ and CH$_3$ groups can make the SAM repelling in nature to metal ions and water$^{106}$ whereas COOH, NH$_2$ and OH groups are hydrophilic and can easily bind hard metal ions (Table 1.1).$^{129}$ Thiol or selenol end groups can bind soft metal ions.

![Figure 1-20. Model diagram of a SAM on a representative Au(111) substrate.](image)

Table 1.1: Classification of hard and soft acids according to Hard-Soft Acid Base Theory (HSAB)$^{130}$

<table>
<thead>
<tr>
<th>Hard</th>
<th>Alkali metal ions Li$^{+}$-Cs$^{+}$, alkaline earth metal ions Be$^{2+}$-Ba$^{2+}$, trivalent lanthanide ions, Ti$^{4+}$, Fe$^{3+}$, Co$^{3+}$, H$^{+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft</td>
<td>Cu$^{+}$, Ag$^{+}$, Hg$^{2+}$, Hg$^{2+}$, Pd$^{2+}$, Pt$^{2+}$, Cd$^{2+}$, Au$^{+}$ (zero-valent base metals), CN$^-$, R$_2$S, RSH, RS$^-$ (soft bases)</td>
</tr>
<tr>
<td>Borderline</td>
<td>Zn$^{2+}$, Ni$^{2+}$, Fe$^{2+}$</td>
</tr>
</tbody>
</table>

Preparing SAMs usually takes place by one of two methods: gas phase adsorption or solution phase deposition. The strong binding of thiols to gold which results in SAMs, can be explained by HSAB. Gold(I) is a soft acid as it is large, relatively polarizable, contains lone pairs of electrons in its valence shells, tends to have a partial positive charge, and has a low energy LUMO. Sulfur is a soft base as is somewhat large, polarizable, is of intermediate electronegativity and has a high energy HOMO. Soft-soft
interactions tend to be strongly covalent. Other methods for the deposition of organic molecules on solid surfaces are also available including Langmuir-Blodgett and Langmuir-Schaefer techniques. Cleanliness of the substrate, precursor compound, and solvent are all critical factors in the preparation of SAMs.

Gas phase deposition typically takes place inside a UHV chamber and offers advantages of having a very controlled working environment and the ability to clean metal substrates by ion sputtering / thermal treatment. Once the substrate is ready for deposition, the precursor compound with a sufficient vapour pressure, for example decanethiol,\textsuperscript{131} may be introduced to the sample chamber, commonly through a leak valve. This allows a good means of studying the early stages of growth and kinetics of SAM formation as the amount of precursor compound exposed to the substrate, gold for example, can be precisely controlled.

Solution phase formation of SAMs has also received a lot of attention owing to its simplicity and ability to produce well-ordered films. One of the first examples of self-assembly on flat surfaces came from the work of Sagiv, who studied the adsorption of mixed monolayers from concentrated solutions of \textit{n}-octadecyltrichlorosilane and long-chain substituted cyanine dyes on surfaces of oxidized polyethylene, evaporated aluminium and smooth glass.\textsuperscript{132} Nuzzo and Allara reported on the self-assembly of a series of substituted bifunctional disulfides on gold surfaces. The prepared samples were characterized by ellipsometry, water contact angle and FTIR measurements.\textsuperscript{133} Deposition times to reach saturation coverage may vary from a period of a few hours up to a few days. Following the deposition of disulfides, work has also been done on sulfides (RSR and/or RSR’), alkane thiols, aromatic thiols, aromatic thiocyanates, alkyl
Figure 1-21. Modified Au(111) surface before and after “click” chemistry between azidoundecanethiol and ferrocenepropynone.\textsuperscript{134}

thiocyanates and aromatic sulfenyl chlorides. An important advantage of solution phase deposition of SAMs is that the modified surface may be immediately modified again. For example, “click” chemistry was applied to a mixed monolayer SAM in which one of the thiols contained a terminal azide group, Figure 1-21.\textsuperscript{134} The azides underwent “click” chemistry with ferrocenepropynone in the presence of a copper II catalyst to form a new 5 membered ring structure containing 3 nitrogens with a ketone ferrocene linkage as one of the substituents. Multiple modified SAMs such as this one, with a hydrolytically and thermally stable triazole, are important because they can form the basis for chemical and biochemical sensors by attaching different groups. Though most SAMs are formed at or near room temperature, altering the temperature can have a strong effect on SAM properties. For instance properties such as desorption, dissociation, solid-solid phase transition and defects are all heavily influenced by temperature.

Two additional types of self-assembly “like” organic modifications of solid surfaces that have seen use in the literature are that of Langmuir-Blodgett and Langmuir-Schaefer films. These films should not be confused with Langmuir films which strictly speaking
refer to a floating monolayer. An example of this is stearic acid in water. After spreading a solution of stearic acid in a volatile solvent over the water surface, at the air-water interface, the hydrophilic –COOH head group will remain submerged while the hydrophobic long chain hydrocarbon tail group will be in the air. This is illustrated in Figure 1-22. Once the volatile solvent has evaporated, there will be a randomly ordered monolayer on the surface, Figure 1-22(a), which can be made into a tightly packed formation by pushing the molecules together. Langmuir-Blodgett films, Figure 1-21(b), are formed by first dipping a slide into a trough containing the desired molecules, and then slowly raising the slide up so that the molecules are drawn up onto the surface along with the water meniscus. The formation of a monolayer is helped by keeping a constant

Figure 1-22. (a) Langmuir film after solvent evaporation, partial compression, and tightly packed formation, (b) Langmuir-Blodgett film deposition on a flat substrate while keeping a constant surface pressure and (c) Langmuir-Schaefer film deposition by the interaction of two hydrophobic tails.
pressure of the molecules along the surface of the water. Once the slide is completely withdrawn, it must be carefully dried in order to remove the water layer and allow binding to the surface. Langmuir-Schaefer films present another form of molecular deposition and are particularly useful for making supported lipid bilayers.\textsuperscript{136} In Figure 1-22(c), this process is shown, where a previously modified solid support, gold for example, contains a monolayer with the hydrophobic tails pointing away from the substrate. These tails are then lowered towards a compressed layer of molecules, and upon interactions between both sets of hydrophobic tails and removal of the substrate, a bilayer is formed.

There are several steps in the process of self-assembly on a Au(111) surface by an alkanethiol. After an initial physisorption of the molecule on the Au(111) surface,\textsuperscript{137} chemisorption on the surface takes place resulting in the formation of a “lying down” phase. This “lying down” phase eventually “stands up” and can have an end result of a densely packed and well-ordered monolayer given enough time which can range from a few hours to a few days.\textsuperscript{138} The nature of the chemisorption process is not well understood, but is believed to occur via oxidative adsorption where gold presumably goes from a 0 to a +1 oxidation state, equation 1.15.\textsuperscript{128}

\[
(CH_3(CH_2)_nSH)_{\text{physAu}} \rightarrow CH_3(CH_2)_nS-Au + 1/2H_2
\]

The mechanism involving production of H\textsubscript{2} is not the only proposed mechanism, but could be an accepted one, equation 1.15. In a recent study, UHV work was done suggesting that the reduction of terminal nitro groups to amine groups during SAM
formation is caused by the hydrogen atoms released during the gold thiolate bond formation. A persisting issue which remains is the unavailability of methods to track the release of thiol hydrogen during or after SAM formation has taken place.

The chemical and thermal stability of SAMs is of utmost importance for technological applications. In ambient conditions, there is evidence that SAMs may degrade to either disulfides and sulfonates, equations 1.16 and 1.17.140,141

\[ 2 \text{RS-Au} \rightarrow \text{RSSR} + 2 \text{Au} \]  

\[ \text{RS-Au} + \text{H}_2\text{O} + \text{O}_3 \rightarrow \text{RSO}_3\text{H} + \text{HO-Au} \]  

Disulfide formation typically occurs in solution. Formation of sulfonates groups is believed to occur both in solution and in air, and has also been shown to occur in air in the absence of light.142

After the degradation reaction has proceeded, the resulting disulfides and sulfonates are not chemisorbed and can be removed lowering the quality of the surface. There are several factors which affect the rate of deterioration including: presence of water,143 oxygen,144 terminal functional group,145 and UV radiation.146 Au(111) is believed to lead to far more rapid degradation of SAMs over gold nanoparticles due to the greater number of defects present in nanostructured materials.147 These include gold islands, adatoms and vacancies.128

The thermal stability of SAMs on gold is particularly important if they are used in electronics. Studies done on dodecanethiol compounds at 373 K showed oxidation to
dodecanethiolates and eventual desorption from the surface. In order to improve thermal stability, several approaches have been put forth including use of electron irradiated aromatic SAMs, silver deposited on the gold surface to obtain thiolate SAMs on silver, and formation of hydrogen bonded network of amide groups.

1.7 Debated Issues in Self-Assembled Monolayers:

There has been a tremendous interest in elucidating the underlying chemistry behind the S-Au bonding interface. The classical picture of organosulfur compounds binding to an unreconstructed Au(111) surface, Figure 1-23(a), with the thiolate bonded to 3-fold hollow sites in agreement with DFT calculations of the time, stood for more than a decade. A new view emerged when evidence from photoelectron diffraction (PED) experiments indicated that methylthiolate binds to an a-top site on Au(111). Low-temperature STM and normal incidence X-ray standing wavefield

Figure 1-23. (a) classical view of an alkanethiol bonded to an unreconstructed Au(111) surface in a (√3 x √3)R30° configuration and (b) model for the proposed thiolate bonding on a-top sites of gold adatoms (adatoms in red, thiolates in blue).
absorption (NIXSW) studies a few year later suggested that this single coordination site arises from Au-adatoms present on the surface, Figure 1-23(b).\textsuperscript{162,163} Understanding the nature of the S/Au interaction and that of the S modified Au surface is important in the hot debate regarding the structure of the thiolate/Au interface in SAMs. With these systems the mobility of the adsorbed species, the coexistence of various phases, the production of etch pits, the initial binding mechanism, and in saturated monolayers, the stoichiometry of adatoms, are among the many important questions that are still not yet absolutely understood.\textsuperscript{128, 160, 164, 165} Current research is now focusing on understanding the nature of the adsorbate and different configurations have been suggested.\textsuperscript{128,160} These involve significant reconstruction of the modified Au surface through formation of Au vacancies\textsuperscript{157} and Au adatoms.\textsuperscript{166,167} The main configurations include bonding of the thiolate to a Au adatom,\textsuperscript{162} and the involvement of Au-adatom dithiolates.\textsuperscript{155}

There have been several issues in regards to SAM formation which have been highly discussed in the literature.\textsuperscript{6,14,128,160} Two of the most popular have been etch-pit production and adsorption site determination. The initial binding mechanism, as mentioned in section 1.4, is something that has been heavily researched.\textsuperscript{6,14,139}

These “etch-pits” are vacancy islands in the gold surface and can contain ordered thiol domains. At one time they were thought to be areas where thiols did not attach to the gold surface.\textsuperscript{168} Etch-pits can form during chemical etching of the gold surface, but also have occurred during UHV deposition of thiols.\textsuperscript{169} Thiols were also thought to be responsible for the etch-pits as gold was detected in the residual thiol solution, but this notion was dispelled when STM observations of thiols on both the outside and inside of the etch-pits were made.\textsuperscript{170} The lifting of the herringbone reconstruction was also thought to be a
potential source of gold adatoms resulting in etch-pit formation. An issue with this however is that the herringbone reconstruction cannot provide enough gold adatoms when considering saturation coverage levels of thiolates. Two current suggestions for the formation of etch pits are: adsorbate-induced stress and incorporation of adatoms into the sulfur-gold bonds. Adsorbate-induced stress has been proposed to be related to a charge redistribution among the sub-surface and surfaces atoms and the electron withdrawing or electron donating groups at the time of adsorption. Herringbone reconstruction, which arises from a charge transfer between the in-plane bonds and dangling bonds at the surface-vacuum interface has been suggested to be related to the adsorbate-induced stress model. The net result is a decrease in the optimal lattice constant caused by the adsorbate-induced enhanced attraction amongst surface atoms.

Bulk metallic gold arranges itself as a face centred cubic lattice with a lattice constant of approximately 4.08 Å. The interactions of the nearest neighbours in close packed systems allow for stability, therefore, surface atoms must undergo a reorganization due to the lack of near neighbours compared to the bulk material. The adsorption of molecules on Au(111) can either be detrimental or alleviate tensile stress. At low coverages, gold atoms may be ejected from the herringbone reconstruction due to the increasing surface lattice constant and may become deposited on terraces as was suggested from chlorine adsorption studies by Friend’s group. With a thiol sulfur atom being an electron acceptor, this should lead to a compressive surface stress after a charge transfer from gold surface weakens the interatomic gold bonds. In this thesis, the possibility of surface stress induced on a Au(111) surface by sulfur adsorption is explored in Chapter 6.
Another proposed mechanism is that the production of etch pits is due to adatoms themselves arising from step edges or terraces which result in frayed edges and etch-pits. Studies have shown that on a clean Au(111) surface, hexagonal pits which are one atom deep can be formed by gentle sputtering at ~500 K, Figure 1-24. Following deposition of the disulphide CH\textsubscript{3}SSCH\textsubscript{3} with heating to 250 K to form the striped phase, the same hexagonal pits became eroded and more circular. Observations with saturating the step edges without heating, lead to no distortion of the initial hexagons.

Adsorption site can be difficult to determine and has been one of the most studied aspects of SAMs in the last decade. Common techniques to determine phases include: LEED, STM and NIXSW. In terms of adsorption site determination, chain length can have a big impact. The (√3×√3)R30° structure is common for alkylthiol SAMs because this structure is due to the sulfur-gold interaction which is present regardless of chain length. Shorter chain lengths such as methanethiol and ethanethiol have one ordered

**Figure 1-24.** Near hexagonal like etch pits formed by sputtering of a clean Au(111) surface at ~500 K, image size 52 x 52 nm\textsuperscript{2}. (Reprinted with permission from Elsevier, Copyright 2010)
structure: typically $(\sqrt{3} \times \sqrt{3})R30^\circ$ and c(4×2) variations. Longer chain SAMs, such as hexanethiol, have not only the $(\sqrt{3} \times \sqrt{3})R30^\circ$, but they also tend to exist in multiple striped structures due to differences in surface coverage. During the adsorption process, as the surface coverage increases, there is a series of $p \times \sqrt{3}$ striped phases made (where $p$ denotes the period) before the final close-packed structure of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase. Low-energy electron diffraction has been used to determine the periodicity of the striped phases from SAMs prepared under UHV conditions with the most common diffraction pattern observed being $(5\sqrt{3} \times \sqrt{3})$ a.k.a. $(7.5 \times \sqrt{3})$ for medium length alkyl

**Figure 1-25.** Proposed models of possible binding sites of 1-octanethiol on Au(111) showing (a) fcc and hcp domain, (b) hcp and atop domains, (c) atop and fcc domain and (d) bridge and low coordination site domains.\textsuperscript{155}
High resolution STM was able to identify the structure and suggest adsorption sites for octanethiol on Au(111). The results proposed a Au-adatom octanethiolate complex in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ orientation from domain boundary imaging when comparing molecules on the inside and outside of an etch pit. A few models, Figure 1-25, were proposed on the assumption that a gold adatom is bound to a single octanethiolate and the underlying Au(111) surface. In Figure 1-25(a), the adatom-thiolates are placed on fcc sites on the upper layer and consequently hcp sites on the lower layer which was found to be the preferred orientation. Having the adatom-thiolates bonded to hcp and atop sites or fcc and atop sites and was deemed not-favourable, Figure 1-25(b)-(c), because for Au-thiolates to be bound to two different sites at the same time on the same surface indicates very little difference in adsorption energy. This was put forth on the assumption that difference in adsorption energy for adatom-thiolates on two very different coordination sites would be similarly large to what was observed from a theoretical study of gold atoms at different adsorption sites, $\sim$0.2 eV between fcc and atop and $\sim$0.014 eV between fcc and hcp. The model in Figure 1-25(d) was rejected outright since bonding on bridge sites on the top layer would mean the bonding would take place on a non-high symmetry site on the lower layer.

Adsorbing compounds on gold allows for the formation of monolayers, but also the potential for multilayers as well. Multilayers can form when $\alpha,\omega$-dithiols are used which can either form disulfides or loop around themselves so both sulfur atoms adsorb to the surface. Rigid $\alpha,\omega$-dithiols may not be flexible enough to form loops, but were observed to oxidatively couple to other dithiols forming disulfide bridges. Another possibility for the formation of multi-layers is if there is still significant charge density on
the gold surface to permit attraction of thiols which are on top of the initial monolayer.\textsuperscript{180}

A different kind of multilayer formation will be explored in Chapter 6 when considering S/Au interactions from a new sulfur deposition compound and Au(111).

\textbf{1.8 Comparison of Gold to Silver:}

Due to the increased price of gold $\sim$ $1850$ CAD/oz. compared to silver $\sim$ $40$ CAD/oz,\textsuperscript{181} silver should be an acceptable substitute due to its position in the periodic table relative to gold and that it is also considered a soft metal which would bind strongly to sulfur. However, gold has certain properties compared to silver which make it more suitable for SAM deposition. Silver is more reactive than gold and readily forms an oxide AgO as its oxidation potential is $1.7$ eV lower than for gold, Table 1.2. The major difference between silver and gold is caused by relativistic effects. Due to the high nuclear charge of gold, the s electrons which can penetrate the nucleus increase their velocity, resulting in an increased mass and leading to a contraction of the s orbitals. The result of contracted s orbitals means that the d and f electrons are more shielded. In addition, gold is after the lanthanide contraction which also results in more strongly bound s electrons. This difference even affects peak to valley roughness at the (111) lattices as the value is $6.0$ kcal/mol for Au(111) and $3.3$ kcal/mol for Ag(111).\textsuperscript{182} What this means is that even if a surface is atomically flat, there remains site selection for adsorption due to the surface still being energetically heterogeneous. For silver there is less discrimination between the hollow sites and the on-top sites compared to gold.\textsuperscript{6}
Table 1.2: Properties of Gold and Silver$^{6,182-185}$

<table>
<thead>
<tr>
<th>Property</th>
<th>Au</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization potential (eV)</td>
<td>$1^{st}$: 9.22</td>
<td>$1^{st}$: 7.57</td>
</tr>
<tr>
<td></td>
<td>$2^{nd}$: 20.19</td>
<td>$2^{nd}$: 21.49</td>
</tr>
<tr>
<td>A-A distance in f.c.c. cells (Å) at 25 °C</td>
<td>2.8840</td>
<td>2.8894</td>
</tr>
<tr>
<td>Peak to valley roughness (kcal/mol)</td>
<td>6.0</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Gold is an attractive surface for binding of organosulfur based SAMs not only because of the strong interaction between the two groups, but also due to gold not readily forming oxides. Au$_2$O$_3$, the most stable gold oxide, is thermodynamically unfavourable with a free energy of formation of $+19.1$ kcal/mol, therefore, sample preparation of gold surfaces do not require inert atmosphere. However, some recent work has revealed that in the presence of ozone and UV light, gold can form an Au$_2$O$_3$ layer at room temperature which cannot be removed by neither water and ethanol washing nor ultra-high vacuum conditions.$^{186}$

1.9 S/Au Interactions: The Highly Debated, High Coverage Sulfur Question

In order to better understand sulfur-gold interactions and to gain possible insights into adsorption site determination sulfur based SAMs, systems involving the deposition of just sulfur on gold have also been thoroughly investigated in the literature, though not without controversy. When considering the shortest thiolate SAM chain, sulfur, experimental evidence has shown that the initial chemisorption on Au(111) takes place at step edges.$^{187}$

A study using sulfur gas, S$_2$, adsorbed on gold, showed the formation of multiple phases of atomic sulfur on Au(111) including a dilute ($5\times5$) phase, Figure 1-26(a) and the
\((\sqrt{3} \times \sqrt{3})R30^\circ\) phase, Figure 1-26(b), which has been assigned to monoatomic sulfur adsorbed on the Au(111) surface. These experiments were studied by LEED and NIXSW techniques.\(^{175}\) The determined amount of surface coverage can give an indication to what species were adsorbed on the surface. At low coverages of \(\sim 0.33\) ML, \((\sqrt{3} \times \sqrt{3})R30^\circ\) phase, sulfur atoms have interatomic distances corresponding to \(\sim 0.5\) nm with adsorption at fcc and hcp hollow sites, similar to what has been reported for selenium.\(^{188}\) When increasing the coverage slightly to greater than 0.40 ML, \(S_2\) was found to be the more stable species on Au(111) compared to just \(S\) according to high-resolution photoemission studies from Rodriguez’s group.\(^{117}\) In addition, phases can also change with increasing or decreasing coverage. For example, coverage of 0.33 ML results primarily in the \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure whereas coverage of 0.51 ML results in a more complicated rectangular structure.\(^{115}\)

At higher coverages, an important question arises which has led to divided opinions in the literature in regards to what the nature of the usually observed rectangular structures
is. X-ray photoelectron studies at high coverages, Figure 1-27(a), usually show the presence of two doublets, with the occasional appearance of a third one. The first doublet which has its S 2p$_{3/2}$ component located at ~161.1 eV has been assigned to monoatomic sulfur bound to the Au(111) surface. At slightly higher binding energies of ~162.2 eV, a view has assigned this peak to sulfur, another to a complex AuS phase, and a third to polymeric sulfur species. Sometimes a third doublet, with the S 2p$_{3/2}$ component located at approximately ~163.5 eV is seen, and is attributed to multilayer sulfur formation on the sample surface.

Figure 1-27. High sulfur coverage on Au(111), (a) XPS spectrum of S 2p region, (b) STM image, 5 x 5 nm$^2$, showing rectangular structures. Models for the debated rectangular structures (c) proposed complex AuS phase and (d) proposed sulfur adlayers.
On one side, the formation of a complex 2D AuS phase has been suggested for the rectangular structures, Figure 1-27(b).\textsuperscript{115,116,175,189,190} A model for this phase have been proposed,\textsuperscript{191} Figure 1-27(c), where the gold atoms are gold and the purple atoms represent sulfur. This conclusion was suggested on the basis of several research groups findings. Initially, sulfur dioxide gas, SO\textsubscript{2}, was used as a sulfur source. A 2D AuS phase was proposed\textsuperscript{115} and explained by large-scale mass transport and a dynamic rearrangement of the surface “landscape”. Experiments were conducted inside a UHV chamber where the herringbone reconstruction was observed by STM. At low surface coverages of 0.05 ML, as measured by Auger electron spectroscopy (AES), the reconstruction become very altered and at 0.1 ML, the herringbone reconstruction is lifted completely. The appearance of frayed step edges upon sulfur adsorption was attributed to compressive surface stress causing gold atoms to be ejected and agglomerate at ascending step edges. An unreconstructed gold surface is stable up to sulfur coverages

\textbf{Figure 1-28.} STM images of sulfur modified Au(111) showing the proposed AuS layer at (a) shortly past 0.33 ML coverage, 113 x 113 nm\textsuperscript{2}, inset 40 x 40 nm\textsuperscript{2} and (b) at saturation coverage, 120 x 120 nm\textsuperscript{2}, inset 4.5 x 5 nm\textsuperscript{2}.\textsuperscript{115} (Reprinted with permission from the ACS, Copyright 2005)
resulting in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ “adlayer”. Sulfur in this form is “claimed” to be too mobile to be imaged by STM, but shortly afterwards, small AuS clusters can be seen, Figure 1-28(a). Further STM observations indicated that at a coverage of ~ 0.6 ML, sulfur has taken on a “sponge-like” appearance, Figure 1-28(b), monoatomic deep etch-pits have formed, and the gold atoms have been absorbed into AuS islands creating the pits. Upon heating to 450 K, the spongelike AuS phase is converted to an ordered 2D AuS phase which the authors claim covers both vacancy islands and terraces uniformly.

Another study conducted inside a UHV chamber used sulfur gas produced from a solid state electrochemical cell to study sulfur-gold interactions. The authors found that the aforementioned dilute (5 x 5) phase was significantly more stable than the $(\sqrt{3} \times \sqrt{3})$, but after dosing with sulfur at room temperature, the Au(111) crystal was cooled to 160 K for subsequent measurements. Heating the $(\sqrt{3} \times \sqrt{3})$ phase to ~ 450 K produced a “complex” LEED pattern which was suggested to be stable over a period of several days at room temperature, but it was not made clear if the sample was kept under UHV conditions during that time. LEED experiments have shown that this complex phase is actually a combination of a small portion of the surface exhibiting incommensurate long range order and the remainder of the surface existing in an unordered state. Normal incidence X-ray standing wavefield absorption experiments suggested that all of sulfur atoms in this phase are nearly at the same level above the underlying Au(111) layer and that they are sitting very close to a-top sites on the gold which implies local commensuration.
Further studies supporting a complex AuS phase were carried out by electrochemical STM (EC-STM). First a Au(111) electrode was modified by cyclic voltammetry in a

**Figure 1-29.** STM images after Au(111) modification and blank electrolyte substitution showing (a) ($\sqrt{3} \times \sqrt{3}$)R30° structure of sulfur, 9.1 x 9.1 nm² and (b) rhombic structure after applying a potential of +400 mV, 3.5 x 3.5 nm². (Reprinted with permission from Elsevier, Copyright 2008)

**Figure 1-30.** STM images, 64 x 64 nm², taken in the order of (a) and then (b) with a 15 minute time period between images, showing the effects of Au mass transport, and growth of the rhombic islands. (Reprinted with permission from Elsevier, Copyright 2008)
NaOH/Na$_2$S solution. Then the electrolyte was exchanged for a blank solution of NaOH after which time the ($\sqrt{3} \times \sqrt{3}$)R30° structure was visible by STM, Figure 1-29(a). When the potential was increased to +400 mV, islands with a rhombic like structure, Figure 1-29(b) were observed. The growth of these islands was attributed to an increase in the local sulfur coverage which was suggested to occur concurrently with the formation of gold vacancies from what were smooth terraces, Figure 1-30. Measurements taken from the apparent AuS islands to the sulfur covered gold substrate indicated a depth of ~ 0.114 nm while going from the substrate to the vacancy islands gave a depth of ~ 0.121 nm resulting in a monoatomic step height of the Au(111) surfaces of 0.235 nm. An increasing number of defects observed in the ($\sqrt{3} \times \sqrt{3}$)R30° S layer was suggested to be due to sulfur atoms being incorporated into the complex AuS phase.

On the other side, the behavior of the rectangles has been attributed to chemisorbed sulfur adlayers, Figure 1-27(d). STM imaging has indicated that several S$_x$ species

![Figure 1-31. High resolution XPS spectra of the Au 4f region of an Au(111) sample after (a) sulfur modification of ~ 0.5 ML and (b) chronoamperometry to form a gold oxide layer. (Reprinted with permission from the ACS, Copyright 2008)](image)
can be observed including \( S_3 \), \( S_4 \), and \( S_8 \).\(^{193}\) A model for the rectangular sulfur structure has been proposed on a gold lattice, with hollow and bridge adsorption sites.\(^{193}\) The interatomic distances of sulfur in this rectangular structure have been previously measured at \( \sim 0.30 \) nm\(^{187}\) which is significantly larger than the interatomic spacing for bulk \( S_8 \) which is \( \sim 0.20 \) nm.\(^{194}\) This indicates a strong interaction between sulfur and the gold substrate. X-ray photoelectron studies of Au(111) with a sulfur coverage of about 0.5 ML, did not give any evidence of oxidized gold which would correspond to an AuS monolayer, Figure 1-31 (a). In order to see if the oxidized gold could be detected, a clean Au(111) sample was modified by chronoamperometry to form a gold oxide layer and then taken for XPS analysis. These results, Figure 1-31(b) do indicate that a new peak is present at \( \sim 85.5 \) eV, however this signal is weak at best when compared to the main gold 4f\(_{5/2}\) and 4f\(_{7/2}\) peaks. The results do indicate that there is no evidence of oxidized gold for the sulfur modified Au(111) sample which supports that the sulfur on the gold surface is in an adlayer form.

Surface enhanced Raman spectroscopy (SERS) experiments were carried out on nanostructured gold after a modification of 40 minutes in 3 mM Na\(_2\)S with 0.1 M NaOH. The results show further support towards sulfur adlayers being present on the gold surface, Figure 1-32.\(^{187}\) In Figure 1-32(a), there is one small peak located 213 cm\(^{-1}\) which has been previously attributed to elemental sulfur, \( S_8 \).\(^{195}\) The band present at 313 cm\(^{-1}\) corresponds to a stretching vibration from S-Au, while the band present at 453 cm\(^{-1}\) is indicative of S-S stretching vibrations from polysulfide species.\(^{195}\) These features are important because they provide support for monoatomic sulfur (S-Au) and polymeric sulfur species (S-S) being present on the gold sample at the same time. There is a
decrease in intensity for the S-S stretching vibrations when going from \textit{ocp}, Figure 1-32(b), to -0.75 V, Figure 1-32(c). This corresponds to the same potential where the rectangular sulfur structures start to exhibit signs of sulfur desorption as indicated by in-situ STM\textsuperscript{193} and suggests that the rectangular structures are related to polymeric sulfur species. The spectrum for clean gold, Figure 1-32(d), serves as a good reference to indicate the presence of peaks and bands for the sulfur modified gold samples in the other spectra.

\textbf{Figure 1-32.} SERS Spectra of nanostructured gold (a) in air after 40 minute solution deposition sulfur modification, (b) same as (a) except in 0.1 M NaOH at \textit{ocp} (red-line), (c) same as (b) except potential was shifted from \textit{ocp} to -0.75V and (d) clean gold.\textsuperscript{185} (Reprinted with permission from the ACS, Copyright 2008)
Sulfur adsorbed onto gold surfaces may not be stationary: there is evidence for mobility of adsorbed sulfur on gold. Density functional theory (DFT) studies on the adsorption of sulfur on Au(111) at various temperatures showed that for $T > 300$ K, sulfur atoms can readily migrate whereas at lower temperatures, the thermal energy barrier to sulfur mobility is calculated to be 25-30 meV.\textsuperscript{196}

The mobility of sulfur atoms on gold is interesting in that sulfur is often considered a poison for many soft metal catalysts due to its high affinity for irreversible binding. Gold-sulfur adducts can be predicted to be stable based on hard soft-acid base (HSAB) theory.\textsuperscript{130} Soft acid and bases are characterized by lower charge density and greater polarizability compared to hard acids and bases. Soft acids have low charge and are in either a +1 or +2 oxidation state, have d orbitals available for $\pi$ bonding, typically have filled or nearly filled d orbitals and high lying LUMOs. Soft bases are highly polarizable, are typically larger ions and have low lying HOMOs. Soft acid-soft base adducts tend to be covalent, and Au-S adducts are strongly covalent in nature.

Sulfur deposition on gold surfaces is usually accomplished in aqueous electrolytic solutions using precursors such as $\text{SH}^-$, $\text{S}^{2-}$ and $\text{H}_2\text{S}$, through spontaneous\textsuperscript{187} or electrochemical conditions.\textsuperscript{118,119,193} In the gas phase, usually inside a UHV chamber, sulfur deposition on gold takes place using sulfur dioxide or sulfur gas.\textsuperscript{115-117} The opportunity to investigate sulfur deposition in an organic solvent on gold, at conditions similar to those used for SAM formation in solution, may elucidate useful information in regards to the S/Au interaction. This forms the basis for Chapters 4, 5 and 6 using a wide variety of different sulfur sources in various organic solvents.
1.10 Scope of Thesis:

This study can be divided into two main parts. In the first part we investigated the effects of a new, efficient and facile means of organically modifying Si(111)-H surfaces which does not require the use of heat or irradiation. The modified surfaces were characterized by a variety of techniques, the details of which are outlined in chapter 2. Chapter 3 will present findings for the electron transfer-initiated organic modification of Si(111)-H.

The second part involved studying the behavior of sulfur on gold by a new means, in organic solvents which are usually reserved for SAM formation. Several new sulfur precursors, some of which are quite different from one another, were used. We have, through the use of two of these sulfur compounds, arrived at an answer for the highly debated question of the structure formed at high sulfur coverages on Au(111). Chapter 4 will detail results of the interaction of thio and dithio-bisphthalimide on polycrystalline gold and Au(111) and a first indication of the high coverage sulfur structure. Chapter 5 will present XPS and STM data from the modification of gold with hexavalent sulfonyl phthalimide compounds. Chapter 6 will provide finding from study of two very reactive compounds with gold that contain N-S linkages and Si-S linkages, and confirmation of high coverage structure on a different level. Chapter 7 will contain a summary of the results and future directions.

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Chapter 2: Experimental Techniques, Chemical & Substrate Preparation

2.1 Introduction:

A variety of surface sensitive techniques, both local and area averages, were used to analyze the modified samples of Si(111), polycrystalline gold and Au(111) on mica in this thesis for purposes of determining surface structure and molecular/elemental composition. These methods included atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), cyclic voltammetry (CV), scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). In addition, theoretical calculations on the precursor molecules from Chapter 3 N-bromosuccinimide (NBS), and the thiobis(hexamethyldisilazane) and hexamethyldisilathiane compounds from Chapter 6, were carried out in order to obtain potential information about the layer thickness, and bond strength. Impurity free chemicals are important for reliable interpretation of surface analysis results. All synthesized chemicals, $S_xPhth_2$ from Chapter 4 and Aryl-$SO_2$-Phth from chapter 5, were purified by hot solvent recrystallization. The hexamethyldisilathiane compound from Chapter 6 was purified by distillation under an argon atmosphere at room temperature. High purity silicon(111)$^1$ and polycrystalline gold$^2$ surfaces were obtained from commercial sources. Au(111) on mica substrates were freshly prepared using an Au evaporation system. Contaminant free substrates are an essential starting point for surface modification. Silicon surfaces were cleaned with hot piranha solution, to remove trace organic material while gold was cleaned with chromosulfuric acid.
2.2 Atomic Force Microscopy (AFM):

Atomic force microscopy was invented by Binnig, Gerber, and Quate\textsuperscript{3} and arose in part from the inefficiency of the STM at imaging insulating surfaces.\textsuperscript{4} AFM generates images of surfaces by tip-surface interactions and may be used on conducting, semiconducting or insulating samples. There are several forces involved between an AFM tip and a surface. When the tip is in close proximity to the surface, van der Waal’s forces dominate. A representative example of this tip-surface interaction is shown in equation

\begin{equation}
U_{vdw} = -\left(\frac{1}{4\pi\varepsilon_0}\right)^2\left(\frac{\mu^4}{3kT} + 2\mu^2\alpha + \frac{3}{4}\alpha^2\hbar\omega\right)\frac{1}{z^6}
\end{equation}

2.1

which gives the van der Waal’s potential between two identical gas molecules, where \(\varepsilon_0\) is the permittivity of free space, \(\mu\) is the dipole moment, \(k\) is the Boltzmann constant, \(T\) is temperature, \(\alpha\) is the polarizability, \(\hbar\omega\) is the ground state energy of the electrons and \(z\) represents the distance between the two molecules.\textsuperscript{5}

If the tip is lifted well above the surface, long range interactions predominate. These interactions act in addition to short range forces between two surfaces, and can be electrostatic in nature, current induced, static-magnetic interactions or capillary forces due to the surface energy of water condensed between sample and tip. Close to the surface, these forces are small compared to van der Waal’s forces. However, farther from the surface, the van der Waal’s interactions become of decreasing importance as shown in Figure 2-1.\textsuperscript{5}
Figure 2-1. Potential energy for the distance between an AFM tip and substrate.

There are three major components of an AFM: cantilever with a sharp tip, scanner and feedback control, Figure 2-2. A sharp tip is mounted to the cantilever which deflects depending on the forces between the sample and the tip. The scanner is controlled in x,y,z directions typically by a piezoelectric tube scanner. The feedback control measures the forces that result from deflection of the cantilever. If the feedback control is turned off, the instrument is in constant height or constant deflection mode which should only be used for flat samples to decrease the chance of crashing the tip. When feedback control is on, the AFM runs in constant force mode or height mode. In this mode of operation, a constant deflection is maintained.

The basic principle of AFM is that the forces between the surface of a sample and the tip result in a deflection of the cantilever. Each cantilever, whether for contact, non-contact modes or tapping modes, will have a small tip located at one end which is
typically composed of silicon or silicon nitride. In contact mode, the force between the tip and the surface is kept constant while scanning by maintaining a constant deflection. Operating in contact mode requires a close tip-sample distance, which can range from a zero force contact point to forces in the repulsive regime, depending on the stability of the surface, or if scratching is desired, to potentially evaluate the thickness of a modified layer(s) on a substrate. Alternatively, an AFM may be operated in non-contact mode, which could be useful when the forces encountered in contact mode may alter the sample.

The cantilever does not touch the surface in this mode, instead relying upon attractive van der Waal’s forces as the tip is oscillating at ~100 Å above the sample surface. Changes in the oscillation of the cantilever are detected by an AC (alternating current) Mode control box and can be displayed for example in terms of topography, amplitude or phase. Tapping mode is popular when imaging sample surfaces that can be damaged by direct

\[\text{Figure 2-2. Schematic diagram of an atomic force microscope setup.}\]
contact with the probe, such as supported lipid bilayers. In this mode, the cantilever is oscillated close to the resonant frequency and alternatingly placed in contact with the sample surface and then lifted up at a very high rate. Due to the intermittent contact, the tip is far less likely to stick to the sample, and because of the van der Waals electrostatic and dipole-dipole forces, there is a decrease in the oscillation amplitude when near the surface, which can help prevent the crashing of the tip.

The primary AFM imaging technique used on the hydrogen-terminated and modified Si(111) substrates in Chapter 3 was contact mode. Imaging was conducted in air using non-conductive silicon nitride cantilevers. Flat terraces could be readily imaged in contact mode on Si(111)-H surfaces. Scratching was done on the modified substrates in order to see the underlying terraces.

2.3 Fourier Transform Infrared Spectroscopy (FTIR):

Fourier transform infrared spectroscopy is a non-destructive method for analyzing the presence of functional groups. This method can be used on thin films, solids, liquids and gases, however, for the scope of this thesis the discussion will be limited to FT-IR on thin films. All spectra acquired in Chapter 3 were conducted on a Thermo Nicolet Nexus 870 FT-IR instrument operated in reflection mode. A freshly prepared piece of hydrogen terminated silicon(111) was used as a background reference.

Chemical bonds absorb frequencies in the electromagnetic spectrum in the region of which is the infrared range. Only bonds which have a change in dipole moment as a function of time can absorb infrared radiation. The vibrational motions are stretching and bending which are amplified by absorption of infrared radiation. For the modified Si(111)
samples of Chapter 3, the key areas of interest are C-H stretches, 2850-2976 cm\(^{-1}\), carbonyl C=O stretches 1690-1760 cm\(^{-1}\), ferrocene ring mode \(\sim 1525\) cm\(^{-1}\) and O-C-C stretches for succinimide, \(\sim 1150\) cm\(^{-1}\).\(^8,9\)

Unlike many other instruments which are dispersive and collect data at certain wavelengths, FT-IR collects data at all wavelengths simultaneously.\(^7\) This is accomplished by collecting an interferogram of a sample signal. The interferogram is a plot of intensity as a function of time. Performing a Fourier transform on the interferogram leads to separation of the individual frequencies and can yield a plot of intensity as a function of absorption frequency.

2.4 Cyclic Voltammetry (CV):

Cyclic voltammetry is a widely used electrochemical technique owing to its ease of setup, and wealth of information that can be obtained about electrode kinetics, electrode thermodynamics and mechanistic information arising from electron transfer processes.\(^10\) A typical electrochemical cell used for CV work contains three electrodes: working, counter and reference. For a CV experiment, potential is varied linearly with time at a fixed rate and changes in the current are monitored. The starting potential, \(E_0\), is chosen in an area where no oxidation or reduction reactions of the material under investigation take place. The potential is then swept towards another potential, \(E_1\), at which point it is reversed and heads back towards the starting potential. Two common types of peaks which are observed in cyclic voltammetry are reversible and irreversible, as illustrated in Figure 2-3.
Within the scope of this thesis, CV studies were used as a tool to evaluate the thermodynamic modification of polycrystalline gold from reactions with several sulfur transfer agents in organic solvents. In all cases for Chapter 4 and Chapter 6, the working electrode was a solid gold electrode and the counter electrode was a piece of platinum foil. The reference electrode was a saturated calomel electrode for the oxidative stripping experiments in sulfuric acid. For electrochemical studies conducted in acetonitrile, a silver wire was used as a quasi-reference electrode, while the real electrode potentials were determined from ferrocene/ferricinium couple which was used as an internal standard.11

2.5 Scanning Tunneling Microscopy (STM):

Scanning tunneling microscopy is an extremely sensitive technique used to probe surfaces at the atomic level.12 In general, the technique involves moving a tip along a
sample surface in the x-y direction. A bias voltage is applied to the tip or the sample and a tunneling current will flow from tip to sample or sample to tip when the distance between the two is sufficiently small, depending on whether the voltage is positive or negative. A STM tip is typically a piece of metallic wire which has been sharpened in some fashion. Scissors can be used to cut a Pt/Ir wire, which is commonly used to image the surface of highly ordered pyrolytic graphite (HOPG). Tungsten wire is another popular choice for STM tips as it can be electrochemically sharpened to become a very fine point at the apex. Very sharp tungsten tips can be routinely made. However, when operating the STM in air, they have to be routinely replaced as the metal wire is prone to oxidation. Tips can also be coated in a variety of materials, such as clear nail polish, Apiezon wax, or hot melt glue for electrochemical STM studies. This coating of tips is required in order to minimize the faradaic current.

Scanning tunneling microscopy studies can be carried out in air, under electrochemical conditions (useful for when potential control experiments are required), or inside an ultra-high vacuum (UHV) chamber. In all cases, due to the small value of the tunneling current, it must be amplified. The tunneling current helps the feedback controls to keep the distance between the tip and the sample constant once the desired value is established. When tunneling current is increased, the tip to sample distance becomes smaller, but if the tunneling current decreases, the feedback controls make the tip to sample distance become larger. Since the current follows exponential behavior, small changes in the distance between the tip and the sample can lead to great increases in the current which is easily measured.
Figure 2-4. Schematic diagram representing the quantum mechanical tunneling of an electron between two materials separated by an insulator.

The principal operation of a STM relies on the quantum mechanical behavior of electron tunneling which is due to the wave-like properties of electrons. From a classical mechanics point of view, if an electron encounters a potential energy barrier, for example air or vacuum, that has a higher energy than its kinetic energy, it will not cross the barrier. In theory the only way for the electron to cross the barrier is to go around it by raising its kinetic energy to a level greater than that of the potential energy barrier. Quantum mechanics however says that there is a finite probability that electrons could tunnel through the barrier if the materials (metal or semiconductor) are sufficiently close enough together, Figure 2-4. When a bias voltage is applied between the two materials, the Fermi level of one material is raised relative to the other such that the electron
wavefunctions from both materials overlap and tunneling may take place. In the case of the example in Figure 2-4, electrons will tunnel from the occupied states of the negatively biased $E_{F1}$ to the unoccupied states of the positively biased $E_{F2}$. The exponential decay length, $\kappa$, of the electron wavefunctions at the Fermi level is given by equation 2.2,

$$\kappa = \frac{\sqrt{2m(V - E)}}{\hbar}$$  \hspace{1cm} 2.2

where $m$ is the mass of an electron, $V$ is the potential energy of the barrier, $E$ is the energy of the electron, and $\hbar$ is Planck’s constant. This quantity, $\kappa$, is related to the probability that the electron will tunnel through the barrier with tunneling current $I$, equation 2.3, and is proportional to the length of the tunneling barrier, $z$.

$$I \propto e^{-2\kappa z}$$  \hspace{1cm} 2.3

A typical STM setup contains a few core components including a metallic or semi-conducting sample, piezoelectric scanner, atomically sharp tip (ideally) and electronic and computer hardware, Figure 2-5. There are two modes of STM operation. In constant current imaging, the tunneling current between the sample and tip (or tip and sample) is kept constant and changes in height ($z$ direction) are monitored. The other mode is constant height mode: the height between the tip and sample is kept constant and changes in current are recorded by the electronics. Scanning in constant height mode can be done at a faster rate than constant current mode, however, there is a higher probability of “crashing” the tip when raster scanning back and forth across the sample. An important note is that in all cases of STM imaging, the actual atomic nuclei (if this resolution is
being achieved) and their positions are not being observed directly, but rather the local
density of states of electrons is being sensed by the microscope, which correlates with the
nuclear positions.

Figure 2-5. Schematic of a scanning tunneling microscope setup.

All STM imaging shown in Chapters 4, 5 and 6 was conducted in air using a
commercial Agilent 5500 scanning probe microscope. The tips were freshly prepared
pieces of tungsten wire, (0.25 mm dia, 99.95%, Alfa Aesar) electrochemically etched in 3
M NaOH (99.99%, Semiconductor Grade, Sigma Aldrich). Images were obtained using
constant current mode at scan rates ranging from 2.0 lines / second to 3.3 lines / second.

2.6 X-ray Photoelectron Spectroscopy (XPS):

X-ray photoelectron spectroscopy (XPS) is a technique widely used in surface science
which can analyze the elemental and chemical nature of the elements present on
surfaces. XPS can provide qualitative data regarding the elemental identities of
components on a surface as well as the chemical nature of these elements. Quantitative
data regarding elemental compositions can also be obtained, but for the scope of this
thesis, the discussion will be geared towards qualitative data. The goal of this section is to
describe: i) the general concept and background of XPS as a technique for analyzing
surfaces, ii) some of the necessary requirements of an XPS system with regard to source
radiation, filter and UHV environment and iii) methods used to analyze spectroscopic
signals and distinguish between real signals and background.

The primary use of XPS is to qualitatively analyze elements present on a surface and a
principal advantage over other surface sensitive techniques such as energy dispersive X-
ray spectroscopy (EDS) is the ability of XPS to identify the chemical state of an
element. Additionally, XPS can be used to probe a thin film in terms of thickness,
uniformity and chemical composition. The primary focus of X-ray photoelectron
spectroscopy for work in this thesis was for the purposes of elemental identification and
in some cases determination of the chemical nature of these elements on the modified
Si(111) and Au(111) surfaces from Chapters 3, 4, 5 and 6. XPS works on the principle of
the photoelectric effect where incoming photons can eject core electrons. A sample is
irradiated with photons and the kinetic energy and number of electrons that escape from
the surface of the material is monitored. The binding energy (\( E_B \)) of an ejected electron
can be calculated and is a key parameter for determining the element and the energy level
that it came from. The spectrometer work function (\( W \)) and the kinetic energy (\( E_k \)) of the
ejected electron are subtracted from the energy of the incoming X-ray photon (\( hv \)) to give
the binding energy as seen in equation 2.4.15

\[
E_B = h\nu - E_k - W
\]

2.4
The photoelectron spectrum (PES) displays counts of ejected electrons as a function of kinetic energy or binding energy. A schematic diagram illustrating the photoemission process itself is shown in Figure 2-6.\cite{15} In addition, the PES also shows those electrons with lower binding energies that were also ejected. Informative signals arise from electrons which are ejected directly from the sample whereas inelastic scattering of electrons contributes to background noise. Other sources of noise arise from the relaxation of the ionized atom by X-ray fluorescence, although due to the low energy of photoelectrons involved, less than 2000 eV for this work, this is unlikely. More likely to occur are Auger peaks which arise from a core vacancy being filled by an electron from a higher energy level. Due to the conservation of energy, another electron must be ejected from the atom. Differentiation of Auger peaks from XPS signals can be

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**Figure 2-6.** Illustration of the photoemission process in XPS.
accomplished by irradiating the same sample with two different X-ray photon sources. XPS satellites occur due to minor resonance lines from the source photons.

Using quartz to filter out the resonance lines from an Al source can remove these additional peaks. Bremsstrahlung radiation is another source of background noise which is due to photon emission due to the conservation of energy which must occur when a particle loses some kinetic energy due to colliding with another particle. Shake up satellites occur due to the interaction of an emitted photoelectron and an electron in the valence band. The emitted photoelectron excites the valence electron, thereby decreasing the shielding of the core electrons leading to a satellite peak with a higher binding energy. Satellite peaks can occur due to excitations caused by resonance lines of the source.$^{15}$

Figure 2-7. X-ray photoelectron spectroscopy setup inside a UHV chamber.
An XPS machine, Figure 2-7, requires some specialized components to ensure reproducible and accurate results. An important requirement is the use of an ultra-high vacuum (UHV) system which has a pressure range between $1 \times 10^{-9}$ mbar to $1 \times 10^{-12}$ mbar.\textsuperscript{16} There are two major reasons for this requirement i) residual gas molecules can easily scatter low energy electrons resulting in a decrease in signal to noise ii) at $10^{-6}$ mbar a monolayer of gas can form at a surface in approximately 1s which is far shorter than the acquisition time for a sample.\textsuperscript{15} The analysis chamber of a UHV machine is primarily composed of Mu metal, which is a nickel-iron alloy. This metal is important because it acts as a shield to magnetic fields, the Earth’s for example, and allows the ejected electrons to travel in a relatively straight line towards the detector. To achieve UHV conditions, a series of pumps work together to maintain the desired pressure. The workhorse of the pumping system is the turbo-molecular pump, which acts as a high speed molecular fan, and exhausts gases out through the roughing pump. The use of these pumps is especially important during the loading and unloading of samples into the system. Titanium sublimation pumps, getter pumps, are important for maintaining pressures inside the preparation chamber and analysis chambers. They trap gases by sputtering a fresh coat of titanium onto the inside walls of the UHV system and rely upon the random motion of gases. Ion pumps ultimately decide the lower limit of pressure inside the UHV chamber. When neutral molecules pass by, they are subject to a high potential field which ionizes them. They are also exposed to a magnetic field which causes them to take an elongated path towards the anodes of the pump, increasing the probability they will strike another neutral gas molecule and ionize it.\textsuperscript{16} This results in a kind of “cascade” type reaction which makes the ion pumps very efficient overall.
The source of the X-rays is also very important because the kinetic energy of the ejected electrons is dependent upon the energy of the source photons. Typically, a twin anode source is used, with the two most common sources being AlK\(_{\alpha}\) and MgK\(_{\alpha}\). The twin anode source is useful for differentiating between XPS signals and Auger peaks. If Auger peaks are obtained with AlK\(_{\alpha}\) radiation, then repeated acquisition of the sample with a MgK\(_{\alpha}\) source will shift Auger peaks by approximately 233 eV\(^{15}\) in terms of binding energy whereas actual XPS peaks will remain in place. The AlK\(_{\alpha}\) source has a photon energy of 1486.6 eV with a full width at half maximum (FWHM) of 0.9 eV. The quartz crystal monochromator used with this source narrows the line width to 0.25 eV resulting in greater resolution for distinguishing different chemical species. The other important part of the XPS is the hemispherical sector analyzer (HSA) which acts as a filter to only allow photoelectrons with a defined energy through. The HSA has a pair of concentric hemispherical electrodes to which a potential difference is applied. Therefore, only electrons with energies as defined by equation 2.5 are allowed through.

\[
E = e\Delta V\left(\frac{R_1R_2}{R_2^2 - R_1^2}\right) \tag{2.5}
\]

E is the kinetic energy, e is the charge of an electron, \(\Delta V\) is the potential difference between the electrodes, \(R_1\) is the radius of the inner electrode and \(R_2\) is the radius of the outer electrode. Since \(R_1\) and \(R_2\) are constant for a certain spectrometer, this equation can be rearranged to obtain:

\[
E = ke\Delta V \tag{2.6}
\]

where \(k\) is the spectrometer constant.

There are two main ways of operating an HSA: constant analyzer energy (CAE) or constant retard ratio (CRR). Since CAE was used for all XPS analysis in this thesis, CRR
will be described only briefly. In CRR mode, electrons are slowed down to a fraction of
energy defined by the operator. In CAE, the energy or range of energies of the electrons
which will pass through the analyzer is selected by the operator. The range of energies
can be wide or narrow. Wide ranges of energy will provide better resolution, but narrow
range selection is useful for determining the chemical states of elements present.

Peaks in the XPS are assigned according to their quantum numbers \((nl_j)\), where \(n\) is the
principal quantum number, \(l\) is the magnetic quantum number and \(j\) is the spin orbit
coupling quantum number. Orbitals with a non-zero angular momentum quantum number
are typically observed as doublets due to \(j = |l+s|\), where \(s\) is the spin quantum number.
The relative intensities of the doublets are due to degeneracies and can be calculated by
the expression \(2j+1\). Chemical shifts can be determined from XPS because when there is
a change in the chemical bonding or chemical environment of an element, there should
also be a change in the core electron’s binding energy. The core binding energies are
electrostatic in nature due to interaction of the core electron(s) with the nucleus, however,
other electrons can shield the core electrons from the nuclear charge, therefore, changes
in the valence electrons impact the core electrons’ binding energies. This means that
oxidation of an element should lead to an increase in binding energy whereas the
reduction of an element should decrease the binding energy. Chemical shifts are due to
either initial state effects which are due to photon absorption and ionization, or final state
effects which occur due to the response of the atom and emission of an electron and
include core hole screening, relaxation of orbitals and polarization of adjacent ions.

Typically, chemical shifts are initial state effects due to the relaxation processes
having a similar magnitude. In addition, spin-orbit splitting (SOS) should be very similar
for the same element in two different chemical environments. The binding energy of an electron is the energy difference between the initial state (n electrons) and the final state (n-1 electron and free photoelectron), equation 2.7.

\[
BE = E_{\text{final}}(n-1) - E_{\text{initial}}(n) \quad 2.7
\]

The chemical shift can be explained by the charged sphere model where for a single atom \( j \) while neglecting relaxation effects, equation 2.8,

\[
E = \frac{q_v e^2}{r_v} \quad 2.8
\]

where \( q_v \) is the number of valence electrons and \( r_v \) is the average radius of the valence electrons.

All X-ray photoelectron spectroscopy (XPS) studies in this thesis were conducted in a commercial ultrahigh vacuum (UHV) system (Omicron) operating at a base pressure of \( 5 \times 10^{-11} \) Torr. X-rays were generated from an Al K\( \alpha \) source (1486.6 eV). The system contains a hemispherical sector analyzer coupled to a multichannel electron detector. The analyzer was operated in constant analyzer energy (CAE) mode with a pass energy of 20 eV. A takeoff angle of 35° was used for all samples. All XPS spectra presented in this work are referenced to binding energies of the bulk Si 2p peak of 99.7 eV for modified Si(111) samples in chapter 3, and the Au 4f\(_{7/2}\) peak at 84.0 eV for the modified gold samples of Chapters 4, 5 and 6. Deconvolution of the XPS peaks was done using XPSPEAK 4.1 software.

### 2.7 Theoretical Calculations:

Computational chemistry is a broad area which covers both molecular mechanics and electronic structure theory. This can be used to calculate the energy of a specific
molecular structure, determine geometry optimizations and determine the vibrational frequencies of molecules. There are two major types of computational methods which are used to determine the properties of molecules i) molecular mechanics and ii) electronic structure methods.

Molecular mechanics is an approach for determination of molecular properties by using tabulated values and set equations. Using this approach, electrons are not treated explicitly which means that this method is computationally inexpensive, but this method does not work well for describing bond breaking and bond forming reactions due to the electron structure not being calculated precisely.

The other general type of computational chemistry is electronic structure methods. The methods which fall under this type are related by the fact that the properties are ultimately obtained by solving the Schrödinger equation (equation 2.9):

\[ H\Psi = E\Psi \tag{2.9} \]

However, for systems which are not very small, exact solutions to the Schrödinger equations are unlikely. The two major types of electronic structure methods are semi-empirical methods and \textit{ab initio} methods.\textsuperscript{17} Semi-empirical methods use experimental data to solve an approximation of the Schrödinger equation. \textit{Ab initio} methods use no experimental parameters and use only quantum mechanics to calculate molecular properties. The only physical constants used in \textit{ab initio} methods are: speed of light, the charge and mass of electrons and nuclei and Planck’s constant. Ab initio methods are more computationally expensive than semi-empirical methods, but provide more accurate results and can be used for a wide variety of systems.
Density Functional Theory (DFT) is an electronic structure method which is similar to \textit{ab initio} methods, but DFT methods include electron correlation. Electron correlation is accounting for the interactions between electrons of opposite spin which is a significant advantage over Hartree-Fock methods which use an average electron density, therefore, DFT methods can be more accurate for certain molecular systems.

There are various methods which are under the umbrella of DFT methods including and are typically made as combinations of exchange and correlation functionals. DFT methods split the overall electronic energy into several components which are calculated separately such as the kinetic energy, the electron-nuclear interaction, Coulomb repulsion and an exchange-correlation functional which itself is divided into an exchange functional and a correlation functional.\textsuperscript{17} The exchange and correlation functionals are further subdivided into two major groups which are local exchange functionals which involve only the actual values of the electron spin densities such as Slater and Xalpha whereas gradient corrected spin densities involve both the values and their accompanying gradients including such functionals as Becke and Lee-Yang-Parr. There is a third type called hybrid functionals which lead to exchange functionals being defined as linear combinations of Hartree-Fock, local and gradient corrected exchange functional combined with either a local or gradient corrected correlation functional. A common hybrid functional is B3LYP which means Becke, three parameter, Lee-Yang-Parr.

The other important component of computational chemistry other than the method is the basis set. A basis set is a mathematical representation of molecular orbitals for a specific molecule. Basis sets are composed of a linear combination of Gaussian functions.
There are several types of basis sets including i) minimal basis sets ii) split basis sets and iii) polarized basis sets.

The focus for this thesis will be on split basis sets and polarized basis sets. Split basis sets use two or more sizes of basis function for each atom. A double zeta basis set such as 6-31G uses two sizes of functions for each atom whereas 6-311G, a triple zeta basis set, uses three sizes of functions for each atom. Polarized basis sets add angular momentum to the orbitals beyond what is required by the ground state. Therefore, p orbitals can be added to hydrogen atoms and d orbitals can be added to other atoms such as carbon and nitrogen. An example of a basis set which uses a polarized function would be 6-31G (d,p) with both polarization for heavy atoms and hydrogen. Another set of functions are diffuse functions which are larger versions of s and p type orbitals. Diffuse functions are of importance for molecules where the electrons occupy space far from the nuclei. Such molecules are those with lone pairs, anions and systems with excessive negative charge in excited states. These basis sets are denoted by + and ++. The ++ is used when diffuse functions are added to hydrogen atoms.

Potential energy surfaces link the molecular structure of a molecule to the molecule’s overall energy. Geometry optimization calculations attempt to find minima on a potential energy surface resulting in a structure for a molecule which should be the most energetically favourable equilibrium structure. Subsequently, single point energy calculations can be performed on these optimized structures and are useful in determining bond dissociation energies. To determine bond dissociation energies, calculations must be run on a molecule and also the radicals which would result from the homolytic bond cleavage of the molecule along the bond of interest. Theoretical calculations were done
on compounds in Chapter 3 and Chapter 6 using the Gaussian 03W software package.\textsuperscript{18,19} Optimization and frequency calculations were done using the B3LYP method with the 6-31G+(d,p) basis set. No imaginary vibrational frequencies were seen.

\section*{2.8 Chemical Preparation:}

N-Bromosuccinimide (NBS), 99 \%, was purchased from Sigma-Aldrich and purified by recrystallization in water. Ferrocene, 98 \%, was purchased from Sigma-Aldrich and purified by sublimation. N-bromophthalimide (NBP), 95 \%, was purchased from Sigma-Aldrich and purified by recrystallization with glacial acetic acid. Acetonitrile, CH\textsubscript{3}CN (HPLC Grade, Caledon Labs) was dried with calcium hydride (Fisher Scientific) and distilled under argon just prior to use. Sulfuric acid, 96 \%, USLI grade, hydrogen peroxide, 30 \%, VSLI grade and ammonium fluoride, 40 \%, USLI grade, were all of semiconductor quality and purchased from GEM Microelectronic Materials L.L.C.. *Calcium gluconate (Sigma-Aldrich) and calcium carbonate (Fisher Scientific) were kept immediately accessible at all times when using NH\textsubscript{4}F as a precautionary measure, in the unlikely event of a spill/burn.

The synthesis of the sulfur bisphthalimide compounds was done according to known literature methods.\textsuperscript{20,21} Under an argon atmosphere, thiobisphthalimide was made from phthalimide dissolved in freshly distilled dimethylformamide (DMF). To this an equimolar amount of sulfur monochloride, S\textsubscript{2}Cl\textsubscript{2}, was added dropwise with stirring over the course of several minutes. After approximately half an hour, a white precipitate formed. The reaction was allowed to continue stirring overnight under argon. Upon
removal of the solvent, the product was washed with cold water to quench any remaining sulfur monochloride and then filtered. After drying, cold finger sublimation was used to remove any remaining yellow crystals of sulfur. Recrystallization was done from a mixture of chloroform and methanol to give a white crystalline product that had a melting point of 318 – 319°C, which is in agreement with literature values of 315 – 317°C.  

Dithiobisphthalimide was also prepared under an argon environment with stirring. A half a molar equivalent of sulfur monochloride was added dropwise to stirred suspension of potassium phthalimide in dry methylene chloride at 0°C. After warming to room temperature and refluxing for a few minutes, the mixture was stirred for an additional 3 hours. The product was then filtered, washed with petroleum ether and cold water, and dried under vacuum. Recrystallization was done from a mixture of chloroform and methanol to yield a white crystalline material which melted at 231°C, in line with values of 227 – 229°C reported by Kalnins, Harpp, Ley and Scammells.  

Sulfonyl phthalimides, both aromatic and alkyl, were prepared from the corresponding sulfonyl chlorides and potassium phthalimide. The resulting compounds were washed with water and purified by recrystallization. Compound purity was checked by melting point, HPLC, and X-ray crystallography.  

Thiobis(hexamethyldisilazane), purity >95%, was purchased from Gilest and used as received.  

Hexamethyldisilathiane was purchased from Sigma-Aldrich and purified by simple distillation. The distillation was done at atmospheric pressure under an inert argon environment according to literature procedures.
2.9 Substrate Preparation: Si(111)-H and Au(111)

Silicon wafers, n-type (doped with phosphorus), resistivity 0.1 - 10 Ωcm, 250 - 300 μm thick, were purchased from SILTRONIX (France). Piranha solution, 3 parts H$_2$SO$_4$ : 1 part H$_2$O$_2$ (Caution: Piranha solution is a very powerful oxidizing agent and care should be taken when handling it) was freshly prepared in Teflon vials just prior to cleaning the silicon shards. Immediately after fluoride ion etching and Si(111)-H formation, the shards were quickly rinsed with MilliQ water, put in a Schlenk tube, and placed under vacuum. Schlenk line techniques were used for all surface modifications of Si(111)-H in order to maintain an inert atmosphere.

Midas is an evaporation system that was used for the preparation of all Au(111) on mica substrates. A gold wire (0.762 mm dia, Premion ®, 99.999%, Alfa Aesar) was evaporated onto freshly cleaved mica (V1 Grade, Ted Pella) in a custom built evaporation system, consisting of a Kurt J. Lesker bell jar, Varian turbo pump, and operating at a pressure of 1 x 10$^{-7}$ Torr. The base plate holding the mica was heated at 600 K for 12 hours prior to depositing the gold and was kept at 600 K for an additional 3 hours after the gold was deposited to help ensure the formation of high quality Au (111) surfaces. Upon removal from the evaporation chamber, the gold samples were cleaned with chromosulfuric acid, (Chromerge ®, Bel-Art), anhydrous ethanol (Commercial Alcohols), and ultra-pure water (Millipore, 18.2 MΩ) and then dried under a nitrogen stream and stored in a dessicator until used.
2.10 References:

[1] SILTRONIX Silicon wafers and Services (http://www.siltronix.com)


Chapter 3: Electron Transfer Initiated Organic Modification of Si(111)

3.1 Introduction:

Silicon is one of the most studied materials on the planet owing to its very high abundance in Earth’s crust and application in the manufacture of cement, silicones, glass and near complete dominance in the semiconductor industry. High-quality wafers are commercially available and relatively inexpensive. Two commonly studied surfaces of silicon are Si(100) and Si(111), both of which are covered by a naturally occurring oxide layer. Direct functionalization of these surfaces can be achieved through the formation of self-assembled monolayers, commonly from various derivatives of trichlorosilane groups. If oxide-free silicon is required for starting from hydrogen terminated surfaces, the oxide layer can be removed with fluoride ion etching, HF or NH₄F, resulting in good hydrogen coverage on both Si(100) and Si(111). Alternatively the oxide layer may be removed by thermal means if operating inside a UHV environment.

Various strategies have been employed to functionalize oxide-free silicon. Two common starting groups are alkenes and alkynes, both of which are known to form densely packed, well-ordered monolayers. Attachment of these groups to form Si-C or Si-C=C linkages is often done by thermal or photochemical means, starting from the hydrogen terminated surface. Depending on the alkene or alkyne chain, subsequent modification of the modified surface can be done. For example copper catalyzed reactions have been used in “click” chemistry, to attach oligo(ethylene glycol) with an azido tag, to a terminal alkyne. Though N-bromosuccinimide (NBS) and N-bromophthalimide (NBP) are well known in organic chemistry as sources of bromine, they have not been used for the direct attachment of the imidyl group to
a silicon substrate which would result in a Si-N linkage. Linkages of this type have been previously reported from the reaction of various amines with both Si(100)-Cl and chlorine terminated porous silicon surfaces which yielded thermally stable Si-N bonds upon modification.\textsuperscript{18}

In this work a facile and efficient method for the modification of Si(111) is demonstrated, which does not involve the use of heat or irradiation. The approach is a radical reaction based on a homogeneous electron transfer between a good electron donor, ferrocene, and a good electron acceptor, NBS/NBP which results in the generation of an imidyl radical from the reduction of the parent structure.\textsuperscript{19} A previous procedure based on the radical initiation/photoirradiation of NBS resulted in the formation of both the imidyl radical and bromine radical which lead to the exclusive deposition of bromine.\textsuperscript{20} Interestingly the data shows ferrocene is on the surface and that both the imidyl and bromine groups are bound to the surface. Nucleophilic substitution studies indicated that the bromine groups could be replaced, for example using succinimide or pentachlorophenol.

3.2 Experimental Procedures:

Freshly prepared Si(111)-H surfaces were used for each of the modifications following the procedure outlined in Chapter 2. Immediately after preparation of the Si(111)-H pieces, they were placed under vacuum on a Schlenk line. De-oxygenated acetonitrile was then added to purified N-bromosuccinimide and ferrocene in separate Schlenk tubes. The solutions, 50 mM, were added simultaneously, drop-wise, by cannula into the Schlenk tube containing the Si(111)-H shard. Upon mixing, the resulting solution immediately turned a dark green colour indicating the formation of the ferricinium cation. After 1 hour in solution, the modified surface was rinsed,
Figure 3-1. Proposed modification mechanism of Si(111)-H surfaces by NBS/ferrocene.

Sonicated, and then rinsed again with acetonitrile and dried under vacuum. This modified surface resulting from the reaction of NBS/ferrocene will be referred to as surface I. A proposed modification mechanism is outlined in Figure 3-1. An electron transfer takes place from the ferrocene to NBS resulting in an imidyl radical, bromine anion, and ferrocinium radical cation. The imidyl radical may then abstract a hydrogen atom from the Si(111)-H surface creating a silicon radical and succinimide. Another imidyl radical could then react with the silicon radical yielding a Si-N type linkage.

Additional study of surface I was undertaken to assess how nucleophilic substitution of the bromine could lead to further modification of the silicon. Two different nucleophiles, succinimide and pentachlorophenol, were used to make mixed layers. These compounds were chosen because of their availability and the presence
of 5 chlorines on the ring should be easily detectable by XPS. For example, succinimide and tetrabutylammonium hydroxide were added to separate Schlenk tubes, dissolved in acetonitrile and then cannulaed into another Schlenk tube containing a surface I modified piece of silicon. After rinsing thoroughly with acetonitrile, sonicating, and rinsing again, the new surface, surface II, was taken for XPS studies. Surface III was prepared in the exact same manner as surface II, however, pentachlorophenol was used as the nucleophile source. Additional exploration of electron transfer initiated organic modification of Si(111)-H was carried out using a different electron acceptor in the form of N-bromophthalimide in a manner similar to surface I.

3.3 Results and Discussion:

Analysis of Surface I was carried out by X-ray photoelectron spectroscopy in order to assess what species may be present on the multilayer surface. Figure 3-2 shows high-resolution XPS data for a surface modified with NBS/ferrocene. Scanning in the Si 2p region yielded four sets of unresolved doublets upon deconvolution with a branching ratio of 2:1 and a spin-orbit splitting of 0.6 eV. The main 2p_{3/2} doublet, located at ~99.7 eV is indicative of bulk silicon. At slightly higher binding energies, ~100.5 eV, there is a second doublet which is attributed to the grafting of bromine to the silicon surface. A third doublet appears at ~102.2 eV and is assigned N-Si from the attachment of the succinimidyl group, while a fourth doublet at ~103.3 eV is attributed to silicon oxide. This may be due to oxide formation, but could also be caused by attachment of the succinimidyl group through the oxygens. Overall these peaks give a first indication that both the succinimidyl and bromine groups are bound to the surface. In the bromine 3d region, the signal could be fitted with one doublet
Figure 3-2. XPS data, binding energy eV scale, of (a) silicon 2p, (b) bromine 3d, (c) nitrogen 1s, (d) carbon 1s, (e) oxygen 1s and (f) iron 2p3/2 regions for a piece of Si(111)-H modified with NBS/Ferrocene.

which has a spin-orbit splitting of 1.0 eV and branching ratio of 3:2.\textsuperscript{22} The doublet has the 3d_{5/2} peak located at \( \sim 69.3 \) eV, is assigned to bromine attached to the silicon surface.\textsuperscript{22,23} This bromine signal may potentially be fitted with two doublets, but further study and experiments would be required to determine the origin of the potential second doublet. Scanning for nitrogen resulted in a signal located at \( \sim 400 \) eV, which is suggested to be N-Si\textsuperscript{24} from the attachment of the succinimidyl group to the surface. Although a signal in the nitrogen 1s region is present, and additional signals may be contained within it, further deconvolution was not attempted due to the lack of resolved peaks. In the carbon 1s region, the main peak is located at \( \sim 285.0 \) eV and assigned to -CH\textsubscript{2}- carbons from the succinimidyl attachment. A little higher in binding energy, a second peak is present at \( \sim 286.6 \) eV corresponding to a N-C...
linkage\textsuperscript{25} and a third peak is resolved at \( \approx 289.0 \) eV. This is assigned to the C=O group.\textsuperscript{26} Oxygen scans showed 2 peaks in the 1s area. The first peak located at \( \approx 532.3 \) eV corresponds to the oxygen region for C=O and Si-O,\textsuperscript{24,26,27} while a small shoulder is present at \( \approx 530.5 \) eV. These results, particularly the bromine and nitrogen scans tend to suggest the successful modification of the Si(111)-H surface.

An additional important observation that was made was the detection of a signal for iron as shown in Figure 3-2(f), with the Fe 2p\textsubscript{3/2} peak located at \( \approx 710.7 \) eV. This indicates that ferrocene is also being incorporated into the structures on surface for the NBP/ferrocene system.\textsuperscript{28} A common “mis-match” that was seen in the carbon 1s XPS scans for all of the surfaces, especially surface I, was the disproportionate relative intensities of -CH\textsubscript{2}- carbons to carbonyl carbons. The addition of ferrocene onto the surface would provide several “extra” carbon-carbon bonds which would make that signal significantly larger than the carbonyl carbon signal. Ferrocene bound to Si(111) surfaces has also been cited a potential candidate for electronic memory storage.\textsuperscript{29}

Subsequent study of surface I by FTIR, Figure 3-3, provided further confirmation of the modified surface. A small, broad signal for a sp\textsuperscript{3} C-H stretch was seen at \( \approx 2966 \) cm\textsuperscript{-1}. This was followed by a clear signal for C=O stretch located at

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{FTIR Spectrum.png}
\caption{FTIR spectrum of surface I.}
\end{figure}
Immediately after the carbonyl signal, there is a medium, broad peak at \( \sim 1527 \text{ cm}^{-1} \) which is attributed to a ferrocene ring mode. \(^{31}\) A fourth peak, attributed to an O-C-C stretch from succinimide is centered at \( \sim 1150 \text{ cm}^{-1} \).

Further analysis of surface I was conducted by atomic force microscopy (AFM). Imaging of the modified surface was conducted in air in contact mode at various times going from freshly prepared to after the sample sat for several days. The results were similar in all cases. In Figure 3-4(a) at a scan size of 4 x 4 \( \mu \text{m}^2 \), the surface looks very rough and there are no terraces visible. However, after scratching the surface, Figure 3-4(b), and then re-imaging, the scratched area can be seen indicating that layers of

Figure 3-4. Contact mode AFM images of a modified surface at scan sizes of (a) 4 x 4 \( \mu \text{m}^2 \), (b) 3 x 3 \( \mu \text{m}^2 \) after scratching the surface, (c) 0.8 x 0.8 \( \mu \text{m}^2 \) inside the scratched area showing atomically flat terraces and (d) a representative line profile illustrating the approximate depth of the multilayers.
molecules have been removed. The scratching force should be sufficient to remove
the molecules, but not so much that the underlying surface is impaired.\textsuperscript{32} Zooming
inside of the scratched area, Figure 3-4(c), clearly shows the atomically flat terraces
of Si(111), which don’t show any visible signs of damage from the scratching. With
the sample sitting for several days in air, this further suggests the successful
modification of the surface because if oxide reformation were to have taken place,
smooth flat terraces would not be visible by AFM. This also implies that the Si-N
bond is stable upon exposure to atmospheric conditions up to a period of a few weeks.
A line profile taken from Figure 3-4(b), is presented in Figure 3-4(d). The drop in
height of ~ 2 nm represents an average value over the range of the line. In all cases
these numbers suggest that multilayers have been formed on the surface bound
species. This is similar to what has been observed in the reduction of diazonium salts
on carbon and silicon surfaces where the reduction proceeds by a radical reaction and
results in the formation of multilayers on the sample surfaces.\textsuperscript{33}

Due to this modification methodology involving radical chemistry, which is known
to be able to branch off in many directions, an exact structure of the modified surface
would be very difficult to determine. Gaussian optimization calculations gave NBS as
a planar molecule. An approximate molecular length of 4.06819 Å was calculated
from midway between the alkane carbons to the bromine atom. Given this length, ~
0.406819 nm vs the depth of the scratched area down to the terraces, ~ 2 nm,
monolayer formation is unlikely. The multilayer formation seen in this work is similar
to what has been observed for the grafting of aromatic diazonium salts on carbon and
silicon surfaces.\textsuperscript{33,34}
The XPS results of surface II are presented in Figure 3-5. Scanning in the Si 2p region, Figure 3-5(a), gave three unresolved doublets, similar in position to surface I. The doublet representing bromine attached to silicon was not present. In the bromine 3d region, there was no peak, which suggests that the substitution did proceed, Figure 3-5(b). The nitrogen 1s area, Figure 3-5(c), yielded a signal similar to what was seen NBS/ferrocene and NBP/ferrocene modified surfaces Si(111)-H surfaces. When looking into the carbon 1s region, the peaks are very similar in position to surface I for the carbonyl, N-C, and -CH2- carbons, Figure 3-5(d).

Further characterization of surface II was done by Fourier transform infrared spectroscopy (FTIR). Figure 3-6 shows FTIR results from a freshly modified surface. There is a small, broad peak, located in the sp3 C-H stretch region. A strong, sharp peak is observed at ~ 1730 cm⁻¹ which represents the C=O stretch of the carbonyl carbons.30 The third peak, located at ~ 1525 cm⁻¹, is of medium intensity, broad and is assigned to a ferrocene ring mode.31 A fourth peak, small and sharp, corresponds to a O-C-C stretch from a succinimidyl group at ~ 1150 cm⁻¹.31
In Figure 3-7, a FTIR spectrum is shown which represents a piece of Si(111) modified for surface III. A strong signal is present for the carbonyl carbon at ~1750 cm\(^{-1}\). The signal for a ferrocene ring mode is present at ~ 1500 cm\(^{-1}\) and provides additional support for the presence of the ferrocene group on the silicon surface. A small, sharp peak is present at ~ 1150 cm\(^{-1}\) and is consistent with a succinimidyl (O-C-C) type structure.
The elemental composition on surface III was studied by XPS and the results are shown in Figure 3-8. Similarly to surface II, there was no signal for bromine which gives a first indication of a successful nucleophilic substitution reaction. Deconvolution of the Si 2p area, Figure 3-8(a) yielded three sets of unresolved doublets with the Si 2p\textsubscript{3/2} components located at ~99.8 eV, ~102.5 eV and ~103.5 eV corresponding to the bulk silicon, Si-N linkages and silicon oxide. Scanning in the carbon 1s region, Figure 3-8(b), shows the expected peaks for -CH\textsubscript{2}- carbons and the carbonyl carbons, at ~285.0 eV and ~289.3 eV.\textsuperscript{25,26} A notable difference between this sample and surfaces I and II is the peak at ~286.5 eV, which is much larger here, than for those surfaces. The peak is in the region for N-C carbons, but also for Cl-C carbons, which is what the large increase in strength is attributed to.\textsuperscript{35} Figure 3-8(c)

![XPS spectra](image)

**Figure 3-8.** XPS spectra, scale in binding energy eV, from surface III showing the (a) S 2p area, (b) C 1s area, (c) N 1s area and (d) Cl 2p area.
shows a signal from the N 1s region giving a further indication that the imidyl group is present on the sample surface. In Figure 3-8(d), there is a clear signal for chlorine, with a branching ratio of 2:1 for the Cl 2p\textsubscript{3/2} and Cl 2p\textsubscript{1/2} peaks and a spin-orbit coupling of \(~1.6\) eV.\textsuperscript{36} The combined XPS signals provide good evidence that pentachlorophenol is a suitable candidate for nucleophilic substitution of the bromine groups from surface I.

Additional XPS data comparing surfaces I and III with survey scans is presented in Figure 3-9. Both scans show the Fe 3p peak at \(~53\) eV, which gives further support for ferrocene being present on the surface. For surface I, the red line, clear signals can be observed for the bromine 3d and 3p areas. The corresponding areas on surface III, the blue line, do not show these peaks. Concurrently on surface III, clear signals are seen for the chlorine 2p and chlorine 2s regions, while the same area on surface I, shows no signals at all. Also of interest are the C 1s signals for both surfaces.

![XPS survey scans](image)

**Figure 3-9.** XPS survey scans, scale in binding energy (eV) for surface’s I (red) and III (blue) showing differences between the C 1s, Br 3p/3d and Cl 2s/2p regions.
surfaces which by their differences in shapes indicates that multiple forms of carbon are present. When considering the relative intensities of the two sets of silicon signals between the samples, Si(111)-NBS/Fc’s Si 2p signal appears to be stronger. This however is likely due to presence of the much larger pentachlorophenolate group (compared to a bromine atom) on surface III which would certainly cover more area on the silicon surface and potentially block some of the silicon electrons from reaching the XPS signal detector.

Further exploration of electron transfer initiated organic modification of Si(111)-H was carried out using a different electron acceptor in the form of N-bromophthalimide. XPS studies were carried out on a piece of Si(111)-H modified with NBP/ferrocene, Figure 3-10, to see if similar signals would be observed as for the NBS/ferrocene system. In Figure 3-10(a), a survey scan for the bromine 3s, 3p and 3d regions is shown. Clear signals are seen for each which gives a good indication that bromine has been successfully deposited on the silicon surface as was suggested for surface I. Scanning in the carbon 1s region, Figure 3-10(b), yielded a signal which could be fit with 3 peaks upon deconvolution. The main peak is located at ~285.0 eV and is attributed to the -CH$_2$- groups from succinimidyl attachment. A second peak,

![Figure 3-10. XPS spectra from a piece of Si(111)-H modified with NBP/ferrocene showing (a) Br survey scan, (b) C 1s region and (c) N 1s region.](image)

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representing nitrogen attached to carbon atoms, is located at a slightly higher binding energy of \( \sim 286.5 \text{ eV} \).\(^{25}\) A third peak, represents a C=O carbon at \( \sim 289.1 \text{ eV} \)\(^{26}\) and gives an indication that the phthalimide group is on the silicon surface. This is further evidenced by the signal in the nitrogen 1s region at \( \sim 400 \text{ eV} \), attributed to N-Si from phthalimidyl attachment, which is in a similar position to the one observed for the same area in surface I, Figure 3-10(c).

Visualization of the NBP/ferrocene modified surface was studied by AFM imaging as shown in Figure 3-11. Scratching the surface, Figure 3-11(a), was again required to see the underlying terraces, the outlines of which are visible in the scratch area, suggesting that the surface modification could be forming multilayers similarly to what was observed for surface I. Zooming inside the scratched area, Figure 3-11(b) clearly shows the flat terraces, giving further credit to NBP/ferrocene as a suitable means to modify Si(111)-H surfaces.

**Figure 3-11.** AFM images, of a piece of Si(111)-H modified with NBP/ferrocene, after scratching at scan sizes of (a) 1.83 x 1.83 \( \mu \text{m}^2 \) and (b) 0.8 x 0.8 \( \mu \text{m}^2 \).
3.4 Summary:

In summary, electron-transfer initiated organic modification of Si(111) has been shown to be a reproducible and viable method for surface modification, which does not require irradiation, heat or UHV conditions. Using N-bromosuccinimide and ferrocene as a model system, XPS confirmed the presence of both the succinimidyl and bromine groups on the silicon surface. FTIR spectroscopy further confirmed the successful modification of the surface as signals for C=O and ferrocene were clearly observed. AFM imaging in contact mode indicated polymerization/multilayer formation on the surface took place as atomically flat terraces could be readily seen after scratching the surface. Both succinimide and pentachlorophenol were successfully used as nucleophiles to substitute bromine resulting in different mixed layers. Other systems involving a good electron donor and a good electron acceptor, such as NBP/ferrocene also allowed for modification of the Si(111)-H surface. In theory, the use of a large number of nucleophiles should allow for attaching a wide variety compounds to the sample surface, which is important as it could lead to a new means of fashioning electronic devices.

3.5 References:


Chapter 4: Study of Thiobisphthalimide and Dithiobisphthalimide Adsorbed on Polycrystalline Gold and Au(111)

4.1 Introduction:

Sulfur transfer agents are known in synthetic chemistry as they provide a source of sulfur that can be utilized in a non-aqueous environment, which is important for moisture-sensitive chemistry.\(^1\) Two well known examples of these are thiobisphthalimide and dithiobisphthalimide.\(^2\) These compounds were first prepared from phthalimide and potassium phthalimide using both sulfur monochloride, S\(_2\)Cl\(_2\), and sulfur dichloride, SCl\(_2\), as sulfur sources.\(^3\) An advantage the phthalimide compounds possess over the S\(_n\)Cl\(_2\) material is they do not have a foul odor associated with them. Although they are not as reactive as other known sulfur transfer agents such as the corresponding imidazole and benzimidazole analogues, they do possess and advantage in that they have better stability.\(^2\) Thiobisphthalimide, although the least reactive, is a suitable candidate for unsymmetrical substitution.\(^2\) Previously thiobisphthalimide has been reacted with R-SH compounds to produce materials containing R-S-S-Phth linkages.\(^4\) This material has also been used as a sulfur source for linking two peptide chains by a trisulfide bridge.\(^5\) Dithiobisphthalimide has been utilized in the synthesis of derivatized iron carbonyl complexes and platinum(IV) complexes.\(^6\) The work of Cava’s group showed that a mixture of anthrone and dithiobisphthalimide in dimethylformamide with pyridine yielded direct crystallization of monothioanthraquinone.\(^7\) A common advantage of both S\(_n\)Phth\(_2\) compounds is they have good leaving groups in the phthalimides, which have been suggested to recombine after sulfur ejection in organic synthesis.\(^2\) Although both thio and dithiobisphthalimide are well established in synthetic chemistry, they have not
before been used as sulfur precursors to study S-Au interactions. This should provide an excellent oppurtunity to compare these studies from a non-aqueous environment to previous results obtained using traditional sulfur precuresors in aqueous solutions (sodium sulfide)\(^8\) or gas phase (sulfur, sulfur dioxide)\(^9,10\) environments.

Thio and dithiobisphthalimide, Scheme 4.1(a) and 4.1(b) were dissolved in acetonitrile and used as new precursors for the deposition of sulfur on gold from solution. The modified surfaces were analyzed by several techniques such as X-ray photoelectron spectroscopy (XPS), electrochemistry and scanning tunnelling microscopy (STM). The reported results indicate that the sulfur deposition is an efficient and fast process and that high coverages can be reached very quickly. Consecutive high resolution STM imaging in air allowed for the direct observation, of the mobility of the rectangular structures as individual units and the binding of the sulfur rectangles on different sites on the gold surface within the same area. The reversible association/dissociation of these rectangles was also seen. The nature of these structures is highly debated in the literature\(^10,11-14\) and the present work provides new insights into their nature using a new sulfur precursor in an organic solution as opposed to the traditional sulfur precursors in aqueous solutions. Our results tend to suggest that these rectangular structures are not a complex AuS phase, but rather sulfur adlayers adsorbed on the gold surface.

Scheme 4.1. (a) Thiobisphthalimide and (b) Dithiobisphthalimide.
4.2 Experimental Methods:

Modification of both polycrystalline gold and Au(111) on mica surfaces was carried out under atmospheric conditions using two different methods. One method was thermodynamic modification by way of solution deposition. Gold slides were dipped into 1 mM and 10 mM solutions of thiobisphthalimide prepared from freshly distilled acetonitrile. Deposition times ranged from a few seconds to several hours. The modification of gold using dithiobisphthalimide was carried out using 1 mM and 3 mM solutions in acetonitrile for a few minutes to a few hours.

The other method was electrochemical modification using reductive cyclic voltammetry experiments. Electrochemical studies were conducted in a three electrode electrochemical cell with a solid gold electrode as the working electrode, platinum foil as the counter electrode and a silver wire as the quasi reference electrode. The solution was 1 mM thiobisphthalimide in acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. Dithiobisphthalimide was also studied in this manner using similar conditions.

In all cases, samples were rinsed thoroughly with acetonitrile and dried under a gentle stream of nitrogen. X-ray photoelectron spectroscopy (XPS) was used to assess the elemental composition of the modified surfaces. Scanning tunneling microscopy (STM) was conducted in air on Au(111) on mica to visualize the sample surfaces.
4.3 Results and Discussion:

Cyclic voltammetry (CV) studies were primarily used as a tool in order to assess the thermodynamic deposition of thiobisphthalimide on gold. Figure 4-1 shows the results from thermodynamic modification of a solid gold electrode. When there was no waiting time for the gold electrode in the cell, the reduction potential was determined to be -1.21 V vs SCE, using the ferrocene/ferrocenium couple as an internal standard. The shape of the reduction peak is very sharp which indicates that a chemical process is taking place along with the reduction of the initial compound at the electrode surface. When the electrode was left in the solution for 2 minutes, and then the CV was run, there was almost no change in the reduction peak potential. The peak is almost, but not quite as strong, which indicates that during the waiting period, there were no signs of any efficient/substantial modification of the electrode surface. A waiting time of 4 minutes produced much the same result, with a slightly reduced peak intensity, but

![Figure 4-1. Cyclic voltammograms after thermodynamic modification of a solid gold electrode using 1 mM thiobisphthalimide in acetonitrile at a sweep rate of 0.2 V/s.](image)
shape and position virtually identical. The trend continued with modification times of 6, 8 and 10 minutes. This data shows that even if there is modification, it is not significant.

When considering electrochemical modification of a solid gold electrode with thiobisphthalimide, a stark contrast was observed in comparison to the thermodynamic modification, as seen in Figure 4-2. After a 10 minute wait in solution, the CV scan looks much the same as if there were no waiting time at all. However, when a second CV was run, after purging, without removing the electrode from the cell and cleaning it, there was a noticeable shift in the reduction peak to more positive potentials, \( \sim -1 \) V vs SCE. This indicates that the electrochemical modification proceeds more efficiently than the thermodynamic modification and in a different manner.

![Cyclic voltammograms of 1 mM thiobisphthalimide, 0.2 V/s, using a solid gold electrode and 0.1 M TBAHFP as the supporting electrolyte illustrating the effect of electrochemical modification.](image)

**Figure 4-2.** Cyclic voltammograms of 1 mM thiobisphthalimide, 0.2 V/s, using a solid gold electrode and 0.1 M TBAHFP as the supporting electrolyte illustrating the effect of electrochemical modification.
Additional electrochemical study was done by way of oxidative stripping voltammograms to determine the extent of modification of the electrode surface from solution deposition. The modification of a solid gold electrode was done from a 1 mM solution of thiobisphthalimide in acetonitrile. Cyclic voltammetry studies were conducted in a 0.5 M H₂SO₄ solution, the results of which are presented in Figure 4-3(a). The black line representing the bare gold electrode (clean) will serve as a reference point. After a modification time of one minute, there is only a very slight change in the oxidation peak indicating an unsubstantial modification of the sample surface. Deposition times of two minutes to five minutes show very similar results to the one minute sample. With 10 minutes there is a small increase from the shorter modification times, but overall very little from the clean gold electrode. Interestingly, when a single CV sweep was run under the same conditions as in Figure 4-1 with no waiting, and then an oxidative stripping

![Figure 4-3](image)

**Figure 4-3.** Oxidative stripping voltammograms, 0.2 V/s, of a polycrystalline gold electrode in 0.5 M H₂SO₄ after (a) thermodynamic modification with 1 mM thiobisphthalimide in acetonitrile and (b) electrochemical modification with 1 CV as in Figure 4-1.
voltammogram was run in 0.5 M H₂SO₄, a significant change was observed, Figure 4-3(b). The oxidative peak for the CV modified gold is substantially larger than for a 10 minute thermodynamic modification of gold. This indicates that electrochemistry is more efficient at modifying gold with thiobisphthalimide than thermodynamic modification is. The apparently slow thermodynamic modification of gold may be partially explained by the fact that reduction of thiobisphthalimide is known to first generate dithiobisphthalimide before being further reduced.¹⁵

X-ray photoelectron spectroscopy studies were conducted in order to assess what species were present on the modified gold surface. A piece of Au(111) on mica was modified with 1 mM thiobisphthalimide for a period of 1 hour, given that the oxidative stripping voltammograms indicated unsubstantial modification at short times. Scanning in the sulfur 2p region, Figure 4-4(a), showed the presence of a peak, albeit weak, which yielded two unresolved doublets upon deconvolution. The first doublet has its S 2p₃/₂ component located at ~ 161.1 eV and is assigned to monoatomic sulfur bound to the gold surface.⁹ A second doublet appears with its S 2p₃/₂ at slightly higher binding energies of ~162.2 eV, and is attributed to polymeric sulfur species on the surface.¹⁴ In order to get a better signal, another sample was modified for a period of 1 hour, but a higher

![Figure 4-4. XPS spectra for pieces of Au(111) on mica modified with thiobisphthalimide in the (a) S 2p area (1 mM), (b) S 2p area (10 mM) and (c) N 1s area (10 mM).](image)
concentration of 10 mM of thiobisphthalimide was used. XPS studies of the S 2p region indicated a signal, Figure 4-4(b), which could be deconvoluted into two sets of unresolved doublets, at binding energies very similar to the ones obtained for the 1 mM sample. There was no signal at all for nitrogen, Figure 4-4(c) which indicates the cleavage of both phthalimide groups during the modification process.

Additional analysis of the 10 mM thiobisphthalimide modification of Au(111) on mica for one hour was done by STM imaging. In general, images of sulfur on gold from this compound were found to be considerably more difficult to obtain then images from dithiobisphthalimide or thiobis(hexamethyldisilazane) and hexamethyldisilathiane from Chapter 6. The image present in Figure 4-5 is noisy, but does show some structural details in the middle portion of the image. The tunneling current was 1.55 nA and the bias voltage was 2.0 V. In the circled area, a rectangular structure can be made out, which is assigned to the presence of polymeric sulfur species. Interestingly on the same plane, a

![Figure 4-5](image)

**Figure 4-5.** STM image, at a scan size of 10 x 10 nm² of a piece of Au(111) on mica modified for 1 hour with 10 mM thiobisphthalimide, at a scan speed of 3.3 ln/s.
lone sulfur atom is present as indicated by the arrow. This is important because it clearly shows the presence of two distinct forms of sulfur, monomeric and polymeric, in the same plane. These results are in excellent agreement with the XPS data from Figure 4-4(b).

Cyclic voltammetry (CV) studies were further utilized in order to assess the thermodynamic modification of Au using dithiobisphthalimide and to provide a direct comparison to the thiobisphthalimide results. A series of cyclic voltammograms after solution deposition with 1 mM dithiobisphthalimide in acetonitrile are presented in Figure 4-6. The initial voltammogram with no waiting in the cell gave a very sharp reduction peak, similar in shape to thiobisphthalimide, but at a more positive potential of ~ -0.89 V vs SCE. After cleaning the electrode and then leaving it in the cell for two minutes, a noticeable change can be seen in the voltammogram. The reduction

![Figure 4-6](image-url)

**Figure 4-6.** Cyclic voltammograms, 0.2 V/s, using a solid gold electrode after solution modification with 1 mM dithiobisphthalimide.
peak has been shifted to a more positive potentials and the apex of the reduction peak is more round than it was before. This indicates that the electrode is being modified substantially after a period of sitting in solution for only two minutes. A similar shift is observed when leaving the electrode for four minutes before running the CV, where the reduction potential is now located at -0.72 V vs SCE. The shift in reduction potential with waiting time begins to slow down after this point indicating the electrode is approaching maximum coverage.

Additionally, electrochemical modification of a solid gold electrode was carried out by running successive CV scans without removing the electrode from the cell and cleaning in between. In Figure 4-7, a series of 6 CVs are shown with only a brief pause in between for purging the solution. The initial scan has a very sharp reduction peak at -0.89 V vs SCE. When the second scan is run however, there is a reduction of peak potential and a large change in peak size. This is an indication that with this compound, one reductive

![Graph](image)

**Figure 4-7.** Electrochemical modification of a solid gold electrode using 1 mM dithiobisphthalimide in acetonitrile with 0.1 M TBAHFP, sweep rate 0.2 V/s.
Figure 4-8. Consecutive reductive CVs, 0.2 V/s, of 1 mM dithiobisphthalimide using a solid gold electrode with a waiting time of 10 minutes in solution.

sweep is enough to substantially modify the electrode surface and that the electrochemical modification of gold with dithiobisphthalimide proceeds more efficiently and in a different manner than the thermodynamic modification. The electrode activity at the reduction peak decreases very little after this point up until the 6th scan. There is almost no reduction peak at all as the gold surface is nearly completely saturated with sulfur at this point.

In order to assess the efficiency of thermodynamic modification of the gold electrode by dithiobisphthalimide, consecutive CVs were run after a solution deposition time of 10 minutes as seen in Figure 4-8. After a 10 minute wait, the reduction peak of the compound was seen at -0.65 V vs SCE. Very interestingly, there were two major observations made after the 2nd scan. The first was there was little change in the reduction potential of the compound. The second was that a large reductive desorption peak was
seen at ~ -2 V vs SCE. This peak indicates sulfur is being removed from the electrode surface. During the 3\textsuperscript{rd} scan, the sulfur desorption peak is also observed but of a lower intensity, and the main reductive peak at -0.65 V vs SCE is small. By the 5\textsuperscript{th} scan, there is very little change in the CV suggesting that the electrode surface is nearing maximum coverage. This behavior also shows that the solution deposition of dithiobisphthalimide on gold modifies the electrode in a different way as opposed to the strictly electrochemical reduction of the compound.

Solution deposition of dithiobisphthalimide was further studied using oxidative stripping voltammograms in a 0.5 M H\textsubscript{2}SO\textsubscript{4} solution. The deposition solution was at a concentration of 3 mM in acetonitrile. Figure 4-9 shows a typical oxidative stripping wave of a modified solid gold electrode. The two voltammograms correspond to the first (blue line) and second (green line) scan in a 0.5 M aqueous H\textsubscript{2}SO\textsubscript{4} solution of a gold electrode.

![Figure 4-9](image)

**Figure 4-9.** Oxidative cyclic voltammograms, 0.2 V/s, in 0.5 M H\textsubscript{2}SO\textsubscript{4}, 1\textsuperscript{st} and 2\textsuperscript{nd} scan after solution deposition using 3 mM dithiobisphthalimide with an inset showing surface coverage as a function of depositions time.
electrode modified in a dithiobisphthalimide (3 mM in CH$_3$CN) for 7 minutes. The oxidation peak in the first scan is significantly larger than that of the second scan, which is similar to the one observed for bare gold. This indicates the complete removal of the deposited sulfur from the electrode surface during the first oxidative scan, and allows determination of the sulfur coverage of the gold electrode considering the involvement of 6 electrons per sulfur atom.$^{16}$ The inset to Figure 4-7 shows the sulfur coverage ($\theta$) as a function of the modification time in minutes, obtained by repeating the same experiment for different modification times. The electrode is cleaned by polishing and sonication with ethanol, and cycling in sulfuric acid after each stripping experiment. The electrochemical data shows that the deposition process occurs very quickly, and at longer modification times very high coverages, exceeding 1.0 ML, can be reached.

X-ray photoelectron spectroscopy studies were conducted in order to see what species were present on the modified gold surface. The XPS data of a modified Au (111) substrate using a solution of dithiobisphthalimide in acetonitrile is shown in Figure 4-10. A clear sulfur signal in the S 2p region is observed. This signal can be fitted with three unresolved doublets that have their S 2p$_{3/2}$ components located at ~161.2 eV, ~162.3 eV and ~163.7 eV. The first doublet has been assigned to monoatomic sulfur adsorbed on gold.$^{9,14}$ The second doublet has been interpreted as either a complex AuS phase,$^{13}$ sulfur,$^{9}$ or polymeric sulfur species.$^{14}$ The third doublet, which is seen on occasion, has been previously assigned to multilayer formation on the gold surface.$^{14}$ No peak is observed for nitrogen in the N 1s region, Figure 4-10(b), which indicates the ejection of the phthalimide groups. Only trace amounts of carbon and oxygen signals were seen and they are attributed to air exposure.
Figure 4-10. XPS spectra of a piece of gold on mica modified with dithiobisphthalimide showing the (a) S 2p region and the (b) N 1s region.

Scanning tunneling microscopy imaging was done in order to see what patterns of sulfur may be present on the modified surface. Sequential high resolution STM imaging provides more insights into the nature of the rectangular species. Figure 4-11, shows STM images of a Au (111) surface modified using a 3 mM dithiobisphthalimide solution in acetonitrile for 7 minutes. These images show interesting features that provide information about the structure of the modified surface and were obtained using tunneling conditions of 1.55 nA and 2.0 V. While the majority of the rectangles are perfectly aligned with each other yielding parallel rows of rectangles, alignment mis-matches can be clearly seen, as illustrated by the proposed model representing Figure 4-11(a). The rectangles pack differently as the lower side of the rectangles above area C are parallel to the upper side of the rectangles on either side of area C leaving a vacancy between the two rows. This could much more easily be explained by structures packing on a surface. Regardless of whether the S is adsorbed on a non-reconstructed (directly) or a reconstructed surface (through adatoms), it is important to note that in the illustration this
alignment mis-match results in a change in the adsorption sites on the Au surface, going from an adsorption involving six hollow sites and two bridge sites to an adsorption involving six hollow sites and two atop sites. Both of these configurations have been previously suggested. An additional important note is that a bright spot is observed within vacancy B suggesting the presence of adsorbed S in a different form than that of the rectangular structures. The height profiles support this as similar heights are observed for the height profile going through the bright spot in vacancy B, Figure 4-12(a) and (b), and going through a step as well, Figure 4-12(a) and (c). A height around 0.14 to 0.15 nm is observed in good agreement with what has been previously reported for sulfur.

**Figure 4-11.** STM images at a scan size of 6 x 6 nm², 1.55 nA and 2.0 V, taken in the order a and then b, in air of a modified Au (111) surface with dithiobisphthalimide (3 mM in CH₃CN for 7 minutes) and their corresponding proposed models.
Figure 4-12. (a) STM image of the S modified Au (111) surface (b) height profile along line A, going through bright spot and (c) line B, going through a through the step.

Additionally, there is a change in the vacancies that is observed going between the two images, Figure 4-11(a) and Figure 4-11(b) which are in the same area, and taken within 3 minutes of each other. It is evident from the two images that two rectangular structures have moved down to fill the lower vacancy (C), as shown in the illustrations in Figure 4-9. The vacancy at the top of the image (A) and the vacancy created by the mobile rectangles (C'), which is now aligned with the longer vacancy at the left of the image (B), are consequently only separated by two rows. The initial vacancies A and C were separated by three rows. This mobility of the individual rectangles has not been previously observed before. These movements are easier to explain by the suggestion that the rectangular structures on the surface correspond to sulfur adlayers and not a complex AuS phase. According to this view, these rectangular structures are formed through interactions between mobile sulfur atoms on the gold surface, that should be associated with a decrease in the interaction between sulfur and gold. The lower mobility of the rectangles compared to sulfur atoms may be interpreted as conflicting with the weaker
interaction with gold. The mobility of the rectangular structures observed in Figure 4-11 illustrates that this is not the case and that the observed stability of the rectangular structures could be due to their efficient packing through adsorbate/adsorbate interactions. Regardless of whether the STM is sensing the local density of states correlating to atomic nuclei positions or bonds between atoms does not change the fact that rectangles moved as individual units.

These results are further supported by Figure 4-13, which shows real-time STM imaging of the right lower corner which is a layer edge. Images a, b and c are scans of the same area taken in sequence within 1 ½ minutes of one another. The vacancy A seen in the first three images provides a reference to understand the changes taking place in the

![Figure 4-13. Real-Time STM Imaging, 1.55 nA and 2.0 V, in the order (a), (b), and (c), of a S modified Au (111) surface in air close to a layer edge showing the dynamic changes of the sulfur adlayer at a scan size: 6.5 x 6.5 nm², and (d) STM image centered at the lower right area of the other images.](image-url)
rest of the imaged area. In Figure 4-13(a), rectangular structures are observed in all the of the image with the exception of the lower right side. Figures 4-13(b) shows a wider disordered area and the appearance of more vacancies, including vacancy B. The appearance of this vacancy B is important as it shows that the rectangular structures above it also moved confirming the mobility of these rectangular structures observed in Figure 4-11. The formation of vacancy B also results in an alignment defect of the rectangular structures as seen by the blue arrow in Figure 4-13(c). Comparing the areas within the blue rectangles in Figure 4-13(a) and Figure 4-13(c), shows that these changes are real and not artifacts, confirming the mobility of the rectangular structures. Another important observation from Figure 4-13(c) is that some rectangles are formed once again. In certain areas the reformation of the rectangular structure is done in a different way than in Figure 4-13(a) as shown by the single row of rectangles separated from the rest of the rows by a new vacancy (C). There is also a small "zig-zag" pattern that is formed at the top of this isolated new row, circled area in Figure 4-13(c), that suggests the potential formation of other forms of S. The noisy area in Figure 4-13(b) reflects the mobility of the atomic structure resulting from the dissociation of these rectangular structures. This mobility leading to unresolved images in air is well known.\textsuperscript{10} Figure 4-13(d) is taken few minutes later and is a scan centered at the lower side area of the previous images (Figure 4-13a-c) to show the edge of the adsorbed layer. The dynamic nature of the sulfur modified Au surface is confirmed as a larger non-ordered area is once again seen. This data shows that the sulfur modified gold surface is dynamic, and that the rectangular structures formed by interaction of sulfur atoms can dissociate and reform. This is also supported by XPS data, Figure 4-10(a) as well as previous studies showing the
coexistence of sulfur signals corresponding to both atomic and polymeric forms even at high sulfur coverage.\textsuperscript{8,9,14} This coexistence of different structures has been previously observed by normal incidence X-ray standing wavefield absorption (NIXSW) experiments.\textsuperscript{13} The association/dissociation reversibility that was directly observed in this work by STM in air, has also already been suggested based on potential control experiments in electrolytic solutions.\textsuperscript{12,16} The formation of trimers and tetramers through interactions of adsorbed sulfur atoms has previously been observed.\textsuperscript{16} The reversibility can be explained by a dynamic sulfur adlayer on gold, where S atoms can associate to form various structures. This dynamic nature is based on an equilibrium between S/Au and S/S interactions at the edge of the adsorbate layer. In SAMs these two types of interactions involving the metal surface and the adsorbed molecule are crucial.

Considering these and the images reported in previous studies of the rectangular structures, it is important to note that while the rectangle’s dimensions and periodicity are similar, the alignment is not always the same. The rectangular structure is general, however the placement of the rectangles towards one another differs between the parallel as observed in this work and in others,\textsuperscript{8,11,14} the staggered,\textsuperscript{17} the mixed (with both parallel and staggered alternating)\textsuperscript{10,11} and the quite random\textsuperscript{8,11,14} as illustrated by Figure 4-14. These are indications that the rectangles are isolated units rather than part of a uniform phase. An important note is that even if the rectangular structures have been widely debated, other phases have also been obtained for both the sulfur and selenium deposition on different surfaces.\textsuperscript{16,18-21} A dynamic sulfur adlayer involving a reversible association/dissociation of sulfur atoms to form different structures could explain these different observed phases.
The deposition mechanism using thio and dithiobisphthalimide is still not understood. The mechanism could be intuitively considered as involving an initial physisorption on gold involving both sulfur atoms in the initial precursor followed by, or concomitant with, the cleavage of both S-N bonds. In organic chemistry however, dithiobisphthalimide has been shown to transfer a single sulfur atom resulting in a combination of the other fragments to yield thiobisphthalimide. Work is underway to elucidate the details of the involved mechanism in this deposition process using both compounds.

4.4 Summary:

In summary, thiobisphthalimide has been shown to modify gold surfaces both from electrochemical deposition and solution deposition. Electrochemical modification of a
solid gold electrode was shown to be more efficient than thermodynamic modification. XPS data indicated a signal for sulfur, but none for nitrogen, suggesting the cleavage of the phthalimide group at some point during the modification process. STM imaging was able to identify the presence of both monomeric and polymeric sulfur species on the Au(111) surface. The deposition of sulfur on gold using dithiobisphthalimide was found to be much more efficient than using thiobisphthalimide, and evidence has clearly been established for the modified surface using electrochemistry, cyclic voltammetry, XPS, and STM. The modification was carried out in an organic solvent, acetonitrile, providing an opportunity to study the S/Au interaction in environments similar to those usually used for SAM formation. The electrochemical and XPS results indicate that the adsorption of sulfur onto the gold surface occurs quickly. Real-time STM imaging provides evidence for the mobility of the sulfur rectangular structures as independent units. They also demonstrate a reversible association/dissociation behavior in air and at room temperature. The results are much more consistent by these rectangular structures being explained as sulfur adlayers on the gold surface rather than a complex AuS phase. Whether the structure is directly adsorbed on the non-reconstructed gold or involves Au adatoms still needs to be investigated.

4.5 References:


Chapter 5: Gold Catalyzed Reduction Aromatic Sulfonyl Phthalimides to Sulfur

5.1 Introduction:

The effects of sulfur interaction with metals is an important area of study owing to the direct impact on several areas, including catalytic removal of carbon monoxide and nitrogen monoxide from automobile exhaust, luminescence and photonic displays (Mn doped ZnS), semiconducting nanocrystals (PbS) and environmental chemistry. Gold is a common metal to study these interactions and one of the most debated questions in this field has been what the rectangular structure observed at high sulfur coverage corresponds to, a complex AuS phase or sulfur adlayers. Sulfur dioxide (SO$_2$) in particular has received a lot of attention as SO$_2$ is a known air pollutant and contributor to acid rain. Both polycrystalline gold and single crystal Au(111) are known to interact weekly with SO$_2$ gas (relative to the dosing quantity) resulting in small amounts of sulfur-oxygen bonds being broken. Sulfur dioxide will form physisorbed layers on Au(111) at temperatures of about 100 K, chemisorbed SO$_2$ at 120 K, but by heating a little further to 180 K, the sulfur signal disappears altogether. The majority of SO$_2$ molecules will desorb from the surface of gold intact at room temperature. In the small amount that does adsorb, loss of oxygen from adsorbed SO$_2$ is thought to occur via an abstraction reaction with excess SO$_2$ forming SO$_3$ or from abstraction with CO. Copper on the other hand will readily dissociate SO$_2$ at room temperature to sulfur, oxygen and sulfur trioxide. When gold and copper nanoparticles are dispersed on metal oxide supports, the catalytic performance at dissociating SO$_2$ of the resulting system is significantly improved. This increase has in part been attributed to low coordination number metal atoms from density
functional calculations. In the gas phase, SO$_2$ from hexavalent sulfur compounds has been shown to migrate via different fragmentation pathways. Sulfonamides, which constitute an important class of medicinal drugs, and sulfonylamines eliminate SO$_2$ entirely from the parent compound through rearrangements caused by collision induced dissociations or thermal transformations. This has been monitored by tandem mass spectrometry. The formation of a positive charge on the aromatic ring, enhanced by electron withdrawing groups present at the para or ortho positions on the aromatic ring, helps to facilitate the removal of the SO$_2$. An important note is that the removal of SO$_2$ from these compounds occurs after ionization to the gas phase. Alternatively, flash vacuum pyrolysis can require very high temperatures, 600°C for the decomposition of N-methylsulfonyl phthalimide for example, in order to eliminate sulfur dioxide from the parent material. Compounds in which sulfur contains six bonds present an intriguing prospect of study in relation to their interaction with metal surfaces.

In this work, we present interesting findings in relation to the interaction of hexavalent sulfonyl phthalimide compounds with both polycrystalline gold and Au(111) through solution deposition at room temperature. Initially we studied these compounds using XPS to determine elemental composition on the sample surface. For oxidized sulfur compounds, such as SO$_2$, and SO$_4$, the S 2$p$ signal is expected at a binding energy of $\sim$ 168 eV.

The adsorption of aromatic sulfonyl phthalimides on gold was studied using p-iodo, p-methoxy, and p-fluorobenzenesulfonyl phthalimide, Scheme 5.1(a)-(c). Our key finding is the decomposition of the compounds on the surface, leaving sulfur bound to the surface with its six chemical bonds broken. X-ray photoelectron spectroscopy (XPS) results show that a sulfur signal is seen on the gold surface, but
Scheme 5.1. (a) p-iodo, (b), p-methoxy and (c) p-fluoro benzenesulfonyl phthalimide.

not at ~168 e.v. which is expected for oxidized sulfur compounds. High-resolution scanning tunneling microscopy (STM) studies indicate several important findings. From the p-iodo compound multiple etch-pit formation is observed where modification can be observed on both the inside and outside of the pit. Studies of the p-methoxy compound showed the dynamic and independent nature of the rectangular structures from two sections of rectangles within close proximity to one another. STM imaging of a p-fluoro modified clearly illustrated (i) new dense sulfur formations, (ii) dynamic rectangular structure changes and (iii) a new 2:1 adsorption pattern, all of which are consistent with sulfur deposition.

5.2 Experimental Methods:

The first of this series of compounds that was analyzed was p-iodobenzenesulfonyl phthalimide in tetrahydrofuran (THF). A piece of polycrystalline gold was modified for various times going from a few minutes to a few days in an argon purged Schlenk tube containing a 1 mM solution. After this time, the samples were removed, rinsed thoroughly with freshly distilled THF, and dried under a gentle stream of nitrogen. A piece of Au(111) on mica was modified in a similar fashion for STM studies. Similar
methods were followed for the modification of gold by p-methoxybenzenesulfonyl phthalimide and p-fluorobenzenesulfonyl phthalimide. Acetonitrile was used as the solvent for p-methoxybenzenesulfonyl phthalimide and a mixture of THF/MeOH (50:50) was used for p-fluorobenzenesulfonyl phthalimide.

5.3 Results and Discussion:

Figure 5-1 shows XPS results of polycrystalline gold modified with 4-Iodobenzenesulfonyl Phthalimide. In the sulfur 2p region, Figure 5-1(a) there are two unresolved doublets. The first, with the S 2p$_{3/2}$ component at a binding energy of ~161.2 eV corresponds to monoatomic sulfur adsorbed on the gold surface.$^{20}$ In the second doublet, the S 2p$_{3/2}$ is located at ~162.0 eV which suggests the formation of polymeric sulfur species,$^{21}$ but also corresponds to the known position for a thiolate-gold bond.$^{22}$ At much shorter modification times, 10 minutes, 1 hour and 1 day, the XPS data for the S 2p region did not show any signs of oxidized sulfur. With the absence of a signal at ~168 eV for this time period, and the lack of an observed signal

![Figure 5-1. XPS spectra of p-iodobenzenesulfonyl phthalimide adsorbed on gold showing the (a) S 2p region and (b) I 3d region, after a modification of 3 days.](image-url)
in the N 1s region, it is likely that at least 5 of the original 6 chemical bonds to sulfur have been broken. In the iodine 3d region, Figure 5-1(b), there is a clear signal which is very interesting. The peaks show an expected 3:2 branching ratio and are positioned at ~618.8 eV for the 3d5/2 component and ~630.4 eV for the 3d3/2 component. This could be the result of the aromatic fragment of the parent compound binding directly to the gold through iodine as has been demonstrated for the self-assembly of (4-iodophenyl)phenyl phosphinic acid, but may also arise from p-Iodobenzene thiolate being adsorbed on the surface.\textsuperscript{23}

Imaging of the sample surface was done under ambient conditions after modifying a piece of Au(111) on mica with p-iodobenzenesulfonyl phthalimide for a period of three days. Tunneling conditions used to image the modified surface were 0.400 nA

Figure 5-2. STM images, 0.4 nA and 0.1 V, of Au(111) on mica modified with p-iodobenzenesulfonyl phthalimide at a scan size of (a) 100 x 100 nm\(^2\), (b) 60 x 60 nm\(^2\) and (c) 20 x 20 nm\(^2\) showing features consistent with sulfur deposition, and line profiles (d) \(\Rightarrow\) (f) corresponding to the three images.
for tunneling current and 0.1 V for the bias voltage. STM studies were conducted with a freshly etched tungsten wire tip, electrochemically sharpened in sodium hydroxide.

In Figure 5-2(a), a large scale STM image is shown. Relatively large flat areas can be observed along with larger sized etch-pits in the left hand side of the image, and small etch-pits on the right hand side of the image. These etch-pits are similar to what has been previously observed for thiol modified gold.24 This is also similar to what has been reported for sulfur on gold systems where it was suggested that the formation of the “vacancy islands” could be due to Ostwald ripening.7 Ostwald ripening refers to a process in liquid or solid solutions where small crystals and/or particles are present along with larger ones. The larger crystals/particles expand by “absorbing” the smaller ones.25 This is due to the fact that it is more energetically favorable for larger crystals because they have a much lower surface atom to bulk atom ratio. A line profile taken across the 4 layers shows heights consistent with gold steps, Figure 5-2(d).

Looking at a slightly smaller area of 60 x 60 nm², Figure 5-2(b), additional features can be observed. The area outside of the etch-pits, about 50%, is seen to be completely modified, albeit in a random fashion. A very interesting note is that inside several of the pits more details can be made out. Looking at the circled area near the top-middle image, formations which may represent sulfur rectangles can be observed. When looking across one of the etch-pits, line B and Figure 5-2(e), a line profile indicates similar heights to the modified gold steps seen in Figure 5-2(a)/(d).

Confirmation of sulfur rectangles on the outside and inside of an etch-pit is seen in Figure 5-2(c). They are random in distribution and give the surface a kind of “sponge-like” appearance. This is also important because it further highlights a controversial point in SAMs which is the production of etch pits. At one time they were thought to be caused by the etching of the gold surface by the thiol compounds as residual traces.
of gold were detected in the ethanol solution after modification had occurred.\textsuperscript{24} This was questioned however, when STM observations were made in which thiolates were seen on both the inside and outside of the pits,\textsuperscript{26} very similar to what was shown in Figure 5-2(c) with sulfur.

X-ray photoelectron spectroscopy studies were carried out on a gold on glass slide that was modified with p-methoxybenzenesulfonyl phthalimide. Figure 5-3(a) presents the results from scanning in the S 2p region. The curve can be fitted with two unresolved doublets. The main doublet has its S 2p\textsubscript{3/2} component at a binding energy of \(~161.2\) eV and is assigned to monoatomic sulfur on the gold surface.\textsuperscript{20} A second unresolved doublet is located at a slightly higher binding energy of \(~162.3\) eV, S 2p\textsubscript{3/2} component, and has been previously attributed to polymeric sulfur species on gold.\textsuperscript{21} The branching ratio is 2:1 for the doublets (2p\textsubscript{3/2}, 2p\textsubscript{1/2}) and the spin-orbit splitting was fixed at a constant 1.2 eV.\textsuperscript{27} Scanning in the carbon 1s region, Figure 5-3(b), yielded one peak which is centered at \(~284.2\) eV. Due to the samples being exposed to atmosphere for a time between transfers to and from the Schlenk tubes, it is difficult to say how much of the signal may be caused by a component of the parent compound still on the surface or adventitious carbon. A conclusion that can be

![Figure 5-3. XPS spectra from p-methoxybenzenesulfonyl phthalimide modified gold on glass, 3 days, showing the (a) S 2p area, (b) C 1s area and (c) O 1s area, scale in binding energy, eV.](image-url)
drawn however is that there is no signal for a carbonyl carbon which would be located at \(~289\) eV. This indicates that the phthalimide group is removed from the parent compound at some point during the modification. However when looking at the O 1s region, Figure 5-3(c), a clear signal for oxygen is observed. This suggests that the aromatic ring with the methoxy group may still be present on the surface, as binding of oxygen directly to gold would give a signal at \(~529\) eV.\(^{21}\)

STM studies were carried out on an Au(111) on mica substrate modified with p-methoxybenzenesulfonyl phthalimide in order to see what structures may be present on the surface. Figure 5-4 illustrates some very interesting results which clearly demonstrate the dynamic nature of the surface. In Figure 5-4(a), two areas have been marked \(\alpha\) and \(\beta\), which will serve as reference points for the changes on the surface. In area \(\alpha\), there are two rows of sulfur rectangles, as indicated by the arrows, which are parallel in both directions, and will remain relatively unchanged over the next 8 scans. Area \(\beta\) is aligned but will be seen to undergo many changes before arriving at rectangular structures that are well aligned with area \(\alpha\). The circle contains a lone rectangle which will shift positions to another area in the next frame, Figure 5-4(b). Along the path of the arrow where the lone rectangle was located, a gap can be seen to be forming. Moving forward one scan, Figure 5-4(c), a gap approximately 3-4 rectangles long is clearly visible, indicating a shift in position of several rectangles. Also important in this frame is the alignment of the rectangles in area \(\beta\) as shown by the arrow. This is clearly at a different alignment then the rectangles in area \(\alpha\) as indicated by two arrows. The area in and around where the circled gap was becomes blurry in Figure 5-4(d), but one frame later, Figure 5-4(e), the sulfur rectangles have reappeared, and their orientation has changed from their previous position a few
Figure 5-4. Consecutive STM images, 0.3 nA and 0.1 V, unfiltered, (a) → (i), at a scan size of 10 x 10 nm² of a piece of Au(111) on mica modified with p-methoxybenzenesulfonyl phthalimide for three days illustrating the dynamic nature of the sulfur rectangles.

frames earlier. They are now starting to align with the structures in area α. Moving ahead to the next frame, Figure 5-4(f), three rectangles in the top left corner are now orientated staggered relative to one another indicating the sulfur rectangles can
occupy different binding sights on the Au(111) surface. This becomes more evident in the same area in the following scan, Figure 5-4(g). The circled area here contains 4 sulfur rectangles, of which three shift positions in the subsequent frame. Another important note in Figure 5-4(h) is the rectangles in the top left part of the image are no longer staggered but now aligned parallel with the rest of the structures in area $\beta$. There is a very noisy part present here as well as indicated by the ellipsoid. In the final frame, Figure 5-4(i), however, the bottom row of rectangles in area $\beta$ has been resolved, is now well aligned with the rest of the frame. The constant shifting of sulfur rectangles provides clear evidence of their dynamic nature on gold, and the final formation gives an indication of the efficient packing of the structures and good adsorbate/adsorbate interactions. Periodicities of the rectangles were measured at \(~0.84 \text{ nm} (\pm 0.05 \text{ nm}) \times \sim 0.90 \text{ nm} (\pm 0.05 \text{ nm})\) which is in excellent agreement with previously published results of sulfur deposition on Au(111).$^7$

Studies of p-fluorobenzenesulfonyl phthalimide were conducted by XPS to see what species may be present on a modified gold surface. For modification times of 10 minutes, 1 hour, and 1 day, there were no signals observed for sulfur or fluorine. This indicates that sulfur is being deposited from this compound on gold at a much slower rate than the $\text{S}_2\text{Phth}_2$ compounds from Chapter 4, and thiobis(hexamethyldisilazane) and hexamethyldisilathiane compounds from Chapter 6. A clear signal for sulfur was seen when scanning in the S 2p region, Figure 5-5(a), after a 3 day modification. Monoatomic sulfur adsorbed on gold is assigned to the first unresolved doublet which is located at a binding energy of \(~161.2 \text{ eV}^\text{,}^{20}\) and for the second doublet, the S 2p\text{\textsubscript{3/2}} is located at \(~162.3 \text{ eV}\) which suggests the formation of polymeric sulfur species.$^{21}$ Scanning in the N 1s region did not yield any signal for nitrogen which suggests that
the phthalimide-sulfur bond is cleaved at some point during the modification process. The expected peak for fluorine, located at ~685 eV, was not observed, which indicates that the aromatic benzene ring is separating itself from the sulfur.

Additional characterization of the modified surface was done by STM. Samples were prepared in a similar manner to XPS, but using a freshly prepared piece of Au(111) on mica as the substrate. Imaging was done in air, using tunneling conditions of 0.150 V for the bias voltage and 0.175 nA for the tunneling current. The tip was a freshly prepared piece of tungsten wire, electrochemically sharpened in 3 M NaOH. Figure 5-6(a) shows high resolution details of the sample surface. One can readily see the presence of three closely related patterns (A, B, and C). The top right portion of the images presents the well known S rectangles characteristic of S deposition on Au(111). The rectangles are well ordered and are parallel to each other in both directions. Measurements of the observed rectangles showed average sizes of 0.59 nm (± 0.05 nm) x 0.51 nm (± 0.05 nm), and a corresponding unit cell of parameters 0.87 nm (± 0.05 nm) x 0.84 nm (± 0.05 nm),
Figure 5-6. High resolution STM images, 0.175 nA and 0.150 V, unfiltered, of a modified piece of gold on mica, from 1 mM p-fluorobenzenesulfonyl phthalimide for 3 days, at scan sizes of (a) 18.1 x 18.1 nm² (b) 10 x 10 nm² showing the three line structure, (c) and (d) 14.5 x 14.5 nm², same area, with 7 ½ minutes between the scans.

in accordance with the previous measurements, further confirming the efficient deposition of S through use of p-fluorophenyl sulfonyl phthalimide. A new pattern (C), as shown in Figure 5-6(b), gives the appearance of a three lines structure. Of particular interest is the alignment of some of the S rectangles in parallel with the three lines, circled area in Figure 5-6(a), suggesting a good alignment between the
two and that the S rectangles may give rise to the 3 line pattern, or vice versa, by a small shift in the position of the atoms. It is important to note that these new phases show similar unit cell dimensions to the ones observed for the well known rectangular structures. Also in Figure 5-6(a), an additional new phase is seen in the top left of the image (B). The structure gives the appearance of densely packed sulfur formations. This may be caused by an efficient and tight packing of sulfur atoms and suggests that a closely related stable sulfur structure has formed, a type which has not been previously observed. This is confirmed by Figures 5-6(c) and 5-6(d) which show a transition of the regular rectangular structure to this new structure when scanning an area showing both phases. The observation of different phases on the same plane is important because it illustrates the stability of different sulfur structures on Au.

An important issue of long standing discussion in the literature has been the debate between whether the common rectangular structures correspond to a complex AuS phase or sulfur adlayers. Experimental evidence has been presented which supports both sides.7,28,29 Figure 5-7 presents consecutive, unfiltered STM images at a scan size of 30 x 30 nm², illustrating the dynamic nature of the modified surface. In Figure 5-7(a), there are 5 separate areas (α, β, γ, δ, and ε) which are labeled and these will serve as reference points for changes in subsequent images. Looking at Figure 5-7(a) in general a number of features can be seen. There are multiple forms of sulfur present, including a 3 line structure, dense sulfur formations and the usual S rectangles, Figure 5-8(a). Considering area immediately below the α symbol, a nearly complete step edge is present. Going to the corresponding area in Figure 5-7(b), the edge is now complete. However in Figure 5-7(c) in this area, a single rectangle wide gap is present showing a missing
Figure 5-7. Consecutive, (a) → (l), high-resolution STM images, unfiltered, 0.175 nA and 0.150 V, at a scan size of 30 x 30 nm², after a 3 day modification of Au(111) on mica from p-fluorobenzenesulfonyl phthalimide, illustrating the very dynamic nature of the sulfur adlayer surface and dissociation/association behavior of the rectangular and filled rectangular structures.
rectangle along the right hand side. The whole row of filled rectangles has shifted in the next frame, Figure 5-7(d), making a gap on the left hand side of the edge. When considering Figure 5-7(e), area $\alpha$, has become slightly noisy, and the filled rectangles along the edge have dissociated completely and do not re-associate over the remainder of the 7 scans. Above area $\alpha$, $\beta$, and $\gamma$ in Figure 5-7(a), randomly aligned S rectangles are present. They remain this way for a brief while until Figure 5-7(d) where they are beginning to form parallel rows in both directions. Also of interest is the area in the top right corner, where a section of rectangles are aligned amongst themselves, but are at an angle relative to the rectangles to their left, and those to their bottom right. Continuing along to the top part of the image in Figure 5-7(f), the dissociation of the rectangles above the $\beta$ area can clearly be seen, but by the next frame, Figure 5-7(g), they can be seen to be re-associating once more. Figure 5-7(h) indicates that the rectangles are now well aligned in two sections separated by an uneven gap in the middle. Looking to the top right corner in Figure 5-7(i) shows that now most the rectangles which were tilted with respect to their neighbours in Figure 5-7(d), are now lined up very well with the rest of their neighbours. This is important because it provides clear evidence of reversible dissociation/association, good adsorbate/adsorbate interaction, and efficient packing of the S rectangular structures.

Area $\beta$ in Figure 5-7(a) shows a section of well aligned S rectangles. Of note in this area is the bottom edge where one can see 9 rectangles in the lowermost row. In Figure 5-7(c), the two on the left are now gone, and in Figure 5-7(d), 4 of the S rectangles have shifted creating two single gaps in the row. One frame later, two of the rectangles have dissociated and the remaining two have shifted to the right resulting in a row of 5. In Figure 5-7(g), one more rectangle is gone and the row is
Figure 5-8. Proposed models for (a) well aligned regular rectangular structures of Figure 5-7, (b) mis-matched area from Figure 5-7(f) as indicated by the arrow, and (c), very randomly oriented sulfur rectangles representing Figure 5-7, area $\varepsilon$.

The area directly beneath the arrow in Figure 5-7(i) is empty, but over the next frame, the rectangles start shifting to the left. In Figure 5-7(k), the row is clearly seen to be 3 rectangles, but in Figure 5-7(l), two more rectangles have re-associated with the others and there is a row of 5. A similar dissociation/association behavior is observed along the edge of the filled S rectangles in area $\gamma$. This is highlighted by the circled areas in Figure 5-7(d) – Figure 5-7(i).

The area surrounding $\delta$ in Figure 5-7(a) shows several uneven gaps in the rectangular structure. Following this area from one frame to the next, the surface can be seen to be very dynamic as the gaps are constantly shifting in position and size. In the area around the arrow in Figure 5-7(f), the S structures are well aligned. What is interesting here is that directly above the arrow, there are two gaps, which has resulted from an opposite side alignment of the S rectangles, Figure 5-8(b). This behavior suggests that the bonding sites for the rectangular $S_8$ structures are not fixed, they can change. The rectangles have reconfigured themselves by the next frame resulting in a wide gap, but soon start to associate once again and end up in a well ordered formation with several single gaps as can be seen in Figure 5-7(l).
Very randomly oriented features are observed in area ε, in Figure 5-7(a). A few frames pass and this area resolves into rectangles, in Figure 5-7(c) for example and illustrated by the model in Figure 5-8(c). These structures shift again by Figure 5-7(g) where most of the rectangles are gone, but one frame later, there is a small well aligned area inside the pit. This association/dissociation behavior is important because it shows that randomly aligned S rectangles can behave in a similar manner to their well-ordered counter parts.

In addition to the rectangular structures observed on the surface, a new adsorption pattern was also observed. Figure 5-9 presents high-resolution STM images, unfiltered, clearly illustrating a 2:1 line pattern. A large scale image at 60 x 60 nm², Figure 5-9(a), shows a well-aligned surface with different domains. Modification is

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**Figure 5-9.** High resolution, unfiltered, STM images, 0.175 nA and 0.150 V, of an area of the modified surface, at sizes of (a) 60 x 60 nm², (b) 10 x 10 nm², and (c) 5 x 5 nm² showing a clear 2:1 adsorption pattern for sulfur and (d) a corresponding proposed model of the sample surface.
seen to take place both on the area outside and on the inside of the etch pits, for
example in the top left corner. Figure 5-9(b) shows a zoomed in area, 10 x 10 nm²,
illustrating a clear 2 parallel lines to a single line pattern. The unit cell for this
structure was calculated at approximately 0.86 nm (± 0.05 nm) x 0.89 nm (± 0.05
nm). A small scan size, 5 x 5 nm², is shown in Figure 5-9(c). Looking at line profiles
taken across this image, there was very little difference in height going from one row
to the next which indicates that the sulfur atoms are all on the same plane. Line A,
Figure 5-9(d), shows a change in height of ~ 5 Å while line B, Figure 5-9(e), has a
difference in height of ~ 3 Å. This adsorption pattern may result from a shift in
position of two atoms within a sulfur rectangle to one side, such that the rectangle
appears to have been separated into a 2:1 line pattern. A model illustrating the
proposed shifting of sulfur atoms is presented in Figure 5-9(f).

5.4 Summary:

In summary, experimental observations of the interaction of a series of aromatic
sulfanyl phthalimides on gold surfaces have been studied. Given enough time, this
leads to the deposition sulfur, the ejection of sulfanyl oxygens, the cleavage of the
phthalimide group and the removal of the aromatic ring. XPS data from the p-iodo
compound has indicated that iodine is present on the gold surface and may still have
the aromatic ring attached to it on the other side. Similarly, the p-methoxy compound
may have the aromatic fragment attached as suggested by the oxygen 1s signal. STM
imaging has indicated a very dynamic and adlayer-like behavior of sulfur on Au(111)
from these compounds which is in excellent agreement with results from Chapter 4
and Chapter 6. This is very important because it shows sulfur rectangles tend to
behave as sulfur adlayers as opposed to a complex AuS phase. Preliminary studies of
alkyl sulfonyl phthalimides also indicated the ejection of sulfonyl oxygens as XPS studies in the S 2p region did now show the expected binding energy of ~168 eV. Elucidation of mechanistic details is currently underway using electrochemistry.

5.5 References:


Chapter 6: Thiobis(hexamethyldisilazane) and Hexamethyldisilathiane Adsorbed on Au(111)

6.1 Introduction:

The synthesis of thiobis(hexamethyldisilazane), Scheme 6.1(a), was first reported by Wannagat’s group from the reaction of sulfur dichloride, SCl₂, with silyl substituted alkyl amides.¹ This compound has been used primarily in inorganic synthesis of nitrogen-chalcogen materials.² For example, the reaction of this material with a mixture of SO₂Cl₂ and SCl₂ produces tetrasulfur tetranitride, S₄N₄ which can be used in ring closing reactions to form heterocyclic compounds.³ There have not been any previous reports of using thiobis(hexamethyldisilazane) as a potential sulfur source to study sulfur-gold interactions. This compound appears colourless and does not have any odor, which is an important advantage over hexamethyldisilathiane.

The use of hexamethyldisilathiane, Scheme 6.1(b), as a sulfur transfer agent in syntheses is well known.⁴-⁶ A distinction that it has in this area is being an aprotic source of sulfur. Hexamethyldisilathiane has been extensively used in the synthesis of nano-materials, PbS for example, as well as the conversion of metal-oxides and metal chlorides into the corresponding metal sulfides.⁷-⁹ The compound itself appears as a colourless liquid and does give off a very foul smell, but has not before been considered as a potential candidate for sulfur deposition on gold surfaces.

Scheme 6.1. (a) Thiobis(hexamethyldisilazane) and (b) Hexamethyldisilathiane.
Thiobis(hexamethyldisilazane) and hexamethyldisilathiane were used as new sulfur precursors, in an organic, non-electrolytic solution, for the deposition of sulfur in conditions usually used for SAM formation. These compounds present the opportunity to study metal sulfur interactions based off the cleavage of two completely different chemical bonds of N-S and Si-S. We have directly observed by high resolution STM the formation of well-defined sulfur rectangles at multiple step edges, and sulfur arranged in a ‘wavelike’ pattern for the first time from the adsorption of thiobis(hexamethyldisilazane) on Au(111). Direct evidence from real-time STM images indicates the formation of well-ordered multilayers within a short period of time from hexamethyldisilathiane. Rectangular structures are clearly observed on the bottom layer and even on the top layer as well. This suggests that in addition to formation on a gold surface, S₈ rectangles may also form on top of another sulfur layer. Both the top and the under layer are dynamic and show the mobility of the rectangles as well as their reversible association/dissociation. Further confirmation of this dynamic behavior was seen along a step edge, in which rectangle positions shifted many times before arriving at a tightly packed parallel rowed structure bordered by trimers.

6.2 Experimental Procedure:

The modification procedure was carried out on the bench top for thiobis(hexamethyldisilazane) and fume hood for hexamethyldisilathiane. Both polycrystalline gold and Au(111) on mica surfaces were dipped into a 1 mM solutions prepared from freshly distilled acetonitrile. Deposition times ranged from a few seconds to several hours. Samples were rinsed thoroughly with acetonitrile and dried under a gentle stream of nitrogen. The modified surfaces have been using a series of
techniques including X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV) and scanning tunneling microscopy (STM). Atomic resolution level images were obtained after modification times of a few minutes minutes.

6.3 Results and Discussion:

XPS provided insights regarding the adsorbed species on the gold surfaces. Thiobis(hexamethyldisilazane) was seen to show a strong sulfur peak in the S 2p region, Figure 6-1(a). The signal could be deconvoluted into two unresolved doublets. The first doublet had the S 2p$_{3/2}$ peak located at ~ 161.2 eV which has been assigned to monoatomic sulfur bound to the gold surface.$^{10,11}$ A second doublet appears at slightly higher binding energies and has its S 2p$_{3/2}$ component centered at ~ 162.3 eV. Previous assignments of this peak have been credited to sulfur,$^{10}$ polymeric sulfur,$^{12}$ or a complex AuS phase.$^{13}$ These multiple components present in the sulfur 2p region suggests the possibility of various forms of sulfur present on the gold substrate at the same time. There is no signal present in the N 1s region, Figure 6-1(b), which suggests that this is a cleavage point for the molecule at some point during the modification process. The modification may begin with an initial physisorption of thiobis(hexamethyldisilazane) as no reduction peak was observed at all when using an inert glassy carbon electrode with 0.1 M TBAHFP as a supporting electrolyte. This could be true assuming that the compound does not follow a reductive adsorption mechanism initiated by an electron transfer from the gold surface which has been suggested in the case of organic thiocyanate modification of gold.$^{14}$ The lack of a reduction peak suggests that the S-N bond for this compound is strong and reduced beyond the solvent wall, ~ -2.8 V vs SCE for this system.
Cyclic voltammetry was also used to provide more confirmation for the S deposition on Au using thiobis(hexamethyldisilazane). The surface coverage was also calculated from CV studies. A solid gold electrode was modified for various times using a 1 mM solution in acetonitrile. Figure 6-2(a) shows oxidative stripping scans of a polycrystalline gold electrode in 0.5 M H₂SO₄ after modification with thiobis(hexamethyldisilazane). Even after a brief modification time of 1 minute, a large oxidative current was observed compared to bare gold in the same region. The calculated surface coverage, θ, for this time, is ~0.25 ML. Increasing the time to 2 minutes gives a coverage of ~0.35 ML, which is just above the 0.33 ML level which has been previously assigned to monoatomic sulfur species bound to gold in a ($\sqrt{3} \times \sqrt{3}$)R30° structure.¹⁵ Further increasing the time shows a rise in coverage, plateauing at ~0.45 ML with the 10 and 30 minute sample times. Coverages were calculated assuming total conversion of sulfur to sulfate according to the reaction for the formation of sulfate species, equation (1), which occurs simultaneously with the formation of a gold oxide monolayer, equation (2)

\[
S + 4H_2O \rightarrow SO_4^{2-} + 8H^+ + 6e^- \quad (1)
\]

\[
Au + H_2O \rightarrow AuO + 2H^+ + 2e^- \quad (2)
\]
Figure 6-2. (a) Cyclic voltammograms, 0.2 V/s, of a polycrystalline gold electrode in 0.5 M H₂SO₄ after modification with 1 mM thiobis(hexamethyldisilazane) in acetonitrile, and (b) the corresponding surface coverages.

An important note is that after each initial oxidative sweep following solution deposition, a second sweep showed a scan profile which was nearly exactly the same as that of a clean bare gold electrode, indicating that sulfur is completely removed during the initial oxidative scan. These high coverages obtained for short deposition times suggest the compound is reacting very rapidly with the gold surface.

Further evidence of the S deposition on Au using thiobis(hexamethyldisilazane) was provided by STM imaging. Densely packed structures are illustrated in Figure 6-3(a) which shows a high resolution, unfiltered, 20 x 20 nm² STM image. This indicates strong rectangular/rectangular interactions and efficient packing within individual sections. Line profiles along line A and line B in Figure 6-3(b) run along one side of a number of rectangles in which sets of three atoms can clearly be observed. Periodicities were measured at ~ 0.85 nm (± 0.05 nm) by ~ 0.89 nm (± 0.05 nm), which is in line with what is known for the octamer structure.¹⁶ Many of the rectangles are lined up parallel in both directions within specific areas. Individual rectangles bordering these areas may be observed to line up in a staggered fashion.
Figure 6-3. (a) High-resolution, unfiltered, STM image, 1.55 nA and 2.0 V, of an Au(111) surface modified with thiobis(hexamethyldisilazane) showing densely packed rectangular structures at a scan size of 20 x 20 nm$^2$ and (b) the line profiles used to determine the periodicity.

which would suggest different binding sites if they are on the same plane, or they may appear staggered relative to the others due to differences in the underlying gold surface.

Additional insights were provided by further STM imaging of a thiobis(hexamethyldisilazane) modified Au(111) surface. Along a multi-step edge, sulfur and sulfur rectangles can be clearly seen in Figure 6-4(a). The initial adsorption of sulfur on gold is known to take place along a step edge resulting in a monoatomic structure.$^{15}$ Sulfur rectangles can be observed in a parallel fashion across different steps. These structures show tight packing which indicates strong adsorbate/adsorbate interactions. In Figure 6-4(b) we observe similar rectangular structures to the previous image, but also an important new feature. The circled area shows an area along a step edge which gives a suggestion of a possible ‘zig-zag’ pattern. This new pattern could be an example of a different stable polymeric sulfur structure which has not been clearly observed before. The lengths of both the horizontal and vertical portion of the
‘zig-zag’ were measured at ~ 0.52 nm (± 0.05 nm) by ~ 0.62 nm (± 0.05 nm). These dimensions are marginally similar to those of the sulfur rectangles themselves which supports the idea that if two ‘zig-zags were to form in close proximity to one another, this may provide a pathway to forming the rectangular structures. Another possibility is that these structures are two sides of sulfur rectangles and the STM tip is not sensing the other half due to the proximity to the step above. Line profiles taken across different areas in Figure 6-4(a) and Figure 6-4(b), indicate step heights of ~ 0.2 nm, Figure 6-4(c) and Figure 6-4(d).

**Figure 6-4.** High-resolution STM images, 1.55 nA and 2.0 V, unfiltered, 10 x 10 nm², of a piece of gold on mica modified with thiobis(hexamethyldisilazane) showing (a) staggered rectangles along step edges, (b) sulfur rectangles and a ‘zig-zag’ structure along a step edge along with (c) line profile of A and (d) line profile of B.
Further investigation of the modified gold on mica surface provided a new ‘wavy’ structure. Figure 6-5(a) shows an unfiltered STM image suggesting the arrangement of sulfur “wavelike” pattern. The individual atoms can be observed when zooming in on the waves, as seen in Figure 6-5(b). A line profile taken across a horizontal portion of the image indicates that the atoms are at approximately the same height. When considering line profile B, in the vertical direction, the periodicity was found to be \( \approx 0.50 \) nm (\( \pm 0.05 \) nm). This wavelike pattern may appear as a result of surface stress on the gold substrate, which is known to arise on both clean surfaces and thiol-modified surfaces.\(^{17,18}\) The thickness of the substrate is also known to be effected by surface stress as a reorientation of ultrathin film of Au(100) to Au(111) was observed with high resolution electron microscopy.\(^{19}\) Surface stress occurs when there is a difference in lattice constant from the bulk compared to the surface layer. Alkanethiols self-assembled from the gas phase have been used to study this behavior with AFM sensor technology.\(^{20}\) Gold is evaporated on one side of the cantilever and then changes in the laser deflection are monitored upon exposure to thiol vapors.
Experimental evidence using gold-coated microcantilever sensors, has been presented which suggests that surface roughness does not play a large role in the stress induced from SAM modification. This is in stark contrast to other studies which indicate high quality gold coated microcantilevers with large grain sizes, induce significantly larger surface stresses upon SAM modification when compared to their small grain counter parts. There has also been direct observations on the effects of a contaminated vs clean microcantilever sensor, which was seen to give two different profiles when looking at surface stress against applied potential. When the waves and/or “rows” in Figure 6-5(a) give a convex appearance which may suggest a compressive surface stress. This could be caused by a charge transfer from the gold surface to the adsorbed sulfur, resulting in elongated gold-gold bonds in effect creating a repulsive force. Another possibility for this appearance however, is that the sulfur atoms may be sitting on an area of Au(100) which has a different surface morphology then that of Au(111). These row type structures have been readily observed for ethane thiol and butane thiol self-assembled on Au(100) surfaces. Sulfide adsorbed on Au(100) in a (\sqrt{2} \times \sqrt{2})R45° is known, but has not been observed before in a wave/row like structure.

XPS provided insights regarding the adsorbed species on the gold surfaces modified by hexamethyldisilathiane. A clear signal was observed for S, Figure 6-6(a), however no peak was seen for Si, Figure 6-6(b), providing hence a first indication that S is deposited on the surface through a process involving the dissociation of both S-Si chemical bonds. This process is also seen to take place very quickly as a sample modified for a few seconds showed a small, but present, signal for sulfur. Under the used modification conditions two main peaks are observed for the S 2p signal. The first peak is an unresolved doublet with the 2p_{3/2} component located at ~161.2 eV. A
Figure 6-6. XPS spectra of a piece of gold on mica modified with 1 mM hexamethyldisilathiane showing the S 2p area (a) and N 1s area (b), scale in binding energy (eV).

second doublet is also observed with its 2p_{3/2} component at ~162.3 eV. There is also a small third doublet at ~163.2 eV which has been assigned to multilayers. These results are in agreement with the previously reported ones for S modified Au surfaces. The first peak at the lowest binding energy has been attributed to monoatomic sulfur adsorbed on the gold surface, while the second peak has been assigned to a complex AuS phase, S, or polymeric sulfur species.

Oxidative cyclic voltammograms were utilized in order to assess the rate at which hexamethyldisilathiane may be modifying gold surfaces, Figure 6-7(a). These modification times ranged from 1 minute to 30 minutes. In all cases, the second CV after each initial modification scan is similar to the one recorded for a bare gold electrode, indicating that sulfur was completely removed from the electrode surface during the first oxidative scan. On the assumption that all of the sulfur was oxidized to sulfate, the surface coverage under these conditions was calculated, Figure 6-7(b). Calculations were made according to peak current densities from the oxidation and reductive peaks. The difference in charge density for the oxidative and reductive peaks of the 7 minute deposition time for example was calculated at ~ 872 µC/cm²,
Figure 6-7. (a) Cyclic voltammograms, 0.2 V/s, of a polycrystalline gold electrode in 0.5 M H₂SO₄ after modification with 1 mM hexamethyldisilathiane in acetonitrile, and (b) the corresponding surface coverages.

which led to a surface coverage calculation of 0.59 ML. This suggests the presence of polymeric sulfur species or multilayers on the gold surface; however, there has been experimental STM evidence that monoatomic sulfur may still be present at close to this coverage,¹¹ as also confirmed by the XPS data in Figure 6-1(a) and Figure 6-6(a).

Additional insights regarding the nature of the S modified generated surfaces were provided by consecutive high resolution STM from a hexamethyldisilathiane modified piece of gold on mica. Figure 6-8 shows sequential imaging of a sample surface using an electrochemically etched tungsten tip and tunneling conditions of 1.55 nA (tunneling current) and 2.00 V (bias potential). In Figure 6-8(a) we observe two patterns, sulfur rectangles near the top of the image, distorted rectangles (a “new phase”) in the middle of the image and sulfur rectangles near the bottom of the image with the 8 individual atoms visible. This “new phase” (distorted rectangles) has a similar unit cell to the rectangular structures and shows only a slight shift in certain positions of the octamer structure. This is the first time such a structure is reported and suggests that different phases are possible considering the dynamic nature of the S modified surface in accordance with new structures seen in Chapter 4 and Chapter
Figure 6-8. Consecutive high-resolution STM images (unfiltered), 1.55 nA and 2.0 V, 9 nm x 9 nm, of a Au (111) on mica slide modified for 7 minutes in a 1 mM solution showing the adsorption of multiple layers of sulfur and mobile sulfur rectangles (a-c) and corresponding proposed structural models (a'-c').

Figure 6-9. Line profiles across different areas in the images in Figure 6-8(a)-(c).
5. Note that other phases have been shown to be present on a S modified gold surface.\footnote{13} In amongst each of the 3 layers themselves, the rectangles are parallel in both directions indicating good adsorbate/adsorbate interactions and efficient packing. Measurements of the sulfur rectangles showed similar average sizes than those reported in Figure 6-3(a). Close inspection of the image reveals that the sulfur layer at the bottom of the image is actually resting on top of the middle sulfur layer. A drop in height of \(~0.15\, \text{nm}\) is observed going from the top layer to the middle layer, and another drop of \(~0.16\, \text{nm}\) from the middle layer to the bottom layer, line A” (Figure 6-8(a) and Figure 6-9A”). Very similar values respectively are observed when going from middle layer to bottom layer, line B” (Figure 6-8(b) and Figure 6-9B”) and from the top layer to the middle layer, line C” (Figure 6-8(c) and Figure 6-9C”). These heights are similar to the ones observed for S monolayer formation on Au, which tends to indicate that these are S multilayers.

This is further confirmed by the following results. Immediately to the top of line A’, Figure 6-8(a), individual atoms can be made out which represents underlying sulfur rectangles. A depth profile taken across this section showed a drop in height of \(~0.15\, \text{nm}\) (Figure 6-9A’). This also very important as, by looking at the 3 images (Figure 6-8a-c), one can clearly see the mobility of the top rectangles across the middle layer. Figure 6-8(a) has a gap two rectangles wide as indicated by the line A’. In the next scan, Figure 6-8(b), the shifting of one rectangle one unit to the left creating two single gaps can clearly be seen. This is supported by the line profile in Figure 6-9B’ which indicates there is an island in the center, surrounded by two single gaps. One more scan later, Figure 6-8(c), two more shifts to the right are observed, one of one rectangle wide and the other of two. Figure 6-9C’ shows that the gap size is now very similar to what it originally was in Figure 6-8A’. This mobility is
illustrated in the models in Figures 6-8a'-c' based on the STM images. The mobility of these rectangular structures on a top layer is evidence to their adsorbate nature. Moreover, rectangular structures on the edge of the middle layer show an association/dissociation behavior. Along this edge, changes can be observed from one image to the other where rectangles are dissociated and bright spots corresponding to mobile S atoms can be observed and vice versa. A vacancy is clearly created, circled areas in Figures 6-8a and Figure 6-8(c) going from the first to the third image.

Further STM imaging provided new findings in relation to the dynamic behavior and stability of different sulfur species on the sample surface. Figure 6-10 shows a series of unfiltered STM images, all taken within a few minutes of each other, in which many changes can be observed along the step edge. Looking at Figure 6-10(a), inside of the circled area, one can see that there is a gap three rectangles wide along the main edge. In the corresponding position a few frames later, Figure 6-10(b), however, a rectangle has moved and filled one of the vacancies leaving the gap now two rectangles wide. Further along the main edge to the right, several more rectangles have changed positions resulting in a new single wide gap as indicated by the arrow. Moving ahead a few frames, the gaps are now gone as more rectangles have moved positions and filled the vacancies. This can be seen in Figure 6-10(c) along the path of the arrow. Looking ahead a few frames to Figure 6-10(d), a single rectangle has moved to a position on top of the main edge. Several changes can be observed in Figure 6-10(e). Many of the rectangles have shifted positions making the part of the edge inside the ellipsoid area less jagged and more square-like then it was a few frames earlier. Jumping ahead a few more frames, Figure 6-10(f), another single rectangle wide gap has formed along the main edge as can be seen in the circled area.
Just to the right of this, two rectangles in parallel can be seen positioned on top of the main edge. Subsequently the gap has been filled after a few more scans in Figure 6-

![Figure 6-10](image)

**Figure 6-10**: Unfiltered STM images, 1.55 nA and 2.0 V, at a scan size of 20 x 20 nm², showing the dynamic behavior of the rectangular structures along a step edge.

10(g). At the top of the image inside the ellipsoid area, the main edge in this area can be seen to be made up of a series of small edges, 1 or 2 rectangles wide. Changes of the rectangles positions in this area are clearly seen a few frames later, where the edge now has much more square-like orientation, Figure 6-10(h). Another gap has formed along the main edge inside the circled area. Going ahead to the final frame, Figure 6-
10(i), the main edge has changed again with no gaps being present and each of the rectangles being bordered by one side of another rectangle. This can be observed along the path of the arrow. The arrangement of these extra edges, most likely made up of 3 atoms, bordering each of the rectangles in a linear fashion is important as it indicates that trimers can be stable structures. This suggests the possibility of forming other intermediate structures between monoatomic and rectangular. Overall, the constant shifting of the rectangular structures, whether due to thermodynamic or tip-induced changes, illustrates that this modified surface, (sulfur on gold) exhibits very dynamic interactions. The final arrangement of rectangles shows structures that are well-ordered and in parallel rows indicating efficient packing and good adsorbate/adsorbate interactions.

This data clearly shows the deposition of S on the Au surface using thiobis(hexamethyldisilazane) and hexamethyldisilathiane as new precursors. Even if a more rigorous investigation is needed to understand the mechanism of the modification process, a number of facts indicate that the mechanism involves the initial physisorption of these sulfur precursor compounds, very quickly followed by or concomitant with the cleavage of the N-S or Si-S chemical bonds. The first fact is that both compounds are not easily reduced. Cyclic voltammetry on a glassy carbon electrode in acetonitrile containing tetrabutyl ammonium tetrafluoroborate (0.1 M) as a supporting electrolyte shows a reduction peak at -2.75 V vs SCE. This value is very close to the solvent wall, -2.8 V vs SCE, for this electrolytic solution. Keeping in mind that thiolate SAMs formed on Au have mainly been explained through a dissociative reductive process involving an electron transfer from the Au surface to the parent substrate, such a process in our case very likely takes place through an initial physisorption of the parent precursor. The second fact, which also supports this
idea, is the strength of the Si-S chemical bond. A B3LYP calculation of hexamethyldisilathiane and its fragments through a homolytic dissociation of the S-Si chemical bond provided a value of 3.56 eV. The dissociation of such a highly stable chemical bond is a further indication of the initial adsorption of the parent molecule. As both Si-S bonds are cleaved, this process likely involves the recombination of the two Me₃Si fragments to form bis-trimethyl disilane CH₃SiSiCH₃. This is somewhat favored by the vicinity of these groups in the starting material as shown in the optimized structure, ~ 3.729 Å, Scheme 6.2(a). This is in line with what has been reported for sulfur transfer reactions in organic chemistry, where a recombination of the two remaining fragments has been observed.²⁸ The recombination of the two fragments make indeed the S transfer more thermodynamically feasible. An estimation of the Si-Si bond dissociation energy in the bis-trimethyl disilane, using DFT calculation at the B3LYP level provided a value of 3.07 eV, Scheme 6.2(b), which still indicates a very strong interaction between the atomic S and Au.

![Scheme 6.2](image)

**Scheme 6.2.** Optimized Structures and bond dissociation energies for (a) hexamethyldisilathiane and (b) bis-trimethyl disilane.

The dissociation of both S-Si chemical bonds is also important in further understanding the SAM formation mechanism through the use of thiols. A controversial mechanistic aspect concerns the occurrence and timing of the S-H dissociation.²⁹-³¹ This is due to the failure of surface characterization techniques to
monitor hydrogen. Our data shows the absence of any trace of Si on the Au surface even for modification time as short as 10s, Figure 6-11, while a clear S peak is observed. A sequential adsorption/dissociation process may allow, depending on the time, observation of Si on the surface considering the fact that two chemical bonds are cleaved. This tends to indicate that the adsorption is rather concomitant with the dissociation of both chemical bonds in a concerted manner. Further investigation is certainly necessary to unravel the intricate details of this deposition process using hexamethyldisilathiane including the formation of multilayers, which the present data still doesn’t explain.

![Figure 6-11. XPS spectra of the S 2p and Si 2p regions after modification with 1 mM hexamethyldisilathiane for 10 seconds.](image)

Evidence has clearly been established for the deposition of S on the Au surface using hexamethyldisilathiane as a new precursor. Given the optimized structure, as seen in Scheme 1, and the lack of a silicon signal from XPS experiments, an initial adsorption of the parent compound very quickly followed by or concomitant with cleavage of both S-Si chemical bonds could be suggested. The formation of a dimer of trimethylsilyl may also provide a driving force for the reaction given the proximity
of the two groups in the optimized structure. Investigations into the mechanism of the sulfur deposition on gold, including multilayer formation, from hexamethyldisilithiane are currently underway.

6.4 Summary:

Thiobis(hexamethyldisilazane) adsorbed on gold and hexamethyldisilathiane adsorbed on gold have been investigated as new compounds to study sulfur/gold interactions using XPS, electrochemistry and STM measurements. Sulfur is readily deposited on gold surfaces by both of these molecules with the two S-N bonds and the two S-Si bonds being cleaved respectively as indicated by XPS. Cyclic voltammetry has indicated a rapid deposition of sulfur on a solid gold electrode. STM observations from thiobis(hexamethyldisilazane) modified gold have shown regular rectangular structures in densely packed formations and staggered, along with interesting new observations of a ‘zig-zag like’ pattern and sulfur orientated in “waves” / “rows”. We have directly observed by high resolution STM that the initial Au modification with S is closely followed by the formation of additional S layers from the study of hexamethyldisilathiane. This implies that sulfur surface coverages above monoatomic (0.33 ML) levels, observed high sulfur coverage structures, such as the pseudo S₈ rectangles, in addition to sitting directly on the gold surface, may also form on top of another layer of sulfur. This is important because it indicates, that the heavily debated rectangular structures correspond to sulfur adlayers, as supposed to an AuS phase. This was further confirmed by the dynamic nature of these top layers where the mobility of the rectangular sulfur structures was directly observed by STM along with their reversible association/dissociation. Further confirmation of this behavior was seen along a step edge in which a series of STM images clearly showed the rectangles
shifting position many times before arriving at a tightly packed, parallel rowed
structure bordered by trimers.

6.5 References:


6153-6159.


11394-11402.


Chapter 7: Summary & Future Work

7.1 Summary:

This thesis has been an investigation of new methodologies in the surface modification of silicon and gold. Hydrogen terminated Si(111) was successfully modified using a new method which did not require the use of irradiation, heat or UHV conditions. A facile electron transfer initiated methodology was employed using NBS/Fc or NBP/Fc as starting points. AFM studies suggested multilayer formation had occurred as scratching was required to see the underlying terraces. XPS data indicated the presence of the expected elements as well as ferrocene and also showed that successful nucleophilic substitution of bromine could take place. Excellent signals for C=O stretches were seen by FTIR. This work also showed that this methodology could be used in general as other combinations of good electron donors and good electron acceptors, in principle should allow for modification of Si(111)-H surfaces. As the leaving group is also deposited, bromine in this study, the use of other nucleophiles should allow for attaching a wide variety of compounds to the surface.

Gold surfaces were modified by seven new and individually different sulfur precursors for the purposes of studying gold sulfur interactions, using a new environment of organic solvents, which is usually used in SAM formation. Cyclic voltammetry studies of the thiobisphthalimide and dithiobisphthalimide compounds showed that electrochemical modification and thermodynamic modification of gold by these compounds proceeds in two different ways and that the electrochemical modification is more efficient. XPS studies showed that from the parent compounds only sulfur is deposited on gold surfaces.
STM studies provided new insights into the behavior of sulfur on Au(111). The direct visualization of sulfur rectangles and a lone sulfur atom on the same plane was observed for thiobisphthalimide modified gold. Dithiobisphthalimide modified gold showed STM images which gave a first indication that sulfur rectangles can move as individual units, which suggests they are in fact sulfur adlayers. A reversible dissociation/association behavior was also observed.

The three aromatic benzene sulfonyl phthalimide compounds, p-iodo, p-methoxy, and p-fluoro, showed very interesting behavior when interacting with gold surfaces in that all six chemical bonds to sulfur were broken as indicated by XPS as well as the presence of iodine for gold modified with the p-iodo compound. STM studies showed patterns and formations consistent with sulfur deposition. A very dynamic and adlayer like behavior for the sulfur rectangles was seen which is in excellent agreement with the \( \text{S}_x\text{Phth}_2 \) compounds. This provided a second observation of adlayer like behavior of the highly debated sulfur structures. A new 2:1 line pattern was also observed which is important as it illustrated the stability of different structures of sulfur on the Au(111) surface.

Both thiobis(hexamethyldisilazane) and hexamethyldisilathiane were shown to react very quickly with gold surfaces as supported by XPS, CV and STM data. XPS and CV studies showed excellent sulfur signals in a matter of minutes. STM imaging showed a wavy pattern from the thiobis(hexamethyldisilazane) compound which might be the result of surface stress and would be the first experimental observation of this phenomena when depositing sulfur. Multilayer formation of sulfur was directly observed by STM for hexamethyldisilathiane modification of Au(111). Moving rectangles were also seen which is a very important point because it provided a third observation and additional
evidence to answering the long-standing debate in the literature of what the high-sulfur coverage rectangles correspond to which is not a complex AuS phase, but rather sulfur adlayers on gold.

7.2 Future Work:

Future work from our group on the modification of silicon could branch off in several different directions. One may be to look into mechanistic details of the modification of Si(111)-H with NBS/Fc for example. Using an NBS derivative with a bulky substituent in place of one of the -CH₂- hydrogens could lead to details on if this is a starting point for the multilayer formation. Another would be to further investigate the effect of different nucleophiles. This could be accomplished by exposing a modified Si(111) surface with a good leaving group, preferably one easily detectable by XPS, to different anions. Also experiments will be conducted to try to elucidate if ferrocene is trapped by the multilayer formation or actually bound to the surface. Scanning electrochemical microscopy (SECM) studies of modified silicon may be undertaken to see if local changes to a surface structure can be induced. Extending the electron transfer method of modification to make other linkages such as Si-C and Si-S may also be done.

Mechanistic studies for the modification of all sulfur precursors on gold are currently underway using electrochemical methods. This could be especially important for the aromatic sulfonyl phthalimide compounds to try and figure out how gold is catalyzing the reduction of all six of the sulfur’s bonds. Obtaining STM images for Au(111) samples modified with the straight chain sulfonyl phthalimides might be done. This could reveal if R-S-Au or S-Au is forming and may provide additional insights into the modification
mechanism. Modifying other metal surfaces with the compounds used in this study could also be done. For example, modifying platinum, copper, and silver may lead to new insights into sulfur-metal interactions. Our group is also interested in making metal-sulfide nanostructures as they have important technological applications. The thio and dithiobisphthalimide compounds as well as thiobis(hexamethyldisilazane) and hexamethyldisilathiane are interesting candidates as potential sulfur precursors as they have been shown to react very quickly with gold.