Characteristics and Use of Thin Metals on Modified Glass Substrates.

Sonya Latrice caston Pierre

Louisiana State University and Agricultural & Mechanical College

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CHARACTERISTICS AND USE OF THIN METALS ON MODIFIED GLASS SUBSTRATES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agriculture and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Sonya C. Pierre
B.S., Jackson State University, 1993
May 2001
For my loving husband, Darren Paul Pierre

Thanks for your support, and understanding when I couldn’t be around. Now we can enjoy our life.

For my parents, Fulton and Artrie Caston

You have shared with me one of your greatest gifts, love. Thank you for your love, inspiration, and support.
Acknowledgements

There are several people that I encountered at Louisiana State University that had a major influence in my life. I am grateful for their contributions towards completing graduate school. For their encouragement, support, and guidance to wait the storm out, I would like to thank Dr. Isiah Warner, Dr. Crystal Williams-Harrell, Dr. Judson Haynes, Dr. Clinton Hunt, and Dr. Tracey Simmons. I am grateful for Teri Lynn Robinson who reminded me to stay focused, Carolyn Faye Jackson who provided a laugh and smile especially when I was feeling down, Margaret Brown who reminded me of the Word, Regina Tolliver who reminded me to stay positive and release the negative energy, and Rose Simon who checked on me during the long night. I want to recognize my road "dawg" and dear friend, Jennifer Lear. We went through some trying times but we made it through. You are still the smart one (inside joke). Thanks Jenn for being there for me, even when you left for the Crescent City in 1997.

I am thankful for my beloved sister, Paulette Anita Caston. You have always been there during the good and bad times. I am glad that God chose me to be you lil' sister. I want to thank my grandmothers, Julius Frank Goodman and Eva Mae Caston. Your wisdom has led our family to acquire a better understanding of life. To my family, thank you for being you and for sharing your love. I love you all. To Superintendent and Mrs. John Pierre, my in-laws, thanks for ministering to me especially when I was unsure of my path.

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fabrication of nanoscopic band electrodes, Paul Moberg for help with the simulations, John Williams for assistance with profilometry, Wanda LeBlanc and Professor Ray Ferrell for obtaining the X-ray diffraction analyses in Chapter 4, Cindy Henk for assistance with SEM and fluorescence microscopy, Bikas Vaidya for fluorescence microscopy, and Dr. Julia Chan for X-ray diffraction analyses in Chapter 3.

Also, special thanks to Dr. Jeffrey D. Zubkowski for inspiring me to obtain a Ph. D. in Chemistry, Germaine Hill for constantly reminding me of important deadlines and requirements to finish graduate school, and Kimberly Hamilton for taking the time to edit my dissertation.

Most importantly, through prayers, focus, and encouragement, God helped me stay my course, complete my graduate school requirements, and earn my Doctor of Philosophy Degree. I offer my most humble praise to God.
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<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>A</td>
<td>geometric area in cm²</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>APS</td>
<td>3-aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>APS/glass</td>
<td>APS on glass</td>
</tr>
<tr>
<td>c</td>
<td>the speed of light</td>
</tr>
<tr>
<td>C</td>
<td>bulk concentration</td>
</tr>
<tr>
<td>C&lt;sub&gt;DL&lt;/sub&gt;</td>
<td>double layer capacitance</td>
</tr>
<tr>
<td>Cr/glass</td>
<td>Cr on glass</td>
</tr>
<tr>
<td>d</td>
<td>spacing between the lowest atom on the tip and highest atom on the sample</td>
</tr>
<tr>
<td>D</td>
<td>film thickness</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>DMAMFc</td>
<td>N,N-dimethylaminomethylferrocene</td>
</tr>
<tr>
<td>DMFc</td>
<td>dimethylferrocene</td>
</tr>
<tr>
<td>e</td>
<td>charge on the electron</td>
</tr>
<tr>
<td>e⁻</td>
<td>electron</td>
</tr>
<tr>
<td>E&lt;sub&gt;f&lt;/sub&gt;</td>
<td>electric field</td>
</tr>
<tr>
<td>E</td>
<td>energy equivalent of an X-ray photon</td>
</tr>
<tr>
<td>E&lt;sub&gt;p,a&lt;/sub&gt;</td>
<td>anodic peak potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;p,c&lt;/sub&gt;</td>
<td>cathodic peak potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;只要&lt;/sub&gt;</td>
<td>formal potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;wk&lt;/sub&gt;</td>
<td>working electrode</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>$F$</td>
<td>force</td>
</tr>
<tr>
<td>$Fc$</td>
<td>ferrocene</td>
</tr>
<tr>
<td>$Fc^*$</td>
<td>bis(pentamethylcyclopentadienyl) iron</td>
</tr>
<tr>
<td>$Fc$-SH</td>
<td>$(C_5H_5)Fe(C_5H_4CO_2(CH_2)_6SH)$</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck's constant</td>
</tr>
<tr>
<td>HOBt</td>
<td>1-hydroxybenzotriazole hydrate</td>
</tr>
<tr>
<td>HTS</td>
<td>methyl-terminated n-hexadecyltrichlorosilane</td>
</tr>
<tr>
<td>$i_{DL}$</td>
<td>current in Amps at a given potential for double layer</td>
</tr>
<tr>
<td>$i_{lim}$</td>
<td>limiting current</td>
</tr>
<tr>
<td>$i_{pa}$</td>
<td>anodic peak current</td>
</tr>
<tr>
<td>$i_{pc}$</td>
<td>cathodic peak current</td>
</tr>
<tr>
<td>$I_0$</td>
<td>intensity of the incident light</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>$k$</td>
<td>spring constant</td>
</tr>
<tr>
<td>$k_i$</td>
<td>refractive index related to the absorption coefficient</td>
</tr>
<tr>
<td>$l$</td>
<td>diffusion length of a molecule</td>
</tr>
<tr>
<td>$M$</td>
<td>magnification</td>
</tr>
<tr>
<td>$m_e$</td>
<td>mass of the electron</td>
</tr>
<tr>
<td>$n$</td>
<td>number of electrons</td>
</tr>
<tr>
<td>$n_2$</td>
<td>refractive index of a film</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>$n$-(6-aminohexyl)-aminoprpyltrimethoxysilan</td>
</tr>
<tr>
<td>NVOC</td>
<td>nitroveratryloxycarbonyl group</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>ox</td>
<td>oxidation</td>
</tr>
<tr>
<td>Q</td>
<td>charge</td>
</tr>
<tr>
<td>QCM</td>
<td>quartz crystal microbalance</td>
</tr>
<tr>
<td>r</td>
<td>radius of the equivalent hemicylinder</td>
</tr>
<tr>
<td>r</td>
<td>distance from the scattering electron to the detector</td>
</tr>
<tr>
<td>RAIRS</td>
<td>reflection-absorption infrared spectroscopy</td>
</tr>
<tr>
<td>red</td>
<td>reduction</td>
</tr>
<tr>
<td>Redox</td>
<td>reduction-oxidation</td>
</tr>
<tr>
<td>Rs</td>
<td>resistance of the solution</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SFM</td>
<td>scanning force microscopy</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscopy</td>
</tr>
<tr>
<td>t</td>
<td>time segment for diffusion</td>
</tr>
<tr>
<td>TMAMFc</td>
<td>trimethylaminomethylferrocene iodide</td>
</tr>
<tr>
<td>v</td>
<td>scan rate</td>
</tr>
<tr>
<td>ν</td>
<td>frequency</td>
</tr>
<tr>
<td>w</td>
<td>width of a single line scan across the sample surface</td>
</tr>
<tr>
<td>W</td>
<td>width of the CRT display</td>
</tr>
<tr>
<td>β</td>
<td>change in phase of the light beam</td>
</tr>
<tr>
<td>φ₂</td>
<td>phase thickness of a film</td>
</tr>
<tr>
<td>λ</td>
<td>wavelength of the radiation reflected</td>
</tr>
<tr>
<td>Γ₀ₓ</td>
<td>surface coverage of the oxidized species</td>
</tr>
<tr>
<td>κ</td>
<td>variable that is dependent on the bias across two electrodes</td>
</tr>
</tbody>
</table>
Abstract

Ultra-thin films of Au are formed on glass by thermal evaporation of Au onto a silane-modified glass surface. Monolayers of 3-aminopropyltriethoxysilane on glass (APS/glass) are outstanding surfaces for the formation of adherent, electrically conductive, smooth, and highly oriented Au films. Scanning tunneling microscopy images indicate that ultra-thin Au films are highly conductive and have a significant \{111\} texture, and X-ray diffraction studies confirm the latter. In addition, Au films on APS/glass surface are not removed by tape tests, pointing to a strong chemical interaction between the Au and amine surface. Unlike metal adhesion promoters, APS layer does not diffuse through Au films, making their use in advanced devices attractive.

Two applications of the Au films on APS/glass substrates are described. First, Au band electrodes with widths ranging from 3 to 150 nm are investigated by obtaining the voltammetric response of a series of substituted ferrocenes in non-aqueous electrolyte. Plots of normalized limiting current for each ferrocene derivative as a function of normalized electrode width reveal a negative response from traditional theoretical predictions. The observed negative responses for electrodes less than 50 nm in width are explained by effects that become important when the sizes of electrode and redox species are comparable. Concerns regarding the real surface area of band electrodes are addressed by labeling of the exposed Au of nanoband electrode with ferrocene-alkanethiol and measurements of double-layer capacitance. Microscopy studies of the epoxy/Au/glass interface point to insufficient insulation of the Au by the epoxy as the result of defects.
Lastly, fabrication methods in previous studies are used to construct laterally patterned metal features through the use of photolithography techniques. A photoprotecting group, nitroveratryloxycarbonyl, is covalently linked to the amine group of the APS monolayers. The sample is patterned by using a mask that allows UV light to reach the nitroveratryloxycarbonyl-APS/glass surface and remove the nitroveratryloxycarbonyl groups in the exposed areas. Gold is then vapor deposited on the patterned surface and the success of the patterning experiments are evaluated by “developing” the Au through the removal of tape.
Chapter 1
Introduction

1.1 Overview of Research Goals

The long-range goal of this research is the production of smooth, electrically conducting, ultra-thin metal films that can be spatially patterned with feature sizes on the sub-micrometer scale. Such films will be formed through the use of surface modifiers that were previously shown by Dunaway and McCarley to substantially affect the properties of evaporated metal films deposited on silicon oxide layers.\(^1,2\) The general approach is outlined in Figure 1.1.

![Figure 1.1 Schematic diagram outlining the research described in this dissertation.](image-url)
development of this strategy for the formation of ultra-thin conducting metal films on insulators will have a major impact on science and engineering fields that target the fabrication of nanoscopic devices. For example, the ability to make ultra-thin conducting metal films on insulating substrates is key in future electronic devices (computer "chips") and analytical microelectromechanical systems where feature size is continuously diminishing (so as to reduce space for devices), but uncomplicated, inexpensive alternatives to device fabrication are lagging.\textsuperscript{3,4} In addition, such metal films/patterned metal features will allow for the study of molecular events, such as diffusion of analytes to molecular-sized electrodes\textsuperscript{5-7}, which could lead to qualitative identification of analytes in mixtures. Also, control over the orientation (crystallographic direction) of the metal films through judicious choice of the surface modifier would provide a much needed alternative route to the production of metal substrates for STM imaging of molecules.\textsuperscript{8} Thus, achievement of the long-term goal of the work described here will be of great benefit to the analytical and materials chemistry, as well as the micromanufacturing fields.

To describe the ultimate goal above, Au films will be thermally evaporated onto amine-terminated silane monolayers supported on glass substrates. Silane monolayers were chosen due to the ability to readily form them on silicon oxide surfaces, such as glass, silica or quartz.\textsuperscript{9} The choice of the amine functionality is based on previous work from the McCarley group\textsuperscript{1} and that of Majda and coworkers\textsuperscript{10} demonstrating the ability of amine-terminated silane layers to act as effective nucleation enhancing surfaces during the vapor deposition of Au films. Although the previous study by Dunaway and McCarley showed that extremely thin (1-10 nm), electrically conductive Au films could
be formed on the amine surfaces, the morphology and crystallographic orientation of the 
Au films was not thoroughly investigated. In addition, the usefulness of such ultra-thin 
films in real-world applications such as electrochemical studies or lithographic 
fabrication procedures was not demonstrated.

Initial studies will target the morphology and texture (crystallographic 
orientation) of Au films, evaporated onto the amine-terminated monolayers supported on 
glass, through the use of scanning probe microscopy and X-ray diffractometry. The 
roughness and crystallinity of the Au films will be compared to those of Au films 
prepared on other “classic” substrates. These studies will allow a basic understanding of 
the properties of the Au films prepared on the amine surfaces and will give an indication 
of the use of such films in a variety of applications. Next, the use of the Au films in the 
construction of nanometer-wide Au electrodes and the electrochemical responses for a 
series of electroactive species will be described; these studies will elucidate whether the 
type of electrode material has an impact on “molecular size effects” seen in previous 
voltammetry studies by White, Murray, and Fritsch. Finally, the use of the 
aminosilane layers in optical lithographic patterning of Au films will be investigated. 
This latter study will help establish the feasibility of utilizing photolabile groups as 
protecting layers (of the amine) during the vapor deposition of Au so that Au deposited in 
the regions containing the photolabile groups can be removed using simple methods, 
whereas the Au in the regions that do not contain the photolabile groups (removed by 
UV-visible light) will remain after such removal methods. Thus, the work described here 
will lay the groundwork for future use of these Au films in a variety of applications and 
future studies that target the use of other metals, such as Ag, Pt and Cu.
1.2 Research Synopsis

The discussion below focuses on investigations of the properties of Au films deposited on 3-aminopropyltriethoxysilane (APS) monolayers and subsequent use of such films in two specific applications. In particular, the studies consist of determinations of the order and structure of evaporated Au films on modified glass surfaces, electrochemical characterization of nanoscopic band electrodes fabricated from the Au thin films, and demonstration of Au film patterning on modified glass through the use of photolithographic methods. Future work with these films includes their use in biological, environmental, and chemical sensors, as well as in the construction of nanoelectronic devices.

Au nucleation and growth on APS-modified glass is compared to that on Cr-treated glass and pristine mica. Scanning tunneling microscopy (STM)\(^{13}\) and X-ray diffraction (XRD)\(^{14,15}\) were used to determine the surface roughness and crystallographic orientation of 10–100-nm-thick evaporated Au films on each of the aforementioned substrates. STM images of 100-nm-thick Au films on APS/glass and mica exhibit flat atomic terraces and single-atom steps indicative of Au(111) surfaces, while those of Au on Cr/glass do not exhibit such flat terraces. X-ray diffractometry confirms the presence of a highly oriented Au film on the APS/glass substrates, as noted by the presence of more than 98% Au(111) texture as compared to only 90% for the Cr/glass and mica substrates.

Gold band electrodes with widths ranging from 3 to 150 nm, fabricated using Au films deposited on APS/glass, are used to investigate the voltammetric response of a series of substituted ferrocenes in non-aqueous electrolyte. The Au electrodes are fabricated by insulating, with an epoxy, all but the edge of an evaporated Au film.
deposited onto a silane-modified glass substrate. Plots of normalized limiting current for each ferrocene derivative as a function of normalized electrode width reveal a negative response from traditional theoretical predictions. The theory used for the band electrodes is based on semiinfinite diffusion of the ferrocenes to a hemicylindrical electrode. The observed negative responses for electrodes less than 50 nm in width are explained by effects that become important when the sizes of the electrode and redox species are comparable. Concerns regarding the real surface area of the band electrodes are addressed by labeling of the exposed Au of the nanoband electrode with a ferrocene-tagged alkanethiol and measurements of double-layer capacitance. These studies indicate that roughly 20-500 times more area is exposed than that calculated from the nominal width and length of the bands, even though X-ray diffraction and stylus profilometry determinations of Au thickness are in agreement with those found by quartz crystal microgravimetry during evaporation of the Au films. Scanning electron microscopy studies of the epoxy/Au/glass interface point to insufficient insulation of the Au by the epoxy as the result of defects.

In the final studies described in this dissertation, the use of photolabile protecting groups, in conjunction with APS/glass surfaces, is investigated as a means of patterning the deposition of Au films. Fodor has used such protection/photodeprotection chemistry to fabricate DNA arrays. APS/glass substrates are reacted with nitroveratryloxy-carbonyl (NVOC) chloride so as to protect the amine groups of the APS monolayers. Upon evaporation of Au films onto the NVOC-APS/glass substrates, no noticeable adhesion of Au was found upon application of the standard tape test, a result that is in clear contrast to that for Au films on APS-treated surfaces. Exposure of the NVOC-APS/glass surfaces to light from a mercury lamp results in removal of the NVOC
protecting group to yield the APS surface; Au films deposited on these photodeprotected surfaces adhere as well as that found for pristine APS surfaces. Patterning of Au films was achieved by exposing the NVOC-APS surfaces to UV light through a variety of masks. Through proper control of the NVOC protection conditions and the photodeprotection steps, Au films with ~micrometer features can be produced. Fluorescence microscopy images of fluorescamine-labeled amine groups liberated during the photolysis procedure confirm that the amine groups of the APS are present in tact after the photolysis reaction.

1.3 Adhesion and Nucleation Promoters for Evaporated Metal Films on Dielectrics

In order to gain some understanding for why it is necessary to use an adhesion/nucleation promoter when evaporating a metal film like Au onto an insulator such as glass, the schematic in Figure 1.2 concerning the growth mechanisms of materials on surfaces is discussed. If the difference in surface energies between the depositing material and the substrate is great, then the depositing material "likes" itself more than the substrate, and large grains of the deposition material result. Another way of thinking of this is that a small degree of attraction between the deposit and the substrate will result in a high rate of diffusion of atoms of the depositing material on the substrate. As a result, the atoms collect together due to their mutual attraction. In such a scenario, if the difference in surface energies is very high, then the deposit will most likely not adhere well to the substrate surface. In addition, such "islanded" films will exhibit low electrical conductivities due to the fact that the crystallites or grains do not interact to a large degree (few contact points between grains); in such a scenario the films are often times electrically discontinuous up to thicknesses of 20 nm. This growth mechanism is often
referred to as the Volmer-Weber growth model. In contrast, if the depositing material interacts greatly with the substrate, then surface diffusion of deposit atoms is reduced (a sticky surface) and smaller grains form. In such cases, the adhesion between the substrate and the deposit is often extremely high. Also, the films are electrically continuous at very low film thickness values.

![Figure 1.2](image)

**Figure 1.2** Growth models of metal deposition demonstrating the impact of deposit-substrate interaction on deposit grain size, with grain size decreasing with increasing interaction between substrate and deposit, A through C.

Previous methods employed to modify glass surfaces for increasing adhesion of metals include coating the glass with silane monolayers, or evaporation of chromium (Cr), tungsten (W), or titanium (Ti) underlayers. The latter approach of first evaporating an ultra-thin (~2 nm) underlayer of a metal (a primer layer) has been the main method for increasing adhesion of metals to glass. However, the resulting metal films are typically rough, must be fairly thick to have reasonable conductivities, and may

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experience contamination or delamination as a result of the primer layer's presence. These concerns are magnified when using ultra-thin films of a metal of interest, for the thickness of the overlaying metal is comparable to that of the primer layer. In particular, a problem encountered when using Cr metal as a modifier is that the Cr diffuses through the metallic layer of interest to its outer surface after only a few days. This is a serious problem when electrochemical or sensor studies are carried out with thin metal films primed with Cr, for the Cr interferes in the analysis.\textsuperscript{26} Also, due to the known diffusion of chromium through metal films like Au, destruction of a given Au crystallographic orientation may result.\textsuperscript{27,28} In addition, although Ti and W do not diffuse through metal overlays to a great extent, metal films deposited on Ti- or W-primed surfaces suffer from delamination from the substrate at some point in the lifetime of the metal film, making their long-term use as an adhesion layer unattractive. Finally, the transparency of the primer layer is sometimes a concern, especially if one is to use the metal/primer/glass assembly as a transparent electrode in spectroelectrochemistry experiments.\textsuperscript{29}

Research here at LSU has previously demonstrated that monolayers of ω-substituted silanes on silicon oxide surfaces can act as effective adhesion promoters for ultra-thin (0.3-10 nm) Au films.\textsuperscript{1,2} In particular, 3-aminopropylsilane (APS) monolayers exhibited striking effects on the morphology and electrical conductivity of evaporated Au films; electrically contiguous films as thin as 3 nm could be produced, and these ultra-thin Au films exhibited extremely small grain sizes (5-9 nm diameter for APS surfaces versus 20-25 nm for bare silicon oxide).\textsuperscript{1} In addition, it was shown that Au films on APS-treated surfaces remains on the modified surface for a minimum of 6.5 months when exposed to the laboratory ambient. It was postulated in the previous studies that the
amine groups of the APS monolayers were hydrogen bonded to an extent that large areas of ordered amines existed. If this were so, then Au films produced on APS surfaces should exhibit extremely high order (preferred crystallographic orientation), such as that observed for Au on mica.\textsuperscript{30}

Coating of APS unto glass (silicon oxide) can be done in several ways. Some methods are dip and spin coating, resulting in polymeric multilayers of APS, while vapor deposition has proven effective for the production of monolayers of APS.\textsuperscript{1,2,16,31} Due to the goal of this research to produce nanoscopic structures, the vapor-phase treatment method was used. In this method, the APS is heated so that vapors of the silane are delivered to the silanol groups on the surface of the glass, which prevents polymerization of the silane. With this method, APS is deposited and cured on the substrate (glass). Such a monolayer-formation mechanism for a variety of substituted silanes is pictorially depicted in Figure 1.3.\textsuperscript{1,2}

![Diagram of monolayer formation](image)

**Figure 1.3** Formation of \(\omega\)-substituted silane monolayers on glass surfaces.

**1.4 Sub-Micrometer Electrodes**

Microelectrodes (smallest dimension of 1–10 \(\mu\)m) have been used for electrochemical studies since the early 1980s. R. Mark Wightman's concept for making smaller electrodes was based on the general idea that smaller is better for analyses in
confined spaces. These electrodes were created with at least one dimension in the 0.1 to 50 μm range. These studies have led to an interesting area of science where the electrochemical response at such electrodes is significantly different than that at macroscopic electrodes (dimensions in the mm or greater range). Further discussion of the characteristics of micro- and nano-electrodes is given in chapters 2 and 4 of this dissertation.

The initial studies with microelectrodes led researchers to ask the question, "what happens to the response of an electrode as one dimension of the electrode approaches molecular sizes?" If the electrode is similar in size to that of the redox species, then traditional theory concerning the voltammetric response should break down, Figure 1.4. This was first addressed in one of Wightman’s early papers on microband electrodes. Such questions have encouraged the production and study of electrodes on the nanometer scale. White, et al. developed nanoscopic band electrodes (2–50 nm wide, ~ 1 cm in length) in the late 1980s. They discovered that nanoband electrodes have similar characteristics to those of microband electrodes (qualitatively similar voltammetric response), but the magnitude of the current response was affected to a greater degree by band width than that expected based on theory available at that time. White observed Faradaic limiting currents (i_{lim}) that changed drastically when the width of the Pt band electrodes were less than ~20 nm, and explained these observations by correcting for the unrealistic view that the concentration of the redox species at the electrode surface cannot be that predicted by classical theory and that the diffusion layer at the electrode surface is roughly the size of the electrical double layer, which will result in a different diffusivity of the redox species than in the bulk. Thus, the redox species will experience a solvent
environment that is more viscous due to the localized increase in the concentration of ions near the electrode surface, and the diffusion laws ordinarily used for deriving equations for the current response at an electrode become discontinuous under such conditions.

**Figure 1.4** Pictorial depiction of molecular species approaching, A, a nanoband electrode and, B, a microband electrode demonstrating that diffusion to molecularly sized electrodes should be different than expected for microelectrodes.

Based on previous work with extremely small electrodes, there are concerns about uncertainty in band geometry and reproducibility of making such molecularly sized electrodes (surface defects). In addition, questions regarding the conductivity of such thin Pt films used in the construction of the electrodes arise. To combat these problems, Fritsch and co-workers have made micromachined band electrodes and have found similar deviations from the expected voltammetric response.

### 1.5 Photolithographic Patterning of Surfaces Utilizing Photolabile Groups

Photolithography is a powerful technique which has expanded the capabilities of research in electrode fabrication. It has allowed for the creation of sensors with selectively immobilized proteins and has been shown to be useful in the promotion of cell growth on surfaces. It also finds utility in electronic applications where selective
metalization of electrodes is desired and in light-directed molecular derivatization of surfaces in the synthesis of peptides (solid-phase peptide synthesis) and oligonucleotides (DNA arrays). In general, photolithography is an outstanding method for making patterned surfaces with micrometer-sized features.

Protecting groups that are light sensitive have been used in the synthesis of complex polyfunctional molecules. Usually, the protecting groups are bonded to molecules that have amino functional groups. This method has been used to synthesize peptides, polysaccharides, and nucleotides. Light-directed synthesis has also been used to pattern colloidal metals on silica surfaces covered with an amine-terminated silane. Using this light-directed photodeprotection method and colloidal metals, one can create complex micro- and nano-devices, including semiconductor devices.

For synthesis of polyfunctional molecules, aromatic nitro compounds, such as 2-nitrobenzylloxy carbonyl group (nitroveratryloxy carbonyl, NVOC), have been used as protecting groups. The removal of the 2-nitrobenzyl group with irradiation was first noted with 2-nitrobenzyl benzoate. During photoremoval of the NVOC protecting group, the nitro group is reduced to nitroso and the oxygen is inserted into the carbon-hydrogen bond at position 2 (see Figure 1.5). Such protecting groups are very useful in syntheses involving protection of amine groups, as shown in Figure 1.6 for the protection of the amine group of APS. The amine group forms a bond to yield the photolabile nitro urethane which can be removed by exposure to light with a wavelength longer than ~320 nm (λ_{max} of NVOC is ~350 nm). Thus, through the use of the NVOC group, APS-modified surfaces, masks, and an arc lamp, one can construct surfaces that would have on them patterned features of evaporated Au.
**Figure 1.5.** Mechanism for conversion of nitroveratryloxycarbonyl group to nitrosoveratryloxycarbonyl group with subsequent removal from the protected “R” group.

**Figure 1.6** Scheme of nitroveratryloxycarbonyl chloride forming a bond with the amino group of APS.
1.6 References


36) Rajasekharan Pillai, V. N. Synthesis 1980, 1, 1.


Chapter 2

Materials and Methods

2.1 Experimental Section

2.1.1 Chemicals

All solvents used were HPLC grade or better and were used as received. Ferrocene (Fc, Aldrich, 98%), 3-aminopropyltriethoxysilane (APS, Aldrich, 99%), bis(pentamethylcyclopentadienyl) iron (Fe*, Aldrich, 95%), dimethylferrocene (DMFc, Aldrich, 97%), methyl iodide (Aldrich, 99.5%), ammonium hexafluorophosphate (Aldrich, 99.99%), 4,5-dimethoxy-2-nitrobenzyl chloroformate (NVOC, Aldrich, 97%), and 1-hydroxybenzotriazole hydrate (HOBt, Aldrich, 99.9%) were used without further purification. The 2-mercaptoethylamine (cysteamine, 95%) was purchased from Sigma. N,N-dimethylaminomethylferrocene (DMAMFc) was purchased from Strem Chemicals. Fluorescamine, a fluorescent probe, was purchased from Molecular Probes. Reagent grade solvents used were 30% hydrogen peroxide, 98% sulfuric acid, and 99.9% pyridine and absolute ethyl alcohol. Tetrabutylammonium perchlorate and \((\text{C}_3\text{H}_5)\text{Fe}((\text{C}_3\text{H}_4\text{CO}_2\text{(CH}_2)_5\text{SH}), \text{referred to as Fc-SH, were from previous studies and synthesized according to literature procedures.}^{1,2}\text{ Ferrocenylmethyltrimethylammonium iodide (referred to as trimethylaminomethylferrocene iodide, TMAMFc) was synthesized by reaction of excess methyl iodide with DMAMFc in toluene. After reaction for 2 h, a slightly yellow precipitate formed. The solvent was rotoevaporated and a light yellow solid was obtained. Conversion to the hexafluorophosphate salt was accomplished by addition of excess aqueous, ammonium hexafluorophosphate to an aqueous solution of trimethylaminomethylferrocene iodide. The tan/yellow solid was dried under vacuum.
and collected by suction filtration. Gold nuggets (99.99%) and Ag wire (99.99%) were purchased from Refining Systems, Inc., Las Vegas, NV.

2.1.2 Fabrication of Band Electrodes

Microscope slide cover glasses, sometimes referred to as coverslips, and microscope slides (Fisherbrand) were used as a substrate support for the evaporated metal films. The glass coverslips/slides were cleaned in piranha solution (1:4 30% H$_2$O$_2$:98% H$_2$SO$_4$) at a temperature of 75 ± 5 °C for 20 min. **CAUTION! The piranha solution is extremely oxidizing and should be disposed of immediately after use so as to prevent explosions.** Then, the glass slips/slides were thoroughly rinsed with 18 MΩ•cm water and dried with a stream of N$_2$. The clean coverslips/slides were subsequently placed on a quartz rack for support during vapor deposition of the silane monolayers. To the vapor deposition chamber was added a mixture of 3 mL of APS and 40 mL of toluene. The chamber was sealed with the supported rack included, and then the chamber was heated for 4 hr at a temperature of 30–40 °C, as measured by a thermometer placed ~5 cm above the microscope glasses/slides. Upon removal of the coverslips/slides from the chamber, they were rinsed with toluene followed by drying with high purity N$_2$. The silane-treated cover glasses/slides were then transferred to a cryogenically pumped vacuum chamber (Edwards Auto 306, base pressure of 2 x 10$^{-7}$ Torr) for evaporation of Au. Gold was evaporated at a rate of 0.01 nm s$^{-1}$ to form metal films on the surface of the treated cover glasses/slides. Film thickness was determined through the use of an in vacuo quartz crystal microbalance (QCM). After evaporation of the metal films, the chamber was back filled with high purity nitrogen or argon and the samples removed. The Au band electrodes were fabricated by coating with epoxy the face of the metal films to within a
millimeter of the edge of glass slide. The epoxy-covered slides were then placed in an oven at 60 °C for 24 h to allow the epoxy to spread out and thermally cure. This method is expected to yield an epoxy/Au/substrate interface at the edge of the glass slide so that band electrodes with nanometer widths can be produced.

2.1.3 Synthesis of NVOC on NH₂-Terminated Surfaces and Subsequent Photolytic Removal of NVOC Groups

The NVOC protecting group was attached to the amine-terminated monolayers by using a simple solution method. A solution composed of approximately 1 mM 4,5 dimethoxy-2-nitrobenzyl chloroformate (NVOC) and 0.05 M HOBt in 1:5 benzene:pyridine was made. Modified glass substrates with an amine terminus (APS/glass) were placed in the above mixture, and the temperature of the solution was raised to and held at 30 °C for 7 h. The amine group of APS reacts with the NVOC to form a urethane linkage.

Because the urethane bond formed between the APS and NVOC groups is weak, light at a wavelength of ~320–350 nm will cause removal of the NVOC group from the amine group. This method is used in the work described here to form patterns of Au on glass surfaces. Through the use of a Ealing mercury arc lamp at 150 Watt equipped with a bandpass filter, water-filled cylinder filter, and an Al mask containing slots or a Cr/quartz mask with a known macroscopic or microscopic pattern, NVOC groups should be removed in the exposed areas. NVOC-protected samples require the use of a spacer (tape) between sample and mask to hold the sample in place. The NVOC/APS/glass samples were irradiated for 45 min to ensure complete removal of the NVOC groups.
2.1.4 Voltammetric Measurements

The measurement of \( i-E \) curves was achieved with an EG&G Princeton Applied Research Model 273A Potentiostat. A Yokogawa 3025 X-Y recorder was used to record the output of the potentiostat. An Ag wire quasi-reference electrode and a Pt wire counter electrode were used throughout the experiments. The working electrodes were Au band electrodes fabricated as outlined above or Au wire electrodes made by sealing Au wire in glass. The three-electrode system was composed of a glass electrochemical cell containing a porous ceramic frit (Ace Glass Inc.) that separated the reference electrode compartment from the auxiliary and working electrode compartment.

2.1.5 Scanning Probe Microscopy

Scanning force microscopy (SFM) and Scanning tunneling microscopy (STM) images were obtained by use of a Nanoscope III Scanning Probe Microscope (Digital Instruments, Santa Barbara, CA). Samples for SFM were glued onto magnetic sample pucks with double-sided adhesive tape and placed on the magnetic head of the piezoelectric scanner. Contact SFM in constant-height mode was used to obtain topographical images of APS monolayers on glass. SFM images of Au nanoband electrodes were acquired in deflection mode so as to examine the epoxy/Au/APS/glass interface for possible defects in the nanoband electrode. STM images of evaporated Au on mica or glass were obtained in the height mode using a freshly cut (or "cleaved") Pt-Ir wire.

2.1.6 Scanning Electron Microscopy

A Cambridge 260 Stereoscan Scanning Electron Microscope (SEM) was used to obtain images of band electrodes that were glued onto a sample holder with double sided adhesive tape and subsequently coated with an Au/Pd film to prevent sample charging.
2.1.7 X-ray Diffraction

A Siemens D5000 Dual Goniometer with a Kevev solid-state detector was used to quantitatively analyze the bulk properties of Au on Emerald muscovite mica (ASTM V-2, grade 3, Lawrence and Co.) or modified glass. The theory associated with determining the thickness of a thin metal film is based on the Scherrer method, as described in Chapter 3. The instrument was also used to determine the crystallographic orientation of the Au metal films on mica or glass.

2.1.8 Profilometry

Profilometry measurements were obtained using a Tencor P-2 Long Scan Profiler. These measurements were used to determine the thickness of evaporated Au on modified glass surfaces.

2.1.9 Infrared Spectroscopy

Infrared (IR) spectroscopy was performed with a Nicolet 740 Fourier transform infrared (FTIR) system using a liquid-nitrogen-cooled, wide-band MCT detector. The analyzing chamber was covered with a poly(ethylene) glove bag and purged with house nitrogen to minimize adsorption of hydrocarbons and H₂O on the samples. All IR samples were evaluated through the use of a commercially available reflectance accessory a with retro-mirror attachment (VRA-RMA, Harrick Scientific) with an incidence angle of 86° with respect to the substrate normal. Incident p-polarized light was achieved by employing a wire grid polarizer (Harrick Scientific). All sample spectra are the result of 1024 scans versus a bare Au background. Nicolet SX software was utilized to remove residual water bands from the spectra and to perform baseline corrections.
2.1.10 Fluorescence Microscopy

The fluorescence microscopy images were obtained with a Nikon microphet-FXA Fluorescence Microscope outfitted with a Nikon Super High Pressure Mercury Lamp Power Supply Model HB-i0101AF. Samples were exposed to dry acetonitrile solutions containing 2 mM fluorescamine for a minimum of 5 min, followed by rinsing with dry acetonitrile and drying with high purity N₂.

2.2 Theory of Electrochemical Measurements

Electrochemistry is a broad subject covering topics such as electron-transfer kinetics to electrosynthesis. Key to the electrochemical process are the currents and potentials involved with electron-transfer events, and in turn, the events that lead up to the observation of a current or potential associated with such events. In particular, upon application of a potential to an electrode immersed in a solution containing an electrolyte and a redox-active species, any observed current for the redox-active species is a combination of currents associated with the electron-transfer process and mass transport of the electroactive species to the electrode surface. However, under certain experimental conditions the observed current can be strictly limited to either the electron transfer process (then the current is a measure of the kinetics of electron transfer) or mass transport (the current is then a measure of the diffusivity of the redox molecules). In addition, electrochemical measurements can be made to have very high responsivities (sensitivities) and very low limits of detection, thus allowing for determinations of various molecular characteristics at exceedingly low concentrations (submicromolar or picomolar concentrations of the redox species of interest). The nanoscopic band electrodes (1 – 50 nm) used in this dissertation have voltammetric characteristics much different than those of macroscopic electrodes. For example, the current response at such
nanoband electrodes are sigmoidal in shape and are characterized by a plateau or limiting current, $i_{\text{lim}}$, that is a direct reflection of the diffusivity of the redox species under investigation, Figure 2.1. In addition, the limiting current is almost unaffected by the rate at which the potential is changed at the electrode surface (at slow potential scan rates, ~ up to 10 V s$^{-1}$). Finally, the currents associated with the redox process are extremely small but appear to be relatively insensitive to the presence of the current associated with the electrical double layer (background current). Thus allows for the analysis of species at much lower concentrations than that achievable with macroscopic electrodes.

![Diagram](image)

**Figure 2.1.** Depiction of the current response during a cyclic voltammetry experiment when using a microelectrode or nanoelectrode at slow potential scan rates.

To understand the characteristics of the sub-micrometer electrodes, one must first gain an understanding of the response of a macroscopic electrode (~0.1 cm diameter disk, for example) immersed in an electrolyte containing a redox-active species. If the potential of the working electrode, $E_{\text{wk}}$—that is the electrode at which the electrochemical response is measured—is moved at a scan rate $v$ (V s$^{-1}$) in a region
where no redox reactions associated with the analyte occur, then a current will flow at the electrode surface that is due to charging the metal–electrolyte interface. This charging current is the result of the requirement that the charge developed on the metal surface be compensated for in solution by ions and/or solvent. As a result, the electrolyte-metal interface resembles a double-layered region of charge of opposing sign, which is why it is called the electrical double layer. In addition, the double layer has the characteristics of a parallel plate capacitor with a capacitance, $C_{DL}$, which can be determined from the current flowing during a potential sweep:

**Equation 2.1.**

$$i_{DL} = C_{DL} \nu A,$$

where $i_{DL}$ is the current in Amps at a given potential and $A$ is the geometric area in cm$^2$ of the electrode. Thus, the capacitive current at a macroelectrode will increase linearly with scan rate and the area of the electrode, giving us our first glimpse of why very small area electrodes lead to low limits of detection for analytes (low capacitive currents).

The reduction-oxidation (redox) current that flows at a macroelectrode when the potential is swept through the region where electron transfer occurs (the formal potential, $E^0$) is a function of time and potential, as seen in Figure 2.2. The potentials at which the current is maximum are referred to as the peak potentials, $E_{p,c}$ and $E_{p,a}$ for the cathodic and anodic peak currents, $i_{p,c}$ and $i_{p,a}$. The voltammogram is peak shaped due to the fact that diffusion of analyte to the electrode surface is slower than the rate of consumption at potentials beyond the formal potential (which is roughly 28 mV negative/positive of the peak cathodic/anodic potentials) of the redox species, leading to a diffusion layer that extends away from the electrode surface into solution and "deepens" with more time or
Figure 2.2. Current response obtained at a macroelectrode for an electrochemically reversible process.

This deepening diffusion layer results from linear diffusion of analyte to the electrode surface. One way of thinking about this event is to recall the fact that the Nernst equation dictates the concentration of the oxidized form of the redox species to be zero at the electrode surface at potentials negative of the formal potential (for an electrochemically reversible reaction) and the rate at which the oxidized form gets converted to the reduced form is a function of the potential. As the potential is made more and more negative, the rate at which oxidized molecules can diffuse to the electrode surface remains the same, but the rate at which they are converted from the oxidized state to the reduced state increases dramatically, leading to a build up of the reduced form and a lack of the oxidized form within the vicinity of the electrode. Thus, the oxidized molecules must diffuse through a layer rich in the reduced form but devoid of the oxidized form, and the thickness of this depletion or diffusion layer increases with time (scan time or potential). Thus, as the potential passes the formal potential, the rate of diffusion can no longer keep up with the rate at which the molecules are converted to the reduced form. This current, which is a measure of the rate of conversion of oxidized
molecules to reduced molecules, is composed of the electron-transfer current and the mass transport or diffusion current. The peak current can be calculated from the Randles-Sevcik equation, Equation 2.2.

Equation 2.2

\[ i_p = 2.69 \times 10^3 n^{1/2} A D^{1/2} C^{1/2} \nu^{1/2} \]

at 25°C

From Equation 2.2 it is immediately noted that the peak current is a function of the potential scan rate to the one-half power and directly related to the concentration of the analyte. Thus, as the concentration of analyte is decreased, the current decreases linearly. In theory, as long as one can have an instrument that can measure the current at the macroelectrode, it should be possible to measure as low a concentration solution of analyte as is desired. However, this discussion has neglected the presence of the charging current, which is typically on the microamp scale. One might suggest that the scan rate be increased so that the analyte signal be made larger, but the charging current will "beat" the increases achieved in the analyte current due to the linear dependence of the capacitive current on potential scan rate. Thus, the minimum concentration detectable by cyclic voltammetry at a macroelectrode is in the micromolar range.

Diffusion to microelectrodes or nanoelectrodes is considerably different than at macroelectrodes when slow potential scan rates are used. Instead of the linear diffusion of analyte to the electrode surface discussed above for macroelectrodes, spherical or radial diffusion of analyte occurs at electrodes with one dimension comparable to or smaller than the diffusion length of a molecule, \( l \) (cm):

Equation 2.3.

\[ l = (2Dt)^{0.5} \]
where \( t \) is the time segment for diffusion and \( D \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)). One way of thinking about why radial diffusion occurs is that the analyte can traverse the diffusion layer at the electrode surface very rapidly, so fast so that the diffusion layer does not grow substantially into solution. As a result, the time it takes for the analyte to diffuse through the depletion layer is fast enough such that the rate of mass transport remains almost constant. In fact, due to the high rates of mass transport, the diffusion layer appears as a hemisphere for a disk electrode or a hemicylinder for a band electrode. This makes sense when one thinks about the fact that the concentration gradient, which is directly linked to the current observed, is not changing with time. Thus, the current should be independent of time (potential scan rate) as long as the time scale of the experiment is long enough for radial diffusion to be the dominant mass transport mechanism. As a result, the voltammograms obtained at micro- and nanoscopic electrodes resemble those obtained at rotated disk macroelectrodes. And similar to rotated disk electrodes, the higher the mass transport rate (smaller electrode dimension), the more sensitive is the voltammetry to electron transfer kinetics (current limited by electron transfer at potentials near the formal potential.

The limiting current at a disk electrode for all scan rates (long or short experimental time frames) is defined as the following.\(^{12}\)

\[
\text{Equation 2.4} \quad i_{\text{elec}} = \frac{nFACbD^{1/2}}{\pi^{1/2} t^{1/2}} + 4nFDrC_o
\]

The first parameter represents the current under linear diffusion conditions and the second parameter represents the current under radial diffusion conditions. If one carries out the experiment on a short time frame (fast potential scan rates), diffusion to the
microelectrode is linear, as was seen for macroelectrodes, and the left-hand term of the equation dominates. At long time frames (slow potential scan rates), the right-hand side of the equation dominates, and a steady-state response or current is obtained due to the radial diffusion profile that results.

The intent of use should first be considered when choosing a microelectrode based on its geometry. Certain standards to consider when choosing an electrode are the actual size, the electrode material, the insulator, the reproducibility after cleaning the electrode surface, and the turnover rate of redox species. The fabrication of submicrometer electrodes has been difficult due to size constraints. Delicate preparation was required to develop an electrode that was stable under electrochemical conditions. The microelectrode geometries consist of a disk cylinder, sphere, hemisphere, ring, and band as noted in Figure 2.3. By scaling down the traditional electrode geometries, microelectrodes were produced from wires, foil, and sputtering metal.

Disk-Cylinder

Hemisphere

Band

Sphere

Ring

Figure 2.3. Typical geometries used for microelectrode fabrication.
Band electrodes were selected for this research to achieve limiting currents based on the width of the metal film applied to the substrate. Band electrodes are equivalent to electrodes with hemicylinder geometry based on the area. This phenomenon is described in Figure 2.4. The similarities of these electrodes are expressed as $A_{\text{band}} = w \times b$ and $A_{\text{hemi}} = \pi \times r \times b$ ($r = w/\pi$) where $A$ is the area, $w$ is the width, $b$ is the length, and $r$ is the radius of electrode. It is shown that a hemicylinder electrode provides radial diffusion that is achieved at the electrode surface. Band electrodes have the same response to diffusion as a hemicylinder electrode.

![Diagram](image)

**Figure 2.4.** The area of the band electrode, in A, is equivalent to the area of a hemicylinder electrode, in B. Each circle represents a redox molecule approaching the electrode.

Assuming long experimental times ($t$ in Equation 2.4 $\to 10$ s), the current for a microband or nanoband electrode is defined as the following.

**Equation 2.5**

$$i(t) = \frac{2nFDIC^b\pi}{\ln\left[\frac{4Dt}{r^2}\right]}$$

In this expression, $D$ is the bulk solution diffusion coefficient, $t$ is time, $n$ is the number of electrons involved in the electron-transfer reaction, $C^b$ is the bulk concentration of the
species undergoing electron-transfer reactions, $F$ is the Faraday constant, and $r$ is the radius of the equivalent hemicylinder of length $l$. For the work in this paper, substitution of $r = w/\pi$\textsuperscript{13} where $w$ is the width of the band electrode, was chosen instead of $r = w/4$.\textsuperscript{14,15} It is important to note that the steady-state current at a band electrode is relatively independent of the electrode width. However, if the electrode is made thin enough, deviations from this relationship are found, as will be seen in Chapter 4.

Although very high mass transport rates are obtainable with micro- and nanoscopic electrodes, the currents at such electrodes are very small, on the nA to pA scale. At first glance, this may seem to be a problem when thinking about the charging current (background current). But, because the area of the electrode dictates the capacitance, Equation 2.1, and the area is extremely small, the background capacitance currents are minute. In addition, the redox current is dependent on the radius of the electrode. As a result, microelectrodes can be used to analyze for extremely low concentrations of materials (in the nM range and below). And, due to their small size, such electrodes can be placed in very small environments, such as in the synaptic gap region of neurons, for studying neurochemical events.\textsuperscript{16} Finally, due to the very low redox currents that come about with the use of micro- and nanoscopic electrodes, the amount of voltage loss between the working and reference electrodes, $iR_s$, where $R_s$ is the resistance of the solution, is very small. Thus, such electrodes can be used in highly resistive media, such as very non-polar solvents.\textsuperscript{17,18}

Cyclic voltammetry can also be used to characterize electroactive species that are confined on the electrode’s surface. For species that are specifically adsorbed to the electrode surface due to strong interactions between the adsorbate species and electrode
surface. The electrochemical response for specifically adsorbed redox-active species is much different than that of dissolved species (freely diffusing analyte). For strongly adsorbed redox species (reversible) the peak potentials for the anodic and cathodic processes are identical, leading to cyclic voltammograms that are symmetric. The voltammograms exhibit peak currents that can be used to calculate the amount of an adsorbate present, i.e.:

\begin{equation}
  i_{p,r} = \frac{n^2 F^2 A \Gamma_{ox}}{4RT}
\end{equation}

where \( \Gamma_{ox} \) represents the surface coverage or excess of the oxidized species, \( ox \), before the potential scan is initiated. However, more accurate values for surface coverages can be obtained by integration of the area under a given peak (the charge, \( Q \)).

\begin{equation}
  \Gamma_{ox} = \frac{Q}{nF}
\end{equation}

The area under the peak is the charge that is associated with the reduction of the absorbed layer of \( ox \). The same expression can be used to calculate the surface coverage of the reduced form of the adsorbate through use of the area under the anodic portion of the curve.

2.3 Theory of Atomic Force Microscopy

Scanning Force Microscopy (SFM), also known as Atomic Force Microscopy (AFM), is used to obtain the topography of surfaces with nm- to \( \mu \)m- resolution. SFM can be used to obtain information regarding the surface characteristics of either
conductive or nonconductive samples. For SFM, a sensor responds to a force that is measured by a detector, Figure 2.5. The sensor is a tip mounted on a cantilever beam with an effective spring constant, \( k \). The spring constant for the cantilevers used here is between 0.06–0.58 Nm\(^{-1}\). The tip of the cantilever is made of Si\(_3\)N\(_4\) and has a pyramidal shape. Deflection of the cantilever occurs as a result of interaction forces between the cantilever tip and the sample surface. In the contact mode of SFM, the cantilever springs up or down depending on the attractive and repulsive forces between the sample and the tip when the sample is moved under the tip. Some forces that are common for SFM are van der Waals, Born repulsion, electrostatic and magnetic forces, friction, and adhesion. The force (\( F \)) needed to displace the tip vertically a given distance \( z \) is related to the force or spring constant of the cantilever \( k \) through Hooke's Law in Equation 2.8.

![Diagram of SFM cantilever substrate and tip](image)

**Figure 2.5.** A. Depiction of SFM cantilever substrate and tip. B. Depiction of optical lever for monitoring SFM tip movement.
Thus, by measuring the displacement of the tip with distance, a force map or "image" of the surface topography is achieved.

There are two types of forces that contribute significantly to the total force measured with SFM. The first force discussed is that having to do with van der Waals forces. These forces are strong enough to cause deflection of the cantilever when the tip is within a few nanometers of the sample surface. The other force that contributes significantly to the total force measured by SFM is repulsion. This is because this force operates over a wide range of distances. The reader is referred to an excellent review of the models that can be applied to describe repulsive forces.  

2.4 Scanning Tunneling Microscopy

Scanning Tunneling Microscopy (STM) came about, in part, from studies of electron tunneling in the 1960's and 1970's. STM was developed in 1982 by Binnig, Rohrer, and Gerber and was shown to be capable of providing atomic-resolution images of surfaces. Surface topographs of samples are obtained by monitoring the tunneling current between a metal tip and conductive surface. The distance of separation between the tip and substrate dictates the magnitude of the tunneling current and as a result, the observed height of features on the sample. Thus, STM is capable of producing 3-D real space images of conducting surfaces with subatomic resolution.

The ultra-high resolution of STM lies in the high sensitivity of the tunneling current to very minute changes in distance between the STM tip and sample surface. By application of a potential between a sharp metal tip in close proximity to a conductive
surface (~1 nm), a tunneling current is achieved and results from overlap of the electron densities of the tip and sample. The tunneling current (A) is defined by

\textbf{Equation 2.9} \quad i \propto e^{-2\kappa d},

where \(i\) is the tunneling current, \(\kappa\) is a variable that is dependent on the bias across two electrodes, and \(d\) is the spacing between the lowest atom on the tip and highest atom on the sample.

There are two modes of operation when imaging with STM. When the STM is operated in constant-current mode, the current is held constant by adjusting the tip-sample separation distance through use of a feedback circuit and piezoelectric positioner that adjusts the tip height when scanning the tip laterally over the sample. This mode results in an image with a contrast that is related to the electron density of the surface.

An alternative mode to the constant-current mode is known as the constant-height mode, where the tip-sample distance is "locked" at a fixed initial value and then the variations in current that result when laterally scanning the tip are recorded.

To scan the structure of a surface (move the tip over the surface), a scanner with piezoelectric capabilities is used. The instrument used in this work is based on a tube scanner made of piezoelectric material. The piezoelectric material is a ceramic that expands in size (the x, y, and z directions) as a result of applied voltages to the piezoelectric tube. A schematic diagram of a piezo tube scanner is shown in Figure 2.6.

When an electric field is applied across the tube (Y and/or X electrodes), the piezoelectric material reacts and moves laterally. For vertical motion of scanning, the voltage is applied between the inside and outside of the tube (Z electrodes). The
maximum x-y resolution achievable lies between 0.1 – 3.0 nm, whereas, the z resolution is roughly 0.01 nm.

Figure 2.6. A typical piezo tube scanner with x, y, z electrodes.

The ideal tip for an STM should have a radius which is much less than 10-20 μm, for this feature determines the resolution and stability of the tunneling current. The single-atom tip model, as seen in Figure 2.7, best describes the structure of the tip. The model suggests that the tunneling tip has at its end a single atom or at the bare minimum, a small atomic cluster. If the end of the tip is “rough” (many asperities closely grouped together—non-uniform at the end), the current travels to the asperity that is closet to the surface at a given point in time and another at some other point in time, leading to distortions in the image of the sample (“double images”). Thus, the tip should be cut/cleaved so that the tip is atomically sharp and will give rise to the best STM images. Interestingly, such well-behaved tips can often times be obtained by simply cutting wires with inexpensive diagonal cutting pliers.
Figure 2.7. Schematic depiction of single-atom tip in STM.

2.5 Theory of Reflection-Absorption Infra-Red Spectroscopy

A technique commonly used in the field of surface science research to study the spectroscopic characteristics of thin films on reflective surfaces is that of reflection-absorption infrared spectroscopy (RAIRS). RAIRS is methodology best used with Fourier transform infrared spectrometers due to the need to signal average the infrared spectra. As with traditional transmission FT-IR experiments, a sample cell is required for RAIRS analysis; however, analytes for investigation by RAIRS are on a reflective surface (adsorbed or coated films), such as a metal like Au, Ag, Pt, Cu, Al, or Ni.

The theory for RAIRS was developed in 1959 by Francis and Ellison. They demonstrated that adsorbed films on reflective surfaces could be analyzed by reflecting IR light off of the film/metal surface at a grazing angle of 18° (with respect to surface normal). Greenler, in 1966, furthered the previous theory by quantitatively examining results from external reflectance infrared spectroscopy experiments. The application of
RAIRS to monolayers of alkanethiols on gold was first demonstrated by Allara and Swalen in 1983.  

To understand why it is possible to obtain the IR spectrum of a monomolecular layer of material on a reflective surface and gain knowledge concerning the orientation of the various moieties in the layer from such spectra, I discuss what happens when IR light reflects off of a metal surface. \(^{25}\) First, when IR radiation is reflected from a plane through a layer (the analyte), the larger the angle with respect to the surface normal (\(\theta\) represents the incident angle), the larger the number of molecules that are probed by the IR beam. This is another way of saying that the absorption intensity is enhanced by increasing the number of film species interrogated, and the increase in the number of species sampled by the IR beam is due to the larger area exposed to the IR light beam. This area is a function of \(\sec \theta\). The total absorption intensity is a function of the incident angle and the amplitude of the electric field, \(E\), and is defined as the function \(E^2 \sec \theta\). Thus, it is straightforward to see why RAIRS experiments are carried out at grazing angles of incidence.

In addition, when infrared radiation in a RAIRS experiment is reflected from a plane through an adsorbed layer, the reflected light loses intensity due to matched frequencies of the light and one of the vibrational modes of the molecules at the surface. However, only one of the components of the electric field is involved in the absorption process (light that is \(p\)-polarized), with the other (\(s\)-polarized light) only adding noise to the RAIRS signal. The \(s\)-polarized component of the IR beam reverses phase by almost exactly 180° at all angles of incidence. Therefore, the vector sum of the incident and reflected beams of \(s\)-polarized light is close to zero in the infrared region for metal
surfaces. Thus, the incident and reflected electric vectors “cancel each other out”,
leading to no noticeable interaction with film species. However, $p$-polarized IR light
exhibits a phase shift of 90° upon reflection at near grazing angles, and the phase shift is
dependent on the angle of incidence from the metal surface. Therefore, the $p$-polarized
light couples strongly to any vibrational modes that have dipoles perpendicular to the
surface. This is more quantitatively stated in Equation 2.10 where the change in phase of
the light beam ($\beta$) caused by the film is defined as

$$\beta = \frac{2\pi \tilde{n}_2 d \cos \phi_2}{\lambda}$$

where $\tilde{n}_2$ is the refractive index of the film, $\phi_2$ is the phase thickness of the film, $d$ is film
thickness, and $\lambda$ is the wavelength of the radiation reflected. Of course the refractive
index is related to the absorption coefficient ($k$), Equation 2.11.

$$\tilde{n}_i = n_i - ik_i$$

Therefore, the amount of light reflected from the film/surface is a function of the film
refractive index, the angle, and the wavelength of IR light used.

2.6 Theory of Scanning Electron Microscopy

A technique that is widely used to obtain structural information and properties of
surfaces is known as Scanning Electron Microscopy (SEM). This method is a very
powerful microscopy technique that can provide 3-dimensional images of surfaces at
magnifications that range from $\sim10\times$ to $10^5\times$ where the resolution is typically on the
scale of nanometers. Samples can be qualitatively and quantitatively studied using SEM, but it has the disadvantage that it requires a high vacuum that could possibly lead to removal of volatile materials from specimens under examination.

In SEM, an electron gun is used to produce electrons that are rastered onto a conductive surface, Figure 2.8. Samples that are conductive do not require any modifications; however, samples that are nonconductive should be prepared by applying an Au/Pd coating using a sputter coater. The electron gun typically consists of a tungsten filament (cathode) that is heated with a potential between 1 to 50 kV and results in emission of electrons. The sample is typically positioned perpendicular to the surface of interest. The emitted electrons pass through a Wehnelt cylinder (anode) that is poised at a negative bias with respect to the electron gun. The Wehnelt cylinder is used to direct...
electrons toward the sample of interest by accelerating and focusing the electron beam to a diameter of 10-50 μm. The electrons then travel through a series of magnetic condenser and objective lenses which results in a focused, fine spot on the sample. The magnetic lenses are used to increase and decrease the throughput of electrons to the surface, whereas the objective lenses collimate the electron beam on the surface to a spot size anywhere from 5 to 200 nm. Scanning coils are used to move the beam back and forth on the sample surface so that the image of the point of interest on the sample can be obtained in a row by row format.

Images of the sample surface are typically obtained by detecting secondary electrons emitted from the surface that result from interaction of the primary electron beam with the sample. The secondary electrons are detected by a cathode-ray tube to yield a map of the sample surface. The magnification of the sample surface is defined by the following equation.

Equation 2.12
\[ M = \frac{W}{w} \]

Magnification is represented by \( M \), the width of the CRT display by \( W \), and the width of a single line scan across the sample surface is represented by \( w \). According to Equation 2.12, when the line width is infinitessimally small; the magnification should be infinitely large. However, the highest magnification possible with most SEMs is limited to roughly 100,000× (~ 6 nm).

2.7 Theory of X-ray Diffraction

In 1895, W. C. Röntgen discovered X-rays. There are currently three areas of science that X-rays are used in. These areas are X-ray radiography, X-ray...
crystallography, and X-ray spectrometry. The technique most widely used in scientific research is X-ray crystallography. Max von Laue developed this experiment in 1912 where the wave character of light was confirmed by diffraction of X-rays from a single crystal.\textsuperscript{27} X-ray powder diffraction is a subfield of X-ray crystallography, an area of structure determination that was founded in 1935 by Le Galley.\textsuperscript{27}

X-rays are relatively short wavelength, high-energy beams of electromagnetic radiation. One can view an X-ray as a wave, which has a sinusoidal oscillating electric field perpendicular to an oscillating magnetic field, Figure 2.9. The X-ray region is located in the electromagnetic spectrum between 0.1 and 100Å. The following equations represent relationships for any electromagnetic radiation.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure.png}
\caption{Electromagnetic radiation represented as electric and magnetic fields at right angles to one another and direction of propagation.}
\end{figure}

\textbf{Equation 2.13} \hspace{1cm} \nu = \frac{c}{\lambda}

\textbf{Equation 2.14} \hspace{1cm} E = hv

\textbf{Equation 2.15} \hspace{1cm} E = \frac{hc}{\lambda}
Frequency represents as $v$, the speed of light represents as $c$, wavelength represents as $\lambda$, and Planck's constant represents as $h$. In Equations 2.14 and 2.15, $E$ is the energy equivalent of an X-ray photon.

The origin of X-rays is understood by addressing the interaction of high-speed electrons with materials. There are three processes associated with particles and radiation resulting from the impingement of fast moving electrons on a material, Figure 2.10. A photoelectron occurs when an electron is removed from its original state,
leading to an atom in an ionized state. The kinetic energy for a photoelectron is the
difference between the energy of the incident electron and the binding energy of the
ejected electron. With the Auger electron effect, the ionization of the inner shell electron
produces photon (resulting from L→K transition) that gets absorbed by an outer shell
electron and results in its ejection. However, the transition of the L electron to the K
vacancy can also result in production of an X-ray photon.

Diffraction occurs when scattered coherent radiation from a surface with periodic
arrays produce constructive interference at specific angles. For coherent scattering, the
oscillating electric field interacts with electrons in matter. The waves that scatter will
have either constructive or destructive interference. Bragg’s analogy is a simpler way to
understand diffraction from a crystal; however, this analogy is not fully accurate. X-rays
of incidence in this analogy are considered to be in phase and reflect from imaginary
planes in two dimension.\textsuperscript{27} In Figure 2.11, the crystallographic planes are described by
Miller indices (hkl). The initial waves on the left are in phase with one another so that
reflection occurs at each plane. The waves in the second and third plane travel a distance
farther than the first plane. Reflecting waves in the second and third planes lag behind
the first plane causing interference of the waves. Bragg’s equation was determined by
measuring the distance between side AB. Diffraction occurs at angle ABC that is equal
to $\lambda$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2_11.png}
\caption{Diffraction of X-rays of each crystallographic plane.}
\end{figure}
Equation 2.16
\[ AB = d_{hkl} \sin \theta \]

Equation 2.17
\[ \lambda = 2d_{hkl} \sin \theta \]

A more realistic approach to explain diffraction was established by P. P. Ewald.\(^{27}\) This method known as the reciprocal lattice considers the reciprocal of \(d_{hkl}\) in its approach to diffraction in three-dimensional space. In Figure 2.12, a depiction of vectors shows projection in all directions, which represent the 3-D vector of the planes in a unit cell. Because the vectors are approaching the origin, Ewald suggested that the reciprocal of \(d_{hkl}\) should be plotted by Equation 2.18.\(^{27}\)

![Figure 2.12](image-url) 3-D vector of the plane in a unit cell. The reciprocal lattice is shown in Figure 2.13.

Equation 2.18
\[ d_{hkl}^* = \frac{1}{d_{hkl}} \]

When the crystal of study is rotated, its reciprocal lattice also rotates (Ewald sphere). Certain indices representing the \(d^*\) value are brought into contact with the sphere for diffraction to occur. Ewald showed that it is necessary to rotate the sample until the
beam can be diffracted. This is an easy concept for obtaining diffraction geometries of complex samples.

![Reciprocal lattice of unit cell](image)

**Figure 2.13.** Reciprocal lattice of unit cell in Figure 2.12.

The intensity of diffraction peaks is understood by studying the behavior of a single electron, the behavior of electrons in space and scattering of atoms in different regions of the unit cell. The intensity scattered from an electron was proven by J. J. Thompson in 1906 to be

\[
I = \frac{I_0}{r^2} \left( \frac{e^2}{m_e c^2} \right)^2 \left( 1 + \cos^2(2\theta) \right) / 2,
\]

where \( I_0 \) represents the intensity of the incidence, \( e \) represents the charge on the electron, \( m_e \) represents the mass of the electron, \( c \) represents the speed of light, and \( r \) represents the distance from the scattering electron to the detector. This equation is only useful for coherently scattered radiation.

The type of sample used in the X-ray diffraction studies described here is polycrystalline. Gold, an evaporated metal, is in a polycrystalline state with random crystal orientation. The use of X-ray powder diffraction is necessary to obtain the
orientation and amount of each orientation in the Au films. To obtain diffraction at a particular plane, the diffraction angle of interest should vary and the intensity as a function of $2\theta$ is measured. Au is cubic where $a = b = c = 4.078 \text{ Å}$ and $\alpha = \gamma = \beta = 90^\circ$.27

2.8 References


3.1 Introduction

The use of modifiers to enhance metal nucleation and adhesion on glass or silica surfaces has been important for production of microdevices\textsuperscript{1} and bioelectronic\textsuperscript{2} devices such as electrodes, sensors, or semiconductors.\textsuperscript{3,4} Increasing metal nucleation and adhesion on such dielectrics is vital for developing thin metal films capable of acting as optically transparent devices or molecularly sized electrodes.\textsuperscript{3-5} In addition, it is imperative to understand the nucleation properties of metals on modified insulators to create smaller devices for future electronic purposes.\textsuperscript{3,4,6,7}

In order to produce electrically continuous ultra-thin metal films on insulators, it is typically necessary for the surface to have a strong interaction with the deposited metal film. For example, if the surface interacts weakly with the metal, the metal adatoms are mobile on the surface, resulting in the formation of large grains/crystallites, leading to poorly conducting metal films at low film thickness.\textsuperscript{3,4,6,8} However, modifiers on glass or silica surfaces can lead to strong interactions between metal and the surface, resulting in small grained metal films that are highly conductive.\textsuperscript{3-5,9-14}

Although, Cr and Ti are popular modifiers that have been used to increase adhesion of Au films on insulators such as silica and glass, both metals tend to cause difficulties in the performance of Au films. For example, the use of Ti often times leads to Au films that delaminate over the lifetime of device use.\textsuperscript{5,15-20} Also, Cr is known to diffuse through ultra-thin Au layers and contaminate the Au surface, rendering them less
effective in a variety of applications. Finally, the use of Cr and Ti as a modifier leads to Au films that are often times rough (vide infra).

A variety of approaches for surface modification of insulators with organic and inorganic materials to enhance metal nucleation/adhesion have been described. More specifically, we are interested in developing ultra-thin metals for use in microelectrochemical applications. Some surface modifications that have been used to construct metal film electrodes include spin-coated polymer films, Langmuir-Blodgett and self-assembling films of amphiphiles, and silanization reactions. Due to the fact that one can form silane monolayers with tailored chemical "tail" functionalities, we have chosen to study the effects of a particular silane monolayer on the formation of Au films due to its previously reported impact on the conductivity and smoothness of evaporated Au films. Dunaway and McCarley have previously shown that vapor deposited Au films (0.1 – 10 nm) on 3-aminopropylsilane monolayers are very adherent to silicon oxide surfaces (oxides on single-crystal Si). In the study at hand, we describe the use of 3-aminopropytriethoxysilane (APS) monolayers to yield Au films on glass substrates that exhibit the positive attributes of Au(111) on mica and Au on Cr. Scanning tunneling microscopy (STM) is used to probe the morphology of Au on APS-treated glass surfaces. The strong adhesion of Au on the NH$_2$-terminated surfaces prevents diffusion of Au atoms and leads to uniform grain size Au films. In addition, the grains are very flat, as noted by STM images. In fact the morphology of Au films on APS/glass are similar to those of Au(111)/mica, a characteristic that is obtained without thermal annealing of the Au on the APS/glass surface. In addition, X-ray diffraction is
used to obtain the crystallinity of evaporated Au on APS-treated glass (APS/glass), Cr-treated glass (Cr/glass), and mica.

3.2 Results and Discussion

As previously reported by this group, APS is an effective promoter of Au adhesion and nucleation on silica surfaces (native and thermal oxides on single-crystal Si). This surface enhancement has noted the extremely uniform and small Au crystallite size (slow adatom diffusion), the onset of electrical continuity at ultra-low values of Au film thickness, and the tenacity of the Au films to remain on the APS-modified surfaces upon repeated application of the standard tape test. These characteristics have led us to utilize such ultra-thin electrically continuous films (~3–10 nm) in the construction of nanoscopic electrodes. However, the morphological and structural properties of thicker Au films on APS-modified surfaces have not yet been investigated.

The effects of substrate on the morphology of vapor-deposited Au films were studied by examination of 100-nm and 10-nm-thick Au films vapor-deposited on APS/glass, Cr/glass, and mica surfaces. Both the Cr/glass and mica substrates were chosen as reference cases due to their known ability to yield either highly ordered Au films or Au films that are strongly adherent to the underlying support. In addition, comparison of two different Au thicknesses was deemed necessary to gain insight into the possible mechanism of Au crystallite growth on the APS/glass surface versus that for the Cr/glass or mica surfaces.

Shown in Figure 3.1A is a representative topographical STM image of a 100-nm-thick Au film on APS/glass, as well as a cross-sectional image of the topograph. In general, the film is characterized by Au grains that exhibit properties similar to those of
Au on mica, Figure 3.2A. The Au grains on APS/glass are for the most part flat and exhibit single-atom steps (0.25 nm height), vide infra. In addition, for the 100 nm films, the grains are 25.2±3.5 nm in diameter, and the surface roughness is 2.35 nm. These values are somewhat similar to those for 100 nm films on mica, with the grain diameter and roughness being 17.9±1.7 nm and 3.51 nm, respectively, for Au on mica. From STM images of 100 nm Au films on Cr/glass, Figure 3.3A, it is clear that use of APS/glass results in a surface that is populated with Au grains that are routinely larger when Cr/glass is used (28.2±1.7 nm diameter), but a surface with slightly higher roughness (2.76 nm). The roughness values and grain diameters are displayed in Table 1. It must be noted that the roughness reflects, in addition to the grain size, the amount of void space between grains (intergrain void space). It is clear that the Au/mica has many

![Figure 3.1](image-url)

**Figure 3.1.** 880 nm x 880 nm STM images of Au on (CH₃O)₃Si(CH₂)₂NH₂-treated glass and representative cross-sections. A. $d_{Au} = 100$ nm and B. $d_{Au} = 10$ nm. Z-range is 25 nm in all cases.
Figure 3.2. 880 nm x 880 nm STM images of Au on mica and representative cross-sections of the images. A. \(d_{Au} = 100\) nm and B. \(d_{Au} = 10\) nm. The z-range is 25 nm in both A and B. Z-range is 25 nm in all cases.

Figure 3.3. 880 nm x 880 nm STM images of Au on 2.5-nm-thick Cr supported on glass. Representative cross sections are shown for each image. A. \(d_{Au} = 100\) nm and B. \(d_{Au} = 10\) nm. Z-range is 25 nm in all cases.

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atomically flat grains, as does the Au/APS/glass, but both of these surfaces have large intergrain void volumes. Thus, although the 100 nm Au films on APS/glass have smaller roughnesses than do those on mica and Cr/glass, the void volume is quite high, indicating a difference in the growth of the grains.

Table 3.1. Roughness values and diameter of Au on various substrates from STM.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Z range (nm)</th>
<th>Rms (nm)</th>
<th>Diameter (nm)</th>
<th>Diameter S.D. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm Au/APS</td>
<td>19.74</td>
<td>2.35</td>
<td>25.15</td>
<td>3.48</td>
</tr>
<tr>
<td>100 nm Au/mica</td>
<td>29.25</td>
<td>3.51</td>
<td>17.86</td>
<td>1.70</td>
</tr>
<tr>
<td>100 nm Au/Cr</td>
<td>21.32</td>
<td>2.76</td>
<td>28.20</td>
<td>1.74</td>
</tr>
<tr>
<td>10 nm Au/APS</td>
<td>14.31</td>
<td>1.72</td>
<td>17.66</td>
<td>0.68</td>
</tr>
<tr>
<td>10 nm Au/mica</td>
<td>23.89</td>
<td>2.53</td>
<td>11.58</td>
<td>0.85</td>
</tr>
<tr>
<td>10 nm Au/Cr</td>
<td>23.57</td>
<td>3.04</td>
<td>19.67</td>
<td>1.66</td>
</tr>
</tbody>
</table>

S.D. represents standard deviation

The investigation of Au films with smaller thicknesses is necessary to understand the initial growth of Au on the APS/glass substrates. Figure 3.1B is a display of a typical STM image of 10-nm-thick Au on APS/glass and a cross-sectional image. The film exhibits Au grains that are round with no indication of single atom steps. The grain size of the Au is ~17.7 nm in diameter which is smaller than the diameter of Au grains in Figure 3.1A. The RMS surface roughness of 10 nm Au on APS/glass is 1.72 nm. It is evident that the void space is much smaller for the 10 nm film. The size of the grains for the 10-nm-thick film on APS/glass is similar to that for equivalent thickness Au films on mica, and the tops of the grains are very rounded. However, the Au grains on mica in Figure 3.2B exhibit flat tops (terraces) which are characteristic of highly ordered Au and are ~11.6 nm in diameter, and the surface roughness for these films is 2.53 nm. In Figure 3.3B, the grains are round and larger in diameter (~19.7 nm) for 10 nm films on Cr/glass. In addition, the uniformity of the film is poor, as evidenced by the larger surface roughness (3.04 nm) of the 10 nm film in comparison to those on mica or APS/glass.
The striking similarity in the morphology Au films on APS/glass to that of Au on mica must be due to the smoothness of the APS surface and the interaction of the initial layer of Au with the amine groups of the APS surface. In addition, the Au-APS interaction must also be the reason that the Au films on APS/glass are less rough than those on mica or Cr/glass. As seen in Figure 3.4, the APS/glass surface is very smooth (RMS roughness of 0.532 nm), but not as smooth as the single-crystal mica surface. Also, the interaction of 5 to 10-nm-thick Au films with the APS surface is very high as judged by standard tape tests; no loss of Au was found upon repeated application/removal of tape. Similar results were found for Cr/glass substrates. However, the Au films on mica were often times readily removed during the tape test. These results indicate that there is relatively little adhesive interaction between the mineral surface and the Au, but a large interaction between the Au and the APS surface (similar to that for Cr/glass). A general theme to explain the overall observations for Au on APS/glass is focused on the fact that the initial deposition of Au on the amine surface is highly uniform due to chemical interactions of Au with the amine groups. The nature of this interaction has been speculated on previously, but the precise mechanism of the Au-amine interaction is not known.³ However, one can hypothesize from the results of our previous work and those from the present study that the first Au atoms to deposit on the APS surface quickly react to form an Au-amine complex that substantially reduces Au atom mobility. This reduced mobility results in the formation of a high density of very small Au grains (large number of nucleation sites)³, which in turn leads to the production of uniformly sized grains as film thickness increases. The high density of grains also leads to a lack of void volume between grains for the APS/glass surface, as evidenced by comparison of the cross-sectional images in 1A and 2A.

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Figure 3.4. 880 nm x 880 nm SFM image of (CH$_3$O)$_3$Si(CH$_2$)$_3$NH$_2$-treated glass and a representative cross-sectional image. Z-range is 8 nm in all cases.

It is not clear why the Au crystallites on the APS surfaces exhibit atomically flat terraces with single-atom steps for, similar to that found for Au on mica, Figure 3.5. There is no evidence to support a high degree of order in the APS layers that could lead to an epitaxial growth of Au. Au films on mica deposited at room temperature exhibit weak epitaxy with respect to the mica surface, and as a result, (see Figure 3.5), ~20–50 nm-diameter crystallites that display single-atom steps and terraces are achieved. (Heating of the substrate during or after evaporation of Au onto mica leads to much larger Au crystallites and strong epitaxy.) Thus, there appears to be some amount of order in the APS monolayers, possibly due to hydrogen bonding between amine groups, and this order of the amine groups results in an ordered deposition of Au atoms. The STM images obtained here for the Au/APS/glass suggest a $\{111\}$ texture due to their similarity to those for Au/mica, but such an assignment cannot be made conclusively.
without atomic-resolution STM images. Thus, we have turned to X-ray diffraction studies to obtain the various orientations of Au crystallites present in the Au films on APS/glass and compared them to those of Au on mica and Au on Cr/glass.

**Figure 3.5.** 200 nm x 200 nm STM images of 100-nm-thick Au on A. (CH₃O)$_3$Si(CH₂-CH₂)$_3$NH₂-treated glass, B. mica, and C. 2.5-nm-thick Cr on glass. Z-range is 15 nm in all cases.

X-ray diffractograms for 100-nm-thick films of Au on APS/glass, Cr/glass and mica are displayed in Figure 3.6A-C. Even though there are other orientations present,
the preferred orientation of the Au in all cases is \{111\} as noted by the diffraction peak at 38.2°. From the diffractogram in Figure 3.6A for the Au/APS/glass case, only a minor component of the film is composed of the \{222\} (3.80% of theoretical intensity for isotropic sample). The diffractogram for Au on APS/glass is very similar to that for Au on mica (no significant intensity for the \{200\}, \{220\}, or \{311\} faces—the peaks near the Au diffraction planes are due to the mica substrate). As suggested by the STM images of Au on Cr/glass, the amount of other textures present in this film is substantially more than for either the APS/glass or mica substrates, most likely the result of disorder in the film caused by the Cr underlayer. What is outstanding about the Au films on APS/glass is that they exhibit a very strong \{111\} preferred orientation with minimal contributions from the other crystallographic faces. This observation is in agreement with the STM images, for the crystallites exhibit atomically flat terraces similar to those for Au/mica.

3.3 Conclusions

Based on the STM, adhesion, and X-ray diffraction data, it is concluded that the APS layers provide a surface that causes evaporated Au to nucleate uniformly and grow in a highly ordered fashion, similar to room-temperature-deposited Au films on mica which exhibit a weak epitaxy. In addition, the adhesion of Au on the APS/glass is far superior to that of Au films on mica and is comparable to that for films on Cr/glass. However, the APS layer is not prone to diffusion through the Au as is Cr. From previous findings, the stability of the adhesive interaction between Au and the APS layer is such that the films can be used to construct electrodes useful in non-aqueous solution-phase electrochemical studies, and the films are not removed from the substrate for periods of up to 6.5 months upon application/removal of tape.

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Figure 3.6. X-ray diffractograms of 100-nm-thick Au on A. (CH$_3$O)$_3$Si(CH$_2$-CH$_2$)$_3$NH$_2$-treated glass, B. mica, and C. 2.5-nm-thick Cr on glass. The large intensity peaks (*) in B are evidently due to the mica substrate.

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3.4 References


Chapter 4

Characteristics of Nanoscopic Au Band Electrodes

4.1 Introduction

Chemical reactions and their possible control in molecularly sized volumes is an important area of science to explore.\(^1\)\(^2\) Many processes in microelectronics fabrication, genetic sequencing, micromachining, tribology, and chemical sensing are intimately involved with events that occur in dimensions that approach the nanometer scale. It has been assumed in the majority of such work that the bulk characteristics of materials hold true in the nanoscopic regime. Only recently, *in situ* techniques of analysis have been developed for studying the characteristics of molecules and their reactions in exceedingly small volumes. The use of microcoils in the construction of nuclear magnetic resonance spectrometers has proven to be an important step toward the development of trace analysis methods for molecules derived from single cells or combinatorial syntheses.\(^3\) Also, electrochemical sensors based on enzyme-modified nanoscopic band electrodes show great promise for use in small volumes.\(^4\) Techniques such as those that make use of the surface forces apparatus\(^5\) or small-angle neutron scattering\(^6\) can lead to an idea of the structure of solution-phase molecules in confined spaces. In addition, the advent of the family of scanning probe microscopes\(^7\)\(^8\) has allowed for the real time visualization of reactions on surfaces with nanometer resolution. It is evident that as technology continues to push toward the use of molecularly sized events and devices, the demand for methods that permit nanoscopic studies will steadily increase.
Electrochemical techniques have been used extensively to investigate the physical properties of molecules and their environments in solutions and the solid state, but these measurements usually yield information which is averaged over the entire electrode/electrolyte region (often > \( \mu \text{m}^2 \)). The development of electrodes with micron-sized dimensions has led to an understanding of microenvironmental effects on the electrochemical response of various analytes. For example, placement of microelectrodes in or near regions such as synaptic gaps, corrosion pits, or picoliter “beakers” has allowed for determination of chemical properties in small localities that would not be possible otherwise. This type of electrochemical interrogation can be further elaborated by use of techniques that permit one to obtain a map of the physical/chemical characteristics of a given environment, such as the scanning electrochemical microscope (SECM) developed by Bard and co-workers, or those methods which provide data on the sub-microsecond time scale.

Information concerning the diffusional characteristics of an analyte in an electrolyte within a few molecular diameters of a surface can be obtained if electrodes of sub-micron size are employed. Murray has shown that such data can be acquired for semi-solid electrolytes (diffusion coefficients of \( \sim 10^{-2} \text{ cm}^2 \text{ s}^{-1} \)) when either microdisks or microbands are used as the working electrode. The use of sub-micron disk electrodes for determining changes in diffusivities near surfaces in room temperature liquids is an option, but as the size of the disk approaches the nanometer range, measurement of such small currents (current response scales with radius) becomes trivial.

Band electrodes with widths of 1-50 nm have been used by White and co-workers to investigate possible changes in the diffusion of analytes to such molecularly sized
electrodes. In their studies, Pt band electrodes fabricated by sealing sputtered Pt/mica in epoxy were used to obtain the voltammetric response of several redox species in aqueous and non-aqueous electrolytes. It was observed that the limiting currents were an order of magnitude lower than that predicted from semiinfinite diffusion of the redox species to a hemicylindrical electrode. Similar observations were obtained by Fritsch. These negative deviations were attributed to changes in the diffusivity of the redox species near the electrode surface as a result of the nature of the liquid at the electrode/electrolyte interface and non-zero concentrations of the redox species at the electrode surface.

Only a few voltammetric observations with ultra-narrow Au bands (<50 nm) have been reported. This relatively low number of voltammetric studies with Au is most likely due to the fact that evaporated Au tends to form discontinuous films (islands) below equivalent film thicknesses of ~15 nm. By use of appropriate modifiers on glass surfaces, we have shown that small-grained, electrically conductive Au films as thin as 3 nm can be made. These films can be used to construct nanoband electrodes by merely insulating the topside of the Au film with an appropriate dielectric.

Reported here are voltammetric observations for a series of ferrocenes in acetonitrile/tetraalkylammonium electrolyte at Au band electrodes ranging in width from 3 to 150 nm. The results are discussed in light of previous data obtained at Pt nanoband electrodes and Au submicrometer band electrodes. Upon labeling the exposed Au of the nanobands with an electroactive adsorbate, real electrode areas much larger than that calculated from the nominal length and width of the bands are obtained. Similarly,
capacitance values point to much larger exposed areas. Scanning electron microscopy studies confirm the presence of excess exposed Au.

4.2 Theory for Microband Electrodes

The expression for the current response following a potential step at a rectangular electrode with one geometric dimension smaller than 20 μm has been shown.\(^{23,24}\)

\[
i(t) = \frac{2nFDIC^b \pi}{\ln \left( \frac{4Dt}{r^2} \right)}
\]

Equation 4.1

In this expression, \(D\) is the bulk solution diffusion coefficient, \(t\) is time, \(n\) is the number of electrons involved in the electron-transfer reaction, \(C^b\) is the bulk concentration of the species undergoing electron-transfer reactions, \(F\) is the Faraday constant, and \(r\) is the radius of the equivalent hemicylinder of length \(l\). For the work in this paper, substitution of \(r = w/\pi\)\(^{24}\), where \(w\) is the width of the band electrode, was chosen instead of \(r = w/4\).\(^{20,25}\) The latter exactly describes the current response of microband electrodes at long electrolysis times in Equation 4.1. However, direct comparison of our results to previous work\(^{18,19}\) requires use of \(r = w/\pi\). When applying Equation 4.1, it is evident that the long-time current response at microscopic band electrodes is not true steady state and is quite insensitive to changes in the width of the band. The relative independence of the current response on the band width is demonstrated by a 65% decrease in the limiting current that is calculated when moving from a 5-μm to 5-nm-wide band electrode (10\(^3\) decrease in width).

In Figure 4.1, cyclic voltammograms of ~1 mM ferrocene (Fc) in 0.1 M \(\text{Bu}_4\text{NClO}_4\text{CH}_3\text{CN}\) electrolyte recorded at 0.04 V s\(^{-1}\) using a 10-nm-wide, 0.90-cm-long
Figure 4.1. A series of cyclic voltammograms of 1.01 mM Fc in 0.1 M Bu₄NClO₄/CH₃CN. Scan rate is 0.04 V s⁻¹. Electrode width is 10 nm, and its length is 0.90 cm. Au band electrode are shown. These voltammograms were obtained during stability studies that employed a scan rate between 0.04 V s⁻¹ to 0.50 V s⁻¹. If the voltammogram of a given band electrode displayed any unexpected changes in current response with scan rate or displayed "peaked" voltammograms due to defects, the electrode was discarded. Electrodes that displayed voltammograms having shapes and limiting currents

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roughly independent of the potential scan rate over the range of $0.01 \text{Vs}^{-1}$ to $0.5 \text{Vs}^{-1}$ were found to be stable for repeated scans, as seen in Figure 4.1. The observed limiting currents in Figure 4.1 were reproducible ($\pm 2\%$) over a period of approximately 1 h. The expected limiting current calculated using Equation 4.1 for a 10-nm-wide, 0.90-cm-long electrode yields a value of 480 nA, a value that is roughly 1.3 times that observed. Similarly, the theoretical limiting current for a 3-nm-wide band calculated using Equation 4.1 is found to be 5.2 times that observed experimentally.

4.3 Theory for Nanoband Electrodes

Wightman, White, and Fritsch have shown that band electrodes with widths less than approximately 25 nm exhibited limiting currents less than that predicted by Equation 4.1. In 1985, Wightman suggested that the use of Equation 4.1 "...is inappropriate for an electrode of this small size (5 nm)...". White and co-workers investigated the negative deviations from Equation 4.1 at Pt nanoband electrodes and derived a theory that explains these deviations. The proposed theory is based on the idea that transport of a redox species to an electrode of near-equivalent dimension is strongly influenced by changes in the fluid properties of the electrolyte near the electrified interface. In addition, the diffusional transport equations were derived for isotropic continuum fluid structure. The diffusion property can be explained by stating that the diffusion layer at a nanoscopic band electrode will be similar to that of the region near a surface where changes occur in the viscosity and density of the electrolyte medium. With this assumption, the change in concentration of a redox species from the bulk value to a surface value of zero is incorrect. Redox species approaching electrodes of comparable size encounter a build up due to the highly structured solvent/electrolyte medium.
environment and the physical impossibility of having their concentration change from bulk values to zero at the electrode surface over distances of a few molecular diameters. In such a nanoscopic scenario, Equation 4.1 must be reassessed. Upon incorporating terms that allow for correction of the non-zero surface concentration of the reacting redox species and changes in the properties of the electrolyte, the following relationship for nanoscopic band electrodes was obtained.

\[
i(t) = 2nFDB^2\pi \left[ \frac{\left(1 + \frac{r}{z}\right)\ln\left(\frac{4D}{r^2}\right) - 8\xi}{\left(1 + \frac{r}{z}\right)\ln^2\left(\frac{4D}{r^2}\right)} \right]^{\frac{1}{2}}
\]

Here, \(z\) is the reaction layer thickness and \(\xi\) is the ratio of the bulk diffusion coefficient \(D\) to the diffusion coefficient of the redox species in the highly structured reaction layer \(D_s\). This expression predicts that the current response is strongly influenced by \(D_s\) and the size of the reacting redox species when the size of the redox species approaches that of the reaction layer (the width of the band).

The dependence of the limiting current on the size of the redox species is tested by obtaining voltammograms of various ferrocene derivatives using Au nanobands ranging in width from 3 to 50 nm. Cyclic voltammograms of \(~1\ \text{mM}\) solutions of decamethylferrocene (Fc*), dimethylferrocene (DMFc), and \(N,N,N\)-trimethylamino-methylferrocene (TMAMFc, a cationic species) in \(0.1\ \text{M}\) \(\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}\) electrolyte recorded at \(0.04\ \text{V s}^{-1}\) using the same (as in Figure 4.1) 10-nm-wide Au band electrode are displayed in Figure 4.2. Results similar to those in Figure 4.1 are observed in Figure 4.2 where the limiting currents are much less than that predicted by Equation 4.1. In Figure 4.2, the voltammograms have shapes and limiting currents roughly independent of the potential scan rate and were found to be stable to repeated scanning. Analysis of the
Figure 4.2. Cyclic voltammograms of 0.99 mM Fc*, A, 1.01 mM DMFc, B, and 0.99 mM TMAMFc, C, in 0.1 M Bu4NClO4/CH3CN. Scan rate is 0.04 V s⁻¹. Same electrode as in Figure 4.1.

The entire voltammetric data set for Fc using Equation 4.2 where \( t = 25 \) s (time needed for a typical scan) led to Figure 4.3, wherein is plotted the normalized limiting current \( \frac{i_{\text{lim}}}{2nFIDc^{b}} \) as a function of the normalized effective electrode width \( \{\ln(4Du/r^{2})\}^{-1} \). The solid line represents the response predicted by Equation 4.1. For band electrodes with widths \( \geq 50 \) nm (data for electrodes between 150 and 500 nm not shown), the observed normalized limiting currents are in good agreement with those values calculated from Equation 4.1. However, as mentioned in the discussion above, the normalized...
limiting currents for electrodes ≤ 50 nm in width are substantially less than what would be expected from Equation 4.1. As the width of the electrode becomes smaller, the deviation becomes greater, with the normalized current approaching a value of roughly 0.008. This trend is more clearly seen when the data for all the ferrocene derivatives are plotted (Figure 4.4). For all of the ferrocenes studied here, the point at which the normalized limiting current begins to deviate from the theoretical line predicted by Equation 4.1 is between 20 and 50 nm.

Figure 4.3. Plot of normalized limiting current $i_{lim}/2nFILD\pi \sqrt{\frac{\pi}{4Dl/r^2}}$ vs $1/\ln[4Dt/r^2]$ obtained for Fe (□) in 0.1 M Bu4NCIO4/CH3CN. The solid line represents the response predicted by Equation 4.1. The width of electrode used for each point is indicated on the plot. Error bars represent one standard deviation, and each reported value is the average of three measurements using the same electrode.
Figure 4.4. Plot of normalized limiting current $i_{\text{lim}}/2nFIDC^b\pi$ vs $1/\ln[4Dt/r^2]$ obtained for Fc (□), Fc* (×), DMFc (●), and TMAMFc (▲) in 0.1 M Bu$_4$NClO$_4$/CH$_3$CN. Error bars represent one standard deviation, and each reported value is the average of three measurements using the same electrode.

Plots of the calculated normalized limiting current vs the normalized effective electrode width using Equation 4.2 with various $\xi$ and $z$ values are displayed in Figure 4.5. It can be seen that our data in Figure 4.5A and Figure 4.5B qualitatively agree with Equation 4.2 when $\xi$ ranges from 2 to 6 and $z$ is in the 0.5 to 6 nm range, respectively. The molecular diameters of the various ferrocene derivatives vary from roughly 0.5 to 1 nm, values that are comparable to those for $z$ in the curves in Figure 4.5. Although it is
impossible to pinpoint the values of $\xi$ from our data set, they are in the range of those previously reported.\textsuperscript{18,19}

![Figure 4.5](image_url)

**Figure 4.5.** Plot of normalized limiting current vs normalized electrode width for various values of $z$, $A$, and $\xi$, $B$ using Equation 4.2. The experimental data set for Fc is shown (■) for comparison. In A, the dotted lines represent the current calculated using various values of $z$; the values of $z$ used are 0.5, 1, 2, 3, 4, and 6 nm for the lines beginning with the line nearest the solid line and then moving downward. In B, $\xi$ values of 2, 3, 4, 5, and 6 were used for the lines beginning with the line nearest the solid line and then moving downward. The diffusion coefficient $D$ used was $2.1 \times 10^{-5}$ cm$^2$ s$^{-1}$ (that of Fc in the bulk) for A and B.

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In summary, the observations noted here are in accord with previous data at Pt nanoscopic band electrodes for Fc, Fc*, and an organoruthenium compound in non-aqueous media and ferrocyanide in aqueous electrolyte.\textsuperscript{18,19} The similarity of our results obtained at Au bands to those of White and co-workers using Pt bands and those of Fritsch with Au micromachined bands\textsuperscript{20} is important due to the fact that the deviation is not specific to the type of material used for the nanoband electrode. Thus, the observed deviation from Equation 4.1 is a general trend.

4.4 Determination of the “Real” Area of Au Nanoband Electrodes

A concern in the construction of any sub-micrometer-sized electrode of a given geometry is proper assessment of the exposed geometric area of the electrode. This is particularly problematic for sub-microscopic band electrodes that are millimeters in length. With band electrodes, there can be variations in the width of the band that can be quite severe owing to the nature of the substrate, metal film, the adhesive interaction between the various components in the band, and the final state of the band surface. In addition, for band electrodes which are fabricated using evaporated or sputtered metal films supported on a dielectric substrate, the width of the band is often times assumed to be the thickness of the metal film as determined by an \textit{in vacuo} quartz crystal microbalance (QCM). Variations in the placement of the substrates in the metal deposition system can lead to serious errors in the true film thickness within a given deposition run.\textsuperscript{12} The nanoband widths reported here were assumed to be the same as those values of the thickness as recorded by our QCM in the metal evaporator, leading to possible sources of error in the normalized effective electrode widths used in plots like those in Figures 4.3 and 4.4 (\textit{vide infra}). Many of these possible sources of variations in

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band width can go unnoticed due to the voltammetric testing protocols that are typically used.

Band electrodes are usually evaluated by obtaining a voltammogram of a reversible redox species at relatively slow potential scan rates in a liquid electrolyte of low viscosity at room temperature.\textsuperscript{23,24,26,28} Excessively "leaky" band electrodes (due to delamination defects) are often easy to identify due to the large resistive/capacitive backgrounds that their cyclic voltammograms display during such testing procedures; however, smaller defects that would result in larger-than-expected exposed electrode areas can go undetected. For example, micro-voids in the insulating material immediately adjacent to the metal film or small protrusions of the metal film beyond the end of the insulator would have little to no effect on steady-state voltammograms. This invisibility of larger-than-expected exposed electrode areas is due to the fact that the testing procedure involves inspection of voltammograms which are dominated by radial diffusion where the voltammetric response is directly proportional to electrode length and is quite insensitive to width and thus, the electrode area.

To accurately determine the true area of a given nanoband electrode using a voltammetric method, one can use a fast potential sweep rate or a highly viscous solvent in order to obtain linear diffusion conditions. The Randles-Sevcik equation\textsuperscript{29,30} governs the electrochemical response at sub-micron-sized band electrodes under linear diffusion conditions, and the real area can be calculated from the peak currents. Murray and co-workers have recently demonstrated that the use of viscous electrolytes and slow scan rates can allow for the determination of the real areas of bands.\textsuperscript{26} Although the method
described by Murray is quite elegant, it requires specialized electrolyte media and, in some cases, specially constructed band electrodes.

An assessment of the amount of exposed Au in our nanoband electrodes can be achieved by chemically labeling the Au with a redox-tagged alkanethiol. Through knowledge of the surface density of the ferrocene-tagged alkanethiol on variously prepared Au surfaces, one can use the charge beneath the surface-confined ferrocene waves to calculate the amount of exposed Au. The thiol used in these experiments is a ferrocenoyl derivative, $(C_5H_5)Fe(C_5H_4CO_2(CH_2)_{16}SH)$, which is denoted as Fc-SH. Previous studies have shown that the surface density of Fc-SH on Au wires and evaporated Au films (corrected for surface roughness) $\Gamma_{Fc-SH}$ is roughly $5 \times 10^{-10}$ mol cm$^{-2}$. Shown in Figure 4.6 are the cyclic voltammograms of a monolayer of Fc-SH on two band electrodes of 10 and 50 nm width in 0.1 M Bu$_4$NClO$_4$/CH$_3$CN electrolyte recorded at 0.10 V s$^{-1}$. These cyclic voltammograms represent the first scan; however, 5 other scans were taken. The anodic and cathodic peaks were reduced when scanning continuous. Upon integration of the anodic and cathodic currents corresponding to the oxidation and subsequent reduction of the ferrocene sites in the monolayers on the 10-and 50-nm-wide bands, apparent surface coverage values $\Gamma_{app}$ of $1.6 \times 10^{-8}$ mol cm$^{-2}$ and $3.5 \times 10^{-8}$ mol cm$^{-2}$ were obtained, respectively. After dividing by $\Gamma_{Fc-SH}$, these apparent surface coverages yield real electrode areas that are 31 and 69 times that of the predicted geometric areas.

The apparent double-layer capacitance values of these ferrocenoylthiol-coated electrodes at +0.1 V are calculated to be $2.6 \times 10^4$ $\mu$F cm$^{-2}$ and $7.3 \times 10^4$ $\mu$F cm$^{-2}$ at the 10 and 50 nm electrodes; if one divides these apparent capacitances by a typical value of the
double-layer capacitance at a ferrocenoylthiol-coated macroscopic Au electrode of known area (~100 μF cm⁻²), the real electrode areas are found to be 260 and 730 times larger than that based on the QCM-determined film thickness. After completing similar investigations of the different-sized band electrodes used in the construction of Figure 4.4, it was found that the real electrode areas were always 30 to 730 times larger than the simple geometric area. In addition, before the electrodes were tagged with Fc-SH, cyclic voltammograms of electrodes in 0.1 M Bu₄NClO₄/CH₃CN electrolyte at 0.10 V s⁻¹ were obtained so as to determine the apparent double-layer capacitance values. When the apparent double-layer capacitance values for the bare 10 and 50 nm Au band electrodes are divided by that at a bare Au macrodisk, the real electrode areas are found to be 281 and 383 times larger than the simple geometric areas. Thus, the real electrode areas obtained from both the double-layer capacitance and Au labeling experiments indicate an excess of Au exposed.

In addition to excess exposed Au, there are other possible factors that could contribute to the large values of surface coverages when determining the true area of the band electrodes when labeling method described here is used. It is possible that Fc-SH could have built up in the crevices near the electrode or adsorbed on the epoxy near the Au, leading to additional current response. Extended exposure of the electrodes to solvent did not lead to any change in the Fc-SH signal, which would indicate that excess Fc-SH in crevices is not a concern. Although, there is no evidence to negate the possible formation of an adsorbed Fc-SH layer on the nearby epoxy, this seems rather improbable.

In Figure 4.7, a plot of the log (normalized capacitance) at Au nanoband electrodes in 0.1 M Bu₄NClO₄/CH₃CN electrolyte versus the log (scan rate) is displayed. The capacitance for both electrodes decreases with increasing scan rate, which suggests...
that the seal between the Au and the glass substrate and/or epoxy is not perfect as shown
by the same plot for a known leaky macrodisk electrode.\textsuperscript{20,32} The Au surface in contact
with electrolyte in cracks or crevices at the edges of the electrode do not give rise to an
increase in capacitance current at higher scan rates due to the increased $iR$ drop at such
Au surfaces.\textsuperscript{20} Based on the capacitance data and the Au labeling experiments, we
conclude that the nanoband electrodes do indeed have excess exposed Au.

![Figure 4.6. Cyclic voltammograms of Fc-SH adsorbed on 10 nm, A, and 50 nm, B,
Au band electrodes. The electrolyte solution is 0.1 M Bu$_4$NClO$_4$/CH$_3$CN, and scan rate is 0.10 V/s.](image)

---

**Figure 4.6.** Cyclic voltammograms of Fc-SH adsorbed on 10 nm, A, and 50 nm, B,
Au band electrodes. The electrolyte solution is 0.1 M Bu$_4$NClO$_4$/CH$_3$CN, and scan rate is 0.10 V/s.

No trend in the amount of excess exposed Au as a function of nominal bandwidth
was observed. Such observations propelled to us investigate whether there was a serious
error in our film thickness as determined by the quartz microbalance.

4.5 **Evaluation of Au Film Thickness**

In order to test the reliability of our QCM with respect to film thickness accuracy,
we used stylus profilometry and X-ray diffraction methods\textsuperscript{33,34} to obtain independent
measurements of Au film thickness. In addition, it could be argued that the sticking probability of Au atoms on the amine-terminated surface is vastly different than that at the Au surface of the microbalance crystal, leading to large differences in the real film thickness in comparison to those recorded by the QCM. Au films with QCM-determined thicknesses ranging from 6 to 100 nm were inspected with profilometry and X-ray diffraction.

![Figure 4.7.](image)

Figure 4.7. Dependence of capacitance (log normalized) on scan rate (log) for a 10 nm band electrode (□), for a 50 nm edge band electrode (●), and for a known leaky 0.5 mm disk electrode (▲). Capacitances were calculated by measuring the charging current from a cyclic voltammogram (0.1 M Bu₄NClO₄/CH₃CN) at 0.3 V and dividing by scan rate and electrode area.

The use of X-ray diffraction for determination of the thickness of Au films is fairly straightforward and is based on measurement of the breadth of the Au(111) diffraction peak at half height. It is known that the full-width-at-half-maximum

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(FWHM) of a given diffraction peak for a thin metal film has a relationship with the film thickness that can be described by

\[ \tau = \frac{K \lambda}{\beta_r \cos \theta}, \]

where \( \lambda \) is the wavelength of the incident X-radiation, \( \theta \) is the angle of diffraction, \( \beta_r \) is the FWHM, and \( K \) is the shape factor. The accuracy of this method for film thicknesses above 30 nm is not good, as has been previously discussed.\(^{35,36} \) In addition, very thin metal films (< 5 nm) tend to yield diffraction peaks that are extremely weak and broad, and thus determinations of film thickness using Equation 4.3 are often prone to large errors.

Shown in Table 1 are Au film thicknesses as determined by quartz crystal microgravimetry \( (d_{QCM}) \), profilometry \( (d_{\text{prof}}) \), and X-ray diffraction \( (d_{X-ray}) \) for a set of Au films deposited on APS-treated glass. As mentioned above and observed here, the use of X-ray diffraction methods does not provide accurate values for films thicker than 30 nm. The three methods yield values which are in good agreement with exception of the \( d_{X-ray} \) measurements above 20 nm (we did not obtain data between 20 and 50 nm). The larger-than-expected areas noted in the thiol labeling experiments can not be due to errors associated with the quartz crystal microbalance. Instead, the larger areas must be the result of defects near the band/electrolyte interface that are diffusonally invisible during the recording of steady-state voltammograms.

### 4.6 Scanning Force Microscopy Studies of Nanoband Electrodes

Traditional microscopy techniques, such as electron and optical, that can be used to interrogate the interface of dissimilar materials were deemed to be unlikely to provide...
information regarding features on the nanometer scale. Therefore, scanning force microscopy (SFM) in deflection mode was used to examine the face of a nanoband assembly. Shown in Figure 4.8A is a scanning force micrograph of a 10-nm-wide Au band electrode. Moving from left to right in the image, one finds three different topographic regions. On the far left is a very smooth surface, which is the epoxy used to insulate the band electrode. The rough terrain on the far right is the end of the glass microscope slide. Similar images were obtained when the SFM tip was manually moved around (using the x-y micrometer stage of the SFM) on the end of the glass slide. As noted by the arrow in the middle of the micrograph, a bright line that closely follows the contour of the epoxy and the glass is quite prominent. The width of this line is roughly 10 nm, which is the expected Au film thickness measured by the QCM. Manual translation of the SFM tip along the interface for distances of ±100 μm revealed a very similar three-component structure, with the bright line having a width of 10-12 nm. Thus, the line is assigned as the Au film of the nanoband.

Table 4.1. QCM Thickness values compared to thickness values from profilometry and X-ray diffraction.

<table>
<thead>
<tr>
<th>d_{QCM} (nm)</th>
<th>d_{Prof} (nm)</th>
<th>d_{X-ray} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>6.3 ±0.4</td>
<td>6.5 ±0.5</td>
</tr>
<tr>
<td>8</td>
<td>8.0 ±0.1</td>
<td>8.2 ±0.2</td>
</tr>
<tr>
<td>10</td>
<td>10.0 ±0.2</td>
<td>9.9 ±0.4</td>
</tr>
<tr>
<td>20</td>
<td>20.0 ±1.3</td>
<td>21.0 ±0.8</td>
</tr>
<tr>
<td>50</td>
<td>51.0 ±1.3</td>
<td>28.0 ±1.4</td>
</tr>
<tr>
<td>100</td>
<td>110.0 ±1.3</td>
<td>38.0 ±2.5</td>
</tr>
</tbody>
</table>

* The QCM manufacturer states a ±5% accuracy when operated under ideal conditions.
Careful inspection of images such as in Figure 4.8A suggest a structure of the nanoband face, which is consistent with incomplete insulation of the Au film on the glass substrate. Thus, the epoxy did not quite completely reach the end of the Au-coated glass. Recall that the band electrodes are not mechanically finished. The epoxy is carefully spread to within a few tenths of a millimeter of the end of the Au-coated slide and then placed in a low-temperature oven to allow the epoxy to spread and subsequently harden. A schematic representation of the structure from Figure 4.8A is shown in Figure 4.8A.
Thus, one can only speculate as to why the Au film edge displays the apparent jump in height at the epoxy/Au/glass interface in Figure 4.8A. Our proposed model in Figure 4.8B shows that the Au film is not completely covered by epoxy, but the Au film edge is flush with the end of the glass support. Apparently, the abrupt change in height at the glass/Au interface is actually due to differences in the mechanical properties of the Au and glass.

The width of the non-insulated Au can be determined by measuring the distance from the bright line to the beginning of the smooth region at the left in Figure 4.8 and is found to vary considerably over the ~200 μm long region inspected for this sample. For example, at point A in Figure 4.8, the width of the non-insulated Au is roughly 90 nm. Further up in the figure at point B, the width is approximately 35 nm, and at point C there appears to be some blocking of the Au band surface by the epoxy. On average, a crude estimate of the area of Au can be provided, which is not covered by the epoxy for this particular electrode. This value is roughly 2-3 times more than the theoretical area calculated by multiplying the nominal width of the band by the length. This is, of course, far less than what is found using the thiol labeling experiments. The small portion of the electrode that was inspected using the scanning force microscope is most likely not representative of the entire nanoband. Thus, if one could image the entire nanoband, it is quite likely that the value obtained for the exposed Au would agree with that found using the thiol labeling experiments. The salient point to take away from the SFM experiment is that the defect, which leads to the larger-than-expected electrode areas, is most likely incomplete insulation by the epoxy. Further microscopy was carried out with SEM to make quantitative assessments of the exposed Au on band electrodes. This study will
allow us to select well-defined band electrodes for use in advanced voltammetric studies at nanoband electrodes.

### 4.7 Scanning Electron Microscopy

Nanoband electrodes were examined with scanning electron microscopy (SEM) to observe the possible presence of any defects at the epoxy – Au – glass interface. A Au band electrode is shown in Figure 4.9A is with a thickness of 10 nm that was imaged from a top view where epoxy is the topmost layer (Figure 4.10). The image clearly demonstrates that an excess of Au is present due to incomplete (spotty) coverage by the epoxy. When fabricating the nanoband electrodes, the epoxy evidently shrinks somewhat when curing and the forces of attraction within the epoxy cause the side of the Au band to be exposed. An estimate of the excess exposed area of Au from the SEM images was measured to be roughly $3.3 \times 10^{-4}$ cm$^2$ to $4.8 \times 10^{-4}$ cm$^2$ or 330 to 480 times larger than the area of the 10-nm-wide Au band. These results indicate that the observed current should be much larger than predicted by Equation 4.1; however, that is not the case with the Au nanoband electrodes used in this study.

In Figure 4.9B, an SEM image of another 10-nm-wide nanoband electrode is displayed. It is clear from the image that cracks can develop in the epoxy near the epoxy–Au–glass interface, which leads to delamination and cracking. The crack at the interface is observed to be roughly 1.25 µm in width; the crack width is reasonably consistent along the length of the electrode. These particular nanobands with delamination and cracking problems do not follow the characteristics of a well-behave electrode. Thus, they do not exhibit behavior characteristic of radial diffusion at any scan rate (always linear diffusion) used here. Nanoband electrodes with this type of defect were not used in studies when calculating the normalized currents.
Figure 4.9. In A, SEM image of a 10-nm-wide Au band electrode with excess exposed Au present. In B, SEM image of a 10-nm-wide Au band electrode where delamination between epoxy and Au layers is present.
Figure 4.10. Schematic depiction of the epoxy/Au/glass interface in Figure 4.9A.
4.8 Possible Manifestations of Larger-Than-Expected Nanoband Areas

Although it is not surprising to find that nanoband electrodes fabricated using the method described here have "excess" areas in comparison to the simple geometric areas defined by the thickness of the Au film and its length, it is quite surprising that the bands can have real areas which are tens to hundreds of times larger than expected but still exhibit the behavior predicted by Equation 4.2 (negative deviation from Equation 4.1). Assuming that the additional Au, as seen in Figure 4.9, actually increases long-range diffusion to the nanoband, one would expect that the point where the limiting currents begin to substantially disagree with Equation 4.1 would be at much larger apparent values of \( (\ln(4Du/r^2))^{-1} \), due to the larger than normal "width" of the band. For example, at the purportedly 10-nm-wide band with Fc as the analyte (Figure 4.3), the normalized limiting current using Equation 4.1 is calculated to be 0.069 if one assumes a width that is 100 times the nominal width (1000 nm). This value is 2.1 times that experimentally observed for the 10-nm-wide band and is above the line predicted by Equation 4.1 in Figure 4.3!

Based on our experimental results in Figures 4.3 and 4.4, it would appear that the excess non-insulated Au, which we believe adds width to the band, is actually diffusional blocked (no addition in current with long-range diffusion). Future work with simulations using the strongly implicit procedure for determining the diffusional mass transport to nanoband electrodes that deviate from ideal behavior as recently outlined by Alden et al., and experiments, as those described by Oldham, to determine the area accessibility factor, and heterogeneity function of the electrodes by obtaining steady-state voltammograms of an electroactive species that undergoes irreversible electron transfer may allow for a better understanding of our observations.
4.9 References


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Chapter 5

Light-Directed Patterning of Evaporated Au on 3-aminopropyltriethoxysilane (APS) Monolayers on Glass

5.1 Introduction

The lateral patterning of metals to create thin film devices has been achieved using techniques ranging from electrodeposition from an STM tip to photolithography using photoresist materials or self-assembled monolayers (SAMs). Etching and shadow-mask evaporation are also widely used to pattern thin metal films. Of these methods, the most popular involves photolithography, wherein exposure of a light-sensitive polymer resist deposited on a surface results in destruction of the polymer backbone; the polymer can then be removed from the irradiated areas to leave behind a template that can be used to etch the underlying metal film or to direct the deposition of a metal film onto the substrate below. This method has advantages over lithography techniques because of ease of use, reduction in fabricating time, and reduction in cost. Under typical operating conditions, the aforementioned methods for laterally patterning metal films result in minimum feature sizes of ~250 nm.

A direction that is currently of great interest is the fabrication of metal films with small lateral dimensions using traditional and "soft" lithographic techniques. The ability to routinely and inexpensively form on a variety of surfaces metal films with widths in hundreds of nanometer scale would be of great importance to the microelectronics and chemistry fields. For example, parallel metal lines with nanometer widths of separation would allow for the measurement of the electronic properties of single molecules. Sub-micrometer-sized electrodes will have a large impact on
microelectromechanical systems targeted for analytical chemistry applications. Although electron-beam and X-ray lithographies allow for the construction of such nanometer-sized metal features, simpler, less expensive methods are currently being investigated, such as microcontact printing and light-directed fabrication of colloids.  

Recently, Vossmeyer et al. showed that the nitroveratryloxycarbonyl (NVOC) group, a photolabile-protecting group, could be used as part of a patterning technique to direct the distribution of Au nanoparticles (colloidal Au) from solution onto modified glass substrates. In this method, a planar surface with ligands that are capable of binding to the surface of colloidal Au particles is first treated with photolabile protecting groups that render the ligands incapable of binding. The protecting groups are selectively removed using masked light, and then Au colloids are allowed to adsorb onto the exposed ligands. To make conducting Au films, multilayer films of the Au colloid are made by alternatingly placing the patterned substrate in a solution of a bifunctional ligand and then Au colloid. This process is time consuming and requires several experimental steps to obtain a conductive, electrically continuous layer of patterned Au.

In this study, evaporated Au metal films are formed on patterned metal-binding substrates. Such a methodology is shown to decrease the fabrication time required for making patterned metal films. Upon photoremoval of NVOC groups from aminopropylsilane monolayers supported on glass, thin Au films are deposited on the entire NVOC/amine and amine surface, then adhesive tape is applied to liberate the Au which does not bind to the NVOC-protected amine sites on the surface. Fluorescence microscopy images of photo-deprotected amine surfaces demonstrate that the amine groups are indeed intact and accessible.
5.2 Results and Discussion

As discussed earlier, the direction of the work described here focuses on new methods for the fabrication of patterned metal films that may eventually be extended so that films with sub-micrometer feature sizes may be constructed. In order to demonstrate that one can use photo-patterned films for constructing patterned evaporated metal films, the Au/APS/glass system was chosen. In this previous work from our laboratories, it was demonstrated that APS monolayers on glass or silica are outstanding adhesion promoters for evaporated Au films ~0.5-150 nm in thickness. In addition, the amine groups in the APS/glass system can be protected with a photolabile group such as NVOC, and then the amine groups can be liberated by photolysis. Thus, it should be possible to selectively form strongly adherent Au films on the exposed amine functionalities. However, the question regarding the adhesion of Au to the NVOC-protected amine groups (a urethane) needs to be addressed. Upon evaporation of Au onto APS surfaces that have been protected with NVOC (minimum time of 7 h exposure of APS layers to 1 mM NVOC), application and subsequent removal of adhesive tape leads to complete removal of the Au. Thus, the use of photo-patterned substrates should result in removal of evaporated Au from the NVOC-protected areas, but not from the amine regions.

Figure 5.1 is a display of optical image of a macroscopic Au pattern formed by evaporation of 17 nm of Au onto an NVOC-protected APS/glass substrate that was photoexposed through a “window pane” mask (0.49 cm x 0.49 cm “windows”) for 45 min. In general, it is evident that the Au was completely removed in the areas where photolysis did not occur. That is, Au was removed in the NVOC-protected areas composed of the cross bar and the exterior edge. The defect in the upper right corner of the image is due to either handling of the sample with tweezers (physical removal of the
protecting group) or incomplete protection of the amine groups with NVOC. The former argument is supported by the fact that NVOC-protected APS layers that have not been exposed to any light do not exhibit this behavior. In addition, scattered light in the microscope slide is not the origin of the lack of NVOC groups in the upper right corner of Figure 5.1 as demonstrated by control experiments. Finally, heat-induced removal of the NVOC protecting groups (heat is released during the resistive heating of the W crucible holding the Au) has not been observed due to the fact that the temperature inside the evaporator was never allowed to go above 40°C.

Figure 5.1. Optical photograph of a patterned Au film with a 17 nm thickness. The dimension of one side of a square is 0.49 cm. The NVOC protecting group was applied using a concentration of 1 mM and a reaction time of 7 h.

Overall, the Au remained on the exposed amine groups of the APS layer; however, there were very small amounts of Au removed from this layer in the squares on the left side if the sample in Figure 5.1. This is perhaps due to regions that were not exposed to the light for the minimum 45 min needed to fully remove the NVOC groups from samples that did not have a mask placed in front of them. I have recently found that full removal of the NVOC groups when using a mask can be achieved for exposures of ~60 min. A possible explanation for the observation that more exposure time is needed
when using a mask is that variations in the light flux on the sample occur due to reflection of light by rough spots on the edge of the masks. There are times when Au remains on an NVOC-protected amine layer if variations in the NVOC protection step are made. For example, when a lower concentration of the NVOC is used but with a longer reaction time, incomplete NVOC coverage is the result. This is illustrated in Figure 5.2 for an APS/glass substrate that was exposed to 0.5 mM NVOC for 17 h versus 7 h to a 1.0 mM NVOC solution for the sample in Figure 5.1. It is evident that Au regions are present in the nonexposed areas of the sample (outer edge and cross bar). This is attributed to incomplete formation of the NVOC layer which leads to free amine groups that bind to the evaporated Au. This observation is not the result of Au binding to the urethane bond between the NVOC and the APS (Au diffuses to the urethane linkage and interacts with it), due to the fact that samples made with higher concentrations of NVOC in the protecting solution do not exhibit this. However, if the solvents used for the protection step are not sufficiently dry, then the NVOC group is cleaved and similar results to that found for the sample in Figure 5.2 are found.

![Figure 5.2](image-url)

**Figure 5.2.** Optical photograph of a patterned Au film with a 17.5 nm thickness. The dimension of one side of a square is 0.49 cm. The NVOC protecting group was applied using a concentration of 0.5 mM and a reaction time of 17 h.
In order to ensure that the amine groups of the APS layers are being regenerated upon photoexposure of the NVOC-APS/glass surfaces and that there is no occurrence of destructive reactions that would lead to loss of the amine sites, fluorescence microscopy has been carried out. This method was also performed to demonstrate that micrometer-sized regions of amines can be formed using the photopatterning method and that such micron-sized regions can then be used to form Au films. In Figure 5.3 is shown the fluorescence micrograph of an APS/glass surface that had on it placed a drop of a solution containing fluorescamine, a common amine-labeling reagent. The region that was exposed to the dye is on the left in Figure 5.3. As evidenced in Figure 5.3, only the region of the APS surface exposed to the dye exhibited fluorescence. After irradiation of an NVOC-protected APS/glass substrate using a mask with a ~150 μm optically transparent feature and then exposure of the entire substrate to the fluorescamine solution, the image in Figure 5.4 was obtained. In the region where the NVOC groups should have been removed to leave behind free amine sites, bright fluorescence is observed, indicating the presence of labeled amine sites. No fluorescence was found in the regions that were covered by the mask except where possible damage to the NVOC layer was possible (tweezers damage from handling). This is confirmed by images of NVOC-protected APS surfaces that have not been exposed to any light; no observable amount of fluorescence was found for such samples after exposure to the fluorescamine. Finally, it can be concluded that the amine groups liberated during the photoexposure step are stable during the exposure step based on the fluorescence microscopy images.

A concern noted as a result of careful inspection of Figure 5.4 and other images like that of Figure 5.4 is that small (~5-10 μm diameter) “spots” that are either dark or light appear speckled across the images. It was hypothesized that this could be due to
impurity solids in the fluorescamine solutions that adsorb on the surface. In order to test this hypothesis, an NVOC-protected APS/glass substrate that had been irradiated over its entire surface had placed on it a drop of the fluorescamine dye. Upon examination of the region that had been exposed to the dye, the expected fluorescence was observed (lower region), as were the “spots” seen previously. Thus, it is concluded that the “spots” are not inhomogeneities in the NVOC or APS surfaces but rather impurities in the fluorescamine solution.

Figure 5.3. Fluorescence microscopy image of APS on glass that was probed with fluorescamine dye on the left. The right side was not probed with dye.

Figure 5.4. Fluorescence microscopy image of a patterned line on an NVOC-APS/glass surface demonstrating the presence of primary amines in the exposed region.
5.3 Summary

The use of NVOC, a photolabile protecting group, is shown to act as an effective protecting group on APS/glass surfaces, and upon selective photoremoval, allows for the construction of patterned Au films on glass. It is shown that the use of an adhesive-tape-based development technique allows for the fabrication of patterned evaporated Au films. Optimization of the conditions to achieve successful patterning include the use of dry solvents for the protection step and use of sufficient times for the protection and deprotection steps. In addition, fluorescence microscopy images of photopatterned NVOC-APS/glass surfaces point to the ability to form Au features with micrometer-sized features using this technique. Thus, future work will target the fabrication of microelectrodes and microelectrode arrays of electrodes using the photopatterning method described here. However, limitations, such as the use of adhesive tape, must be overcome. A possible route to overcome this limitation is that which utilizes solvent streams directed at the surface of the Au/patterned-NVOC-APS/glass substrate that would dislodge the Au film on the NVOC regions but not on the APS regions. Initial investigations indicate that such solvent-based development methods will require the use of dry solvents in order to prevent removal of the NVOC groups.

5.4 References


6.1 Summary of Conclusions and Observations Supporting Conclusions

Evaporated Au on amine-terminated glass was characterized to understand the properties that cause the metal to adhere to the modified glass. The modifier used in this study was aminopropylsilane (APS). Monolayers of APS were assembled on clean glass by using a vaporization method. The heat provided during the vaporization process cures the monolayer onto the glass surface so that the modifier is strongly bound to the glass. To complete sample preparation for STM and X-ray diffraction analyses, Au was vapor deposited onto the APS-modified glass. The procedure used has led to the development of nanodevices for surface studies, nanoband electrodes investigated with electrochemical methods, and patterned metal devices using light-directed methods.

The nucleation properties of Au on modified glass were examined by STM and X-ray diffractometry. STM analyses were performed on Au samples that were 10 and 100 nm thick on APS-modified glass (APS/glass), mica, and Cr on glass (Cr/glass). From STM images of 100-nm-thick Au films on APS/glass, it was found that the Au grains were flat and had single-atom step edges indicating that the metal on the modified substrate was highly ordered. Grains of Au on Cr/glass were smaller than grains of Au on APS/glass. Although there was some indication of step edges when Au was on Cr/glass, the step edges were not as defined as Au on APS/glass. However, Au grains on mica were very flat, and the step edges were well defined. The surface roughness of Au on mica was larger than the surface roughness of Au on APS/glass due to islands that were stacked on one another, creating deeper voids between each grain. However,
APS/glass was a suitable substrate for producing Au that was flat, and electrically continuous when the thickness of the layer was greater than 10 nm. Grains of Au on APS/glass were similar to grains on mica when Au was 100-nm-thick. Further surface analysis using X-ray diffraction was used to determine the orientation (texture) of the Au crystallites on the various substrates. The preferred plane for Au on APS/glass, Cr/glass and mica was \{111\}. The orientation of Au from X-ray analysis indicated its metallic surface was flat regardless of the type of substrate used. However, the STM images proved that Au on APS/glass was better than Au on Cr/glass because the grains were flatter on the surface. These studies and experimental methods led to the fabrication of nanoscopic Au band electrodes and the patterning of Au on glass to develop thin metal devices. APS was chosen as the modifier to adhere Au to glass because it allowed Au to adhere for a minimum of 6.5 months.

Nanoband electrodes and patterned nanodevices were developed from the method described in Chapter 2. After fabricating nanoband electrodes having widths between 3 and 150 nm, the electrodes were characterized by electrochemical methods. The currents generated by these electrodes were compared to theoretical predictions under controlled electrochemical conditions. In these studies, ferrocene (Fc) and Fc derivatives were the redox species of interest. Each derivative of Fc gave similar voltammetric results for Au band electrodes having widths of 3 to 10 nm, but the response deviated from ideal behavior (theory). Band electrodes with widths between 20 and 150 nm gave electrochemical responses that were in agreement with theory. The electrodes that deviated from ideal behavior were further studied because it was speculated that fabrication problems arose in regard to the true thickness of Au or the area of the nanoband electrode. Additional measurements of the thickness of Au were necessary to
address the accuracy of QCM measurements during evaporation of the Au. The thickness measured by QCM was compared to values obtained via profilometry and X-ray diffractometry. It was found that the QCM values were in agreement with the thicknesses determined using the other methods.

The area of the nanoband electrodes was determined with surface labeling experiments, SFM, and SEM. Gold band electrodes that were 10 and 50 nm wide were labeled with Fc-SH. The surface coverage calculated for each electrode indicated that the apparent area was larger than that of a typical planar electrode. The use of epoxy as an electrode sealant generated this commonly observed problem because of its nonuniformity of spreading at the edge of the electrode. As a result, an undesired portion of the Au was exposed. This nonuniform coverage of the epoxy was observed in SFM and SEM images.

Nanoscopic Au band electrodes have led to the development of other devices through the use of photopatterning techniques. To pattern Au on modified glass, a photoprotecting group known as NVOC was covalently attached to the amine-terminated groups of APS/glass. Before applying evaporated Au onto modified glass, light-directed procedures were employed to deprotect NVOC from amines of APS. The coverage of NVOC on APS-treated glass was examined with RAIRS and fluorescence microscopy.

Before the pattern nanodevices were fabricated, RAIR spectra were obtained to show that NVOC can bond with amine-terminated surfaces. The sample investigated by RAIRS was that of an amine-terminated thiol on Au on Cr-modified glass. A background spectrum was obtained before adsorbing cysteamine to the Au. Cysteamine was adsorbed onto the reflective side until a monolayer formed on the surface. A spectrum of cysteamine/Au was subtracted from the background spectrum to obtain the
analysis for cysteamine (see Appendix). The spectrum of interest was the fingerprint of NVOC on the surface (see Appendix). It was found that NVOC was covalently bound to the amine-terminated Au surface within minutes.

Along with RAIRS, the reaction of NVOC to amines of APS/glass was studied using fluorescence microscopy. The amino groups on glass were labeled with a fluorescent dye, fluorescamine, to show that the dye is capable of labeling surface amino groups. Fluorescence of the amino groups occurred when obtaining the image of the modified glass. However, the NVOC-treated amine surfaces did not fluoresce, which indicated that NVOC completely covered the amino groups of APS after the protection step.

To complete the fabrication of patterning Au, a mask was placed on the modified glass. The mask directed UV radiation at ~340 nm to NVOC areas that were exposed. NVOC was removed from the exposed area leaving free amines present on the substrate. Evaporated Au films ~17 nm in thickness were applied to the sample so that Au would bond to amine groups and not with NVOC groups. To remove the Au from the NVOC layer, tape was used to develop the pattern. Pictures of the patterned Au nanodevices were obtained to show that Au was removed from NVOC surfaces but remained on amine groups of the sample.

6.2 Future Directions

6.2.1 Simulation of Diffusional Mass Transport at Nanoscopic Band Electrodes

Continuing with studies of fabricated Au nanoband electrodes, it is desirable to further characterize these electrodes by examining their diffusional mass transport properties. By using simulations (strongly implicit procedure) developed by Alden et al., one can model our band electrodes and compare them to other custom-made band
electrodes. AFM and SEM images of the nanoband electrode were previously obtained to describe the elevated Au surface and its shape on a microscopic glass slide. The nanoband electrode parameters will be incorporated in the simulation to obtain its current response. Normally, chronoamperometry responses were based on Oldham’s equation for short times.

Equation 6.1

\[ I = F a_{\text{bulk}} D \left( \frac{A}{\pi^{1/2} D^{1/2} t^{1/2}} + \frac{P}{2} \right) \]

Equation 6.2

\[ I = F a_{\text{bulk}} D w \left( \frac{1}{\pi^{1/2} \theta^{1/2}} + 1 \right) \]

Here, \( \theta \) is equivalent to \( D t / x_e^2 \), \( P \) is the length of the electrode perimeter, \( A \) is the electrode area, \( w \) is the width, \( x_e \) is the electrode width, and \( a_{\text{bulk}} \) is the bulk concentration of the electroactive species of diffusion coefficient \( D \). Using cyclic voltammetry, the electrochemical response will be obtained and simulated for diffusion from elevated electrodes using Equation 6.3

Equation 6.3

\[ I = F a_{\text{bulk}} D w \left( \frac{\Delta x^{K_{E}}}{\Delta y} \sum_{i=1}^{K_{E}} a_{i,k} \right) + \left( \frac{\Delta y^{K_{E}}}{\Delta x} \sum_{j=0}^{K_{E}} a_{j,K_{E+1}} \right) \]

where \( w \) is the electrode length, \( x \) is electrode width, and \( a \) is the bulk concentration.

This observation will provide knowledge of when the redox species will be depleted at the electrode surface once achieving linear diffusion effects for short and longer times. It is predicted that the more elevated the electrode, the more current will be passed during the transient. Such responses could be compared to that of other electrodes that are of the recessed and flat forms using simulations based on Alden’s method. Other analyses will

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be supported when comparing Oldham’s, Cottrell’s, and elevated equations in a plot of $I$ versus $r^{1/2}$. Further simulations will consist of using different parameters that are typical of nanoband electrodes where the width is between 3 nm to 50 nm. With these observations, the similarities or differences in the diffusion will be determined based on band electrode width.

6.2.2 The Coverage of Fc-SH Beyond the Adsorption on Au

A previous concern in Chapter 4 was the accuracy of tagging Fc-SH to band electrodes to determine the area of the Au exposed during cyclic voltammetry. It is possible that the Fc-SH could have accumulated in crevices of the epoxy or adsorbed to the epoxy while adsorbing to the Au surface of the electrode. The problem can be approached by XPS or tagging the Fc-SH monolayer on Au with a fluorescent dye.

6.2.3 Surface Enhanced Raman Scattering of Self Assembled Monolayers

Raman spectroscopy is unique in that its peaks are quite narrow where the source provides an image with contrasting effects. Self-assembled monolayers on Au (SAM/Au) should be further characterized to determine the dimensions of the pattern and the assembly of monolayers on the Au surface. Surface-enhanced Raman scattering (SERS) can possibly determine the enhancement of Au on glass based on the type of buffer used. For these studies, 3-aminopropyltriethoxysilane has been used as a buffer to adhere Au to glass when fabricating nanodevices. It was determined from STM and X-ray diffraction studies that APS was suitable for making nanodevices. However, other organic buffers could have yielded better enhancement of Au on glass than APS. With SERS, the best organic buffer to adhere Au to glass can possibly be evaluated from a variety of silanes. The best adherence of Au on glass depends on the formation of islands and the increase in surface roughness from the thin metal film layer. Glass slides will be
prepared by applying APS by vapor deposition as described in Chapter 2. Thickness of Au applied should be around 20 nm so that the SERS signal is achieved from the "back side" approach. At higher metal thicknesses the SERS signal is weak. The SAM will be chemisorbed on the thin metal film to ensure a signal. Each spectrum of the SAM will be compared based on the modifier used. By observing the stronger signals, the SERS results will indicate which organic buffer is better for adhesion. Results can also be compared to modifiers on roughened glass. The roughened glass was previously shown to provide a better SERS signal of the SAM on Au than on nonroughened glass.4

Another property to examine with SERS is the coverage of NVOC and other protecting groups on amino groups of APS. While evaporating Au onto NVOC, the Au grains had a tendency to move pass the NVOC to the amino group. Since Au is attracted to amines, the Au can not be removed from the NVOC layer during tape or solvent tests. It is proposed that one should examine NVOC and other protecting groups to determine the best surface coverage on amines using SERS. This method will suggest the best protecting group that prevents the Au layer from adsorbing to the amino groups of the NVOC-APS bond.

6.2.4 Diffusion Ordered Nuclear Magnetic Resonance Spectroscopy of Ferrocene and Ferrocene Derivatives

To understand the diffusional properties of a redox species traveling through an electrolytic medium, it is necessary to obtain data from cyclic voltammograms by use of a rotating ring electrode or viscometer. While studying nanoband electrodes, a concern about the actual diffusion and viscosity of Fc and Fc derivatives in electrolytic solution was raised. Determining the diffusion coefficient involved several calculations when using the rotating ring electrode. A simpler technique to obtain the diffusion coefficient
would be diffusion ordered nuclear magnetic resonance spectroscopy (DOSY). The diffusion coefficient from DOSY should be compared to results from rotating ring disk and viscometer calculations in order to evaluate the accuracy of this procedure. If the values from DOSY agree with values from rotating ring disk and viscometer calculations, then DOSY would be the suitable choice for determining diffusion coefficient of other redox species. DOSY can also be used to determine the diffusion coefficient of complex mixtures.

Fc and Fc derivatives should be prepared in CD$_3$CN with 0.1 M TBAP. To acquire high-resolution NMR spectra, a longitudinal encode-decode (LED) pulse sequence and actively shielded gradient coils should be used. The spectra from LED will be obtained as a function of $(\gamma g \delta)^2$ where $\gamma$ is the magnetogyric ratio, $g$ is the gradient pulse amplitude and $\delta$ is the duration. This function is used to extract the diffusion coefficient of Fc and Fc derivatives. The transport properties of molecules and ions are determined by the Debye-Einstein theory.

Equation 6.4

$$D = \frac{k_B T}{6\pi \eta r_H}$$

The properties in Equation 6.4 are represented as diffusion coefficient ($D$), Boltzmann constant ($k_B$), absolute temperature ($T$), solvent viscosity ($\eta$), and hydrodynamic radius of a spherical particle ($r_H$).

6.2.5 Patterning Au using Photolabile Protecting Groups

It is necessary to continue the investigation of patterning Au by deprotecting NVOC from slides using UV radiation at ~350 nm. It is possible that photolabile
protecting groups rather than photoresists can provide spatial positioning of Au. We have fabricated macroscopic patterns of Au using photopatterning methods. However, microscopic thin metal devices have not been developed using vapor-deposited Au to date. The microscopic patterning should be possible using procedures described in Chapter 5. After fabricating the microscopic device, the conductivity should be tested by electrochemical methods. The device should have similar current values when compared to devices that are developed by shadowing mask methods. Patterned devices fabricated by photochemical methods and evaporation using shadow masking can be labeled with Fc-SH to obtain surface coverage values from cyclic voltammograms. The surface coverage and capacitance of the double layer from the patterned thin metal devices should have similar values to those fabricated by shadow mask methods.

Patterning Au on APS/glass by removing NVOC using UV radiation between 320-350 nm was previously discussed. However, Giasson et al. have shown that NVOC was not the best when it came to removal efficiencies. They reported that the α,α-dimethyl-3,5-dimethoxybenzyloxy carbonyl (DDZ) group has better coverage on amines than NVOC. Thus, APS/glass could be prepared by immersing the slide in a 1 mM solution of DDZ in 5 mL pyridine and 3 mL of ethyl acetate. The slide and mixture would be heated at 40 °C for 12 h to react DDZ with the amines of APS. Before preparing solutions, the solvents used should be dried. UV radiation should be set at 254 nm to ensure removal of DDZ within 15 to 60 min. Patterns should be obtained on the macroscopic scale before investigating patterns on the microscopic scale to examine the patterning capabilities of vapor-deposited Au.

After obtaining pictures of the Au patterned on the macroscopic scale, patterning on the microscopic scale should be investigated. Fluorescence microscopy allows for
simple investigation of amines after irradiation at 254 nm as seen in Chapter 5. The presence of amines will indicate that APS was left intact on the glass substrate during UV radiation. Fluorescence microscopy can determine the timescale by which amines begin to leave the surface based on irradiation. After obtaining the image using fluorescence microscopy, microscopic patterning of Au should be performed. After proving that NVOC or DDZ can be used to pattern metals on modified glass, devices on the exact scale can be fabricated as microelectrodes or arrays of microelectrodes on a chip to ensure reproducibility of thin metal devices.

The light-directed assembly of Au on glass leads to the fabrication of electronic microdevices. This method allows one to further enhance the thin metal film with a SAM. Information storage devices may be developed more effectively with the use of SAMs on Au. SAMs on Au could also prevent cross talking that occurs with metals on the micro- or nano-scale when placed on a chip. These surfaces modified with organosilanes can be characterized by SERS. This particular instrument is found to provide imaging where the resolution is approximately 2 μm on non-roughened evaporated silver surfaces. It is possible that SERS could observe SAMs on evaporated Au to determine their physical properties.

6.2.6 Developing Two-Dimensional Adsorption of Au Nanoparticles at Heterogeneous Molecular Surfaces

Previously, Schultz et al. showed that heterogeneous molecular surfaces can provide for the ability to carry out two-dimensional (2-D) adsorption of Au nanoparticles. Molecular surfaces were developed by dip coating a silicon wafer in methyl-terminated n-hexadecyltrichlorosilane (HTS) or in amine-terminated n-(6-aminohexyl)-aminopropyltrimethoxysilane (NH₂) for 10 h. After applying the first
monolayer (either NH$_2$ or HTS) to the surface, the second molecular phase was solvent-deposited for 10 h in either organosilane. Thereafter, HTS on NH$_2$ and NH$_2$ on HTS heterogeneous surfaces were developed to study the aggregation and pattern formation of Au colloids on surfaces.

In the future, we would like to reduce the size scaling effects of organosilanes by adhering the first and second phases to the surface using vapor phase deposition.$^{10-12}$ It is possible that NH$_2$ or HTS domains at 50 nm can be reduced to the size of a nanoparticle (25 nm) to study Au colloid aggregates on a 2-D surface. The first phase for modifying glass slides will be prepared as described in Chapter 2 when using vapor phase treatment of glass. The second phase will be prepared in the same manner to develop a heterogeneous molecular surface on glass. The slides will be immersed in an aqueous solution of Au colloids (HAuCl$_4$) for 5 min then rinsed with nanopure water. The 2-D aggregates and pattern of Au nanoparticles can be examined by AFM to note their growth and network due to a heterogeneous surface.

6.3 References


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Appendix

RAIRS Spectra of Cysteamine/Au and NVOC/Cysteamine/Au

Figure A.1. RAIRS of A. cysteamine/Au and B. NVOC/cysteamine/Au.
Vita

Sonya Latrice Caston, now Sonya Caston Pierre, was born at Forest General Hospital in Hattiesburg, Mississippi to Fulton and Artrie Caston on September 21, 1971. She is the youngest sister of Paulette Anita Caston. Sonya attended Baker’s preschool at age 4 in Hattiesburg, Mississippi. Thereafter, her father moved the family to Frankfort, Kentucky in 1976. While in Frankfort, Sonya attended Capitol Day Private School, Collins Lane Elementary School, and Bondurant Middle School. In 1984 prior to entering the eighth grade, her father moved the family to Jackson, Mississippi. She attended Powell Junior High School and Callaway Senior High School. In the fall of 1989, she attended undergraduate school at Jackson State University in Jackson, Mississippi. Sonya was awarded a Bachelors of Science degree in December 1993 from Jackson State University. On February 5, 2000, she was married to Darren Paul Pierre of New Orleans, Louisiana. Currently, Sonya is attending Louisiana State University in Baton Rouge to complete the requirements to receive a Doctor of Philosophy degree in Chemistry.
Candidate: Sonya C. Pierre

Major Field: Chemistry

Title of Dissertation: Characteristics and Use of Thin Metals on Modified Glass Substrates

Approved:

[Signature]

Major Professor and Chairman

[Signature]

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

April 9, 2001