2007

Development of gradient-based surface methods

Erin Louise Ratcliff
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd
Part of the Analytical Chemistry Commons, and the Physical Chemistry Commons

Recommended Citation
https://lib.dr.iastate.edu/rtd/15962

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Development of gradient-based surface methods

by

Erin Louise Ratcliff

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Physical Chemistry

Program of Study Committee:
Andrew C. Hillier, Major Professor
  Kurt Hebert
  Hans Stauffer
  Pat Thiel
  Ed Yeung

Iowa State University

Ames, Iowa

2007
# TABLE OF CONTENTS

LIST OF FIGURES........................................................................................................................................ iv

ABSTRACT.................................................................................................................................................... vii

CHAPTER 1. INTRODUCTION .......................................................................................................................... 1
  1.1 GENERAL INTRODUCTION........................................................................................................................ 1
  1.2 BACKGROUND............................................................................................................................................ 5
  1.3 OBJECTIVE............................................................................................................................................... 8
  1.4 THESIS ORGANIZATION........................................................................................................................... 10
  1.5 REFERENCES.......................................................................................................................................... 10

CHAPTER 2: RAPID AND REVERSIBLE GENERATION OF A MICROSCALE pH GRADIENT USING SURFACE ELECTRIC FIELDS .................................................................................................................. 15
  ABSTRACT................................................................................................................................................... 15
  2.1 INTRODUCTION....................................................................................................................................... 15
  2.2 EXPERIMENTAL SECTION........................................................................................................................ 18
  2.3 RESULTS AND DISCUSSION................................................................................................................... 23
  2.4 CONCLUSIONS........................................................................................................................................ 36
  2.5 REFERENCES.......................................................................................................................................... 36

CHAPTER 3: MASKLESS ELECTRODEPOSITION OF POLYMER FILMS USING SPATIALLY CONTROLLABLE ELECTRIC FIELD GRADIENTS ................................................................................................................... 40
  ABSTRACT................................................................................................................................................... 40
  3.1 INTRODUCTION....................................................................................................................................... 40
  3.2 EXPERIMENTAL SECTION........................................................................................................................ 42
  3.3 RESULTS AND DISCUSSION................................................................................................................... 45
  3.4 CONCLUSIONS........................................................................................................................................ 59
  3.5 REFERENCES.......................................................................................................................................... 60

CHAPTER 4. THE SPATIAL CONTROL OF METAL AND METAL OXIDES USING SURFACE ELECTRIC FIELDS .................................................................................................................................................. 64
  ABSTRACT................................................................................................................................................... 64
  4.1 INTRODUCTION....................................................................................................................................... 64
  4.2 EXPERIMENTAL METHODS...................................................................................................................... 67
  4.3 RESULTS AND DISCUSSION................................................................................................................... 71
  4.4 CONCLUSIONS........................................................................................................................................ 79
  4.5 REFERENCES.......................................................................................................................................... 80

CHAPTER 5. ELECTROCHEMICAL AND ELLIPSOMETRIC STUDY OF POTENTIAL-CONTROLLED SPATIAL ADSORPTION OF DOPC ON Au ............................................................................................................ 82
  ABSTRACT................................................................................................................................................... 82
  5.1 INTRODUCTION....................................................................................................................................... 82
  5.2 EXPERIMENTAL METHODS...................................................................................................................... 85
CHAPTER 6. LOW PRECIOUS METAL CONTENT MONOLAYER-COATED CATALYSTS ......................................................... 104
   ABSTRACT ........................................................................................................... 104
   6.1 INTRODUCTION .......................................................................................... 104
   6.2 EXPERIMENTAL METHODS ....................................................................... 111
   6.3 RESULTS AND DISCUSSION ..................................................................... 113
   6.4 CONCLUSIONS ............................................................................................ 119
   6.5 REFERENCES ............................................................................................... 120

CHAPTER 7. CONCLUSIONS AND FUTURE DIRECTIONS ......................... 121

APPENDIX: NULL ELLIPSMOMETRY ................................................................. 127

ACKNOWLEDGEMENTS .................................................................................. 133
LIST OF FIGURES

Figure 1.1  Schematic of an in-plate linear potential gradient 5
Figure 1.2  Schematic representation of an in-plane potential gradient spatially controlling electrochemical reactions 6
Figure 1.3  Schematic of a two dimensional electric field gradient with a four electrode set-up 7
Figure 2.1  Cyclic voltammetry of electrodeposited platinum on ITO and bare ITO in 0.1 M Na$_2$SO$_4$ 24
Figure 2.2  Measured pH profile along electrode surface determined using IrO$_2$ micro-pH electrode 25
Figure 2.3  Examples of spatially controllable linear pH gradients in a macro flow cell imaged with pH responsive fluorescence 27
Figure 2.4  Examples of spatially controllable two-dimensional pH gradients in a macro cell using pH responsive fluorescence 29
Figure 2.5  Optical imaging of several pH gradients in micro flow cell 30
Figure 2.6  Optical imaging of time-dependent pH gradient development 32
Figure 2.7  Simulated pH gradient development in a micro-channel 34
Figure 3.1  Cyclic voltammograms of polymer film growth on ITO 46
Figure 3.2  PANI-PPO two band sample on ITO 48
Figure 3.3  Null-ellipsometry mapping of PANI-PPO two band sample on ITO 50
Figure 3.4  Three band PAPO-PANI-PAPO sample on ITO 52
Figure 3.5  Null-ellipsometry mapping of PAPO-PANI-PAPO on ITO 53
Figure 3.6  Examples of polymer band constructions 54
| Figure 6.2 | Cost vs. particle size | 106 |
| Figure 6.3 | Schematic of the under potential deposition (UPD) of copper followed by the redox replacement deposition (RRD) of platinum monolayers on gold | 108 |
| Figure 6.4 | Work function vs. standard reduction potentials | 110 |
| Figure 6.5 | Pourbaix diagram for nickel | 111 |
| Figure 6.6 | Cyclic voltammetry of nickel and platinum coated nickel wires | 113 |
| Figure 6.7 | Cyclic voltammetry of template stripped nickel and platinum coated nickel surfaces | 115 |
| Figure 6.8 | Atomic force microscopy (AFM) images of pH-dependent platinum films on nickel | 116 |
| Figure 6.9 | Cyclic voltamagrams of platinum coated nickel nanoparticles | 118 |
| Figure A1 | A schematic of p and s polarized light | 128 |
| Figure A2 | Ellipsometer in PCSA-configuration | 129 |
| Figure A3 | Reflection and transmission of a plane wave by an ambient – film – substrate system | 131 |
ABSTRACT

This work is a detailed study concerning the development and investigation of surface electric field gradients to spatially control the magnitude and locale of electrochemical reactions on surfaces. It will be illustrated that the use of surface potential gradients enables the simultaneous driving of both oxidation and reduction reactions on the same electrode surface. We anticipate that these features will have broad impact over a wide range of applications including microscale devices, sensors, analytical testing devices, and biological applications requiring spatial control of electrochemical phenomena. One example which will be presented in this work of such an application is the development of a spatially controllable pH gradient within a microfluidic channel for isoelectric focusing. Spatial control will also be demonstrated for the local control of adsorbates. In particular, surface potential gradients are used for the maskless patterning of polymers for corrosion protection and sensor applications. Further exploration will delve into the spatial control of metal supported phospholipids, a model system for biological membranes. One final application of surface electric fields will consist of the spatial control of metal electrodeposition and spatiotemporal control of passivating metal oxide film growth, important in studies of catalysis. A separate project will also be discussed concerning the fabrication of low precious metal content monolayer coated nanoscale catalysts for applications in fuel cells. This project utilizes recently developed redox replacement reactions to reduce the amount of catalytic platinum used to only a single monolayer.
CHAPTER 1. INTRODUCTION

1.1 GENERAL INTRODUCTION

Gradients are defined as lateral changes in a function (i.e. concentration, potential, etc.) with respect to displacement. Specifically, chemical gradients are spatial changes in concentration with respect to location. The focus of this work is the fabrication of chemical gradients across a surface formed by the application of gradients in electrical potential. Chemical gradients for a variety of species including redox species in solution (i.e. H\(^+\), OH\(^-\)), electrodeposited polymers, adsorbed phospholipid bi-layers and metal/metal oxide electrochemical systems will be discussed.

Chemical gradients are abundant in a variety of biological systems and essential to vital biological processes. One example is the chemical gradient created across a cell membrane formed by cells pumping ions from one side of a membrane to the other. Specifically, sodium ions are pumped from one side of an epithelium to the other to form an osmotic gradient, which drives the absorption of water – a key function of the cells located in the small intestine [1,2]. In cardiac cells, there are potassium channels which create gradients across the cell membrane, such that cells usually have a higher concentration of potassium ions (K\(^+\)) on the inside of the cell relative to the outside of the cell [3,4]. The regulation of potassium ions help maintain membrane potential, forming the basis for excitability in both nerve and muscle cells. Mitochondria, essential for cell energy production, pump protons out of the inner membrane in order to maintain an electrochemical gradient across the membrane [5]. The electrochemical gradient is critical to the synthesis of ATP [5,6].
The biological implications of chemical gradients are not limited to changes in chemical potential across a membrane. It is well documented that a variety of cells will migrate with respect to gradient orientation [7,8]. When cell mobility is modulated by the sensing of chemical signals in the environment, the resulting mobility is called chemotaxis. There are numerous examples of chemotaxis ranging from protozoa [9,10] to bacteria [11-13] to human cells [14]. For example, it has recently been demonstrated that sperm cells are able to detect and locate ovarian cells due to a chemical gradient produced by the ovarian cells [15-18]. Protein gradients along the spinal cord attract growing neurons toward the brain and may be useful for the repairing of spinal cord injuries [19].

The application of gradients is not limited only to biological systems; gradients have also proven to be extremely applicable to a variety of chemical systems, particularly the discovery of new materials. For example, gradients have been employed to determine ideal percentages of metals for fuel cell catalysts [20-22]. Materials discovery using gradients has also been utilized for binary polymer combinations for polymer based sensors [23, 24]. When a gradient is formed, it contains all permissible combinations of starting and ending concentrations. Using this technique, the amount of necessary substrate fabrication is reduced drastically from discrete composition samples. Furthermore, all combinations may be compared at once, under the same set of conditions. Gradients permit the rapid discovery of ideal candidates within a single experiment.

Further applications of gradients include chemical sensor calibration [24-27], surface fabrication [26,28-34] and patterning [35-37]. Gradients have also been employed in a variety of technologies such as material discovery and sensor design [38-40], microfabrication [41], bonding techniques [31], surface modification and design of interfaces [28].
The formation of gradients has been accomplished using a variety of different techniques. A very popular method is the implementation of micro fluidics. Applications include phenomena that require a gradient in concentration; namely biological studies involving cell biology (ex. chemotaxis [42-46]) as well as chemical gradients [41,47,48], pH gradients for electrophoresis [49,50] and surface chemistry (etching) [51]. Microfluidic devices are contingent upon a series of channel networks between inlet and outlet reservoirs. Gradient control is maintained using syringe pumps to mediate the flow through the channels. Resolution is on the order of millimeters to as small as several microns [51]. Spatial control is achieved, but to a limiting degree. In order to reverse the direction of the gradient, solutions in both the inlet and outlet reservoirs must be changed and time is a factor. Furthermore, gradient smearing occurs when streams of different compositions are merged at the end of a micro channel [44, 52]. A second limitation of many microfluidic methods stems from the time and skill required in soft lithographic techniques to construct channels.

A second very popular technique for gradient formation is the employment of diffusion due to the simplicity of the technique. A species of interest is introduced into a medium such as a gel or a solution via a pipette tip or reservoir. The gradient is created by the migration of the species through the medium. The highest concentration remains at the point of introduction and concentration decreases with respect to displacement. More diverse gradients can be formed by employing multiple entry points and multiple species of varying migration velocities [53,54]. Techniques include diffusion-controlled vapor deposition [55], cross diffusion [56,57] and diffusion through a gel [34,53,54,58]. Applications include both biological and chemical aspects such as cell processes (i.e. chemotaxis and morphogenesis [54]) cell adhesion [34], self-assembled monolayers [56,57] and catalysts [53]. However,
these methods are limiting in terms of resolution, shape and spatial control because they rely on simple diffusion between a source and a sink and have no other spatial control [59-61]. Spatial resolution is typically only on the order of millimeters [44].

A third technique for the fabrication of gradients on a surface takes advantage of the simplicity of the diffusion technique and eliminates time constraints and complicated lithography techniques associated with micro fluidics. Spatial control is obtained by employing an electric field gradient to a surface. The electric field controls the local concentrations of the redox species present in solution with respect to local applied potential, creating a gradient in concentration in the double layer above the surface. The gradient can be controlled in both direction and magnitude by adjustment of the terminally applied potentials. The only requirement is a sufficiently resistive surface that can support the potential gradient and the presence of electroactive species in solution. Applications include non-uniform self-assembled monolayer (SAM) composition gradients [36,37,62-66], metal deposition [63,67,68], peptide monolayer formation [69,70], non-uniform catalysis gradients [32], PtOx studies [33], pH gradients [71], and maskless patterning of polymers [72]. The surface electric field technique has inherent advantages over other techniques presented in that it is fast and easily controlled as well as inexpensive to construct. Limitations include the necessity for sufficiently resistive surfaces to support the potential gradients as well as electroactive species. The use of surface electric fields to produce, control and employ for surface modification is the focus of this work.
1.2 BACKGROUND

An in-plane potential gradient can be created by applying two different potentials at spatially distinct locations (E₁ and E₂) on a sufficiently resistive surface such as a thin gold film (t<50 nm) or indium tin oxide on glass (~100 Ω/in). The potential gradient on the surface can be described by a linear relationship (eqn 1),

\[ V(x) = V(o) + \int \frac{i \rho}{A} dx \]  

(1)

where \( i \) is the electrical current, \( V(o) \) is the applied potential, \( V(x) \) is the offset potential at some distance \( x \) along the surface, \( \rho \) is the surface resistivity and \( A \) is the cross-sectional area (figure 1.1). The local surface potential can be used to drive electrochemical reactions with varying surface rates. For example, the reduction of an electroactive species may occur near one potential (E₁) on the substrate while the oxidation of the species occurs near a second potential (E₂). A corresponding composition gradient in concentration will be formed between the two

![Figure 1.1](image-url)
electrodes (figure 1.2). The magnitude of the composition gradient is controlled both by the applied potentials and the kinetics associated with each electrochemical reaction.

In-plane potential gradients are not limited to specific size scales—surface electric fields have been developed on both the macro and micro scale [36,71]. In-plane potential gradients are not limited to only linear, one-dimensional surfaces. By expanding eqn 1 to two dimensions,

\[ V(x, y) = V(x_0, y_0) + \iint \frac{\rho(x, y)}{A} \, dx \, dy \]  

(2)

where \( i \) is the position dependent current based on the system and terminal voltages. The local potential can be a combination of several competing linear potential gradients. An example of a two dimensional surface gradient profile is given in Figure 1.3.

Surface electric field gradients were first employed to create a varying composition of alkane thiols adsorbed on a thin film gold surface (~50 nm) [66]. Briefly, a hydrophobic alkane thiol was self-adsorbed across the entire gold surface. Thiol terminated monolayers have a widely understood chemistry and will desorb at a specific electrochemical potential.

**Figure 1.2.** Schematic representation of an in-plane potential gradient spatially controlling electrochemical reactions.
A potential gradient was applied across the surface that included potentials below and above the desorption potential. Thiols were stripped from regions of the surface where the local potential was cathodic of the desorption potential. The result was a spatial variation in coverage. Wettibility and surface plasmon resonance (SPR) experiments demonstrated active spatiotemporal control of the electrochemical reactions by applying a variety of electric field gradients. A two-component gradient could also be created by back-filling the freshly exposed gold regions with a second self-assembled monolayer, such as a hydrophilic carboxylic acid terminated alkane thiol.

The ability to create surface composition gradients of self-assembled monolayers paved the way for a variety of applications for surface electric fields.

**Figure 1.3.** Example of a two dimensional surface electric field controlled by four spatially distinct applied potentials $E_1$, $E_2$, $E_3$, and $E_4$. 
Functionalization of the head groups on self-assembled monolayers adhered to gold can be tailored to provide specific binding sites on other molecules. Gradients in surface density of proteins or lipids, once elusive, can be created, applicable to many biological systems such as cell adhesion and motility [37,69,70].

1.3 OBJECTIVE

Much of the work on surface density gradients of self-assembled monolayers created by in-plane electrochemical gradients has focused on proof of concept and verification of gradient control. This work attempts to expand beyond the basic proof of concept and exploit underlying advantages to creating a continuous electric field which spans a surface. By spatially controlling the local reduction or oxidation of species at the electrode surface, one is able to not only generate gradients in surface coverage or composition but also locally control the concentration of redox species. It is possible to not only create a gradient on the surface, but to also create a gradient in the solution above the surface. For example, we will demonstrate within the scope of this work that surface electric fields may be combined with the diffusion of ions in a solution to create a gradient in pH. Such an application is advantageous for the production of chemical gradients within a solution.

Spatial control of oxidative species at an electrode surface has also created potential for maskless patterning capabilities. One case in point involves the maskless patterning of polymers. A particular polymer will deposit at potential values greater than the oxidation potential of the respective monomer. By controlling the electric field over the area of the substrate with arrays of electrode contacts, it is possible to create patterns of bands of deposited polymers on a surface in the absence of a mask.
Maskless patterning may also be extended to metal and metal oxide systems. Metal ions are readily reduced from solution at their respective reduction potentials. By applying potential gradients which encompass a specific metal ion’s reduction potential, gradients in metal composition can be generated across a surface. Further control of metal systems may be achieved by spatially controlling the growth of metal oxides. Again, there are specific potentials at which oxide growth commences. The application of potential gradients across a metal surface can promote oxide growth at one end of the substrate where local potential exceeds the potential for oxide growth while there is no oxide growth at the other end of the substrate at local potentials below the potential for oxide film formation.

Surface electric fields may also be used to pattern surfaces with macromolecules such as phospholipids. Phospholipids are known to adsorb at or near the potential of zero charge ($pzc$) of an electrode and will not adsorb on charged electrode surfaces. By adjusting the terminal applied potentials and the resulting potential gradient, the location of the $pzc$ can be moved around the surface. Phospholipids will adsorb only at the potentials near the $pzc$ and not at other locations, creating localized areas of adsorption.

Each of these systems previously described is unique in its application of surface electric fields to spatially control electrochemical reactions along a surface. Our discussion will not be limited to only linear gradients, but will be the first evidence of expansion into two dimensions. All prior work has focused only on linear gradients employed for spatial control.
1.4 THESIS ORGANIZATION

The spatial control of electric field gradients and in turn, the surface composition gradients which they produce will be investigated and developed in this dissertation. A series of applications are presented; each a unique electrochemical system with broader scientific impact above the simple implementation of a surface electric field. The advantages associated with the use of surface electric fields over state of the art techniques are presented for each.

The development and validation of an electric field generated pH gradient will be discussed in Chapter 2. Results demonstrate that our gradient is superior in time over state of the art electrochemical methods. Chapter 3 is a discussion of the maskless patterning of polymers on an indium tin oxide (ITO) surface using surface electric fields. Chapter 4 deals with the use of surface electric fields to control the deposition of copper as well as the spatial control of platinum oxide on a thin platinum film. Potential and position dependent control of gold oxide and the adsorption of a lipid on a thin gold film are discussed in Chapter 5. A separate project from spatial electric fields is presented in Chapter 6. The fabrication and characterization of low precious metal nanoparticles for potential fuel cell catalysts is presented. Conclusions and future directs are given in Chapter 7. An appendix is also given stating an introduction to the null ellipsometry technique.

1.5 REFERENCES


CHAPTER 2: RAPID AND REVERSIBLE GENERATION OF A MICROSCALE pH GRADIENT USING SURFACE ELECTRIC FIELDS

Adapted from a manuscript published in *Analytical Chemistry* 2005, 77(19), 6487-6492.

Erin L. May and Andrew C. Hillier

ABSTRACT

We report a method for the rapid and reversible generation of microscale pH gradients using a spatially varied electric field. A linear gradient in electrochemical potential is produced on an electrode surface consisting of a platinum catalyst layer on indium-tin-oxide coated glass by the application of two different potential values at spatially distinct surface locations. The resulting potential gradient drives the oxidation and reduction of water at different rates along the surface, as dictated by the local applied potential. A non-uniform distribution of pH in the neighboring solution results due to the variation in surface reaction rates. The extent and magnitude of the pH gradient can be controlled by the appropriate selection of applied potential values. In addition, the gradient can be rapidly turned on or off and reversibly switched between various profiles. The size of the pH gradient can be readily modified by changing the dimensions of the electrode and contact pads to allow integration into chip-scale devices. Characteristics of the pH gradient are described, including experimental and theoretical evidence of significant improvement in time response over competing methods for the generation of microscale pH gradients.

2.1 INTRODUCTION

Lab on a chip concepts for micro fabricated analytical devices consisting of various functions and sample preparation capabilities on a miniaturized scale have become
increasingly popular due to portability, disposability and on-demand processing capabilities [1-3]. For analytical techniques, the reduction in size can significantly reduce sample consumption, decrease the time required to isolate a compound [4] and is more conducive to parallel processing, providing the capability for high throughput analysis [5].

A variety of miniaturized devices and components have been demonstrated. Examples include a variety of macro scale devices fabricated in the micro scale, such as pumps, valves, sensors, power supplies, and fluidic processes [6-9]. Furthermore, a variety of analytical methods have been reduced to practice on the microscale, including gas chromatography [10], liquid chromatography [11,12], flow cytometry [13,14], and mass spectrometry [15-17]. Improved performance for chip-based analytics include electrophoresis [18-20] devices that can separate nucleic acids in less than one minute [21] and perform more complicated tasks such as DNA sequencing in less than twenty minutes [22].

Miniaturizing analytical devices involves solving a variety of challenges. Simple tasks such as sample injection and flow control require new technologies at the microscale. The challenges increase for more complicated processes involving mixing, reaction and detection at the microscale. Electrophoresis represents a relatively straight-forward process to miniaturize. However, performing isoelectric focusing on the micro-scale is considerably more complex. The requisite pH gradient combined with the applied electric field needed to isolate compounds by charge must be generated and placed with spatial control within a microscale platform. At the macro-scale, pH gradients are generated from the migration of heterogeneous mixtures of carrier ampholytes in an electric field or through interdiffusion of reservoirs of acidic and alkaline buffers [23]. The major difficulty in miniaturization of
isoelectric focusing is to decrease the physical size of the pH gradient while still maintaining control over a wide range of pH values.

The most popular method for creating micro-scale pH gradients has involved exploiting microfluidic processing, where buffers are mechanically pumped from reservoirs into channels to create gradients based upon flow/diffusion. However, these methods have not shown significant improvements over macro-scale methods, with separation times involving fractions of hours [24] and length scales only on the order of centimeters [25]. Further drawbacks of microfluidic processing include high cost instrumentation [24], the need for mechanical movement of liquid that results in parabolic velocity profiles and band broadening [26,27], and high electric fields, which lead to Joule heating effects [28] and the possibility of gas evolution.

An alternative method employs a two-terminal electrochemical process to create a “natural” pH gradient in a simple buffer system [25,27]. Two opposing electrodes placed within a fluid channel are used to create a pH gradient by the electrolysis of water. The pH gradient forms by diffusion of \( \text{OH}^- \) and \( \text{H}^+ \) between the anode and cathode across the channel. The ability to use electric fields on the order of a few volts rather than the kilovolts needed with fluidic methods minimizes problems associated with Joule heating and gas evolution [25,27].

Although the two-terminal electrochemical method has some advantages over microfluidic techniques, both methods suffer from slow response times. In this manuscript, we describe a method for generation of a micro-scale pH gradient that is simple, easily implemented at the microscale, controllable, reversible, and capable of generating a fully developed pH gradient on the time-scale of seconds.
The method of pH gradient generation described here is based upon exploiting a surface electric field gradient. Surface electric field gradients have been previously used for a variety of applications [29-35]. This technique develops a linear potential gradient on a surface by forcing current through a resistive electrode or by holding discrete electrode locations at different applied potentials. The resulting gradient in surface potential can be used to drive electrochemical reactions that vary as a function of location on a surface. This method has been used to create surfaces with non-uniform coverage of self-assembled monolayers [29,32,34,35] to map the potential dependence of copper deposition on gold [33], to create non-uniform catalyst gradients [36] and to study peptide monolayer formation on gold [7,31]. In this manuscript, we describe the application of a surface potential gradient to create a dynamic and controllable pH gradient. The oxidation and reduction of water on a platinum-coated indium tin oxide electrode is manipulated by the application of a surface electric field to locally control the proton concentration in solution and generate a pH gradient near the electrode surface. The pH gradient is readily controllable, both in magnitude and direction, by simple manipulation of the applied potential values. The size of the pH gradient can be readily modified by changing the dimensions of the electrode and contact pads to allow integration into chip-scale devices. In addition, the geometry and format of this system provide a fully developed pH gradient on the time-scale of seconds, as opposed to minutes or hours for competing technologies.

2.2 EXPERIMENTAL SECTION

Materials and Reagents. Metal salts (H$_2$PtCl$_6$·6H$_2$O and IrCl$_4$) were purchased from Aldrich (Milwaukee, WI). A pH sensitive fluorescent probe quinine (Alfa Aesar, Lancaster,
England) and universal indicator (Spectrum Chemical Mfg. Corp., Gardena, CA) were used as received. Citric acid buffers used for pH calibration were made by titrating a solution of 0.1 M citric acid monohydride, 0.1 M Na$_2$SO$_4$, $\leq$ 1 mM universal indicator, and 0.1 mM EDTA (for preservative) with 1.0 M NaOH (Aldrich, Milwaukee, WI) to the desired pH, using a MA130 Ion Meter (Meter-Toledo, Inc., Columbus, OH). When not in use, buffers were stored in a refrigerator and allowed to reach room temperature prior to use. Unless otherwise noted, solutions were prepared from as-received reagents from Fisher Scientific (Fair Lawn, NJ) in 18 MΩ deionized water (NANOPure, Barnstead, Dubuque, IA) and purged for 15 minutes in nitrogen before each use. Metal patterning was done with gold (Ernest F. Fullam, Inc., Latha, NY) and photoresist (Microposit S1813 Photoresist, Shipley, Marlborough, MA). Platinum-iridium wire (0.025 mm Pt90/Ir10, Goodfellow Cambridge Limited, Cambridge, England) was used for counter and pH electrodes.

Substrate Fabrication. Glass slides coated with indium-tin oxide (ITO) with a surface resistance of 100 Ω/inch (Delta Technologies, Stillwater, MN) were patterned with photoresist to form conducting and insulating bands of different sizes using a previously published procedure [36]. Platinum was electrodeposited onto the exposed ITO bands from a solution of ~10 mM H$_2$PtCl$_6$·6H$_2$O and 0.1 M Na$_2$SO$_4$ using a potentiostat (Model CH1030, CH Instruments Inc., Austin, TX). A square wave potential program with limits of 0 and -1.5 V (vs. Hg/Hg$_2$SO$_4$) at a frequency of 100 Hz was applied for 2 minutes to create a uniform layer of platinum. Contact pads to connect to the ends of the platinum-coated ITO regions were then fabricated by depositing gold through a mask that exposed the edges of the sample. Approximately 100 nm of gold was vapor-deposited (Denton Vacuum Turbo III,
Morristown, NJ) onto the ends of the substrate at a pressure of ~7x10^{-5} Torr under nitrogen atmosphere at a rate of 1-2 Å/sec.

**Macro-scale Cell.** pH gradients were initially generated and analyzed on a large sample in a macro-scale electrochemical cell (Figure 2.3A). The substrate consisted of a banded electrode with alternating Pt on ITO and insulating glass regions. The total electrode area was 12 mm x 24 mm. Gold was vapor-deposited onto the edges of the substrate to provide electrical contact to the ITO surface. The gold was connected to copper wires and secured using silver epoxy (H20E parts A and B, Epoxy Technologies, Billerica, MA) followed by an insulating epoxy (QuickSet Epoxy Gel, Hentel Consumer Adhesives, Inc., Avon, OH). Finally, the gold was insulated from the solution by Microstop stop-off lacquer (Pyramid Plastics Inc., Hope, AR). The sample was then immersed in an open-top beaker cell for analysis. Electrochemical measurements were carried out in 0.1 M Na$_2$SO$_4$ purged with N$_2$. The electrochemical cell used a quasi Ag/AgCl reference electrode and Pt-Ir on Ti mesh counter electrode. The counter electrode was separated from the substrate electrode by a salt bridge. The potential was controlled by a biopotentiostat (AFRDE5 Bi-potentiostat, Pine Instrument Company, Grove City, PA) with the two working electrodes connected to opposite ends of the substrate.

**Micro-scale Flow Cell.** Miniaturized pH gradients were created and analyzed in a micro-scale flow cell. A glass microscope slide was cut to 24 mm x 24 mm and cleaned by successive sonication in 50:50 ethanol/DI water and DI water and dried in a nitrogen stream. Double-sided adhesive tape ~250 µm thick was placed on the slide to form a channel approximately 1000 µm wide and 2.5 cm long. An ITO coated glass was then cut to size and patterned with platinum bands and attached to the glass slide. The tape formed the flow
channel between patterned ITO and glass pieces (Figure 2.4A). The exposed Pt bordered by the tape defined the electrode area. The channel was filled by capillary action and monitored with an optical microscope (Epiphot, Nikon). Electrochemical measurements were carried out in 0.1 M Na$_2$SO$_4$ purged with N$_2$ that also contained a universal pH indicator. Linear potential gradients were created using either the bipotentiostat or a DC power supply (PA36-3A, Kenwood Corporation, Tokyo, Japan).

**Fluorescence.** Fluorescence measurements were performed by adding quinine to the electrolyte solution and illuminating the macro-cell from the top with a 365 nm UV source (Spectroline Model SB-100P, Spectronics Corp., Westbury, NY). Fluorescence was monitored with a high resolution CCD camera (Model VCC 3972, Sanyo) equipped with a variable zoom lens (Zoom 7000, Navitar), placed perpendicular to the substrate. Images were captured using commercially available software on a personal computer equipped with a frame grabber card (Pinnacle Systems, Inc., Mountain View, CA). Fluorescence intensity versus distance plots were obtained using Image J software to collect grey scale plot profiles of the fluorescence images with respect to position within the macro-channel.

**Micro-pH Electrode.** pH profiles were measured in the macro-cell using a miniature pH-electrode. This electrode was prepared using published procedures [37]. Briefly, 250 µm diameter platinum-iridium wire was cleaned by soaking for approximately 15 minutes in concentrated HNO$_3$ (Fisher Scientific, Fair Lawn, NJ) and rinsed with water. Iridium was electrodeposited from a solution of 0.5 mM iridium (IV) chloride and 0.1 M Na$_2$SO$_4$, using a square wave potential program with limits of 0 and -1.5 V (vs. Hg/Hg$_2$SO$_4$) at a frequency of 100 Hz applied for 2 minutes. Immediately following electrodeposition, the wire was soaked in a solution of 2 M NaOH for 20 minutes, followed by thermal oxidation in air at 800 °C for
1 hour. The NaOH / thermal treatment was repeated three times until a uniform purple-grey coating formed on the wire. The wire was then soaked in deionized water for three days. The oxide coating was stripped from one end of the wire, which was then connected to a copper contact wire using silver epoxy (H20E parts A and B, Epoxy Technologies, Billerica, MA). The Pt/Ir wire was then inserted into a glass capillary (M1B000-4, World Precision Instruments, Sarasota, FL) and secured with epoxy (Quickset Epoxy Gel, Henkel Consumer Adhesives, Inc., Avon, OH) such that approximately 5 mm of iridium oxide coated wire protruded from one end of the capillary. Microstop stop-off lacquer (Pyramid Plastics Inc., Hope, AR) was used to coat the exposed sides of the wire, leaving only the end for solution contact. The open circuit potential of this electrode was then measured versus a mercury/mercury sulfate reference electrode. The voltage response of the pH electrode was calibrated against citric acid buffers using a pH meter (MA130 Ion meter, Meter-Toledo, Inc., Columbus, OH).

**pH Imaging with Universal Indicator.** pH profiles in the micro-scale flow channel were measured using a universal pH indicator. Images of the indicator profile within the flow channel were acquired using an optical microscope and a color CCD camera (**vide supra**). pH profiles were then generated by taking these images and loading them into a commercial graphics software package (Canvas, Deneba). Red, orange, yellow, green, and blue hues were isolated within the images using color filters. Background images were then subtracted from the color images, and plot profiles for each of the isolated hues were obtained. An algorithm relating the five hues to the solution pH was then applied to develop the pH line profiles. The algorithm consisted of a five-term linear expression relating each hue to the pH. The parameters were determined by calibration of color versus pH for a set of
uniform pH standards. Notably, this procedure is limited by the nonlinearity of the CCD camera as well as optical artifacts and defects in the sample. As such, these results are limited to a precision of ± 1 pH unit.

2.3 RESULTS AND DISCUSSION

The method used in this work to generate a controllable pH gradient involved applying different potential values to two spatially distinct locations on a resistive electrode surface in a manner similar to the technique originally developed by Bohn and co-workers [34, 35]. By driving current between two distinct surface locations, a drop in electrode potential ($\Delta V$) is created that follows a simple, linear relationship (Eqn.1).

$$\Delta V = \frac{i \rho}{A} \Delta l$$

where $i$ is the electrical current, $A$ is the cross-sectional area, $\rho$ is the surface resistivity and $\Delta l$ is the distance along the surface. A constant surface resistivity gives a linear drop in potential between two points. When immersed in a solution, this variation in surface electrode potential can be used to drive electrochemical reactions with rates that vary along the electrode surface [29-33].

We have exploited this method of generating a surface potential gradient to produce controllable pH gradients via oxidation and reduction reactions in water. The governing electrochemical processes include pH increasing and pH decreasing reactions facilitated by a thin platinum catalyst layer. In an acidic solution, these reactions are given by

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \hspace{1cm} E^0 \text{ (NHE)} = 1.229 \text{ V} \hspace{1cm} (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \hspace{1cm} E^0 \text{ (NHE)} = 0.0 \text{ V} \hspace{1cm} (3)$$
The first reaction oxidizes water to produce protons and decreases the pH near the electrode surface while the second reduces the proton concentration to increase the pH. In basic solution, the reactions become

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad E^0 (NHE) = -0.828 \text{ V} \quad (4) \]

\[ 2OH^- \rightarrow O_2 + 2H^+ + 2e^- \quad E^0 (NHE) = 0.401 \text{ V} \quad (5) \]

In each case, the reduction reaction increases the pH by either consuming protons or producing hydroxyls. The oxidation reaction lowers the pH by either generating protons or consuming hydroxyls. These reactions are also accompanied by the formation of gases, namely hydrogen and oxygen. At sufficiently large potential values, the rate of gas evolution can exceed the solubility limit of these gases, which leads to bubble formation on the electrode. This can be problematic in microfluidic applications. However, we have found that by carefully controlling the potential limits one can minimize and even eliminate bubble formation.

An example of reactions (2) and (3) occurring at pH 4 for both ITO and platinum surfaces are shown in the cyclic voltammetry in Figure 2.1. The response for Pt (Fig. 2.1, curve A)
depicts the characteristic response for this metal. The pH increases near the negative potential limit due to proton reduction (Eqn.2) and decreases at the positive potential limit due to water oxidation (Eqn.3). At intermediate potentials, the interfacial pH can be modified to a smaller extent due to the formation and removal of platinum oxides and underpotential proton adsorption. The result of these processes is an increase of solution pH near the electrode at negative potential values and a pH decrease at positive potentials. In contrast, the response of ITO (Fig. 2.1, curve B) shows limited activity in the same potential range due to the sluggish kinetics it displays for the reactions described in Eqns.(2)-(5). The Pt layer serves to facilitate pH changes by catalyzing these pH-changing reactions.

The ability to locally control and manipulate the potential drop across the platinum coated electrode allows precise control of the resulting pH gradient. An example pH gradient is shown in Fig. 2.2 for a platinum-coated ITO electrode with 17 mm length. The pH profile was quantified with a custom micro-pH electrode that was scanned across the surface using a micro-positioning system at a separation distance of ~ 100 µm. In the absence of the applied potential gradient, there is a uniform pH across the electrode surface, with a value slightly less than four (Fig. 2.2, curve A), which is the same as that of bulk solution.

Figure 2.2. Measured pH profile along electrode surface determined using IrO₂ micro-pH electrode. Curve A: no applied potential. Curve B: applied potential of -1 V at left and 1 V at right.
pH. A potential gradient was then applied, with the potential at the left held at $E_1 = -1$ V and the potential at the right held at $E_2 = +1$ V. In the presence of this electric field, a pH gradient develops near the electrode surface, with pH values ranging from approximately pH 10 at 0 mm to pH 3 at 17 mm. The gradient is consistent with the pH changing reactions in Eqns. (2)-(5), where a high pH is observed at negative applied potentials and a low pH is seen at positive potentials. In addition to the variation in surface reaction rate, diffusion of ions within the liquid near the electrode surface plays a role in the shape of the pH profile.

Manipulation of the pH gradient can be readily achieved by switching of the applied potential values to influence the local rate of reaction on the electrode. Fig. 2.3 depicts a series of images of a Pt/ITO band electrode (Fig. 2.3A) where various pH gradients are generated. Visualization of the pH profile is achieved with the pH-sensitive fluorescence indicator quinine [38], which fluoresces in its acidic form at pH values below its pK$_a$ ($\sim$4.9), but remains dark in its basic form at higher pH values.

For example, Fig. 2.3B depicts a pH gradient generated with an applied potential of $E_1 = 1$ V and $E_2 = 0.2$ V. The resulting pH gradient varies from a low of 2 at the left to a high of 6 at the right. As depicted in the line plot, the fluorescence intensity is high near 1.0 V on the left side of the sample, indicating an acidic pH. In contrast, the fluorescence intensity is low at 0.2 V on the right side of the sample, consistent with a slightly basic pH. Gradient reversal can be readily visualized by reversing the applied potential to $E_1 = 0.2$ V and $E_2 = 1$ V (Fig.
Figure 2.3. Examples of spatially controllable pH gradients in macro-cell as visualized by fluorescence imaging. (A) Schematic of macro-scale sample. Platinum bands ~1 mm x 25 mm are placed on an indium-tin-oxide (ITO) substrate with gold (Au) contact pads. (B-E) Fluorescence images (left) and line plots versus distance (right) across the channel under various applied potentials in a solution of 0.1 M Na₂SO₄ with initial pH of 4. The line plots (right) depict both the fluorescence intensity (solid line) and applied potential (dashed line). (B) 1 V to 0.2 V at E₁ and E₂, corresponding to a pH gradient of 2 to 6. (C) 0.2 V to 1 V (pH gradient 6 to 2). (D) -1 V to 1 V (pH gradient 10 to 2). (E) Rapid manual field switching from 1 V and -1 V to -1 V and 1 V applied to E₁ and E₂. The applied potential in (E) represents a combination of the two potential profiles denoted 1 and 2 in the line plot.

2.3C). The corresponding pH gradient is reversed and now spans from pH 6 at the left to pH 2 at the right. Additional manipulation of the pH range is shown in Fig. 2.3D, where the absolute difference between E₁ and E₂ is increased by setting E₁ = -1 V and E₂ = 1 V. This results in an increase in observed fluorescence profile, corresponding to a pH gradient with an increased width from 4 pH units to almost 8 pH units, spanning from pH 10 to pH ~2. More complex gradients can also be created. For example, Fig. 2.3E depicts the result of
dynamic switching of applied potentials. A rapid manual switching of the applied potential between \( E_1 = -1 \text{ V} \) and \( E_2 = 1 \text{ V} \) (curve 1) to \( E_1 = 1 \text{ V} \) and \( E_2 = -1 \text{ V} \) (curve 2). This yields a parabolic pH profile where the ends are at a low pH while the center is at a higher pH.

The spatial gradient control in figure 2.3 may also be expanded into two dimensions, again using the fluorescence pH indicator quinine. Samples were arrays of 1 x 1 mm electrodeposited platinum grid squares on ITO. An electrode contact was placed in each of the four corners, illustrated by the schematic given in Figure 2.4 A. As in all previous cases, electrode contact was insulated from solution using epoxy. Figure 2.4 (B-D) shows examples of spatially controllable two-dimensional pH gradients. Fluorescence imaging has been reversed in order to increase contrast against the platinum grid. The reverse fluorescent images are on the left, such that areas of low pH (high fluorescence) appear dark and areas of neutral or high pH (no fluorescence) appear bright. On the right are potential profiles used to generate the pH gradients found on the left. Figure 2.4B and 2.4C illustrate linear gradients generated from four corner electrodes as opposed to two band electrodes. Figure 2.4B has a linear gradient in potential of 2.0V on the top (\( E_1 \) and \( E_2 \)) and 0.0 V on the bottom (\( E_3 \) and \( E_4 \)), which correlates with a pH gradient of pH 2 on the top of the sample and pH 6 on the bottom. A similar gradient is shown in figure 2.4C, with \( E_1 = E_4 = 0.6 \text{ V} \) and \( E_2 = E_3 = 2.0 \text{ V} \), resulting in a pH gradient of pH ~5 on the left and pH~2 on the right. Finally, figure 2.4D illustrates complex spatial control of a two dimensional gradient by applying different potentials to neighboring electrodes (\( E_1 = 0.9 \text{ V} \), \( E_2 = 2.0 \text{ V} \), \( E_3 = 0.9 \text{ V} \), \( E_4 = 2.0 \text{ V} \)). The corresponding pH gradient has pH values of pH 2 in corners \( E_1 \) and \( E_3 \) and pH ~5 in corners \( E_2 \) and \( E_4 \). As with the linear gradient, the two dimensional pH gradients are generated in a matter of seconds and can easily be reversed by flipping the potentials.
The results from Figs. 2.3 and 2.4 illustrate that this surface potential-generated pH gradient is easily controllable in both position and magnitude. This method enables pH gradients to be manipulated to encompass a large range of desirable pH values and physically moved along a surface. We next attempted to reduce the scale of this system to allow generation of micro-scale pH gradients for potential application in miniaturized analytical devices such as isoelectric focusing.
In order to demonstrate the ability to form a miniaturized pH gradient, we devised a micro-scale cell that consists of a single fluid channel of 1000 \( \mu \)m width, 15 mm length and 250 \( \mu \)m depth, with entry/exit ports and a defined flow path (Figure 2.5A). Two gold contact pads were used to make electrical contact to a 3 mm wide swath of ITO that was coated with a thin layer of Pt. The 1000 \( \mu \)m width for the flow channel was created by masking with a 250 \( \mu \)m thick tape. The potential gradient was generated by forcing current through the ITO layer between the two gold contact pads. Observation of pH changes was achieved using a universal pH indicator, which consisted of a mixture of pH sensitive chromatic dyes with a detectable pH range of 3 to 10.

![Figure 2.5. A.) Schematic of micro-scale flow cell containing gold contact pads, platinum catalyst region and flow channel. (B-D) pH profile measured with universal indicator across the micro-channel under various applied potentials. (B) No applied potential (\( \Delta E = 0 \) V). (C) \( \Delta E = 1.86 \) V. (D) \( \Delta E = -2.35 \) V. The dashed line in (C) and (D) represents the initial pH within the channel while the solid lines represent a polynomial fit to the data as a guide to the eye.](image-url)
The response of the universal indicator within the micro-channel cell with various electric fields is shown in Figure 2.5 (B-D). These data were produced by acquiring color images of the pH indicator, isolating various hues in the form of intensity with respect to channel position, and then converting them to pH values using a conversion algorithm. In absence of an applied electric field, the pH across the electrode surface remains equal to that of the bulk at ~ 4 (Fig.2.5B). The application of a positive electric field with \( \Delta E = E_1 - E_2 = +1.86 \text{ V} \) (Fig.2.5C) generates an increasing pH gradient with a low pH on the left (pH~3) and high pH on the right (pH\( \geq 9 \)). This gradient is due to oxidation occurring near the left region of the electrode and reduction occurring at the right. By reversing the applied potential (\( \Delta E = -2.35 \text{ V} \)), the pH profile across the channel transforms to a decreasing gradient with a high value on the left and a low value on the right (Fig. 2.5D). The pH gradient in Fig. 2.5D is approximately the same magnitude as in Fig. 2.5C, but in the opposite direction (pH 9 to 3). As with the macro-scale pH gradient demonstrated earlier with quinine, the micro pH gradient is controllable in both position and direction. However, this gradient is produced on a length scale that is considerably smaller.

In addition to the reduced length scale, the pH gradient produced with a surface electric field can respond on a much smaller time-scale than competing technologies. As a comparison, two micro-scale flow channels of the same size were fabricated, one as described above, with a platinum layer spanning the channel and two gold contact pads. A second channel was fabricated that possessed two-terminal electrodes on a glass slide, with no connecting platinum on ITO layer. This latter configuration is reminiscent of the “natural” pH gradient method [25,27]. The channels were filled with the same solution and an identical potential drop was applied across each channel (\( \Delta E = 1.12 \text{ V} \)). The pH response
was monitored with the universal indicator. Just before the potential was applied, both the gradient (Fig. 2.6A) and two-terminal (Fig. 2.6D) configurations showed a nearly constant pH value of ~ 4, consistent with the bulk solution. After 15 sec, the gradient system showed the formation of a substantial pH profile (Fig. 2.6B) while the two-terminal system exhibited no measurable change (Fig. 2.6E). For the gradient sample, a pH variation ranging from a low of 3 at the left to a high of 9 at the right appeared after just 15 seconds while the two-terminal showed no deviation from bulk pH at this time. Only after 5 minutes did the two-terminal electrode system exhibit a developed pH profile of magnitude similar to the gradient.

**Figure 2.6.** pH profiles within micro-channel as measured with universal indicator for (A-C) potential gradient and (D-F) two-terminal electrode configuration. The data reflects pH profiles at 0 sec (A & D), 15 sec (B & E), and 5 min after a potential difference of $\Delta E = 1.12$ V is applied to the edges of each sample. Solid lines represent a polynomial fit to the data as a guide to the eye.
surface (Fig. 2.6F). The gradient pH profile remained stable over this time period (Fig. 2.6C). After 20 minutes, both pH profiles were stable and exhibited a comparable magnitude.

The time difference required to develop a pH gradient using the surface potential gradient versus the two-terminal “natural” gradient were compared theoretically in order to understand the origins for these differences. The local change in concentration within the micro-channel was modeled by Fick’s second law, using the following differential equation:

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right)$$

(7)

where $C$ is proton concentration, $t$ is time, $D$ is the proton diffusion coefficient ($9.31 \times 10^{-5}$ cm$^2$ s$^{-1}$), and $x$ and $y$ are spatial dimensions (width and height) within the channel.

Both channels were simulated with a width of 1000 µm. Boundary conditions for the pH changing reactions were defined by the Butler-Volmer equation

$$i = -i_{o,c} e^{-\frac{nF}{RT}(E-E_{o,c})} + i_{o,a} e^{\frac{nF}{RT}(E-E_{o,a})}$$

(8)

where the exchange currents for cathodic and anodic reactions ($i_{o,c}$ and $i_{o,a}$) and the formal potentials ($E_{o,c}$ and $E_{o,a}$) were fit to experimental data for platinum in water (Fig.2.1A). With this information for the electrochemical current, the potential applied to the terminal electrodes or present along the surface potential gradient would dictate the local rate of electrochemical reaction. Both channels assumed potential values of -1.5 V at $x = 0$ and +1.5 V at $x = 1000$ µm for comparison. For the sample possessing a surface potential gradient, a linear potential profile is applied to the lower boundary between these two limits. The
remaining boundaries are treated as insulating. Finite element analysis was used to simulate the proton concentration within the channels for the two configurations. Results for the proton concentration for each of the two configurations are plotted in Figure 2.7 in terms of the change in pH ($\Delta pH$). Figure 2.7A shows the time evolution at $t = 0.145, 1.45$ and $14.5$ seconds for a surface potential gradient. After only a short time, the pH has started to change within the channel having a surface potential gradient. At $\sim 1.5$ sec, the pH at the left side of the channel has dropped by almost one-half a pH unit. At $\sim 15$ sec, the pH has changed by nearly a full pH unit on each side of the channel. Although this change is not as large as was seen experimentally, the trend is similar. Experimentally, after $15$ sec., there was a pH gradient formed that ranged from pH of 3 to pH of 9. Theoretically, after $15$ sec, the pH gradient was calculated.
to range from a change of -0.5 pH units to 0.2 pH units (or from pH 6.5 to pH 7.2). This is due to only estimating the change in pH from the change in proton concentration at the surface and the assumption that the initial pH was near neutral. The pH gradient is experimentally formed from both the generation of protons at one end of the gradient and the generation of hydroxide ions at the opposite end of the gradient and diffusion of these ions through solution. For theoretical comparison with the natural gradient, Fig. 2.7B shows that the evolution of pH in the two-terminal configuration is much slower than the surface generated pH gradient. At ~ 1.5 sec, the pH has changed only slightly at the edges of the channel. Further changes in the pH have occurred by ~ 15 sec, but not near the magnitude of that seen in the gradient system. In order to achieve a pH change of similar magnitude to that seen for the potential gradient at 15 sec, the two-terminal system requires 290 sec or ~ 5 min. This difference in time-scale is a factor of almost twenty.

The substantially decreased time-scale required to develop a pH gradient using an electrode with a surface potential as compared to the two-terminal system can be rationalized by considering the role of diffusion. In the two-terminal system, a fully established pH profile requires that protons or hydroxyls diffuse across the channel width. In contrast, the potential gradient involves a much smaller diffusion path. Since the reaction is occurring along the surface of the channel, we can assume that protons and hydroxyls are produced instantaneously at the channel floor and then need only to diffuse the height of the channel. Since the time required for diffusion is proportional to the square of the distance involved, diffusion across the 1000 µm channel width takes 25 times longer than diffusion up the 200 µm channel height. This difference is nearly identical to the experimentally observed and theoretically predicted variation between the two systems.
2.4 CONCLUSIONS

This report describes a method for the rapid and reversible generation of a microscale pH gradient using a spatially varied, surface electric field. Benefits of using this method to produce a pH gradient include the ability to readily control both the position and magnitude of the pH gradient. In addition, this method is scalable allowing the formation of gradients ranging from centimeters in size down to micrometers, depending upon the length over which the electric field is applied. The time-response of this method when working in a thin channel or microscale platform is considerably improved over competing technologies. Indeed, the ability to modulate the pH within a micro-scale channel within mere seconds is a substantial advance for chip-scale separation devices. It is anticipated that this work will impact on a variety of chip-scale analytical devices, protein separation techniques, and combinatorial pH studies. The ability to create a variable pH profile might have further application in the study of, corrosion processes, metal deposition, enzyme reactions, metabolic processes, or any other chemical system involving pH as a variable.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the National Science Foundation (CTS 9875496) and Iowa State University for partial support of this work.

2.5 REFERENCES


CHAPTER 3: MASKLESS ELECTRODEPOSITION OF POLYMER FILMS USING SPATIALLY CONTROLLABLE ELECTRIC FIELD GRADIENTS

Adapted from a manuscript submitted to *Langmuir* 2007.

Erin L. Ratcliff and Andrew C. Hillier

ABSTRACT

We report a method for the maskless electrodeposition of polymer films in various patterns using spatially controllable electric field gradients. One and two-dimensional surface electric field gradients were produced by applying different potential values at spatially distinct locations on an electrode surface. Variations in the resulting local electrochemical potentials were used to spatially manipulate the rate of electrodeposition of several polymers. By controlling the electric field gradient in the presence of sequentially varying deposition solutions, complex polymer patterns could be produced. One-dimensional structures consisting of alternating bands of poly(aniline) and either phenol or aminophenol were produced, as well as more complex two-dimensional structures. Film characterization was achieved through optical imaging, UV-VIS spectroscopy and ellipsometry. Results indicate that this maskless patterning technique is a simple strategy to create complex, millimeter-sized surface patterns of electrodeposited materials.

3.1 INTRODUCTION

Maskless patterning strategies have become increasingly popular as a means of producing complex surface structures. Maskless patterning can eliminate some of the difficulty and
expense of typical photoresist processing [1] as well as provide potential improvements over conventional methods [2]. Examples of maskless patterning have been described for the fabrication of polymer light-emitting devices [3], semiconductor materials [1,2], metals [4], and lab-on-a-chip devices [3,5,6].

Some of the more common maskless patterning methods use lasers [2,7-9], electron beams [10] or ion beams [11,12] to locally control the rates of deposition or dissolution of a material on a surface. Material is either deposited or etched from a surface in the path of the laser or ion beam [2]. The main advantages of these techniques include the intrinsic spatial resolution and design flexibility [2,10-12]. However, they are limited to low throughput applications due to their serial nature.

Maskless fabrication has also been demonstrated using electrostatic fields to create patterns of colloidal particles [1,13]. In this technique, a surface is modified with a pattern of electric charges derived from voltage pulses applied by the conductive tip of an atomic force microscope (AFM). Charged nanoparticles of opposite polarity are then deposited onto these modified locations. This technique has been employed to deposit both SiO$_2$ [13] and Au particles [1]. The major advantage of this method is the high resolution and spatial control, allowing adsorption of patterned nanoparticles (~20 nm dia) on a surface. However, this technique is limited by the range of materials that can be employed [1].

Recently, a technique for maskless patterning has been demonstrated using surface electric fields to spatially control electrochemical reactions and locally control rates of deposition or dissolution [14-16]. This technique permits the fabrication of substrates with spatially controllable components varying compositions and thicknesses. Examples include
self-assembled monolayer gradients [15,17-19], electrodeposited copper gradients [20], patterned peptide monolayers [21], combinatorial catalyst libraries [22], and spatially controllable pH gradients [23].

In this work, we demonstrate the use of surface electric fields to generate spatially patterned films of electrodeposited polymers. A non-uniform electric field is applied to a resistive electrode surface in order to locally vary the deposition rate of either a conducting or insulating polymer film derived from aniline, phenol or aminophenol monomers. At locations where the electrode potential is less than the deposition potential, no polymer is deposited, while at potentials exceeding the deposition potential, a thin polymer film grows on the surface. By varying the magnitude of the applied potential values through a sequence of monomer-containing solutions, a variety of one and two-dimensional film patterns were created. A combination of optical and electrochemical measurements was used to characterize the polymer structures. In particular, scanning UV-Vis spectroscopy was used to determine the location of particular polymers with respect to distance along the surface. Null ellipsometry was also performed to monitor the change in thickness along the different polymer regions. This maskless deposition strategy produces structures of alternating conducting and insulating polymers that are spatially controllable in thickness, location and shape.

3.2 EXPERIMENTAL SECTION

Materials and Reagents. Polymer electrodeposition was performed in solutions containing either 0.5 M sulfuric acid (Fisher Scientific, Fair Lawn, NJ) and 0.1 M aniline (Aldrich, Milwaukee, WI) or 0.1 M monobasic sodium phosphate (Fisher) and 10 mM
phenol (Aldrich) or aminophenol (Aldrich), with pH adjusted to ~ 7.0 with 1 M NaOH (Fisher). All experiments were performed in deionized water (NANOpure, Barnstead, Dubuque, IA).

**Substrate Fabrication.** Slides of indium tin oxide (ITO) coated float glass (Delta Technologies, Inc Stillwater, MN) with a surface resistance of $R_s \sim 100 \ \Omega \ \text{square}^{-1}$ were cut to size (10 mm x 25 mm or 25 mm x 25 mm), rinsed in DI water, sonicated in a 50:50 solution of DI water and ethanol, sonicated in pure DI water, and dried under nitrogen. Electrical contacts to the ITO electrode were made by attaching copper wires to the ITO with silver epoxy (H2OE parts A and B, Epoxy Technologies, Billerica, MA) and then coating the connections with an insulating epoxy (QuickSet Epox Gel, Hentel Consumer Adhesives, Inc., Avon, OH).

**Electrochemistry.** Electrodeposition was achieved in a cell consisting of the ITO as working electrode, a Hg/HgSO$_4$ reference electrode, and a Pt-Ir on Ti mesh counter electrode. For one-dimensional patterns, the electrode potentials were controlled with a bi-potentiostat (AFRDE5 Bi-potentiostat, Pine Instrument Co., Grove City, PA), with the two working electrodes ($E_1$ and $E_2$) connected to opposite ends of the substrate electrode. Polymer bands were formed by applying different potential values to the edges of the ITO to create a potential gradient along the surface. Two-dimensional patterns were created by controlling the potential at four different locations on the ITO substrate using a multi-electrode potentiostat (CH1030, CH Instruments, Austin, TX). Four electrode potentials ($E_1$, $E_2$, $E_3$, and $E_4$) were applied at the corners of a 25 mm x 25 mm square of the ITO substrate.

**Imaging.** Images of the various samples were acquired with a high resolution CCD
camera (Model VCC 3972, Sanyo) equipped with a variable zoom lens (Zoom 7000, Navitar). The camera was interfaced to a computer by a frame grabber card (Pinnacle Systems, Inc., Mountain View, CA) and images were captured using commercially available software (Studio 8, Pinnacle Systems). Image analysis was performed with Image J (National Institutes of Health).

**Optical Spectroscopy.** A fiber optic spectrometer with reflectance probe (S2000 Minature Fiber Optic Spectrometer, Ocean Optics, Inc., Dunedin, FL) and deuterium tungsten halogen light source (DT-MINI, Ocean Optics) was used to measure the absorbance at 750 nm, with a wavelength resolution of ~0.4 nm. The reflectance probe sampled a spot size of ~1 mm diameter on the sample. Measurements were enhanced by placing the sample on a first surface mirror and using a large integration time (2500 msec). The probe was held in place by a fitted holder while a computer controlled positioning motor (T-LS, Zaber Technologies Inc., Richmond, BC) was used to move the cell to the desired position beneath the optical fiber probe with a resolution of approximately 0.1 µm. Both the positioning motor and the data collection were controlled via a homemade LabView program (National Instruments Corp., Austin, TX).

**Ellipsometry.** Null-ellipsometry measurements were performed using an automated, multi-functional optical system (Multiskop, Optrel GbR, Berlin, Germany) with spatial mapping capabilities. Ellipsometric data was obtained at a single-wavelength (632.8 nm beam with ~0.6 mm diameter) in the PCSA configuration at 70º angle of incidence. Film calculations were performed using a commercial software package (Elli, Optrel GbR, Berlin, Germany). The refractive index, n, and absorption coefficient, k, of the substrate (ITO: n =
1.7, k = 0.0; float glass: n = 1.5, k = 0.153) were determined using a 3-phase model (air/ITO/float glass). Ellipsometric angles $\Delta$ and $\Psi$ were recorded with respect to position by translating the sample using an integrated stepper motor. The thickness of the polymer films with respect to position were calculated using a 4-phase model (air/polymer/ITO/float glass) using an estimate for the optical constants of the polymers (n = 1.5, k = 0).

3.3 RESULTS AND DISCUSSION

In this work, we have exploited the spatial control provided by surface electric field gradients to perform mask-free surface patterning with electrodeposited polymers. Patterns were constructed with a combination of the conducting polymer polyaniline (PANI) and insulating polymers poly(phenylene oxide) (PPO) and poly(aminophenylene oxide) (PAPO). The electrodeposition and growth behavior of these polymers is fairly well understood [24-27]. PANI films are frequently grown by potential cycling or constant potential methods in acidic solutions [24-28]. The resulting films form a dense, fibrous network with potential application in sensing and controlled delivery [29-31], corrosion prevention [32-34], and electrochromic displays [24,35]. Figure 3.1A shows a typical cyclic voltammogram for PANI during a growth cycle on an ITO electrode from a solution containing 0.5 M H$_2$SO$_4$ and 0.1 M aniline. Film growth occurs while cycling the potential between -0.6 and 0.6 V vs Hg/HgSO$_4$ at 5 mV/s. The large anodic peak at ~0.6 V corresponds to aniline monomer oxidation, while the pair of peaks at +/- 0.1 V reflects polymer oxidation/reduction and the transition between the yellow, fully reduced leucoemeraldine state to the green, half-oxidized emeraldine state. Growth of the polymer is indicated by the increasing current with each potential cycle. The thickness of the PANI film has been shown to increase in relation to the
total charge passed during cycling [27,28,36].

While oxidation of aniline monomer forms conductive PANI films, oxidation of phenol [37-40] and aminophenol [41] at an electrode surface produces insulating films of poly(phenylene oxide) (PPO) and poly(aminophenylene oxide) (PAPO), respectively. An example of the electrodeposition of a film of PPO on ITO in 0.1 M phosphate buffer (pH 7) containing 10 mM phenol is shown in Figure 3.1B. During the first anodic scan, a large peak appears at ~0.5 V, corresponding to the oxidation of phenol monomer. Subsequent cycles show significantly reduced currents. This behavior is consistent with the formation of a thin, compact and insulating film of PPO on the electrode surface.[40] The self-limiting growth of these films has prompted their use as thin insulators for the fabrication of microelectrodes.
and organic devices [37,39,41,42].

Poly(aminophenylene oxide) (PAPO) growth follows a similar mechanism to PPO, although it has been suggested that both the hydroxyl and amino groups participate in the electropolymerization [41]. The electrodeposition of PAPO on ITO in 0.1 M phosphate buffer (pH 7) containing 10 mM aminophenol is shown in Figure 3.1C. An oxidation peak is observed at 0.3 V during the first anodic cycle, with subsequent cycles showing a decrease in current. This behavior is also consistent with the formation of a compact, insulating film.

The electrochemical behavior depicted in Figure 3.1 for these three polymer systems illustrates the fact that film formation proceeds at a potential where monomer oxidation occurs. Therefore, in addition to potential cycling [38,40,41], films may be formed by constant potential deposition. For aniline, monomer oxidation occurs at ~0.6 V, while for phenol and aminophenol, oxidation occurs at 0.5 and 0.3 V, respectively. At potentials significantly below these values, monomer oxidation does not occur, while at and above these potentials, monomer oxidation results in polymer growth. Thus, each monomer exhibits a potential where the onset of polymerization occurs.

One can exploit this behavior to spatially localize deposition and pattern surfaces using a surface electric field. A simple example of polymer patterning is shown if Figure 3.2, where two distinct regions of PANI and PPO have been electropolymerized onto ITO. A 25 mm long strip of ITO was placed in a solution of phenol and a potential gradient was applied between the two edges. $E_1$ at the left of the sample was held at a potential of -0.1 V, while $E_2$ at the right edge of the sample was held at 0.6 V, which created a linear potential drop across the electrode (Figure 3.2A, curve i). This potential profile was held for a period of 10 min
and a PPO film grew on the right half of the electrode where the surface potential exceeded the monomer oxidation potential. Subsequently, the substrate was placed in an aniline solution and the entire substrate was held at 0.7 V for 2 min (Figure 3.2A, curve ii). This resulted in a PANI film being deposited in regions free of PPO, which served as a barrier to deposition. In the absence of the PPO film, PANI deposition would have been uniform over the surface of the ITO. This procedure resulted in a surface with an alternating region of PANI on the left and PPO on the right.

The presence and location of PANI and PPO films were verified using scanning UV-VIS spectroscopy. A reflectance probe was scanned across the surface using a micro-positioning...
system and absorbance data was collected every 1 mm at a wavelength of 750 nm. The 750 nm band corresponds to absorbance from the conducting emeraldine state of PANI [43-45]. Absorbance with respect to position is plotted in Figure 3.2B for the PANI-PPO sample and for bare ITO. For the bare ITO curve, the surface is featureless due to the transparency of the ITO sample in this wavelength region. In the presence of the polymer film there is a strong absorbance on the left side of the sample, corresponding to the PANI film, and a weak absorbance on the right where the PPO is located. At ~10 mm, there is a sharp decrease in absorbance, consistent with the sharp boundary between PANI and PPO films. A schematic for the proposed surface containing the PANI and PPO regions is depicted in Figure 3.2C.

Scanning null ellipsometry was used to further quantify the nature of the PANI and PPO films. Figures 3.3A and B depict values of Δ (Δ) and Ψ (Ψ) acquired while scanning along bare ITO and the PANI-PPO coated sample in Figure 3.2. For the bare sample, Δ and Ψ maintain constant values consistent with a thin film of ITO on glass in air. On the PANI-PPO sample, the values of Δ and Ψ vary as the thickness and optical properties of the polymer film varies. At the far left, Δ is constant with a value near 16 deg, which then decreases as the sample is transversed from left to right. Near the center of the sample at ~ 10 mm, Δ plateaus at a near constant value of 4 deg (Figure 3.3A). Conversely, Ψ is low and constant at the left of the sample then increases from the left to the right side (Figure 3.3B). For both Δ and Ψ, a distinct transition appears near the middle of the sample at ~10 mm, corresponding to the boundary between PANI and PPO regions. Estimates of the film thickness and refractive index (n) are provided in Figures 3.3C and D. These numbers were determined using a four layer model of the interface (air/polymer/ITO/float glass). The calculated thickness (Figure 3.3C) varies from a maximum near 180 nm for the PANI film to
a minimum of 120 nm for the thinnest region of the PPO film. Simultaneously, the refractive index (n) varies between 1.7 and 1.5 for the PANI film, while maintaining a constant value of 1.5 for PPO (Figure 3.3D).

Film thicknesses were estimated using a four-layer interface model, with the thickness and refractive index of the PANI and PPO films used as the fitting parameters and the extinction coefficient was fixed at zero. Notably, previous ellipsometry studies of PANI films have shown that both the refractive index and extinction coefficient vary with film thickness and polymer oxidation state [25-27]. As noted in Figure 3.3C, PANI film thickness was found to vary from ~180 nm on the far left of the sample down to ~140 nm near the center. The thickest region of the PANI film had an estimated refractive index of 1.68 and a decreasing refractive index as the center of the sample was approached, corresponding to a parallel decrease in film thickness; such a correlation between PANI film thickness and refractive index has been noted in the

---

**Figure 3.3** Null-ellipsometry mapping of PANI-PPO two band sample on ITO. Raw null-ellipsometry results: (A) Delta (Δ) and (B) Psi (Ψ) for both bare ITO and PANI-PPO film. Modeled null-ellipsometry results: (C) thickness (t) and (D) refractive index (n) for PANI-PPO film.
Although the PANI film appeared to decrease in thickness across the sample, the PPO film maintained a consistent thickness near ~120 nm. This PPO film was found to be somewhat thicker than previous literature values of 10-100 nm [29,41]. The authors suspect that the difference in film thickness from that reported in previous studies is related to the film growth technique. In this study, the PPO film was grown at a constant potential as opposed to cycling, which is the method typically used for growth. A constant potential deposition might lend itself to a thicker film growth due to lower efficiency in filling of the pin holes in the film.

The ability to manipulate surface electric fields to localize polymer growth can readily be extended to more complex patterns. Figure 3.4 depicts the results of a three-step deposition process to create a sample with three different polymer regions. This sample consists of a central band of PANI surrounded by two neighboring bands of PAPO. The potential profile used for this deposition is shown in Figure 4A. Initially, a band of PAPO was deposited on the left side of the sample by holding \( E_1 \) at 0.4 V and \( E_2 \) at -0.2 V in a solution containing 10 mM aminophenol (curve i in Figure 3.4A). A second PAPO band was then formed on the right side of the sample by holding \( E_1 \) at -0.6 V and \( E_2 \) at 0.4 V (curve ii in Figure 3.4A). The sample was subsequently placed in an aniline solution and both \( E_1 \) and \( E_2 \) were held at 0.7 V to promote PANI deposition at uncoated sample regions (curve iii in Figure 3.4A). This procedure resulted in PAPO deposition at the right and left sides of the sample, with PANI deposition in the center. Scanning absorbance spectroscopy results in Figure 3.4B illustrates the PANI and PAPO coverage with respect to position. The results show a small absorbance
for PAPO over the ITO substrate on the right and left sides of the sample, while PANI appears as a strong absorbance covering the center region of the sample. A schematic of this sample is provided in Figure 3.4C. The slightly wider PAPO region on the left part of the sample compared to that at the right was formed by design as a result of the different potential profiles applied as shown in Figure 3.4A profiles (i) and (ii), which deposit a wider band PAPO on the left side of the sample.

Scanning null-ellipsometry was performed to determine the film thickness and refractive index along this three-band sample surface. The measured Delta and Psi with respect to position are given in figures 3.5A and 3.5B, respectively. The data shows the PANI region in the center having a higher

---

**Figure 3.4.** Three band PAPO-PANI-PAPO sample on ITO. (A) Potential profiles used to electrodeposit polymer bands. (i) $E_1 = 0.4$ V, $E_2 = -0.2$ V in aminophenol solution. (ii) $E_1 = -0.6$ V, $E_2 = 0.4$ V in aminophenol solution. (iii) $E_1 = E_2 = 0.7$ V in aniline solution. (B) Absorbance profile at 750 nm with respect to position of along sample showing bare ITO and PAPO-PANI-PAPO film. (C) Schematic of ITO substrate with polymer films.
Delta value and a lower Psi value than PAPO on the edges. Thickness was then determined with respect to position (Figure 3.5C) using the same four layer model as described previously. The results indicate a nearly constant thickness of 110 nm for the PAPO region at the left between 0 to 7 mm. At positions beyond approximately 7 mm, there is a steady increase in thickness due to the PANI film, which reaches a maximum thickness of 170 nm at about 15 mm. The film height then decreases and levels off at 110 nm for second PAPO band. A variation in refractive index between PAPO and PANI regions is also observed (Figure 3.5D), which is consistent with the two-band result.

The ability to spatially control polymer deposition with well-defined electric fields can be further extended to create more complex patterns. Figure 3.6 depicts a series of samples in

**Figure 3.5.** Null-ellipsometry mapping of three-band sample on ITO. Raw null-ellipsometry results: (A) Delta (Δ) and (B) Psi (Ψ) for bare ITO and PAPO-PANI-PAPO film. Modeled null-ellipsometry results: (C) thickness (t) and (D) refractive index (n).
which an increasing number of polymer bands are created by sequential deposition of PANI and PPO or PAPO layers. Figure 3.6A depicts a two band sample, with PPO on the left and PANI on the right. PPO was first deposited by holding \( E_1 = 0.6 \) V and \( E_2 = -0.1 \) V in a phenol containing solution. The entire substrate was then held at 0.7 V in aniline containing solution to deposit PANI, which formed on the PPO-free regions. The optical image (Figure 3.6A) depicts a clear PPO film on the left and a sharp transition to a dark PANI film on the right. This sample is a mirror image of that described in Figure 3.2. Figure 3.6B is a three band sample with alternating regions PANI-PAPO-PANI. In order to create this surface, a PANI band was first formed on the left edge of the sample by holding \( E_1 = 0.7 \) V and \( E_2 = -0.2 \) V in an aniline containing solution. A PAPO film was then deposited over the PANI film and over the center portion of the substrate by holding \( E_1 = 0.3 \) and \( E_2 = -0.2 \) V in an aminophenol-containing solution. PANI was then deposited on the remaining exposed

**Figure 3.6.** Optical images of four different polymer band constructions possessing alternating regions of insulating (PPO, PAPO) and conducting (PANI) polymer films. (A) Two band: PPO-PANI, (B) three band: PANI-PAPO-PANI, (C) four band: PANI-PAPO-PANI-PAPO and (D) five band: PANI-PPO-PANI-PPO-PANI. Each image is 0.5 cm x 2.5 cm.
substrate by applying a uniform potential of 0.7 V over the entire surface. The sample image shows a dark region on the left and right sides of the sample corresponding to PANI and a light region in the center corresponding to PAPO. Figure 3.6C is a four band sample consisting of PANI-PAPO-PANI-PAPO regions deposited via the following sequence: (i) $E_1 = 0.7$ V, $E_2 = -0.3$ V in aniline; (ii) $E_1 = 0.3$ V, $E_2 = -0.2$ V in aminophenol; (iii) $E_1 = -0.4$ V, $E_2 = 0.3$ V in aminophenol; and (iv) $E_1 = E_2 = 0.7$ V in aniline. This results in PANI on the far left, a region of PAPO, PANI at the center-right, and then PAPO again at the far right. Figure 3.6D is a five band sample of PANI-PPO-PANI-PPO-PANI deposited by: (i) $E_1 = 0.7$ V, $E_2 = -0.3$ V in aniline solution; (ii) $E_1 = 0.6$ V, $E_2 = -0.1$ V in phenol; (iii) $E_1 = -0.1$ V, $E_2 = 0.7$ V in aniline; (iv) $E_1 = -0.2$ V, $E_2 = 0.6$ V in phenol; and (v) $E_1 = E_2 = 0.7$ V in aniline. Along a one-dimensional sample, this operation could be performed an increasing number of times to add additional bands of polymer and create a highly complex structure.

The ability to control deposition via surface electric field gradients can be further extended to two-dimensions to create more complex patterns. Examples of various two-dimensional polymer patterns are shown in Figures 3.7, 3.8 and 3.9. In this system, four working electrodes are independently controlled to produce a variety of two-dimensional patterns. Figure 3.7 depicts two-dimensional potential profiles and an optical image of a simple pattern created with this four electrode system. A PANI film was electrodeposited at the top right and bottom left corners by holding $E_1$ and $E_3$ at -0.2 V and $E_2$ and $E_4$ at 0.7 V for 30 seconds in an aniline containing solution. Figure 3.7A is a contour plot of the calculated electric field on the two dimensional surface. Figure 3.7B depicts the sample following deposition, with dark regions in the upper right and lower left, corresponding to regions of PANI deposition. There is good agreement between the modeled potential profile and the
sample structure, with PANI thickest in areas with applied potentials exceeding the value required for monomer oxidation (~0.6 V for aniline) and a decrease in thickness as the applied surface potential drops below that value. The film extends only to the region of surface potential values near 0.4 V, which corresponds to the onset of oxidation as seen in Figure 3.1A.

![Figure 3.7. Construction of two-dimensional PANI surface pattern. (A) Contour plot of computed surface electric field generated by holding E₁ and E₃ at -0.2 V and E₂ and E₄ at 0.7 V. (B) Sample Image with PANI film formed using potential profile described in (A), with deposition in top right and bottom left corners of sample.](image)

More complex surface patterns can also be created. Figure 3.8 is an example of a three-step pattern resulting in five different polymer regions, with PPO deposited in the four corners and PANI deposited in the center. To create this surface, PPO is first deposited at the top left and bottom right corner by holding E₁ and E₃ at 0.6 V and E₂ and E₄ at 0.25 V for 10 minutes in a solution containing phenol. Figures 3.8A is a surface plot of the applied electric field. The PPO film only forms on regions of the surface with an applied potential greater
than 0.4 V, corresponding to the upper left and lower right sample regions. The deposition of PPO in these two corners is followed by deposition of PPO in the upper right and lower left corners by holding $E_1$ and $E_3$ at -0.25 V and $E_2$ and $E_4$ at 0.6 V for 10 minutes in phenol containing solution. Figure 3.8B is a contour plot of the associated electric field on the surface. The films formed in the first step, on the top left ($E_1$) and bottom right corners ($E_3$), are insulating. Thus, the potential variation in the second step is confined to

**Figure 3.8.** Construction of two-dimensional surface pattern of PPO and PANI films. (A) Contour plot of electric field used to deposit PPO at top left and bottom right corners. (B) Contour plot of electric field used to deposit PPO at top right and bottom left corners. (C) Contour plot of electric field used to deposit PANI in center of sample. (D) Optical image of sample containing PPO in four corners and PANI in the center.
the diagonal between upper right and lower left regions of the film. As with the first step, the PPO film only forms at regions of applied potential greater than 0.4 V, which occur at the upper right and lower left regions of the sample. The final deposition involves creating a PANI film in the center of the substrate. This is achieved by holding all four corners at 0.7 V in the presence of aniline. The surface electric field under these conditions is illustrated as a contour plot in Figure 3.8C. The PPO films deposited in the first and second steps are insulating and prevent PANI deposition at the corners of the sample. The PANI film only deposits on the exposed ITO surface in the center of the substrate. Figure 3.8D is an optical image of the resulting polymer surface. The dark regions near the center of the sample correspond to PANI, while the light regions at the sample edges are covered with PPO film.

A variety of other two-dimensional surface patterns can be created by changing the potential profile along the surface and the sequence of deposition steps. Figure 3.9 is a compilation of patterns produced with this four electrode system. The simplest pattern is shown in Figure 3.9A, which depicts a PANI film deposited at $E_2$ and $E_4$ following the procedure outlined for Figure 3.7. Figure 3.9B is continuation of Figure 3.9A, with all four corners having PANI deposits. In this case, PANI was deposited at $E_2$ and $E_4$ by the same technique as in Figure 3.9A. Then, the electric field was reversed, such that $E_1$ and $E_3$ were held at 0.7 V and $E_2$ and $E_4$ were held at -0.2 V. Figure 3.9C demonstrates a more complex, two-dimensional pattern. In this sample, PANI was initially coated at the upper left and lower right corners by holding $E_1$ and $E_3$ at 0.7 with $E_2$ and $E_4$ at -0.25 V in an aniline containing solution. An insulating layer of PPO was then formed over this PANI deposit and extending towards the sample center by holding $E_1$ and $E_3$ at 0.6 V and $E_2$ and $E_4$ at -0.3 V. The process was repeated for the remaining two corners by holding $E_2$ and $E_4$ at 0.7 and $E_1$
and \( E_3 \) at -0.25 V in the presence of aniline and then \( E_2 \) and \( E_4 \) at 0.6 V and \( E_1 \) and \( E_3 \) at -0.3 V in a phenol solution. This produced a sample with PANI deposited at the four corners and a layer of PPO the extended in a ring away from the corners towards the center of the sample. In the last step, the entire sample was held at 0.7 V, resulting in PANI deposition over the remaining bare surface at the sample center. The result of this deposition procedure is a complex, two-dimensional polymer pattern containing both PANI and PPO films. A variety of additional patterns with increasing complexity can be readily envisioned.

### 3.4 CONCLUSIONS

This paper describes a method for the maskless patterning of electrode surfaces using surface electric fields to localize deposition at desired sample locations. The technique requires no prior surface treatments and is an inexpensive technique; there is no requisite clean room or high cost instrumentation involved. Furthermore, the technique has potential for parallel processing and high -
throughput fabrication since it is not limited to serial processing and time constraints associated with previously described maskless patterning techniques. Surfaces with lateral permutations in polymer coverage are applicable to a variety of studies of both single and co-polymer characteristics, including wettibility, conductivity, thickness, optical properties, and use as permeselective membranes. Applications include but are not limited to polymer light-emitting devices, semiconductor, metal patterning and polymer and protein chip devices.

3.5. REFERENCES


CHAPTER 4. THE SPATIAL CONTROL OF METAL AND METAL OXIDES
USING SURFACE ELECTRIC FIELDS.

ABSTRACT

The formation of in-plane electrodeposited copper gradients on indium tin oxide (ITO) in both one and two dimensions is presented. Copper was selectively deposited onto the surface by applying surface potential gradients that span the reduction potential of \( \text{Cu}^{2+}/\text{Cu}^0 \). Areas of the electrode for which the applied potential is less than the oxidation potential have copper deposits while areas of applied potential greater than the oxidation potential have no copper. Cyclic voltammetry, optical imaging and transmission spectroscopy are used to demonstrate spatial control of copper electrodeposition. The spatial control of platinum oxide films formed by in-plane potential gradients is also discussed. Ellipsometry and electrochemistry is employed to verify the position and potential dependence of platinum oxide film growth. Results indicate that this is a simple technique to create one and two dimensional patterns of metal and metal oxide systems in a high-throughput manner.

4.1 INTRODUCTION

Metal/metal oxide systems are an important area of focus in surface chemistry. Metal oxides are known to have different properties from their bulk metal counterparts including passivating characteristics for corrosion protection (i.e. \( \text{Al}_2\text{O}_3 \) protective layer on pop cans), color (i.e. the rusting of iron), loss of malleability and reactivity (i.e. formation of bases in water).
There have been a variety of techniques employed in order to create patterned deposits of metal surfaces such as evaporation, sputtering, chemical vapor deposition (CVD) electrodeposition. Electrodeposition has seen an increased interest because of use in the fabrication of integrated circuits, deposition of magnetic recording devices, and the deposition of multilayered structures. In particular, electrodeposition methods represent an attractive alternative to conventional fabrication methods such as sputter coating and chemical vapor deposition; electrodeposition is able to deposit material in places not accessible to sputter coating and vapor deposition, such as interconnects for electronics.

The electrodeposition of metals is a common industrial process. In the food and beverage industry, steel cans may be electrochemically coated in a thin coat of tin, in order to provide protection of the iron from rusting. Galvanized iron is formed by electrochemically depositing a layer of zinc on iron. The automotive industry uses a chrome plating to enhance the corrosion protection. There are various aspects of the electronics industry which employ electrochemical methods of metal deposition for such applications in macro and micro electronics, optics, and sensors. In particular, the electrodeposition of copper has generated a strong interest since its integration into computer chips, when it was first used for electrical contact by IBM in the 1990’s [1] and has since become one of the most important processes for the fabrication of on-chip interconnects [2,3].

The implementation of a gradient to study metal systems has become increasingly popular. Gradients permit exploration of all thickness values from starting to final in a continuous manner, permitting comparison under a single basis of conditions. There are numerous examples of metal gradients prepared using various techniques. Recently, binary (Pt-Ru) [4,5] and tertiary (Pt-Ru-Rh, Pt-Ru-Mo) [4,6] component gradients have been formed
using the diffusion of metal salts through a gel followed by electrochemical reduction of the
metals. These gradients have been useful in the study of ideal fuel cell catalysts. However,
diffusion limits spatial control of a gradient because it relies solely on the diffusion between
a sink and a source separated by a pre-determined distance and not on any external control.

Other methods have been employed to create metal gradients. Palladium metal
gradients have been produced on cellulose substrates by heating a palladium wire as a source,
creating a gradient with respect to distance [7]. Still other gradient formation techniques rely
on sputtering of materials such as nickel [8] or aluminum [9] as well as tertiary components
[10]. Again, these gradients are difficult to control spatially.

It has previously been shown that copper will electrodeposit on a gold substrate in the
presence of a surface potential gradient and was verified using XPS [11,12]. This work will
focus on expanding the concept of gradients of electrodeposited metals to high-throughput
applications, using copper deposition as an example. This work will demonstrate that copper
gradients can be generated on transparent indium tin oxide (ITO) substrates. Indium tin
oxide was chosen as a substrate because of its transparent nature. Copper deposits could be
readily visualized and analysis can be performed quickly, applicable to high-throughput
processing. All previous work has focused only on the electrodeposition of copper in one
dimension; this work expands copper deposition into two dimensions. This study also
extends the application of surface electric fields to metal oxide systems. Platinum was
chosen as a substrate for its easily recognizable classic electrochemical behavior. The
formation of platinum oxide on platinum surfaces is well documented and characterized by
ellipsometry. Issues with corrosion of the platinum surface are avoided because once
deposited, platinum requires rather high potentials to strip it from the surface.
We report the use of potential gradients in order to spatially control the electrodeposition of copper in one and two dimensions on an indium tin oxide (ITO) substrate. By adjusting the magnitude of the potential gradient, we demonstrate the ability to control the width of the copper gradient as well as the degree of coverage. We also report the spatial control of a thin film of platinum oxide electrochemically grown on an electrodeposited platinum band. The results of both studies can be combined for the development of complex metal/metal oxide systems with multiple components.

4.2 EXPERIMENTAL METHODS

Materials and Reagents. All experiments were performed in 18 MΩ de-ionized water (E-Pure, Barnstead, Dubuque, IA). Electrochemical measurements were performed in solutions containing as-received 0.1 M sodium sulfate (Na₂SO₄) and 5 mM copper sulfate (CuSO₄, Aldrich, Milwaukee, WI). Deposits of Pt were obtained by electrodeposition (vide infra) from solutions containing 1-10mM H₂PtCl₆·6H₂O (Strem Chemicals, Newburyport, MA) in 0.1 M Na₂SO₄.

Electrochemistry. Experiments were performed in an open cell with a Ag/AgCl as a reference electrode and an Pt-Ir on Ti mesh counter electrode. Potential was controlled using a multi-potentiostat from CH Instruments (model CH1030, Austin, TX). Copper gradients were formed using two or four electrode configurations.

Substrate Fabrication. Glass slides coated with indium tin oxide (ITO) with a surface resistance of 100 Ω/in. (Delta Technologies, Stillwater, MN) were cut to 10 x 25 or 25 x 25 mm² and cleaned by sonication in successive 50:50 ethanol/DI water and DI water and dried in a stream of N₂. For platinum bands, ITO slides were patterned with photoresist
to form alternating bands of exposed and insulated ITO 2 mm wide and 25 mm across using a previously described procedure [13]. Briefly, a uniform layer of platinum was electrodeposited onto exposed indium tin oxide (ITO) using a square wave potential program with limits of 0 and -1.5 V (vs Hg/Hg$_2$SO$_4$) at a frequency of 100 Hz applied for 2 minutes. Contact pads to connect to the ends of the platinum-coated ITO regions were then fabricated by depositing gold through a mask that exposed only the terminal edges of the sample. Approximately 100 nm of gold was vapor-deposited (Denton Vacuum Turbo III, Morristown, NJ) onto the ends of the substrate at a pressure of ~7 x 10$^{-5}$ Torr under nitrogen atmosphere at a rate of 1-2 Å/s. Electrical contact was made with copper wires secured with silver epoxy (H20E parts A and B, Epoxy Technologies, Billerica, MA) followed by an insulating epoxy (QuickSet Epoxy Gel, Hentel Consumer Adhesives, Inc., Avon, OH). The gold was isolated from solution by Microstop stop-off lacquer (Pyramid Plastics Inc., Hope, AR). Copper was electrodeposited onto freshly cleaned ITO slides and electrical contact was made using copper wires adhered with silver epoxy followed by insulating epoxy. The applied potential gradient was held for 3-5 minutes, until there was visible copper coverage.

**Optical Images.** Images were collected using a high resolution CCD camera (Model VCC 3972, Sanyo) equipped with a variable zoom lens (Zoom 7000, Navitar), placed perpendicular to the substrate. Images were captured using commercially available software on a personal computer equipped with a frame grabber card (Pinnacle Systems, Inc., Mountain View, CA).

**Thickness Estimation: Copper Gradient.** Copper thickness measurements were made using a laser ($\lambda = 632.8$ nm) aligned to a photo detector. A positioning motor was used
to move the sample along the x axis, or along the axis of the potential gradient. Changes in light intensity can be correlated to film thickness (t) using Beer’s Law,

\[-\ln \left( \frac{I}{I_0} \right) = \frac{4\pi k}{\lambda} t\]

or

\[t = \lambda \frac{-\ln \left( \frac{I}{I_0} \right)}{4\pi k}\]  \hspace{1cm} (1)

where n and k are the ellipsometry constants for copper (n = 2.43, k = 3.46), \(\lambda\) is the wavelength of the laser light (632.8 nm), and I and I_0 are the spatially dependent values of the intensity of the laser light at the photo detector in the presence and absence of the copper gradient, respectively.

**Ellipsometry.** An in situ ellipsometry cell was fabricated from a piece of Delrin® and glass microscope slides. A 7.5 x 5.1 x 1 cm^3 piece of Delrin was machined along two parallel sides at 20°. Glass slides were glued (QuickTite Super Glue, Manco, Inc., Avon, OH) to the Delrin to provide optical access to the sample at a 70° angle of incidence. Two more glass slides were adhered to the remaining ends to create a closed cell. The cell wall joints were then covered with an inert organic lacquer (Microstop stop-off lacquer, Pyramid Plastics Inc., Hope, AR). For ellipsometry measurements, the substrate consisted of a layer of platinum electrodeposited deposited between gold contact pads on an ITO substrate. Ag/AgCl reference and Pt/Ir counter electrodes were suspended in the cell for potential control. Experiments were performed in a solution of 0.1 M Na_2SO_4 and potentials have been adjusted with respect to RHE.

Null-ellipsometry measurements were performed using an automated, multi-functional optical system (Multiskop, Optrel GbR, Berlin, Germany) with spatial mapping capabilities.
Ellipsometric data was acquired at a single-wavelength (632.8 nm) with a beam diameter of \(~0.6\) mm in the PCSA configuration at 70\(^\circ\) angle of incidence. Film calculations were performed using a commercial software package (Elli, Optrel GbR, Berlin, Germany). The refractive index, \(n\), and absorption coefficient, \(k\), of the substrate \((n = 2.062, k = -0.860)\) were determined using a 2-phase model (water/substrate) at a potential of 0.0 V (vs NHE). The absorption coefficient used here varies from that observed for bulk Pt electrodes \((k = -4.6)\) [14]. This difference is most likely due to the semi-transparent nature of our Pt-coated ITO film. The thickness of the platinum oxide film was then calculated as a function of applied potential using a 3-phase model (water/film/substrate) using estimated optical constants \((n = 2.8, k = -0.3)\). Ellipsometry mapping experiments were performed by translating the sample along the direction of the applied potential gradient using an integrated stepper motor and recording Delta and Psi with a uniform potential of 0 V and in the presence of an applied potential gradient. The change in Delta and Psi at each position was used to determine the oxide thickness.

\[\text{Figure 4.1. Cyclic voltammogram of ITO in (A) 0.1 M Na}_2\text{SO}_4 + 5 \text{ mM CuSO}_4 \text{ and (B) 0.1 M Na}_2\text{SO}_4 \text{ at 0.1 V/s.}\]
4.3 RESULTS AND DISCUSSION

Figure 4.1 shows a typical cyclic voltammogram of 5 mM CuSO$_4$ in 0.1 M Na$_2$SO$_4$ (Fig. 4.1A) on indium tin oxide (ITO) and the cyclic voltammogram of ITO in the base electrolyte (Figure 4.1B). There is a clear deposition peak at which at ~-0.3 V and a corresponding stripping peak at ~0.4 V. This is consistent with the literature; copper will electrodeposit at negative potentials and will be stripped from the surface at positive potentials [11, 12].

A gradient of copper on the surface of ITO is demonstrated in figure 5.2. An electric field was applied such that the left side of the ITO substrate was held at -0.6 V ($E_1$) and the right was held at 0.2 V ($E_2$). An optical image of the resulting copper gradient is given in Figure 4.2 A. The copper can be visualized on the left side of the sample, consistent with a negative applied potential while the absence of copper on the right side of the

**Figure 4.2.** Thickness determination for a spatial gradient of copper on ITO. (A) Image of substrate. (B) Thickness estimate (left axis) and potential gradient (right axis) (C) Schematic of copper gradient on ITO surface.
sample is consistent with positive local potential. Figure 4.2B is an estimation of copper thickness (left axis) and applied potential (right axis) with respect to position. Thickness was estimated using Beer’s law, which correlates changes in intensity of laser light of a known wavelength light to film thickness. Briefly, light from a laser ($\lambda = 632.8$ nm) was transmitted through bare ITO and the intensity was measured by a photo detector. Then the copper film was deposited and changes in light intensity were measured with respect to position. Measurements were taken every 1 mm, using a positioning motor to move the sample across the laser beam path. On the left side of the sample, there is a maximum thickness of ~17 nm, which steadily decreases as one moves from left to right or from negative to positive potentials across the substrate. At the middle of the sample (15 mm), the thickness of the copper levels off at zero, coinciding with potentials greater than 0 V. Figure 4.2 C is a schematic illustrating the copper gradient formed on the ITO surface. By controlling the applied potentials at $E_1$ and $E_2$, the width of the gradient along the surface can be manipulated.

Figure 4.3 illustrates further spatial control of copper on ITO through application of various potential gradients. Optical images of the copper coated surfaces are on the left and on the right are corresponding thickness (left axis) and potential (right axis) plots with respect to position on the surface. Figure 4.3 A is the result of gradient of $E_1 = -0.6$ V to $E_2 = 0.6$ V. There is copper only in regions corresponding to potentials lower than -0.2 V, from approximately 0 to 8 mm along the substrate. Figure 4.3 B and Figure 4.3C correspond to subsequently increasing width in copper gradients, corresponding to decreasing ranges in potential. Figure 4.3 D demonstrates that by reversing the direction of the electric field, the copper gradient is relocated to the other side of the substrate.
Copper gradients are not limited to one dimension, but can be expanded to two dimensions using a four-electrode configuration; one electrode at each corner of a square. Figure 4.4 illustrates copper gradients in two dimensions, using optical images of the substrates on the left and simulated plots of the applied electric field used to generate the samples. Figure 4.4A uses a configuration of the top left (E₁) and bottom right (E₃) held to -0.6 V while the top right (E₂) and bottom left (E₄) were held at 0.2 V. Copper is electrodeposited at the top right and the bottom left corners and no copper is found at the bottom left and top right corners. Figure 4.4B is the result of reversing the applied potentials such that the top left (E₁) and bottom right (E₂) have an applied potential of 0.2 V and the top right (E₂) and bottom left (E₄) have an applied potential of -0.6 V. Copper is etched from the
top left and bottom right corners and is deposited on the top right and bottom left corners. The result of this deposition procedure is a complex, two-dimensional metal pattern. A variety of additional patterns with increasing complexity can readily be envisioned. Further complexity can be achieved by expanding this technique to multi-component systems.

The electrodeposition of metals is not the only application for surface electric fields to metal systems. Surface electric fields may also be employed to spatially control the

**Figure 4.4.** Two dimensional spatial control of electrodeposition of copper. (A) $E_1 = E_3 = -0.6$, $E_2 = E_4 = +0.2$ V (B) $E_1 = E_3 = +0.2$ V, $E_2 = E_4 = -0.6$ V.
electrochemical response of metals once they are adsorbed onto a substrate. For example, by controlling the applied potential along a surface of platinum, one can spatially control the position of an oxide film grown on the platinum [17].

Cyclic voltammetry of an electrodeposited thin platinum film on an ITO electrode in a solution of 5 mM H₂SO₄ / 0.1 M Na₂SO₄ displays the features typical of platinum in an acidic solution (Figure 4.5). Hydrogen underpotential deposition (UPD) peaks are evident at potentials just positive of 0 V (vs NHE). Oxide formation is indicated by the broad oxidation at more positive electrode potentials and by the symmetric reduction peak in the reverse scan. Platinum oxides would be expected to appear as the potential approaches and exceeds ~0.6 V (vs NHE).

In-situ ellipsometry measurements were performed for thin platinum films on ITO. Figure 4.6 depicts null ellipsometry results for an electrodeposited platinum film on ITO while the entire film was cycled between 0 and 1.4 V (vs NHE) in a solution of 5 mM H₂SO₄ / 0.1 M Na₂SO₄. Figure 4.6A is a schematic of a platinum band on ITO, with gold electrode contacts for potential control on either side. Figure 4.6B shows the change in Delta as a function of applied potential while Figure 4.6C shows the change in Psi. During the forward potential scan, Delta decreases gradually between 0.0 and 0.8 V, and then decreases rapidly
with further increasing potential. Psi, in contrast, increases steadily over the same range in potential. The increase in Delta of approximately four degrees suggests the formation of an oxide film [15]. The changes appear at potentials consistent with the oxidation current observed in the cyclic voltammetry (Figure 4.5).

During the return sweep in potential from 1.4 V to 0 V, Delta increases while Psi decreases until they reach their original values at 0.0 V. In both, a rapid change is observed at a potential corresponding to the oxide reduction peak in Figure 4.5.

Previously, ellipsometric measurements on bulk platinum electrodes found that changes in Delta and Psi could be used to deduce the potential-dependent thickness of a growing oxide film [14, 16]. In order to convert the changes in Delta and Psi measured here to an estimate

**Figure 4.6.** (A) Schematic of platinum bands on ITO with gold contacts. Potential-dependent null-ellipsometry on platinum-coated ITO surface showing (B) Delta (□) and (C) Psi (○) versus applied potential. (D) Plot of oxide thickness versus potential (D) as determined by fitting potential-dependent ellipsometry results to three-layer model.
of the oxide thickness, a three layer optical model (water-oxide-substrate) was used. Optical constants for the platinum-coated ITO substrate were first determined at a potential of 0.0 V ($n = 2.062$ and $k = -0.860$). The changes in Delta and Psi were then fit to a three layer model using estimated optical constants for the oxide ($n = 2.8$, $k = -0.3$) to determine the thickness of the oxide film. Results of this fitting procedure (Figure 4.6D) indicate a slow film growth starting at ~0.6 V and then a rapid increase in thickness to a maximum of ~2.3 nm near 1.6 V. During the reverse scan, the oxide film is removed rapidly as the potential decreases below ~0.8 V. The potentials at which the oxide film forms and is removed are consistent with the cyclic voltammetry shown in Figure 4.5. Notably, the oxide thickness observed here is somewhat larger than that reported for short time-scale oxide growth on bulk Pt electrodes [14, 16]. This difference in measured oxide thickness could be influenced by the time scale of the experiments as well as the nature of the electrodes examined.

In order to quantify the nature of the oxide film formed in the presence of a surface potential gradient, null-ellipsometry mapping experiments were performed. A platinum-coated ITO electrode was prepared and in situ ellipsometry mapping was performed along the surface in the presence of a linear potential gradient. Since small variations in the quality of the substrate resulted in changes in the measured optical constants whose values exceeded those induced by an applied potential, the ellipsometry results are reported as the change in Delta and Psi at each location. This change refers to that measured in the presence of the surface potential gradient with respect to the same locations measured with a uniform potential of 0.0 V. Changes in Delta (Figure 4.7A) and Psi (Figure 4.7B) were monitored with respect to electrode position for a surface potential gradient spanning 0.0 to 1.6 V. The observed changes in these parameters are consistent with that observed at a fixed location.
during potential cycling. As the potential increases along the gradient from the left to the right of the sample, Delta decreases gradually at first and then more rapidly as the potential reaches and exceeds ~0.6 V (Figure 4.7A). Similarly, Psi increases gradually at low potentials on the left and then more rapidly at higher potentials on the right (Figure 4.7B). The only anomalous result appears to be the Psi value measured at the far right side of the sample. The lower value measured here could be due to overlap with the gold contact pad at this location [17]. Nevertheless, the thickness of the oxide layer could be determined as a function of position in the presence of the potential gradient from these results using a three-layer model (Figure 4.7C). The thickness of the oxide layer versus position and potential is consistent with that observed in

![Figure 4.7](image-url)
the potential cycling results. A variation in oxide thickness between 0 and ~2.3 nm is observed along the gradient.

The spatial control of the electrodeposition of copper and platinum oxide film growth represent examples to the capabilities of high-throughput applications for surface electric fields. These systems can be expanded in complexity for a variety of applications such as corrosion, metal alloy and catalytic studies by adding multiple metal components. Other applications include electrochemical sensors. Each metal has a specific potential at which it will electrodeposit; by using surface electric fields, these materials could be separated from solution and spatially resolved for easy detection.

4.4 CONCLUSIONS

It has been demonstrated that the electrodeposition of copper is spatially controllable in both one and two dimensions on an indium tin oxide (ITO) substrate. Boundaries between copper film and substrate are sharp and can be controlled by manipulating gradient width. Future work would include boundary analysis using surface techniques such as AFM and XPS to determine sharpness as well as copper roughness. The influence of solution additives to copper deposits is also of interest, particularly to the application of copper electrodeposits as interconnects in the electronics industry. It was also verified that the growth of an oxide film on platinum is controllable with respect to potential, as demonstrated by ellipsometry. By employing a surface electric field, platinum oxide film growth can be spatially controlled to create areas of passivated surface neighboring active regions of exposed platinum as a way to pattern surfaces. Discrete regions of oxide bands or spots could be formed to protect the underlying platinum surface from a chemical treatment and then be removed to expose
patterned platinum substrates. Both of these systems suggest that metal and metal oxide systems are spatially controllable by the local applied potential and applicable to more complex multi-component systems. Applications include high through-put processing of metal/metal oxide systems as well as applications in corrosion studies, metal alloy combinatorics, catalysts, and electrochemical sensors.

4.5 REFERENCES


CHAPTER 5. ELECTROCHEMICAL AND ELLIPSOMETRIC STUDY OF
POTENTIAL-CONTROLLED SPATIAL ADSORPTION OF DOPC ON AU

A paper to be submitted to *Langmuir*

Erin L. Ratcliff and Andrew C. Hillier

ABSTRACT

The potential and position-dependent adsorption of 1,2-dioleoyl-sn-3-phosphocholine (DOPC) on a thin gold film (~20 nm) using spatially controllable electric fields is reported. An electric field gradient was produced by applying different potentials at spatially distinct locations on an electrode surface. The resulting variations in local potential were employed to spatially control the adsorption of DOPC as well as the growth of gold oxide. In situ null-ellipsometry was used to detect and characterize film formation with respect to potential and position in the presence of an electric field. DOPC was found to adsorb only at or near the potential of zero charge (pzc) of the gold electrode, creating spots or bands of adsorbed phospholipid. The use of potential gradients allows the localized adsorption of DOPC molecules on an electrode surface. Results indicate that this technique can be used to pattern phospholipids with high resolution on an electrode surface.

5.1 INTRODUCTION

The study of the properties and structures associated with biological membranes is important to the understanding of biological processes of living organisms. One popular model to study these structural systems are membranes supported on solid surfaces [1]. Phospholipid bi-layers represent one key group of such model systems and are applicable in
other fields such as biofunctionalization of inorganic solids (ex. semiconductors and optoelectronic devices) [2,3], biosensors [4,5], surface modification of implants [6-8], immobilization of proteins [9], and catalytic interfaces [10].

There are numerous techniques to construct metal substrate supported phospholipid bi-layers. Many focus on the deposition of phospholipids onto a mercury drop electrode. A drop of mercury is coated in the phospholipid by dropping the mercury through a monolayer spread on a gas-solution interface [11-14]. A second approach involves the attachment of a phospholipids to a thiol monolayer tethered to gold, forming a “stacked” layer structure [13,15-19]. Still other techniques prepare supported bi-layers using Langmuir-Blodgett methods [20] or the spontaneous fusion of the phospholipids vesicles [21-25]. Supported membranes on metal substrates can be studied by many surface-sensitive techniques such as microinterferometry [26,27], ellipsometry [28-30], surface plasmon spectroscopy [31,32], Fourier transform infrared (FTIR) spectroscopy [28,33], nuclear magnetic resonance (NMR) [34], total internal reflection fluorescence [20,35-37] and neutron and x-ray surface reflectivity [38,39].

It has been observed that phospholipid bi-layers will adsorb on metal electrodes and pass through a phase transition with respect to applied potential [1,14,32,40,41]. Structural changes associated with these phase transitions have been examined using polarized attenuated total reflection (ATR) spectroscopy on phospholipid multi-layers sandwiched between two germanium electrodes [42]. Further work has focused on the potential-dependent orientation of the bi-layer on gold using photon polarization modulation infrared reflection absorption spectroscopy (PPM-FTIRRAS) [1,43]. Moreover, it has been found that not only the orientation of the phospholipids but also the specific act of adsorption is
potential dependent [41]. Using electrochemical quartz crystal microbalance (EQCM), Hoffmannova et. al. verified that 1,2-dioleoyl-\textit{sn}-glycero-3-phosphocholine (DOPC) vesicles will adsorb at potentials only near the potential of zero charge (\textit{pzc}) of a gold electrode [41].

Until now, no work has been done to study the spatial control of phospholipids with respect to an electric field. Surface electric fields have been used to probe the adsorption of several species with respect to applied potential on a surface such as self-assembled monolayers [44-48], polymers [49-51], metal oxide [52] and metal deposition [53, 54]. When two spatially separate distinct potentials are applied to a sufficiently resistive thin gold film (t \leq 50 \text{ nm}), a corresponding in-plane surface electric field gradient is formed [44-48]. The potential varies linearly with respect to position on the substrate. This method permits spatially tunable gradients in both magnitude and width and readily lends itself to mapping the electro-adsorption of such species as alkane thiols [44-48] or phospholipids. This work will focus on the adsorption of phospholipid molecules on a surface at high resolution.

The goal of this study is to establish that surface electric fields can be employed to spatially control the adsorption of a phospholipid 1,2-dioleoyl-\textit{sn}-glycero-3-phosphocholine (DOPC, Schematic 5.1) using a combination of electrochemistry and ellipsometry. It will be demonstrated that DOPC will adsorb on an electrode surface only at potentials at or near the potential of zero charge. High resolution spatial control of the phospholipid adsorption is achieved. Results will be compared with the behavior of the gold substrate in only the bulk electrolyte. Gold oxide film growth is characterized with cyclic voltammetry and ellipsometry. The ellipsometric mapping of the spatial control of gold oxide film is presented.
5.2 EXPERIMENTAL METHODS

Materials and Reagents. All experiments were performed in 0.05 M KCl (Aldrich, Milwaukee, WI) in deionized water (NANOpure, Barnstead, Dubuque, IA). The 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) and was purchased from Avanti Polar Lipids, Inc. (Alabaster, AL) and used as received.

Substrate Fabrication. Pieces of glass were cut to 1 cm x 2.8 cm and were cleaned by sonicating in 50:50 ethanol/water followed by sonication in water and dried under a stream of nitrogen. In order to promote adhesion of gold to the glass surface, the glass was functionalized using a silane monolayer. Briefly, glass slides were sonicated for 10 minutes in cyclohexane and dried with nitrogen. Then slides were immersed in Piranha solution (75% H₂SO₄ + 25% H₂O₂) for 30 minutes. Slides were rinsed with deionized H₂O and dried again with nitrogen. Finally, the glass slides were placed in a solution of 5 mM 3-mercaptopropyltrimethoxysilane in toluene for 6 hours or overnight followed by sonication in toluene for 10 seconds and dried in N₂. Substrates were placed immediately in a vacuum deposition chamber and ~20-25 nm of gold was vapor deposited. A subsequent gold vapor
deposition added 110 nm of gold to the terminal edges of the substrates for electrical contact. The thick regions of gold were connected to copper wires and secured using silver epoxy (H20E parts A and B, Epoxy Technologies, Billerica, MA) followed by an insulating epoxy (QuickSet Epoxy Gel, Hentel Consumer Adhesives, Inc., Avon, OH).

**Electrochemistry.** Cyclic voltammetry and differential capacity measurements were all carried out in a three-electrode glass cell. The cyclic voltammetry curves were recorded at a scan rate of 50 mV/s. The differential capacity curves were determined using a scan rate 10 mV/s and an AC perturbation of 1000 Hz frequency and 5 mV rms amplitude using a polycrystalline disk gold electrode. All measurements were performed using a multipotentiotstat (CH760 B, CH Instruments, Austin, TX). Solutions of 0.05 M KCl and various solutions of DOPC were purged under a stream of nitrogen for 15 minutes. All potentials are reported with respect to an Ag/AgCl reference electrode. A Pt-Ir on Ti mesh was used as a counter electrode.

**Ellipsometry.** An in-situ ellipsometry cell was fabricated from a piece of Delrin and glass microscope slides. A 7.5 x 5.1 x 1 cm$^3$ piece of Delrin was machined along two parallel sides at 20º. Glass slides were glued (QuickTite Super Glue, Manco, Inc., Avon, OH) to the Delrin to provide optical access to the sample at a 70º angle of incidence. Two more glass slides were adhered to the remaining ends to create a closed cell. The cell wall joints were then covered with an inert organic lacquer (Microstop stop-off lacquer, Pyramid Plastics Inc., Hope, AR). For ellipsometry measurements, the substrate consisted of a layer of vapor deposited gold on a glass slide. Electrical contact to the substrates was achieved by attaching a copper wire to the gold contact pads using a conductive silver epoxy (H20E,
Epoxy Technologies, Billerica, MA), followed by an insulating epoxy (QuickSet Epoxy Gel, Hentel Consumer Adhesives Inc., Avon, OH).

Null-ellipsometry measurements were performed using an automated, multifunctional optical system (Multiskop, Optrel GbR, Berlin, Germany) with spatial mapping capabilities. Ellipsometric data was acquired at a single-wavelength (632.8 nm) with a beam diameter of ~0.6 mm in the PCSA configuration at 70° angle of incidence. Film calculations were performed using a commercial software package (Elli, Optrel GbR, Berlin, Germany). The estimation of film thickness will be discussed in the text. Ellipsometry mapping experiments were performed by translating the sample along the direction of the applied potential gradient using an integrated stepper motor and recording delta and psi with a uniform potential of -1.0 V and in the presence of an applied potential gradient. The changes in delta and psi at each position with respect to the uncoated substrate were used to determine the film thickness.

5.3 **RESULTS AND DISCUSSION**

Cyclic voltammetry of a polycrystalline gold electrode in a solution of 0.05 M KCl exhibits the typical response for gold in a neutral solution (Figure 5.1). Oxide formation is indicated by the broad peak beginning at ~0.4 V and by the symmetric reduction peak at ~0.2 V in the reverse scan. Potentials negative of -0.9 V correspond to the reduction of protons at the gold surface.

The electrochemical behavior of gold, particularly oxide film composition and structure along with growth mechanisms have been studied extensively [55-64]. Previous ellipsometric measurements on bulk gold electrodes suggest that changes in delta and psi
may be used to determine the potential-dependent thickness of a growing oxide film [55,56,63,64]. Figure 5.2 depicts null-ellipsometry results for a vapor deposited gold film (~25 nm) on a glass slide while being cycled from -1.0 to 1.1 V (vs Ag/AgCl) at 5 mV/s in a solution of 0.05 M KCl. Figure 5.2 A shows the change in delta as a function of applied potential and

Figure 5.1. Cyclic voltammogram of vapor deposited Au on glass electrode in a nitrogen-purged solution of 0.05 M KCl at 100 mV/s.

Figure 5.2 B shows the change in psi. During the forward potential scan delta decreases gradually between -1.0 and 0.3 V and then decreases rapidly with further increasing potential. Psi shows a similar trend and decreases with increasing potential. The decrease in delta of approximately 1.3° suggests the formation of an oxide film. The changes appear at potentials consistent with the oxidation current observed in cyclic voltammetry in Figure 5.1. During the return sweep in potential from 1.1 to -1.0 V, delta and psi both increase until they reach their original values. A rapid change in delta and psi is observed at a potential corresponding to the oxide reduction peak (Figure 5.1).
The changes in delta and psi were correlated to a four-layer model (water-oxide-gold-glass) to estimate the oxide thickness. Results of this fitting procedure (Figure 5.2 C) indicate a slow film growth initiating at ~0.2 V and then a rapid increase in thickness to a maximum of 0.6 nm near 1.1 V. During the reverse scan, the oxide film is rapidly removed as the potential decreases below 0.2 V. The potentials at which the oxide forms and is removed are consistent with the cyclic voltammetry shown in Figure 5.1. An oxide thickness of approximately 0.5 nm is consistent with values reported in the literature for this scan rate [55,56]. Figure 5.2 D is a schematic of surface charge and oxide coverage. On the left, at potentials below the potential of zero charge (E < E_{pzc}), there is a negative charge on the
metal. In the middle is a schematic of a positively charged metal surface at potentials above the $E_{pzc}$ ($E > E_{pzc}$). Finally, on the right, for potentials greater than 0.4 V, there is oxide film growth on the gold surface.

Null-ellipsometry mapping experiments were used in order to quantify the gold oxide in the presence of a surface potential gradient. This experiment was performed in order to quickly verify that the gold films were sufficiently resistive to maintain a potential gradient in the presence of film growth. Briefly, a thin gold film electrode was prepared and in-situ ellipsometry measurements were performed in the presence of a linear potential gradient. Due to the nature of the gold electrode, small variations are present spatially over a distance of 21 mm. The variations result in differences in the optical parameters which are greater than the differences associated with the gold oxide film. Therefore, it was necessary to monitor changes in delta and psi with respect to location both prior and after the application of the electric field. An applied potential of -1.0 V was used as a base potential and optical parameters with respect to location were collected. Second, a surface potential gradient was applied and changes in the optical parameters from -1.0 V were measured with respect to location. Results of modeled gold oxide thickness with respect to location for three potential gradients are given in Figure 5.3, using the four-layer model previously described. Potential gradients are shown on the right ( - - ) along with estimated thickness (○) with respect to position on the right. Figure 5.3 A is an example of an electric field which spans from 1.0 V on the left to -0.2 V on the right over a distance of 21 mm. Data collected for Figure 5.3 A was collected after a time of 3 minutes. There is a maximum in oxide thickness of 0.8 nm on the left side of the sample, at 1.0 V. Oxide thickness decreases with respect to position from 0 mm to ~10 mm, which corresponds to local potential values of 1.0 to 0.4 V, respectively.
At potentials below 0.4 V, there is no oxide film present, consistent with cyclic voltammetry results in Figure 5.1. Figure 5.3 B is an example of an electric field spanning more negative potentials, with the application of -1.0 V on the left side (0 mm) and 1.0 V on the right side (21 mm). The data in Figure 5.3 B was collected after only two minutes. Like Figure 5.3A, maximum film thickness occurs at positive potentials, with maximum film growth at 1.0 V (0 mm) and decreasing as one progresses from left to right. However, maximum film thickness is only 0.5 nm at 1.0 V, indicating a dependence on both potential and time for oxide film growth, consistent with the literature.
Figure 5.3C reverses the direction of the potential gradient used in Figure 5.3 B, with -1.0 V on the left (0 mm) and 1.0 V on the right (21 mm). Data was collected 2 minutes after application of the electric field. The result is a reverse of Figure 5.3B. Thickness increases, starting at positive potentials, as one moves from left to right, with maximum thickness of approximately 0.45 nm at 1.0 V (21 mm). Figure 5.3 D is a schematic illustrating oxide growth on the surface may be spatially controlled by adjusting the terminally applied potentials.

Null-ellipsometry results indicate that oxide film formation is dependent on potential, but also is dependent on the time the electric field is applied. Oxide film growth initiates at positive potentials, with rapid film growth of over 0.2 nm occurring after just three minutes at potentials greater than 0.4 V. The adsorption of DOPC is known to occur over a much longer time span, with sufficient adsorption occurring after 60 minutes [1,41]. The important outcome of the ellipsometry studies of gold oxide film growth is that potentials at which gold oxide film growth occurs must be avoided in order to study the adsorption of DOPC. Therefore, we will restrict our study to potentials below 0.2 V.

It has been previously reported that DOPC will adsorb on a gold surface only at potentials near the potential of zero charge ($pzc$) [41]. Cyclic voltammetry performed in a solution of $1.2 \times 10^{-6}$ M DOPC and 0.05 M KCl showed little deviation in behavior from the behavior of gold in bulk electrolyte, indicating the DOPC molecules show no electroactive activity. Differential capacitance was used as a more sensitive technique to verify DOPC adsorption at the potential of zero charge ($pzc$) for gold electrodes in 0.05 M KCl. The potential of zero charge is defined as the potential at which the charge on the electrical double layer is zero. Figure 5.4 A (curve i) is a plot of capacitance versus potential for a
polycrystalline gold disk electrode in 0.05 M KCl. The relative minimum at approximately -0.15 V corresponds to the onset of the specific adsorption of Cl\(^-\) ions and is the \( pzc \) of the electrode. At potentials below the \( E_{pzc} \), Cl\(^-\) ions will desorb as the electrode becomes negatively charged. This value is consistent with the literature for a KCl electrolyte. Vapor deposited gold substrates showed analogous behavior.

Differential capacitance curves for the supporting electrolyte and several concentrations of DOPC are given in Figure 5.4. Results presented are for a polycrystalline gold disk electrode and are comparative with vapor deposited gold. The C-E curves for the solutions containing DOPC show a decrease in capacitance with increasing DOPC concentration, indicating adsorption on the gold surface. There is a slight shift in the

![Figure 5.4.](image-url)
pzc of the electrode upon DOPC adsorption to slightly higher potentials, again reflecting DOPC adsorption.

The minimum capacitance with respect to DOPC concentration is plotted in Figure 5.4 B. The decrease in capacitance relative to the capacitance of the gold electrode in bulk electrolyte suggests DOPC adsorption on the electrode surface. The decrease in capacitance with respect to increasing DOPC concentration is consistent with the lower dielectric constant associated with organic adsorbates on metal electrodes.

Ellipsometry can also be used to measure the potential-dependent adsorption of 1,2-dioleoyl-sn-3-phosphocholine vesicles onto a gold electrode. Figure 5.5 shows the changes in ellipsometric parameters delta (Fig. 5.5 A) and psi (Fig. 5.5 B) as measured with respect to time for 60 minutes at a single point on the substrate held at a specified potential. Figure 5.5A illustrates a decrease in delta with time for potentials near the pzc of the electrode, at -0.2 V. Specifically, the total magnitude of overall decrease in delta increases as the potential increases from -0.3 V (○) to -0.2 V (□). However, the total magnitude of change in delta

![Figure 5.5](image-url)
decreases as potentials increase above -0.2 V, at -0.1 V (\(\Delta\)) and 0.0 V (+). This is consistent with maximum adsorption of DOPC vesicles near the \(pzc\) of the electrode at -0.2 V. Figure 5.5 B shows the changes in psi over 60 minutes at specified potentials. In this case, psi increases with time for all potentials. The largest change in psi over time occurs at a potential of -0.2 V, or the \(pzc\) of the electrode.

The final changes in the values of delta and psi after 60 minutes are presented in Figure 5.6 A and B, respectively. Figure 5.6 A shows delta decreasing from -0.3 V to approximately -0.2 V, at which point it again begins to increase and then levels off near zero. Figure 5.6 B shows psi increasing from -0.3 V to -0.2 V and decreasing before leveling off at potentials greater than -0.2 V. Delta and psi show respective minimums and maximums at ~-0.2 V, suggesting maximum absorbance at the potential of zero charge (\(pzc\)) of a gold electrode in 0.05 M KCl. Previous studies of the potential-dependent adsorption of DOPC on gold occurs at the \(pzc\) of the gold electrode, which is dependent on the supporting electrolyte [23,41]. It is believed that vesicle adsorption is restricted to potentials close to the \(pzc\) with vesicle deformation into bilayers occurring at potentials deviating slightly from the \(pzc\) prior to complete desorption at sufficiently charged surfaces [1]. At potentials where the electrode is charged, the kinetics of vesicle rupture are faster than the kinetics of vesicle adsorption [41] and adsorption does not take place.

The corresponding bi-layer thickness was calculated using a four-layer model (water-DOPC-gold-glass) and given in Figure 5.6 C. A refractive index of \(n = 1.4\) was used for the bi-layer [1,65,66]. There is a maximum in thickness of approximately 8 nm at the \(pzc\) of the gold electrode. The thickness of the adsorbate decreases sharply as applied potential deviates from the \(pzc\). The thickness values for DOPC obtained on a thin gold film are comparable to
other techniques. High-resolution synchrotron x-ray data found the cross sectional area of a vesicle of the lipid suspended in liquid to be 72.1 Å² (dia. ~9.6 Å) and bilayer thickness is approximated at 4.5 nm [67]. Ellipsometry of DMPC (1,2-dimyristoyl-sn-glycero-3-phosphocholine) was found to have a thickness of ~5 nm on SiO₂ after 1 hr (20 % coverage) [30] while photon polarization modulation infrared reflection absorption spectroscopy estimated a bilayer of DOPC on Au(111) thickness of ~5 nm [1]. Our result of maximum thickness of 8 nm is slightly larger

Figure 5.6. Potential-dependent null ellipsometry on a ~25 nm vapor deposited Au on glass surface in 0.05 M KCl + 1.2 x 10⁻⁵ M DOPC showing the (A) change in delta (○) and (B) change in psi (Δ) after 60 minutes versus applied potential. (C) Plot of bi-layer thickness versus potential (□) as determined by fitting potential-dependent ellipsometry results to a four-layer model. (D) Schematic of surface charge and gold surface with adsorbed bi-layer.
than reported values of bi-layer thickness but is still smaller than the diameter of the free vesicle.

The adsorption of DOPC only near the pzc of the gold electrode makes it ideal for creating isolated domains of phospholipids as either bands or discrete spots. Such spatial control of the adsorption of DOPC on gold using potential gradients is illustrated in Figure 5.7.

Null-ellipsometry methods were used, analogous to those used for the thin gold oxide films. The potential gradients are given on the right (- -) and the corresponding DOPC thicknesses are given on the left (□) for three unique potential gradients. Figure 5.7 A is a

Figure 5.7. Position-dependent null ellipsometry on vapor deposited Au on glass in 0.05 M KCl and 1.2 x 10-5 M DOPC in the presence of applied potential gradients (A) 0.2 to -0.6 V, (B) -1.0 to 0.1 V and (C) 0.1 to -1.0 V. Respective oxide thickness (□) vs position with the applied potential gradient ( - - ) over a region spanning 0 to 21 mm. (D) Schematic of bilayer on gold.
potential gradient which spans from 0.2 V on the left (0 mm) to -0.6 V on the right (21 mm). There is an increase in thickness beginning at about 5 mm, which shows a relative maximum at 11 mm before decreasing again. This corresponds to a sharp DOPC adsorbance near the \( pzc \) of the gold electrode, as predicted by Figure 5.6. Figure 5.7 B is a potential gradient larger in magnitude, ranging from -1.0 V on the left to 0.2 V on the right. The \( pzc \) of the gold electrode has shifted to the right to about 15 mm, with a parallel shift in the maximum thickness to the right. If the gradient is reversed such that 0.2 V is applied to the left and -1.0 V to the right, as in figure 5.7 C, there is a respective shift in the \( pzc \) and the maximum thickness to 5 mm, a mirror image of Figure 5.7 B. The results in Figure 5.7 demonstrate that the adsorption of DOPC in the presence of a potential gradient is localized only to domains with local applied potential near the \( pzc \) of the electrode. Furthermore, by changing the terminal applied potentials, the location of the DOPC adsorption site can be manipulated and the DOPC can be moved around on the surface. In theory, by chemically linking the DOPC to the surface, successive electric fields could be applied so that several discrete areas of DOPC patches could be created.

5.4 CONCLUSIONS

We have demonstrated the ability to use electrochemistry and null-ellipsometry to investigate the localized adsorption of DOPC with respect to the \( pzc \) of the electrode using potential gradients. The adsorption of the phospholipid DOPC was verified to be both potential and position dependent in the presence of a surface electric field gradient. Restrictions are placed on the range of potentials used in the potential surface gradients by the growth of gold oxide film, which may perturb DOPC adsorption. This technique can be
utilized to perform a mask-free patterning of phospholipids on a gold surface and can be expanded to create areas of biofunctionalization on metal electrodes. Future work will focus on the spatial control of other organic molecules as a way to pattern surfaces using “bottom up building” techniques. Focus will be devoted to the fabrication of isolated domains of organic films with application for the immobilization of proteins, biosensors, and catalytic interfaces.

5.5 REFERENCES


CHAPTER 6. LOW PRECIOUS METAL CONTENT MONOLAYER-COATED CATALYSTS

ABSTRACT

The desire to construct tailored nanostructured metallic catalysts with low precious metal content (i.e. platinum) for proton exchange membrane (PEM) fuel cells is in high demand in order to reduce catalyst loading costs. A strategy to fabricate nanoparticle catalysts which contain only a monolayer of platinum is presented. A single under-potential deposited (UPD) monolayer of copper is formed on nickel core nanoparticles, followed by the redox replacement with Pt\(^{2+}\) to yield a monolayer of Pt on nickel. The ultra-thin coating of platinum on nickel is verified with cyclic voltammetry and atomic force microscopy (AFM) for bulk template stripped nickel as well as commercial and synthesized nickel nanoparticles. Issues associated with oxide passivation and pH are presented and discussed.

6.1 INTRODUCTION

Proton exchange membrane (PEM) fuel cells are compact, renewable power sources with low environmental impact. Chemical energy is converted to electrical energy by electrochemical reactions. At the anode, hydrogen molecules are oxidized to protons, which migrate through the proton exchange membrane to the cathode. At the cathode, the protons combine with oxygen from the air and are expelled from the cell as water. The electrons generated from the splitting of the hydrogen molecule travel through an alternate path and can be used by the fuel cell for electrical work (figure 6.1). The major barrier limiting the commercialization and application of the fuel cell to such consumer products as automobiles is cost associated with high catalyst loading.
Catalyst loading is defined by eqn. 1, where \( m \) is the mass of the catalyst used and \( A \) is the surface area of the catalyst. High cost materials, particularly platinum, are often used as catalysts. Platinum can cost over $18,000 per kilogram [1]. For a PEM, 55% of the total cost is from the fuel cell stack, with 25% of the total cost is associated with the catalyst cost. The Department of Energy has set a goal of $7.2 per kW in order to make fuel cells economically feasible [2]. Currently, a platinum fuel cell has a power density of 0.6 W/cm\(^2\) and a loading of ~0.8 mg/cm\(^2\) [3], which corresponds to a total platinum cost of ~$26/kW,

\[
\text{Loading} = \frac{m}{A} \tag{1}
\]
three times the necessary DOE goal.\textsuperscript{1} In order to utilize fuel cells as a primary energy source, the catalyst cost must be reduced.

A substantial amount of the fuel cell cost is devoted to catalyst material; an obvious solution would be to reduce the cost of the catalyst, or reduce the loading associated with the catalyst. Referring to eqn 1, loading can be reduced by either reducing the mass of the catalyst used or increasing the surface area per mass. Smaller spherical particles will have a lower loading than larger particles because of a larger surface area to volume ratio. A decrease in particle size also increases the surface area due to a higher percentage of total atoms being surface atoms instead of bulk atoms. The state of the art fuel cell takes advantage of

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{figure6.2.png}
\caption{Cost per unit area for (A) a pure platinum particle and (B) a single monolayer of platinum on an inexpensive core material.}
\end{figure}

\textsuperscript{1} Power Density: 0.6 V at 1 A/cm\textsuperscript{2}, Power Density = 0.6 V x 1 A/cm\textsuperscript{2} = 0.6 W/cm\textsuperscript{2}
Total Pt loading/power density = 0.8/0.6 = 1.3 g Pt per kW * cost of Pt = $26/kW.
These calculations are based upon using pure hydrogen as a fuel.
small catalyst particles, using Pt or Pt-Rh \(~3.5\) nm diameter nanoparticles embedded in porous carbon to yield a loading of \(~0.8\) mg/cm$^2$ [4].

Cost can also be improved by eliminating the core of “expensive” atoms not taking part in the electrochemical reaction and replacing them with “inexpensive” atoms. Figure 6.2 A is a plot of loading with respect to size for a pure platinum nanoparticle. By comparison, figure 6.2 B is a plot for particles with only a single monolayer of platinum on an inexpensive support material core. Cost for monolayer coatings levels off for larger particles, while solid particles linearly increase with radius. True advantages are seen at small particle size. For example, for a radius of 15 nm, the cost for using particles with only a monolayer of platinum is 100 times lower than using pure platinum particles. Using this novel architecture of inexpensive core material and platinum monolayer coating, there is a significant reduction in catalyst loading.

There are several examples of the application of the core and monolayer architecture to reduce catalytic loading available in the literature. One strategy to form materials with low precious metal content but having high activity involves the spontaneous deposition (SD) of platinum on the surface of ruthenium nanoparticles. The ruthenium particles are introduced to a solution of platinum ions, which spontaneously deposit on the surface. The platinum forms a monolayer or submonolayer coating on the ruthenium particles and has shown evidence of exhibiting significant activity towards the oxidation of hydrogen [5,6]. However, there are few materials onto which platinum will spontaneously deposit.

A second technique for precious metal monolayer deposition onto a second metal core involves a two step process: an under-potential deposition (UPD) followed by a redox replacement deposition (RRD). For example, on a gold surface or nanoparticle, it has been
found that copper will form a monolayer when deposited at a potential below its bulk electrochemical deposition potential, or its UPD potential [7-10]. When the copper monolayer is exposed to a more noble metal such as platinum, platinum will replace the copper on the surface following an electrochemical surface redox reaction (figure 6.3) [7-10]. The result is a monolayer or submonolayer of platinum on a gold surface that exhibits high catalytic activity.

The above studies demonstrate the ability to reduce the platinum content to extremely low levels by creating an active surface of the platinum while replacing the core with another material. However, gold and ruthenium are still relatively costly materials. Our goal for this project was to construct nanoparticles with a platinum monolayer or submonolayer on a core of an inexpensive material other than gold. These nanoparticles should significantly reduce the loading by creating a surface of active catalyst on a nominally less active core.

There are several factors that need to be considered when choosing a core material. In particular, one needs to consider the method by which the platinum monolayer will form.

**Figure 6.3.** Schematic of the under potential deposition (UPD) of copper followed by the redox replacement deposition (RRD) of platinum monolayers on Au.
Under-potential deposition (UPD) typically occurs by the formation of adlayers of a foreign material on the surface of a different metal. Several underlying or core materials that display this behavior are Pt, Au, and Ag. For UPD, the substrate metal must have a higher work function than the adlayer. During UPD, the adlayer will deposit as a monolayer or submonolayer on the substrate at a potential positive of its standard reduction potential, causing an underpotential shift ($\Delta E_{\text{upd}}$). The underpotential shift represents the difference in bond energies between the bond between the metal adatom with the substrate and a bond with itself. The correlation between the underpotential shift ($\Delta E_{\text{upd}}$) and the work function ($\Psi$) of the metal is given in eqn 2, where $a = 0.5$ V/e [11].

$$\Delta E_{\text{upd}} = a \Delta \Psi$$

(2)

The result of this relationship is the general rule that UPD occurs when the work function of the substrate ($\Psi_{\text{sub}}$) is greater than the work function of the adlayer material ($\Psi_{\text{upd}}$).

$$\Psi_{\text{sub}} > \Psi_{\text{upd}}$$

(3)

Figure 6.4 plots the work functions of a variety of metals versus their standard reduction potentials [12]. Materials with large work functions would be suitable substrates (---) for UPD while materials with lower work functions would be more suited for adlayers (- -).

A key point of figure 6.4 is that the UPD method is not likely to create Pt monolayers on a substrate, since Pt has the highest work function and will not under-potential deposit. Therefore, it is necessary to employ a second method, namely using redox reduction deposition (RRD), which occurs by the redox replacement of a UPD layer with another metal. The reaction mechanism is as follows:

$$M_{\text{UPD}}^{0} + (m/z)M_{T}^{z+} \rightarrow M^{m+} + (m/z)M_{T}^{0}$$

(4)
where \( M_{\text{UPD}}^0 \) is the UPD metal such as Cu and \( M_T^0 \) is a nobler transition metal acting as the replacement metal such as Pt. The requirement for eqn. 4 to occur is that the standard reduction potential of the replacement metal \( M_T^0 \) must be greater than the standard reduction potential of the UPD metal \( M_{\text{UPD}}^0 \).

\[
\Delta E_{M_T^{1+/M_T^0}} > \Delta E_{M_{\text{UPD}}^{1+/M_{\text{UPD}}^0}}
\]

A contributing factor to the monolayer coverage is the stoichiometric relationship \((m/z)\) between the metal salts used. If \((m/z) = 1\), there will be a full monolayer (1 ML). If \((m/z) = 0.5\), there would be 0.5 ML and conversely, if \((m/z) = 2\), there would be 2 ML coverage.

The goal of this research project was to successfully form a monolayer of platinum on an inexpensive core material (other than gold) using the criteria outlined in (3) and (5). Core metal candidates were eliminated based upon their Pourbaix diagrams, which suggested that surface passivation due to oxide formations would limit either UPD or the RRD of Pt. Nickel was chosen as a core metal because of its low cost and resistance to surface passivation at low pH values, demonstrated by the Pourbaix diagram of nickel (figure 6.5) [13].
6.2 EXPERIMENTAL METHODS

Materials and Reagents. Nickel wire (0.25 mm) was obtained from Goodfellow Cambridge Limited (Cambridge, England) and was used as both an electrode and for vapor deposition. Metal salts (CuSO$_4$·5H$_2$O, NiCl$_2$·6H$_2$O and K$_2$PtCl$_4$) were purchased from (Sigma-Aldrich). The cationic surfactant cetyltrimethylammonium bromide (CTAB) was obtained from Acros Organics (Belgium). The cationic co-surfactant tetradodecylammonium bromide (TC$_{12}$AB) was supplied by Fluka. Hydrazine, acetone, and NaOH were obtained from Sigma-Aldrich. Unless otherwise noted, solutions were prepared from 0.1 M H$_2$SO$_4$ (Fisher Scientific, Fair Lawn, NJ) in 18-MΩ deionized water (NANOPure, Barnstead, Dubuque, IA) and purged for 15 min in nitrogen before each use.

Template stripped nickel surface preparation. Template stripped nickel was used as 111 crystallographic planes for imaging and electrochemistry experiments. Nickel

---

**Figure 6.5.** Pourbaix diagram for nickel. Acidic pH values are required to prevent passivation of the nickel surface by oxide formation.
films (75 – 125 nm) used in atomic force microscopy (AFM) experiments were deposited by vapor deposition on freshly cleaved mica. The exposed nickel film was adhered to clean glass slides using Epo-Tek 377 parts A and B (Epoxy Technologies, Billerica, MA), forming a mica, nickel and glass “sandwich.” The epoxy was cured at 150°C for 1-2 hours. The mica was removed by placing the substrates in THF (Fischer Scientific, Fair Lawn, NJ) for 1-3 minutes and rinsed with ethanol and dried in a stream of nitrogen.

**Nickel Nanoparticle Synthesis.** Nickel nanoparticles were synthesized by the reduction of nickel chloride with hydrazine in the presence of cationic surfactants CTAB/TC\textsubscript{12}AB\cite{14}. Briefly, 50 mL of aqueous solutions were prepared by dissolving CTAB (0.025 M), TC\textsubscript{12}AB (0.5 mg/mL) and nickel chloride (0.005 – 0.1 M) and trace amounts of acetone (10\textmu L/mL) in water. Then, hydrazine (1.15 M) and trace NaOH solution (1.0 M, 20 \textmu L/mL) were added. Nickel nanoparticles were formed after about 1 hour at a temperature of 60°C. Solution was filtered and remaining particles were placed in furnace at 700°C for 3 hours to remove surfactants and dry particles. Nickel nanoparticles were attached to glassy carbon electrodes using Nafion (Aldrich). Platinum coatings were formed by placing a drop of 10 mM K\textsubscript{2}PtCl\textsubscript{4} in 0.1 M H\textsubscript{2}SO\textsubscript{4} (pH <2) onto the Nafion film and allowed to dry. Remaining Pt\textsuperscript{2+} ions were expunged from the electrode surface by cycling between 0 and 0.9 V at 0.05 V/s. A similar procedure was also repeated for commercially purchased nickel nanoparticles from Quantum Sphere, Inc.

**Electrochemistry.** All electrochemistry was performed in 0.1 M H\textsubscript{2}SO\textsubscript{4} deoxygenated with nitrogen gas for 15 minutes at a scan rate of 0.05 V/s, unless otherwise stated. An Ag/AgCl reference electrode and Pt/Ir on Ti mesh counter electrode were used.
Atomic Force Microscopy. All images were taken in tapping mode at 0.5 Hz and are a scan size of 10.0 µm.

6.3 RESULTS AND DISCUSSION

Nickel surfaces were characterized using electrochemistry. Figure 6.6A plots the current versus potential for a nickel wire electrode in 0.1 M H$_2$SO$_4$. The peak from A to B to C represents the active region of the nickel surface; the response in this area is highly pH dependent and may include the formation of complex metal ions or the dissolution of the nickel surface to Ni$^{2+}$. Curve C to D is the passivation of the nickel surface, forming oxides such as NiO and Ni$_2$O$_3$, which are pH dependent. Curve D to E is the transpassive region; the nickel surface is electrochemically inactive due to the insulating oxide layer. Curve E to F shows an increase in the dissolution of nickel.

Figure 6.6. Plot of current versus potential (vs Ag/AgCl) for a bare nickel wire electrode before (A) and after (B) the UPD of Cu followed by RRD of Pt.
rate, suggesting a removal of the passivation layer prior to the production of oxygen in curve F to G. It is important to note that the passivation of the nickel surface occurs at potentials much higher than the standard reduction potential for copper.

To verify the UPD of copper followed by the RRD of platinum on nickel, a bare nickel wire electrode was placed in a solution of 5 mM CuSO$_4$ and 0.1 M H$_2$SO$_4$ and held at -0.1 V (vs Ag/AgCl) for three minutes, sufficient time to coat the nickel wire in at least a monolayer of copper. A copper color was visible on the wire. Then the copper coated nickel electrode was placed in a solution of 5 mM K$_2$PtCl$_4$ and 0.1 M H$_2$SO$_4$. The cyclic voltammogram of the resulting surface is shown in figure 6.6B and current response is consistent with a platinum electrode. However, control experiments with nickel electrodes submerged in platinum salt showed no platinum behavior after five minutes of submersion. This result may be due to the annealing processes used to form nickel wire.

The surface coverage ($\Gamma$) of platinum can be calculated from the charge of the adsorbed hydrogen peak ($Q_{H,ads}$) using equation (6), where

\[
Q_{H,ads} = nFA\Gamma \\
\Gamma = \frac{Q_{H,ads}}{nFA}
\]  

(6)

$n$ is the number of electrons in the half reaction, $F$ is Faraday’s constant and $A$ is the area of the electrode. Experimental surface coverage was found to be $3.3 \times 10^{-8}$ mols/cm$^2$, well over a monolayer of platinum. This result indicates that simple UPD of copper followed by RRD with platinum is not taking place, but that platinum appears to be replacing nickel atoms as well.
The above experiment was repeated for an atomically flat surface of template stripped nickel adhered to a glass surface. This technique results in flat planes of 111 nickel that can be imaged using atomic force microscopy. It also avoids issues caused by annealing nickel wire. Indeed, the platinum was able to spontaneously deposit onto the nickel surface and did not require the intermediate UPD step of copper. This is consistent with the standard reduction potential of platinum being greater than that of nickel. One would predict that there would be an electrochemical redox reaction at the surface when the nickel surface came into contact with Pt$^{2+}$ cations. The result is that platinum will continuously replace the

Figure 6.7. Cyclic voltammograms of template stripped nickel surfaces before (A) and after (B) exposure to 5 mM K$_2$PtCl$_4$ +0.1 M H$_2$SO$_4$. 
nickel until there are no longer available nickel atoms. Platinum growth can not be controlled and limited to a single monolayer.

The cyclic voltammograms for the bare nickel surface and the platinum (SD) on the nickel surface are shown in figure 6.7 A and B, respectively. Figure 6.7A shows nickel oxide film growth on the first scan, initiating at approximately 0.2V. Subsequent scans show a reduction in current from 0.2 to 1.0 V, indicating passivation of the nickel surface by the oxide layer. Results are consistent with Ni(111), while figure 6.6 A is consistent with polycrystalline nickel behavior. Figure 6.7B is consistent with the presence of platinum on the surface. There is a platinum oxide peak at ~0.4 V and the beginning of hydrogen adsorption peaks at -0.2 V.

Atomic force microscopy (AFM) was used to confirm the passivation of the nickel surface and to probe the affect of pH on the spontaneous deposition of the platinum onto the nickel surface.

Figure 6.8 depicts AFM scans after exposing the template stripped nickel to 5 mM K₂PtCl₄ at (A)  

![Figure 6.8](image)

Figure 6.8 Atomic force microscopy (AFM) images of template stripped nickel surfaces exposed to 5 mM K₂PtCl₄ at various pH values. (A) pH ~ 2.5 (B) pH ~ 4 (C) pH ~ 6.
pH ~ 2.5, (B) pH ~4 and (C) pH ~ 6. There is a decrease in coverage of platinum islands on the flat surface as the pH increases from 2.5 to 4, with very little coverage at pH ~ 6 and no coverage at pH ~8 (not shown). This result is consistent with formation of NiOx, as shown in the Pourbaix diagram (figure 6.5) for pH >6 and no applied potential. Average platinum particle size also changes with pH, suggesting the presence of oxides on certain sites over others at near neutral pH values. For a pH ~2.5, particles are small (40 ± 20 nm) and cover the majority of the nickel surface while for pH ~ 4, particles are 225 ± 50 nm and for pH ~ 6, particles are 325 ± 50 nm. The increase in particle size suggests that platinum is grouping in areas of exposed nickel surface, while other parts of the nickel surface may be passivated.

The spontaneous deposition of platinum on nickel was also explored on nickel nanoparticles. Two types of nanoparticles were used; a commercially available nickel nanoparticle and an in-lab synthesized nickel nanoparticle using a cationic surfactant method [14]. Briefly, nickel nanoparticles are formed in the presence of a surfactant, which forms micelles in solution. The size distribution of the particles is controlled by the kinetics associated with the formation of the micelles. The commercially obtained nickel particles were used to test electrochemical methods as well as used as controls for testing the removal of the surfactant from synthesized particles.

The nickel nanoparticle synthesis resulted in particles with an average size of 50 ±25 nm. This included nickel cores surrounded by a micelle structure of surfactant. The nanoparticles were placed in a furnace at 700°C for 3 hours in order to remove the surfactant micelle encapsulating them. Post furnace treatment, nanoparticles had an average diameter of 10 ± 10 nm indicating removal of the surfactant micelles surrounding the nickel nanoparticles. The particle size distribution was rather disperse in diameter due to
“clumping” upon removal of the surfactant layer. Commercially obtained nickel nanoparticles were a mixture of 5-20 nm in diameter.

Platinum was deposited by spontaneous deposition. Briefly, commercial or heat-treated nickel nanoparticles were adhered to a glassy carbon electrode using a Nafion film. A small drop of a solution of 10 mM K₂SO₄ and 0.1 M H₂SO₄ (pH < 2 to avoid nickel oxide) was placed on the electrode surface and allowed to dry. Electrodes were cycled from 0 to 0.9 V for 20 cycles in 0.1 M H₂SO₄ to expunge any remaining Pt²⁺ ions from the film prior to cycling from -0.8 to 0.8 V. Cyclic voltammograms for both the commercially purchased (A) and the synthesized nanoparticles (B) coated in platinum are given in figure 6.9. Both plots demonstrate classic, stable platinum behavior as previously described, with

![Cyclic voltammograms of platinum coated nickel nanoparticles obtained (A) commercially and (B) in lab, treated with 700 C to remove surfactant.](image)
platinum oxide peak at ~0.2 V and the onset of hydrogen reduction at -0.6 V and oxygen reduction initiating at 0.6 V.

Results presented suggest that nickel platforms are not suitable for the construction of platinum monolayers. The work function and standard reduction potential of platinum are significantly larger than the respective values for nickel. Electrochemical results suggest that platinum will replace nickel surface atoms as well as etch its way into nickel bulk atoms. In order to make nickel substrates feasible, a protective layer must be formed as a barrier between nickel and platinum.

6.4 CONCLUSIONS

This work represents some preliminary results for the fabrication of low precious metal content nanocatalysts for PEM fuel cells. We were able to successfully deposit platinum onto several nickel surfaces, including a nickel wire, template stripped nickel, and both commercial and synthesized nickel nanoparticles. There is a clear dependence of platinum deposition on pH, due to the formation of passivating nickel oxides at pH values greater than four. Issues with uncontrollable platinum deposition on nickel surfaces and recently published results have deterred authors from further study. Zhang et al. have since published a related work that focus on first protecting nickel particles with a monolayer of gold, followed by UPD/RRD with copper and platinum [15]. The gold acts as a protective layer for the nickel since its standard reduction potential is greater than the standard reduction potential for platinum. Therefore, platinum deposition could be controlled to only a single monolayer.
REFERENCES

CHAPTER 7. CONCLUSIONS AND FUTURE DIRECTIONS

This work focused on the development and application of surface electric fields to spatially control local electrochemical reactions along a surface. Gradients have been characterized using a variety of surface scanning techniques (namely, ellipsometry and optical screening). The spatial control of these systems was demonstrated and manipulated in both one and two dimensions as well as over both macro and micro scales. Surface electric fields provide inherent temporal control advantages over many other gradient generation techniques since they are only limited by mass transport and the kinetics of the employed electrochemical reactions. Spatial control can be established in a matter of seconds as opposed to minutes or even fractions of an hour. Other advantages include low cost and elimination of clean room techniques such as vapor deposition. The following conclusions and future directions can be drawn from each presented project:

**Rapid and reversible generation of a microscale pH gradient (Chapter 2):** In this section, a method to electrochemically generate and control a pH gradient along a thin surface of platinum was presented. The presence of the pH gradient was verified using a micro pH electrode scanned across the surface. Spatial control and gradient manipulation in both one and two dimensions was visualized on the macro scale using the optical screening of a pH-dependent fluorescence probe quinine. The pH gradient was reduced to a micro flow channel and spatial control was shown using mathematical processing of optical images of universal pH indicator dye. It was established that pH control can be achieved in a matter of seconds in a micro channel, demonstrating superiority over previously published microfluidic
and electrochemical devices. Mathematical simulations were also performed to illustrate that the presented electrochemically generated pH gradient was superior in time over current state of the art electrochemical techniques. Both experimental and theoretical results prove our gradient could be formed and manipulated 20 times faster than current methods. Applications of this work include a lab on chip devices, systems involving electrophoresis and isoelectric focusing, as well as a variety of systems concerning pH as a variable such as corrosion, metal deposition, polymer synthesis and metabolic and enzymatic processes.

The use of surface electric fields to spatially control the local oxidation and reduction of chemical species across a surface can be expanded to a variety of applications. In chapter 2, it was demonstrated that local H⁺ and OH⁻ concentration could be controlled by linear variations in applied potentials. In theory, this technique could be expanded to any system which has potential-dependent concentrations of species in solution. For example, in chapter 1, it was discussed that a major application of gradients is biological systems, such as chemical gradients across cell membranes. Using surface electric fields and appropriate substrates and redox species, gradients in other simple ions such as K⁺, Cl⁻, and Ca²⁺ could be generated and readily controlled for biological processes.

**Maskless electrodeposition of polymer films (Chapter 3):** This section expounds on the application of surface electric fields to spatially control electrochemical reactions along a surface. The application of potential gradients in subsequent solutions of monomers were employed to fabricate alternating bands of polymers in both one and two dimensions. Electrochemistry was used to verify polymer electrosynthesis on indium tin oxide from solutions containing one of the precursor monomers (phenol, aminophenol, or aniline). Simple two and three band structures were distinguished from one another using scanning
UV-Vis spectroscopy and optical screening methods. Ellipsometry was employed to demonstrate spatial control and estimate polymer film thickness. More complex band structures as well as substrates with two dimensional structures are also presented. The use of potential gradients for polymer film growth provides a unique method for spatial control that is inexpensive and requires no clean room techniques, providing advantages over current techniques. The only limitation is that polymers must be able to be grown under potential control and substrates of interest must be capable of supporting potential gradients. The spatial control of electrochemically synthesized polymers at the surface has numerous applications including electrochromatic devices, corrosion prevention, sensor development, and semiconductors.

Future work involving the maskless patterning of polymers would be expansion into co-polymer systems. There are a variety of unique properties that are derived when two polymers are co-synthesized; material properties are also dependent on relative concentrations of monomer units in the final structures. The use of potential gradients could be employed to generate gradients of co-polymers that encompass all possible combinations of monomers on a single sample.

Spatial control of metal and metal oxides (Chapter 4): In this section, it was demonstrated that copper could be electrodeposited with sharp boundaries on both one and two dimensions by controlling the magnitude of the electric field. Laser transmission and optical image processing were used to verify gradients in copper coverage. Simulations in two dimensional applied potential gradients are also presented. Future work would explore the boundaries between electrodeposited copper and substrate on the micro scale, as
applicable to interconnects for the electronics industry. Useful tools would include atomic force microscopy (AFM) and x-ray photon spectroscopy (XPS). Further exploration would involve the application of surface electric fields for spatially controlled metal deposition for a variety of metal ions. In particular, multi-component metal systems for high throughput processing could be created by combining two or even three metals.

A second system involving potential-dependent growth of platinum oxide films on electrodeposited platinum was also explored. Ellipsometry was used to verify platinum oxide film growth with respect to potential. Scanning ellipsometry was utilized to illustrate that potential gradients could be used to create localized platinum oxide growth. This study serves as a platform for high throughput experimental data on catalysts. Future work would focus on the passivation of platinum by oxide film growth at high positive potentials. For example, platinum oxide restricts potentials for oxygen reduction, useful in proton exchange membrane (PEM) fuel cells. Further applications include the fabrication of discrete regions of oxide bands or spots to protect the underlying platinum surface from a chemical treatment. Oxide films could then be reduced electrochemically to expose patterned platinum substrates. Both the copper electrodeposition and platinum oxide systems suggest that metal and metal oxide systems are spatially controllable by the local applied potential and applicable to more complex multi-component systems. Applications include high-throughput processing of metal/metal oxide systems as well as applications in corrosion studies, metal alloy combinatorics, catalysts, and electrochemical sensors.

Potential-controlled adsorption of DOPC on gold (Chapter 5): The idea of mask free spatial control of adsorbates on a surface was expanded in this section to spatial control
of the adsorption of a lipid, using 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) on thin gold films. Gold substrates were first characterized using cyclic voltammetry and ellipsometry to probe gold oxide film growth. Characterization of the gold surface involved ellipsometric monitoring of gold oxide film growth with respect to potential followed by the demonstration of spatial control of gold oxide film growth using scanning ellipsometry. Results suggest that applied potentials above 0.4 V (vs Ag/AgCl) should be avoided in order to prevent gold oxide film from interfering with DOPC adsorption.

Capacitance measurements were used to determine the \( pzc \) of the thin gold film with respect to the chosen electrolyte KCl. Capacitance was also found to decrease with increasing DOPC concentration, indicating DOPC adsorption on the surface. Most importantly, it was demonstrated that the adsorption of DOPC is limited to potentials near the potential of zero charge (\( pzc \)) of the electrode, as determined by the electrolyte. By applying gradients which span the \( pzc \), spatial control is achieved through localized adsorption. Ellipsometry was used to verify adsorption at potentials near the \( pzc \). Position-dependent adsorption with respect to linear potential gradients was also verified with ellipsometry. Future work includes study into high resolution control of the adsorption of DOPC for the biofunctionalization of metal electrodes. In particular, chemistries of interest include protein or macromolecule immobilization onto localized domains of adsorbed DOCP as a technique for maskless patterning. Future work will focus on “building from bottom up” techniques to fabricate stacked substrates for high throughput processing.

**Low precious metal content monolayer coated catalysts (Chapter 6):** In this final section, galvanic replacement of nickel with platinum was achieved to fabricate low precious
metal content catalysts for applications in fuel cells was presented. The advantages of using nanoparticles to reduce catalyst loading was discussed. Platinum monolayers on nickel nanoparticles were selected as key players; platinum for its high exchange current and nickel for its low cost. Cyclic voltammetry was used to show the characteristic behavior of bare nickel and platinum substrates. Platinum were deposited on template stripped nickel substrates and characterized using atomic force microscopy (AFM) and cyclic voltammetry. The pH dependence on nickel oxide film growth as a passivating layer to platinum film growth was illustrated. Platinum was successfully adsorbed onto synthesized and commercially available nickel nanoparticles and characteristic electrochemical platinum behavior is shown. On all surfaces, platinum adsorbance was not restricted to single monolayers, as expected, but would replace bulk nickel atoms as well. Further work needs to be done to protect nickel nanoparticles from entire redox replacement of platinum. Future work would focus on compositional measurements of the platinum coated nickel nanoparticles to check for the presence of Ni-Pt alloys.
APPENDIX: NULL ELLIPSOMETRY

This appendix presents the basics of the ellipsometry technique for measuring film thickness on a surface. Ellipsometry measures the changes in the state of polarization of light upon reflection from the surface of interest. Wavelengths used to probe the surface are on the order of 500 nm and the only requirement is that samples reflect laser light. Due to its simple nature, ellipsometry is an ideal tool for surface analysis to probe interfaces. Ideal cases can measure thin films to within Å accuracy.

Maxwell’s theory provides the foundation for the properties of light as electromagnetic waves as applicable to ellipsometry. Material properties are described by the refractive index \( n + ik \). An electromagnetic wave is composed of an electric field \( E \) and a magnetic field \( B \), which are mutually perpendicular to each other as well as the propagation direction given by the wave vector \( k \). The states of polarization are classified with respect to one period trace of the electrical field vector. Linearly polarized light implies the electrical field vector is oscillating within a plane while elliptically polarized light suggests the trace of the electric field vector is an ellipse. Mathematically, the polarization of two linearly polarized light waves is

\[
\mathbf{E}(r, t) = \begin{pmatrix} |E_p| \cos(2\pi vt - k \cdot r + \delta_p) \\ |E_s| \cos(2\pi vt - k \cdot r + \delta_s) \end{pmatrix}
\]

(1)

where \( |E_p| \) and \( |E_s| \) are the amplitudes, \( \delta_p \) and \( \delta_s \) are the phase angles, \( |k| = 2\pi/\lambda \) is the magnitude of the wave vector and \( v \) in the frequency. Only the phases and the amplitudes are required for complete representation of the state of polarization and the result is called the Jones vector.
The state of polarization is linear if $\delta_p - \delta_s = 0$ or $\pi$, is elliptical if $\delta_p \neq \delta_s$ and $|E_p| \neq |E_s|$, and circular for the special case where $\delta_p - \delta_s = \pi/2$ and $|E_p| = |E_s|$.

![Figure A1. A schematic of p and s polarized light.](image)

In ellipsometry, light with a well defined state of polarization is incident upon a sample. The reflected light usually differs in its state of polarization; it is these changes that are measured and quantified in ellipsometry. The mathematical definitions of ellipsometric parameters are defined in reference to the plane of incidence, as defined by the propagation direction of the beam and the normal to the reflecting surface. Light with an electric field vector oscillating within the plane of incidence is labeled p-polarized light and light oscillating perpendicular to the plane is defined as s-polarized light as shown in figure A1. Upon reflection, both s and p light remain linearly polarized. The incident and reflected light can also be defined by Jones vectors:
The two quantities $\Psi$ and $\Delta$ are the parameters used to describe the changes in the state of polarization.

$$\Delta = (\delta_p^r - \delta_s^r) - (\delta_p^i - \delta_s^i) \quad (4)$$

$$\Psi = \frac{|E_p'|/|E_p|}{|E_s'|/|E_s|} \quad (5)$$

**Figure A2.** Ellipsometer in a PCSA-configuration.

The layout of a typical ellipsometer is given in figure A2. The main components are a polarizer (P) which produces linearly polarized light, a compensator (C) which introduces a defined phase retardation of one of the field components with respect to the orthogonal one, the sample (S), the analyzer (A) and a detector. This is referred to as the PCSA-
configuration. This setup permits the determination of the unknown ellipsometric angles and can be operated in various modes. Each optical component modifies the state of polarization. Linear polarized light exits the polarizer then is rotated in the coordinate system of the compensator. When light exits the compensator, the light is circularly polarized. Light is reflected off of the sample and is polarized elliptically. Specifically, for null-ellipsometry, the setting of the optical components is chosen such that the light at the detector vanishes. The null settings of the polarizer \( P_0 \) and the analyzer \( A_0 \) can be linked to the quantities \( \Delta \) and \( \Psi \) by the following equation
\[
\tan \Psi e^{i\Delta} = \frac{r_p}{r_s} = \pm \tan A_0 \exp[i(\pm 2P_0 + \frac{\pi}{2})]
\] (6)
where \( r_p \) and \( r_s \) are the unknown reflectivity coefficients.

Ellipsometry is not an indirect method in that the measured \( \Delta \) and \( \Psi \) cannot be directly converted into the material properties (i.e. refractive index and thickness parameters). Direct conversion is only possible for the very simple theoretical case of isotropic, homogeneous and infinitely thick films. In all other cases, a layer model must be employed which first considers the optical constants and thickness parameters of each separate layer in the corresponding sequence of incidence. A least-squares minimization technique is used, in which the unknown optical constants and/or thickness parameters are varied. Values of \( \Delta \) and \( \Psi \) are calculated using the Fresnel equations; calculations of optical constants and/or thickness are continued until modeled values of \( \Delta \) and \( \Psi \) best fit experimentally determined values.

Assume that a film with thickness \( d \) is formed on a substrate in ambient conditions and that all are homogeneous and optically isotropic with refractive indices \( N_0 \), \( N_1 \), and \( N_2 \).
for the ambient, film, and substrate, respectively. This three-layer model can be visualized in Figure A3, where $\Theta_1$, $\Theta_2$ and $\Theta_3$ are the angles of refraction in ambient, film and substrate.

When the incident wave first meets the ambient-film interface, a portion of the wave is reflected while a portion is transmitted through the film. The Fresnel reflection coefficients for both p and s light at the ambient-film and film-substrate interfaces will be denoted $r_{01}$ and $r_{12}$, respectively. The presented coefficients can be derived using Snell’s law ($N_0\sin\Theta_0 = N_1\sin\Theta_1$).
\[
\begin{align*}
    r_{01p} &= \frac{N_1 \cos \Theta_0 - N_0 \cos \Theta_1}{N_1 \cos \Theta_0 + N_0 \cos \Theta_1} \\
    r_{12p} &= \frac{N_2 \cos \Theta_1 - N_1 \cos \Theta_2}{N_2 \cos \Theta_1 + N_1 \cos \Theta_2} \\
    r_{01s} &= \frac{N_0 \cos \Theta_0 - N_1 \cos \Theta_1}{N_0 \cos \Theta_0 + N_1 \cos \Theta_1} \\
    r_{12s} &= \frac{N_1 \cos \Theta_1 - N_2 \cos \Theta_2}{N_1 \cos \Theta_1 + N_2 \cos \Theta_2}
\end{align*}
\]

Information about the polarization of light can be retrieved such that

\[
\begin{align*}
    R_p &= \frac{r_{01p} + r_{12p}e^{-j2\beta}}{1 + r_{01p}r_{12p}e^{-j2\beta}} \\
    R_s &= \frac{r_{01s} + r_{12s}e^{-j2\beta}}{1 + r_{01s}r_{12s}e^{-j2\beta}}
\end{align*}
\]

where \( j \) is used to denote an imaginary number \( (\sqrt{-1}) \) and \( \beta \) is the phase change that the reflected wave inside the film experiences as it transverses the film between boundaries given by

\[
\beta = 2\pi \left( \frac{1}{\lambda} \right) \left( N_1^2 - N_0^2 \sin^2 \Theta_0 \right)^{1/2}
\]

and \( \lambda \) is the wavelength of light used.
ACKNOWLEDGEMENTS

First and foremost, I would like to thank Dr. Hillier for all of his support and guidance along the way. Most importantly, I would like to thank him for always believing that I can do it, even when I didn’t think that I could.

I would also like to thank my husband Kyle for providing support through the entire process of earning my degree. He was there to celebrate the triumphs and to encourage me on the failures. Moving to Iowa was the greatest thing anyone has ever done for me and I am eternally grateful for his sacrifices.

My friends and family have also been a huge support. I would like to thank my parents for encouraging me and helping me find my way in the world. To my dad, thank you for giving me a goal for which to strive. To my mom, thank you for pointing me in the direction of science and lending a sympathetic ear along the way. My brother, my buddy, thank you for always listening to me on my struggles – I hope you find success in your science endeavors. Also, to my partner in crime Kathy, thank you for being there on a day to day basis through it all. Most importantly, thank you for providing the necessary distractions to get me through the rough patches and always making me laugh.

I would also like to thank my undergraduate advisor Prof. Mary Walczak for being a great mentor, both in and out of the laboratory. Without you Mary, I wouldn’t have found my passion for surface chemistry and I certainly wouldn’t have come to Iowa State.

I would also like to express my appreciation for my fellow members of the Hillier group – Chang-Hoon, Bipin, Yi, Suhda and Kousik for all the useful discussions. In particular, thank you to Chang-Hoon and Bipin for always having time to talk.
To my fellow chemistry students, thanks for all the great times. And finally, I would like to also thank all of the professors, secretaries and other members of the support staff at Iowa State University for helping make my time at here memorable.