In compliance with the
Canadian Privacy Legislation
some supporting forms
may have been removed from
this dissertation.

While these forms may be included
in the document page count,
their removal does not represent
any loss of content from the dissertation.

**Electrochemical Characterization of Alkyl
Modified Si(111) by Varying Organic Functional
Groups**

© 2003

Dalbinder Colman

All Rights Reserved

National Library
of Canada

Bibliothèque nationale
du Canada

Acquisitions and
Bibliographic Services

Acquisitions et
services bibliographiques

395 Wellington Street
Ottawa ON K1A 0N4
Canada

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

ISBN: 0-612-88767-7

Our file Notre référence

ISBN: 0-612-88767-7

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

Canada

The undersigned hereby recommend to
the Faculty of Graduate Studies and Research
acceptance of the thesis

**Electrochemical Modification of Alkyl Modified Si(111)
by Varying Organic Functional Groups**

Submitted by

Dalbinder Colman, B.Sc.

in partial fulfilment of the requirements
for the degree of Masters of Science

Chair, Department of Chemistry

D. Wayner, Thesis Co-Supervisor

R. Crutchley, Thesis Co-Supervisor

Carleton University

Abstract

The electrochemical properties of alkyl modified Si(111) are examined in both aqueous and organic solvents. In particular, H-Si, undecylenic acid, N-Hydroxysuccinimide, and aromatic hydrazides are tested. Capacitive properties, impedance measurements and band bending are correlated with dipole characteristics of the terminal group. The amount of band bending is demonstrated to be dependent on the polarity of a substance. A visible decrease in band bending is found with monolayers that withdraw electron density away from the electrode. These measurements are confirmed using solid-state Kelvin probe data. Impedance Measurements evaluated at flatband enable the determination of defects as a function of modification and surface treatment. It is found that defects increase with subsequent surface treatments. The insulating capacity of the monolayer is also examined utilizing impedance measurements.

Acknowledgments

A culmination of time, particularly a research project, into ninety odd pages leaves much of a story left untold. Several people have contributed to the completion of this work. I offer my heartfelt gratitude to my advisor Dan Wayner, for the tremendous opportunity to conduct my research at the National Research Council. Thank you so much for your advice and guidance. It has forced me to set higher standards for my work. I would also sincerely like to thank Greg Lopinski who has offered me advice and instruction with a good dose of humour.

To the Langlois family I offer my appreciation, love and friendship. I have found a home amongst your family. You've been surrogates for me when I could not be near to my own.

I thank my family, who are so precious to me, for all their love and support. Particular my father, who taught me to enjoy the simple pleasures of life. Most importantly to my husband, I cannot express my gratitude for your support, patience and love during this time.

Table of Contents

1	Introduction.....	1
1.1	Overview:.....	1
1.1.1	A Brief Review of Semiconductor Electrochemistry:	2
1.1.2	The Energy Band Model:.....	2
1.1.3	Charge Carriers & The Fermi Level:	5
1.1.4	Doping:	6
1.2	Physical Properties of Si:	8
1.3	The Semiconductor/Electrolyte Interface:	10
1.3.1	The Space Charge Layer:.....	11
1.3.2	Helmholtz Layer:	12
1.3.3	The Guoy Layer:.....	12
1.3.4	Depletion & Inversion:	13
1.3.5	Accumulation & Flatband:.....	15
1.3.6	Surface states:	16
1.4	Hydrogen terminated Si(111)	17
1.4.1	Stability of H-Si(111)	19
1.5	Alkylation of H-Si(111):.....	20
1.5.1	Alternate means of creating Si-C bonds	23
1.5.2	Subsequent Modification of Alkyl Monolayers on Si(111):.....	24
1.6	Electrochemistry of Alkyl modified Si(111):	25
2	Experimental.....	28
2.1	Sample Preparation	28
2.2	Ellipsometric Measurements.....	30
2.3	Attenuated Total Reflection (ATR) Fourier Transform Infrared Spectroscopy (FTIR):	31

2.4	Electrochemical Measurements	33
2.5	The Kelvin Probe	35
3	Results & Discussion: Electrochemical Characterization of Modified Si(111) in an Aqueous Environment	37
3.1	Native Oxide	37
3.2	Hydrogen terminated Si(111):	40
3.3	Undecylenic Acid modified Si(111)	48
3.4	N-Hydroxysuccinimide modified Si(111):	58
3.5	Phenylhydrazine Modified Si(111).....	62
3.6	Nitrophenylhydrazine Modified Si(111).....	66
3.7	Dinitrophenylhydrazine Modified Si(111)	71
3.8	Substrate Quality and Surface States	74
4	Results & Discussion: A Study of Modified Si(111) in ACN/0.1 M TBAPF ₆	80
4.1	UDA modified Si(111):	80
4.2	NHS Modified Si(111).....	85
4.3	Phenylhydrazide Modified Si(111).....	89
4.4	Nitrophenylhydrazide Modified Si(111).....	91
4.5	Electrical Properties of modified Silicon(111) in Acetonitrile	95
5	Conclusions:.....	96
	References.....	99

Index of Figures

Figure 1. Band Diagram for an Intrinsic Semiconductor.....	4
Figure 2. Band Diagram for an n-type Semiconductor.....	7
Figure 3 Silicon Unit Cell.....	8
Figure 4. Regions of Charge at the Semiconductor/Electrolyte Interface	10
Figure 5 Modes of Band Bending for an n-type Semiconductor.....	15
Figure 6. Reaction Scheme for the H-Si(111) Surface and Subsequent Modifications....	29
Figure 7. General Schematic for Ellipsometric Spectrometer	31
Figure 8. Kelvin Probe Schematic at Open Circuit.....	35
Figure 9. Kelvin Probe Schematic at Closed Circuit	36
Figure 10. Capacitance Curves for Native Oxide on Si(111) in 0.1 M H ₂ SO ₄ Measured in Accumulation. Fits are not shown	39
Figure 11. Circuit Model for the Solution/Semiconductor Interface.....	40
Figure 12. Capacitance Curves for Hydrogen terminated Si(111) in 0.1 M H ₂ SO ₄ Measured in Accumulation. Fits are not shown.....	43
Figure 13. Complex Impedance plot for the Si-H surface in 0.1M H ₂ SO ₄ , where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element. Measurements are taken 0.4V in accumulation.....	44
Figure 14. Simple RC circuit model representing the Dashed Lines in all Impedance Arcs	45
Figure 15. Simple CPE circuit model representing the Solid Lines in all Impedance Arcs	46
Figure 16. FTIR Spectrum for UDA Modified Si(111).....	48

Figure 17. Mott-Schottky plot for Undecylenic Acid in 0.1M H ₂ SO ₄ Measured in the Depletion Region at 50 kHz. Fits are not shown.	51
Figure 18. Equivalent Circuit Model for an Alkyl Modified Si(111) Electrode	52
Figure 19. Complex Impedance plot for the UDA surface in 0.1M H ₂ SO ₄ , where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element. Measurements are taken 0.35 V in accumulation	53
Figure 20. Band Representation Kelvin Probe Measurements	56
Figure 21. Surface Voltage for independent samples of UDA modified Si(111) in Dark and under Illumination. Higher Plateaus are Measured in the Dark and Lower Values Correspond with Light.	57
Figure 22. FTIR Spectrum of NHS modified Si(111)	58
Figure 23. Complex Impedance plot for the NHS surface in 0.1M H ₂ SO ₄ , where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element. Measurements are taken 0.3V in accumulation	61
Figure 24. Surface Voltage for PH modified Si(111) in Dark and under Illumination. Higher Plateaus are Measured in the Dark and Lower Values Correspond with Light.	64
Figure 25. Complex Impedance plot for the PH surface in 0.1M H ₂ SO ₄ , where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element. Measurements are taken 0.3V in accumulation	66
Figure 26. FTIR Spectrum of NPH.....	66

Figure 27. Surface Voltage for NPH modified Si(111) in Dark and under Illumination. Higher Plateaus are Measured in the Dark and Lower Values Correspond with Light.	70
Figure 28. Complex Impedance plot for the NPH surface in 0.1M H ₂ SO ₄ , where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element. Measurements are taken 0.3V in accumulation	71
Figure 29. Surface Voltage for DN PH modified Si(111) in Dark and under Illumination. Higher Plateaus are Measured in the Dark and Lower Values Correspond with Light.	73
Figure 30. Complex Impedance plot for the NPH surface in 0.1M H ₂ SO ₄ , where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element. Measurements are taken 0.35V in accumulation. Where $R_{p1} = 320$, T_{c1} $= 4.63E-6$, $C_1 = 0.021$ uF are the values for the first arc and $R_{p2} = 780$, $T_{c2} = 1.28E-$ 3 , $C_2 = 2.35uF$ represent the second arc.	74
Figure 31. Capacitance curves of the UDA, NHS, and DNPH measured in 0.1 M H ₂ SO ₄ . Fits not shown.	75
Figure 32. Capacitance curves of the UDA, NHS, and DNPH. In order of increasing surface state Capacitance.	76
Figure 33. Complex Impedance Arcs for PH in 0.1M H ₂ SO ₄ at E_{fb} where the Solid Line Represents the Fit of a simple RC circuit.	77
Figure 34. Capacitance curves measured in Accumulation of UDA modified Si (111) in ACN/0.1 M TBAPF ₆ . Fits are not shown.	83

Figure 35. Complex Impedance Arcs for UDA in 0.1M ACN/0.1 M TBAPF ₆ 0.4V in accumulation, where the Solid Line Represents the Fit of a simple RC circuit.	84
Figure 36. Capacitance curves measured in Accumulation of NHS modified Si (111) in ACN/0.1 M TBAPF ₆ . Fits are not shown.	88
Figure 37. Capacitance curves measured in Accumulation of PH modified Si (111) in ACN/0.1 M TBAPF ₆ . Fits are not shown.	90
Figure 38. Complex Impedance Arcs for NPH in 0.1M ACN/0.1 M TBAPF ₆ 0.4V in accumulation, where the Solid Line Represents the Fit of a simple RC circuit.	93
Figure 39. Capacitance curves measured in Accumulation of NPH modified Si (111) in ACN/0.1 M TBAPF ₆ . Fits are not shown	94

Index of Tables

Table 1. Physical Characterstics of Silicon.....	9
Table 2. Rectangular form of Impedance Circuit Elements.	34
Table 3. Flatband, OCP potential and Dopant Densities for Native Oxide measured in 0.1M H ₂ SO ₄	38
Table 4. Flatband potential, OCP, and Dopant Densities for Hydrogen terminated Si(111) measured in 0.1M H ₂ SO ₄	41
Table 5. Flatband potential, OCP, and Dopant Densities the UDA Modified Si(111) measured in 0.1M H ₂ SO ₄	50
Table 6. Total and Monolayer Capacitance, Effective dielectric and Thicknesses for UDA modified Si(111) in 0.1 M H ₂ SO ₄	52
Table 7. Flatband potential, OCP, and Dopant Densities the NHS Modified Si(111) measured in 0.1M H ₂ SO ₄	59
Table 8. Monolayer Capacitance, Effective Dielectric constant, and Monolayer thickness of N-Hydroxysuccinimide modified Si(111) measured in 0.1M H ₂ SO ₄	60
Table 9. Surface voltage measurements for N-Hydroxysuccinimide modified Si(111) in 0.1M H ₂ SO ₄	61
Table 10. Flatband potential, OCP, and Dopant Densities the PH Modified Si(111) measured in 0.1M H ₂ SO ₄	62
Table 11. Monolayer Capacitance, Effective Dielectric constant, and Monolayer thicknesses for PH modified Si(111) measured in 0.1M H ₂ SO ₄	65
Table 12. Flatband potential, OCP, and Dopant Densities the NPH Modified Si(111) measured in 0.1M H ₂ SO ₄	68

Table 13. Monolayer Capacitance, Effective Dielectric constant, and Monolayer thickness for Nitrophenylhydrazide modified Si(111) measured in 0.1M H ₂ SO ₄	69
Table 14. Flatband potential, OCP, and Dopant Densities the DNPH Modified Si(111) measured in 0.1M H ₂ SO ₄	72
Table 15. Monolayer Capacitance, Effective Dielectric constant, and Monolayer thickness of Dinitrophenylhydrazide modified Si(111) measured in 0.1M H ₂ SO ₄ .	72
Table 16. The Number of Surface states, Monolayer & Surface State Capacitance for Modified Si(111).....	78
Table 17. Summary of Electrical Properties of modified Silicon(111) in Sulfuric Acid	78
Table 18. Flatband potential, OCP, and Dopant Densities for UDA terminated Si(111) measured in ACN/0.1M TBAPF ₆	81
Table 19. Capacitance, Effective dielectric and Thicknesses for UDA modified Si(111)	83
Table 20. Flatband potential, OCP, and Dopant Densities for NHS terminated Si(111) measured in ACN/0.1M TBAPF ₆	86
Table 21. Capacitance, Effective dielectric and thicknesses for NHS modified Si(111) .	88
Table 22. Flatband potential, OCP, and Dopant Densities for PH terminated Si(111) measured in ACN/0.1M TBAPF ₆	89
Table 23. Flatband potential, OCP, and Dopant Densities for NPH terminated Si(111) measured in ACN/0.1M TBAPF ₆	92
Table 24. Summary of Electrical Properties of modified Silicon(111) in Acetonitrile	95

List of Acronyms

ω	= Angular Frequency
ACN	= Acetonitrile
AFM	= Atomic Force Microscopy
ATR	= Attenuated Total Reflectance
C	= Capacitance
C_H	= Helmholtz Capacitance
C_m	= Monolayer Capacitance
CPE	= Constant Phase Element
C_{SC}	= Space-Charge Capacitance
DNPH	= 2, 4 - Dinitrophenylhydrazine
E_{fb}	= Flatband Potential Energy
FTIR	= Fourier Transform Spectroscopy
HREELS	= High Resolution Electron Energy Loss Spectroscopy
L	= Inductor
N_d	= Dopant Density
NHS	= N-Hydroxysuccinimide
NPH	= 4-Nitrophenylhydrazine
OCP	= Open Circuit Potential
PED	= Photoelectron Diffraction
R	= Resistor
R_p	= Parallel Resistance
R_s	= Series Resistance

SCE	= Saturated Calomel Electrode
STM	= Scanning Tunneling Microscopy
TBAPF ₆	= Tetrabutylammonium Hexafluorophosphate
T _c , τ	= Time Constant
TCE	= Trichloroethane
THF	= Tetrahydrofuran
UDA	= Undecylenic Acid
XPS	= X-ray Photoemission Spectroscopy
Z	= Impedance

1 Introduction

1.1 Overview:

Microelectronics play a strong role in everyone's day-to-day activities. Over the past century, society's dependence on technology has grown dramatically. In particular, a predominant trend towards miniaturization has become evident. Small hand held electronics are becoming the norm of late. Electronic devices are rapidly decreasing in size. The components of these devices are getting smaller, but not at the same speed. This is because the semiconductor industry is reaching its limit for technological innovation. The physical restrictions of silicon technology will be met in the near future. This curbs the variety and quality of the electronics available. As a result the scientific community has witnessed a push towards research in molecular electronics.

Molecular electronics is indeed a general term for a very broad area of research. Recent reviews by Vilan *et al.* and Mark Ratner provide a comprehensive introduction to the topic.^{1,2} It seeks to replace conventional electrical components with molecules that perform similar functions. If this exploration is successful, the implications are far reaching. Computer chips will become smaller and faster. There is also the possibility of using the functionality of molecules for biomedical research. Many possible scenarios exist.

Research in molecular electronics has stemmed from the computer industry and its need to have smaller system components. A device built with molecules would be a thousand times smaller than silicon-based device, which may result in a faster processing time. The cost of production of electronic devices would likely decrease with size as well.

The combination of using less material along with the increased density of components translates into reduced manufacturing costs.

In order for research to move forward, fundamental scientific questions need further examination. Issues such as how molecular geometry affects charge transport or the effect of impurities on electrical measurements still need to be addressed.^{1,2}

The critical processes involved in molecular electronics are charge injection and charge transport. The electrochemical properties of a metal/molecular or semiconductor/molecular system are key in determining whether a given system is appropriate as an electrical component.

Scientists have developed several different synthetic approaches to producing semiconductor electrodes modified with molecular systems. In order to correctly interpret physical measurements of a semiconductor modified surface, a grasp of semiconductor electrochemistry is required.

1.1.1 A Brief Review of Semiconductor Electrochemistry:

Understanding the energetic behaviour of a semiconductor electrode requires knowledge of the Energy Band Model. Because silicon is used extensively, it is focus of the experimental observations that follow. The electrochemistry of silicon will be discussed in general terms that can readily apply to other semiconductors.

1.1.2 The Energy Band Model:

An energy band model for a metal would show the valence band partially submerged in the conduction band. There is little or theoretically no barrier to electron

transfer. That's is what makes a metal a good conductor. An insulator in contrast requires a large amount of energy to move an electron from the valence to conduction band because it has a large band gap. Semiconductors are the bridge between these two extremes. (See Figure 1.)

A single atom of silicon has ten of its fourteen electrons tightly bound to its core. The remaining four valence electrons, are free to occupy four of the eight remaining energy states. In a semiconductor, atoms could maintain separate and identical energy states if they are non-interacting or far enough apart. A semiconductor cannot be treated as a single atom by virtue of its connectivity. They are not discrete molecules, but rather you have a network of atoms. If a given number of silicon atoms come into contact, as in crystalline silicon, it is reasonable to expect an adjustment in the energy levels of the valence electrons. Molecular orbital theory states that an energy level that exists between two atoms splits into many closely packed levels in a network solid.⁵ In accordance to the Pauli exclusion principle, the energy states of identical overlapping electronic orbitals cannot be equal. A given number of Si atoms in a crystal will combine, half becoming lower in energy while the other half is raised in energy.³ Since the atoms are almost identical in term of energy states they form a continuum or band. In particular, the valence and conduction bands are formed. For example N isolated Si atoms could combine (making $6N$ p-states, $2N$ s-states) creating $4N$ allowed states in the conduction and valence bands.³ A forbidden region known as the band gap separates the bands.

The free electron model has been used to explain the photoelectric effect for metals. The model assumes that electrons in a metal are free to move within the bounds of given potentials. The minimum energy required to remove an electron to vacuum is the

work function of the material. If the electron is not bound (free electrons), a continuous energy region is created. If the electrons are strongly bound (electrons in the potential field of one ion), sharp energy levels are formed. If the electron moves in a periodic potential field (as in a solid) energy bands are created.⁴ This is the case for atoms in a semiconductor. The analysis of periodic potentials is required to find energy levels in a semiconductor. This is how bands and band gaps are defined. The behavior of electrons at the top and bottom of such a band is similar to that of a free electron. However, the electrons are affected by the presence of the periodic potential. The width of the band gap depends on the strength of the chemical bonds of the solid. The positions of the edges of the valence and conduction band on an energy scale also contribute to the electrochemical characteristics of a semiconductor.

Figure 1. Band Diagram for an Intrinsic Semiconductor

Electrons will tend to migrate toward the region of lower energy. Since the valence band has $4N$ allowed states and there are $4N$ electrons, the valence band will be almost completely filled.

It is important to note that unlike isolated Si atoms, the electrons in a crystal are free to move about. They are not connected to any one particular atom. However, it is typical that four electrons are found shared among an atom and its nearest neighbours. In an intrinsic (undoped) semiconductor (depicted in Figure 1 where the dashed line is the fermi) the number of holes and electrons are equal. At 0 K the valence band is completely filled and conduction band is empty. At room temperature the conductivity is still very small. A Si atom has 5×10^{22} atoms/cm³. Only one out of 10^{13} bonds per cm³ is broken at room temperature.⁴

1.1.3 Charge Carriers & The Fermi Level:

Once a clear image of energetic states has been formed, knowledge of the occupiers of these states is also needed to understand semiconductor electrochemical behaviour. The most commonly known form of charge carrier is an electron. Excitation of valence band electrons into the conduction band creates carriers. This may happen via thermal excitation, doping, or photo-excitation. Just as important, a charge carrier is the absence of an electron, otherwise known as a hole. A hole is an empty level that is also considered to be a carrier.

The Fermi level is a fundamental concept in understanding semiconductor electrochemistry. It is the energy at which the probability of an energy level being occupied is precisely one-half.⁴ The odds of occupancy increase moving down the energy scale, beneath the Fermi level and decrease above it. The Fermi level can also be thought of as the electrochemical potential of an electron in the semiconductor. The band gap region of a semiconductor is considered a forbidden region. There should be no states in

the gap. If some impurity or adsorbed species is situated at an energy level aligned with the Fermi level, it can become fixed. It should also be understood that the Fermi level does not really exist. It only serves as a reference point. It is more of an indicator that provides information about the doping level and the nature of the semiconductor. An applied potential affects the position of the Fermi level. The level shifts in relation to the sign of the applied voltage. This external field alters the relative occupancy of the valence and conduction bands.

1.1.4 Doping:

It is important to note the difference between a perfect crystal and a semiconductor with defects. A perfect crystal has a fully occupied valence band. This means there is no charge mobility. The band gap is large enough to discourage free movement of charge.

A semiconductor of high crystallinity and limited impurities is known as an intrinsic semiconductor. Impurities in a crystal often create localized energy levels. Such impurities can also lead to the creation of carriers in the conduction or valence band. The Fermi level of an intrinsic semiconductor is approximately at midgap. This is a condition of the Fermi-Dirac distribution function.⁵

$$F(E) = (1 + \exp^{[(E-E_f)/kT]})^{-1} \quad \text{Equation 1}$$

Since the valence band is almost entirely occupied, the distribution function goes to one. The conduction band is virtually empty so the function approaches zero.

Deliberate introduction of an impurity, specifically electron donors or acceptors, is known as doping. Generally, dopants are introduced just below the conduction band or just above the valence band. A group V element like phosphorous has five valence electrons. Phosphorous will take the place of a silicon atom in the bond structure with one electron left over. The electron is only weakly bound to the donor site. Phosphorous has an energy level just beneath the conduction band edge that facilitates the donation charge to the conduction band. Figure 2 shows an n-type semiconductor. At room temperature this electron is readily free to wander the lattice structure. By analogy, group III elements are electron acceptors, and create a mobile hole. Semiconductors doped with electrons are called n-type semiconductors since electrons are the majority carrier. (The most abundant charge carrier in a semiconductor). Similarly, acceptors are called p-type semiconductors and have holes as the majority carrier. Doping levels in silicon can range over several orders of magnitude from 10^{15} - 10^{19} .⁵ Depending on the dopant and concentration, the Fermi level can shift to within 0.1eV of either band edge.⁵ The purpose of doping is to increase the conductivities of wide band gap semiconductors.

Figure 2. Band Diagram for an n-type Semiconductor

Some mention of band bending should be made to show an accurate picture of the behaviour of a semiconductor. This topic is discussed further in section 1.3

Conduction and valence band edges are fixed in band diagrams. When a voltage is applied to a working silicon electrode, the electrode will donate or accept electrons depending on its doping. This phenomenon is called band bending. A physical representation is depicted in Figure 4. Some inherent band bending may exist due to a dipole on the surface and interactions that push the semiconductor to accept or donate charge.⁵ A semiconductor is said to be in accumulation when it has excess majority carriers, and is depleted when the minority carrier dominates. A semiconductor is said to be in inversion when under depletion conditions the density of minority carriers near the surface exceeds that of the bulk majority.

1.2 Physical Properties of Si:

Silicon is a main component of microelectronic circuits today. As a result it has been extensively characterized. It has an intrinsic conductivity of $4.3 \times 10^{-6} \text{ ohms}^{-1} \text{ cm}^{-1}$ and a band gap of 1.12 eV at 300K. The diamond crystal structure is due to the Silicon's tetrahedral coordination. Surface characteristics depend largely on the orientation of the crystal. Physical characteristics (below) and the structure of Si unit cell (adjacent) are shown.

Figure 3 Silicon Unit Cell

Number of Si atoms (cm^{-3})	5×10^{22}
Atomic Weight	28.09
Crystal structure	Diamond
Density (g/cm^3)	2.328
Dielectric Constant	11.9
Density of states in the conduction band (cm^{-3})	2.8×10^{19}
Density of states in the valence band (cm^{-3})	1.04×10^{19}
Band gap at 300K (eV)	1.12
Intrinsic Carrier Concentration (cm^{-3})	1.45×10^{10}
Resistivity ($\Omega\text{-cm}$)	2.3×10^5
Lattice Constant Å	5.43

Table 1. Physical Characteristics of Silicon

The crystal structure of silicon can be described by examining its three-dimensional unit cell. The simple cubic cell has an atom positioned at each corner. Single crystals commonly used in device processing are oriented such that the Si(111) and Si(100) crystal planes are the structure on the top of a wafer. These provide the Miller indices for any given plane of atoms. The numbers in brackets provide x, y, and z Cartesian coordinates. In Figure 3, the unit cell above, the (111) surface would be represented by slicing a section from one corner to the opposite diagonal corner. The silicon (100) surface is the plane represented by moving one unit in the direction of the x axis.

Because of its extensive use in the electronics industry and its physical properties, silicon will be the only semiconductor subsequently examined. The Si(111) plane in particular will be studied.

1.3 The Semiconductor/Electrolyte Interface:

When a semiconductor and electrolyte solution are brought into contact with one another an equilibrium process occurs. The Fermi level and redox potential must be equal at the interface. These two concepts are analogous. If the Fermi level is higher than the redox potential, electrons will flow into the solution. The contrary occurs when the Fermi level is lower than the electrolyte potential. The semiconductor/electrolyte interface can be broken up into roughly three areas of interest: the Space-charge layer, the Helmholtz layer and the Guoy-Chapman layer.

Figure 4. Regions of Charge at the Semiconductor/Electrolyte Interface

1.3.1 The Space Charge Layer:

This region of charge occurs due to carriers moving in and out of the semiconductor. Unlike a metal, the electrons are not on the surface. The space charge layer can be a result of charged impurities, adsorbed ions, or the simple accumulation of free charge. The electric field of a solution is felt within some distance of the semiconductor. Fixed charges at the surface can trap an electron or hole rendering it immobile whereas the rest of the charge in the semiconductor is free to move in response to an applied field.

Electron transfer from the bulk of the semiconductor to the surface is negligible. The amount of charge transferred from the bulk, corresponds to approximately 10^{12} cm^{-2} or less.⁵ In contrast, the Helmholtz region has charge on the order of 10^{15} cm^{-2} . As a result, it is clear that any potential drop will occur in the space charge layer. This potential drop is known as band bending.

The magnitude of the band bending is either inherent or a result of an applied potential. It is important to note that it is the Fermi level that changes with the applied potential and not the conduction and valence bands, which are fixed. Similarly, the edges that extend into the bulk, away from the space charge region, are subject to an applied potential and bend accordingly.

When a semiconductor has no excess charge, the space charge region ceases to exist. The voltage at which this occurs is known as the flatband potential (E_{fb} or V_{fb}). The E_{fb} connects the Fermi level to the redox potential. Band bending can be quantified by the following equation.

$$V_{fb} = V_{measured} - V_{spacecharge} \quad \text{Equation 2}$$

Three different scenarios exist when applying a potential to a semiconductor. The first case is when the applied potential flattens the bands. Applied potential can also cause the space-charge layer to be occupied with majority carriers or depleted of them.

1.3.2 Helmholtz Layer:

The innermost layer is the electrical double layer. Ions adsorbed on the surface of the electrode produce the inner Helmholtz layer. Solvated ions that cannot approach the electrode directly create the outer Helmholtz plane. The potential drop in the solution that counteracts the space charge region occurs almost entirely in the Helmholtz plane. The size of the double layer is largely dependent on the type/strength of the adsorption/desorption process. The resulting structure is very similar to a capacitor.

1.3.3 The Guoy Layer:

The Guoy layer describes charge due to an excess of either positive or negative free ions. These ions are attracted to the Helmholtz layer. The ions gather in this region to negate any electric field present that the Helmholtz plane has not compensated for. Quantitatively, this area of charge alone could not compensate for the charge on the electrode. It provides the bulk diffuse ions to balance the field from the electrode. In reality, in a concentrated solution, the Guoy layer is extremely thin.³ The layer virtually disappears as the Helmholtz layer assimilates the charge. In high concentrations, ions are more readily able to compensate for charge in the space charge region.

1.3.4 Depletion & Inversion:

When the semiconductor is exhausted of majority carriers it is said to be in depletion. In the case of an n-type semiconductor this would imply that the surface region has a positive charge on it. For an n-type semiconductor this occurs when a positive potential w.r.t. the flatband is applied to the electrode. The depletion layer has no mobile carriers. The dopant atoms are fixed. For a p-type semiconductor, the depletion region occurs when negative potentials w.r.t. to the flatband are applied. The space charge region has a different width in depletion than the accumulation layer.⁵ This is a result of the fact that in accumulation, majority carriers can quickly respond to an applied potential because there are more of them. Minority carriers, or holes from ionized dopants are more dispersed and cannot compensate in the same way by virtue of their smaller number. The charge distribution in the space charge region can be quantified by the Poisson equation:

$$\frac{d^2 V}{dx^2} = \frac{e}{\epsilon \epsilon_0} [N_d - N_a - n(x) - p(x)] \quad \text{Equation 3}$$

Where N_d and N_a are the donor and acceptor densities, $n(x)$ and $p(x)$ are the electron and hole densities and x is the distance to the surface. The electron and hole densities follow the Boltzmann distribution:

$$n(x) = n_0 e^{[-eV/kT]} \quad \text{Similarly, } p(x) = p_0 e^{[-eV/kT]} \quad \text{Equation 4}$$

The dopant density N_d and N_a can be equated with n_0 and p_0 . For an n-type material the Poisson equation will reduce to:

$$\frac{d^2V}{dx^2} = \frac{-e}{\epsilon\epsilon_0} N_d [e^{[-eV/kT]} - 1] \quad \text{Equation 5}$$

Integration of the above equation (at $V = 0$) and using Gauss's Law:

$$\frac{dV}{dx} = \frac{Q_{sc}}{\epsilon\epsilon_0} = \frac{eN_d x_0}{\epsilon\epsilon_0} = \left\{ \frac{2eN_d}{\epsilon\epsilon_0} \left[V_s - \frac{kT}{e} \right] \right\}^{\frac{1}{2}} \quad \text{Equation 6}$$

The capacitance of the space charge layer is equivalent to dQ_{sc}/dV_{sc}

Differentiating the above results in the Mott-Schottky equation:⁵ For a more detailed explanation of the derivation it can be found in *Semiconductor Electrochemistry*.⁵

$$C_{sc}^{-2} = \frac{2}{e\epsilon\epsilon_0 N_d} \left(V - \frac{kT}{e} \right) \quad \text{Equation 7}$$

The Mott-Schottky equation is important because it relates the space charge capacity to the magnitude of band bending. Both the flatband potential and the dopant density can be extrapolated from the Mott-Schottky equation.

Just as there exists a depletion region other modes of band bending also occur. When the magnitude of band bending is so large that the number of minority carriers exceeds the majority carriers, the semiconductor is said to be in inversion. Note that this

only happens in the space charge region and not in the bulk. An inversion layer seldom arises since minority carriers are rapidly reacting with solution species at the interface.

Figure 5 Modes of Band Bending for an n-type Semiconductor

1.3.5 Accumulation & Flatband:

When the surface region has an excess of majority carriers, an accumulation of charge occurs. This is analogous to depletion except that all the signs are exchanged. For n-type semiconductors this occurs at negative potentials w.r.t. the flatband and for p-type it occurs at positive potentials w.r.t. E_{fb} . If the band bending is large enough to move the Fermi level into the conduction or valence band, the semiconductor is said to be degenerate. At this point the electrode behaves more like a metal than a semiconductor.

The charge transfer abilities of an electrode largely depend on whether the electrode is in accumulation or depletion. If the electrode is in accumulation, majority carriers are abundant and charge is readily transferred. In depletion however, there are very few mobile carriers and electron transfer occurs slowly.

The applied potential that exactly counteracts the magnitude of the band-bending is E_{fb} . Surfaces generally have some measure of inherent band bending because ideal surfaces are rarely achieved. Applying a potential such that no charge exists at the interface provides a surface with a band diagram similar to Figure 1 or Figure 2.

1.3.6 Surface states:

Surface states are energy levels that are confined to the surface. They mediate transfer between the surface and solution. Surface states can have a large impact on band bending when located between the band edges. These energy levels arise for a variety of reasons. For example, an intrinsic surface state develops from dangling bonds on the silicon surface. These are semiconductor atoms in the crystal lattice that are missing at least one neighbour.⁵ Energy states in the band gap that trap electroactive species by adsorption also qualify as surface states. Variations in surface morphology contribute to the presence of surface states as well.⁵ The ability of these energetic states to charge and discharge contributes to the overall electrochemical behaviour of the electrode. When solution interactions can be ignored and the measurements are taken at low frequencies, the quantity of surface states can be obtained by this equation⁵,

$$C_{ss} = N_{ss} e^2 / 4kT \quad \text{Equation 8}$$

An interesting situation arises when the capacitance due to surface states is larger than the space charge region. The Fermi level becomes fixed and any potential change no longer occurs in the space charge region. The potential drop is entirely in the Helmholtz layer. Since the Fermi level is pinned and the redox potential of the solution is fixed, the potential barrier (Schottky barrier) between the conduction band and redox potential is constant. In such a case, electrochemical measurements do not provide information about the electrode.

1.4 Hydrogen terminated Si(111)

It is very difficult to obtain a clean Si surface. Adsorbed species on the surface are always a source of contamination. Metal ions and surface reactions with water and air can also contaminate the substrate.⁵ These phenomena combined create a heterogeneous surface with oxide, adsorbed species, hydroxyl species and other adsorbates. Ensuring the quality of the semiconductor surface is important for a number of reasons. If care is not taken, it is difficult to measure electrical properties of the surface. Subsequent modifications to the monolayer may also suffer. The contaminants will be measured along with the substrate providing only an approximate measurement. This makes it difficult to discern whether results should be attributed to the surface or the contaminants. An ideal surface is free of surface states. Experimentally, this is a very difficult achievement. The first step in creating a clean surface is etching process.

The semiconductor is etched to provide a relatively clean and stable electrode surface. This is basically the process of removing SiO_2 by dissolution. A suggested mechanism for the etching of oxide can be found in *Semiconductor Electrochemistry*.⁵

Hydrogen termination of silicon is typically prepared by chemical etching in hydrofluoric acid (HF). The semiconductor industry has produced high quality silicon surfaces with HF acid for quite some time. Interest in hydrogen-terminated silicon (H-Si) surfaces has grown over the years. One of the first studies to examine the etching process more closely was performed by Higashi *et al.*⁶ In it, infrared absorption spectroscopy was used to study the effect of varying the pH of the etching solution on the Si(111) surface. It was found that this alters the roughness of the surface and influences the number of defects. More basic HF solutions, using ammonium fluoride as a buffering agent, created ideally terminated Si(111). The expectation of etching at a higher pH is to obtain a flat silicon surface terminated with monohydrides. The reality of a simple HF etch is quite different. Using IR spectroscopy, Chabal *et al.* showed that the surface of the silicon was microscopically rough.⁷ A pH of less than four revealed a large defect density as well as surface roughness. The presence of trihydrides on the Si(111) surface implied hydrogen adsorbed at defect sites. However, the IR spectrum of Si(111) etched in a basic solution revealed a small defect density. This value was calculated by estimating the area under the s-polarized spectrum. The implication is that the vibrational component of hydrogen at a defect site is parallel to the surface. In contrast, the p-polarized spectrum of a sample etched in a basic solution showed a strong, sharp peak. This implies that the hydrogen is perpendicular to the surface. The mechanism for hydrogen termination was proposed to be preferential, anisotropic etching attacking step edges.

A facet of the hydrogen termination that had not been previously explained was the presence of triangular etch pits on the terraces of Si(111). To compensate for this phenomenon, Chidsey *et al.* further modified the etching procedure by simply using forty

percent aqueous ammonium fluoride purged with Argon instead of HF.⁸ Using Scanning Tunneling Microscopy (STM) it was shown that dissolved O₂ was responsible for the etch pits. It was suggested that at fairly negative open circuit potentials of hydrogen terminated Si(111), dioxygen reduces to the superoxide radical anion. The radical anion can then abstract hydrogen from the terrace. This would leave a silicon radical that is vulnerable to attack by solution species such as hydroxide. As the process continues, an etch pit is formed. Purging the etching solution creates a relatively ideal H-Si(111) surface with a more uniform morphology.

The etching mechanism proposed by Chabal and his colleagues was further modified by Allongue *et al.*⁹ Etching is initiated by hydrolysis of the Si-H surface bond at a kink site. The hydroxyl group is substituted for a fluoride atom. This in turn polarizes the Si-Si back bonds due to the large difference in electronegativity. One of the back bonds breaks, ejecting the fluoride bound silicon atom. The silicon bound to the fluoride (Si^{+δ+}) picks up another hydroxyl group. This continues until the silicon atom enters the solution as HSiF(X)₂. The silicon on the surface is left intact, terminated by hydrogen.

1.4.1 Stability of H-Si(111)

Stability of the hydrogen terminated silicon (111) surface is crucial for accurate characterization and potential device applications. The main concern about such surfaces is contamination. Native oxide is the most likely source of initial contamination in a controlled system. Oxide appears to form as a result of H-Si(111) exposure to water and dioxygen. The mechanisms of oxidation by both species were shown in a recent review of organic modification of H-Si surfaces.¹⁰

Morita *et al.*¹¹ demonstrated the stability of H-Si(100) wafers in both air and water. The study examined the growth of native oxide as a function of exposure time to air and ultrapure water. Very little native oxide, no more than 2-3 Å, was present after two hundred minutes of exposure to air with 42% relative humidity. Similarly, native oxide had a very low growth rate for the first 100 minutes immersed in ultrapure water.¹² HF treatment of Si(100) examined by XPS and HREELS revealed that it took about one week to form a monolayer of native oxide on the surface. A similar study examined the stability of the surfaces in air. Utilizing XPS and EELS, p-type H-Si(100) wafers were examined for surface oxidation. A monolayer of oxide is reached after roughly one week of storage in air.¹³ Infrared studies revealed that the Si-H stretch is dependent on humidity, which confirms the findings of these previous studies.¹⁴ Collectively, these imply that the H-Si(111) surface is stable and can be easily characterized.

1.5 Alkylation of H-Si(111):

Until recently, alkylation of silicon via a covalent link had not been successfully accomplished. Novel experiments by Chidsey and his colleagues produced densely packed alkyl monolayer covalently bound to Si(111).^{15,16} The original study produced these surfaces by pyrolysis of diacyl peroxides.¹⁵ The diacyl peroxides decompose and produce an alkyl radical. The possibility of a dangling silicon bond causing the break up of the diacyl peroxide was noted by the authors. This would create a Si-OC(O)CH₂- bond instead of the desired Si-CH₂- bond. The surfaces were characterized by IR, XPS and ellipsometric measurements. A weak carbonyl stretch of 1715cm⁻¹ indicated the formation of Si-OC(O)CH₂-. It is estimated to account for roughly 30% of the monolayer.

Stability of these surfaces was demonstrated by boiling the samples in chloroform and in water. The acyl peroxide link is expected to hydrolyzed under such conditions. The percentage of minor linkage was determined by measuring loss of the monolayer. It should be noted that confirmation of the covalent bond was assumed and not known for certain.

Chidsey *et al.* continued their investigations by studying the characteristics of Si(111) modified by neat olefins, diacyl peroxide and a mixture of olefin and diacyl peroxide.¹⁶ To determine whether the alkyl monolayer on silicon was established by the olefin or the diacyl peroxide deuterium the peroxide was labeled. Their data suggests that 90% of the monolayer is derived from the olefin. The proposed mechanism for bonding of the olefin onto the Si(111) surface follows:

The last radical may then abstract hydrogen from an unreacted olefin or from another silicon atom terminated with hydrogen. The stability of these films was confirmed when an XPS spectrum of a sample, boiled in chloroform and water and exposed to air for eleven weeks, showed only a small increase in oxidation. It should be noted that because the silicon atoms on a Si(111) surface are 3.84 Å apart and the diameter of the alkyl chains is about 4.2 Å, complete coverage of the surface is not possible.

Evidence of a direct Si-C bond was reported utilizing photoelectron diffraction (PED).¹⁷ Generally a PED spectrum is difficult to interpret because there are several

carbon atoms in an alkyl chain bound to silicon. However, it was demonstrated that decomposing the core level spectrum at each photon energy level into its chemically shifted components could isolate the signal of just one type of site. A shift in the binding energy of about 1 eV was due to the polarization of the Si-C bond. Further evidence for the covalent Si-C bond confirmed this. Using electron energy loss spectroscopy (EELS) the thermal stability of alkyl modified Si(111) was examined.¹⁷ A vibrational transition became evident at about 780 cm⁻¹. The disappearance of this absorption above 615 K and the reappearance of a Si-H stretch suggest that thermal desorption was occurring. The olefin and hydrogen terminated surfaces were being reformed.

While the covalent link between silicon and carbon has been clearly established, the mechanism of alkylation had yet to be verified. Bateman *et al.* attempted to test the hypothesis of the radical chain reaction.¹⁸ The surface of a Si(111) surface was deuterated and then heated in a weak alkene solution dissolved in toluene. The mechanism implies that the heavy hydrogen should be found at the second carbon of the neighbouring alkyl chain. But no such carbon-deuterium stretch was detected. In contrast, Lopinski *et al.* reported indirect evidence to confirm the mechanism proposed by Chidsey and his colleagues.¹⁹ Dangling bonds created by an STM tip on Si(100) were exposed to vaporized styrene under ultra-high vacuum. Regions of the Si(100) revealed surface short lines beginning to form and continuing to grow. This evidence supports the chain reaction mechanism. A dangling bond would react with the terminal alkene, causing the C₂ to become a radical. That radical would abstract an adjacent hydrogen and continue to propagate in a line. The longest line of styrene formed was approximately 130 Å. Si(111)

was studied in a similar fashion.²⁰ In this case clusters of styrene molecules were found. This is consistent with the differing geometry of Si(111).

1.5.1 Alternate means of creating Si-C bonds

Formation of Si-C bonds does not occur only by alkylation via olefin reactions. Several other modes of alkylation have been explored since the seminal work of Chidsey *et al.*^{15,16} Halogenation to passivate the surface has been confirmed several times. Bansal *et al.* demonstrated the formation of a monolayer by chlorination of the H-Si(111) surface. The halogenated surface is further modified with a Grignard reagent. This creates a monolayer with the desired alkyl chain.²¹ He *et al.* illustrated how a brominated surface could be further reacted with lithiated thiophenes to modify the silicon surface.²² Several different agents for halogenation were utilized for the formation of the monolayer. Similarly, Boukherroub *et al.* were able to modify the Si(111)-H directly using a Grignard reagent.²³ The surprising result of this study was that halogenation of the surface was not required for passivation by the Grignard.

Organic monolayers on Si(111) have also been produced by electrochemical methods.²⁴ Phenyl groups were bound to silicon by reduction of $^+N_2-Ar-X$. The substituent (X) can be Br, NO₂, COOH, CN or an alkyl chain. The studies were performed in 0.1M H₂SO₄ and 2% HF. The HF ensured a relatively oxide free surface. No loss of Br was detected after six months, demonstrating that the surfaces were quite stable. Over time, oxide was found beneath the halogenated surface. A dip of the aged sample in HF was found to remove the oxide and organic molecules. Methylation of the

Si(111) surface was confirmed by cyclic voltammetry when an anodic current of between 0.1 to 5 Amps was applied to the wafer in the presence of a Grignard reagent.²⁵

1.5.2 Subsequent Modification of Alkyl Monolayers on Si(111):

Creating a monolayer on the surface of silicon that has specific electronic properties requires sequential reactions to functionalize the thin film. A film that is easily modified would be ideal. This facet is most important when determining the potential of different organics for use as electrical components. Electrochemical measurements characterize the monolayer and allow for adjustments to fit desired electrical parameters. Only a few instances exist where organic films have effectively been sequentially modified.

Sievel *et al.* used olefins terminated by ester groups to further modify a Si(100)-H surface.²⁶ The ester was hydrolyzed to form a carboxylic acid group. Another reaction pathway reduced the ester to make an alcohol. But, the environmental conditions for these reactions were too harsh to be of practical use.

It was found that the photochemical reaction of ethyl undecylenate could be used on Si(111)-H to passivate the surface.²⁷ Neat ethyl undecylenate was reduced producing an alcohol. Esterification of the alkyl provided unique possibilities for functionalization. Similar methodology prompted the formation of tert-butylhydrazide groups on H-Si(111).²⁸ Photochemically modified undecylenic acid (UDA) Si(111) was activated with N-hydroxysuccinimide (NHS). NHS is a good leaving group so this surface can be further modified to produce the desired tert-butylhydrazide. This last approach is the focus of this thesis.

1.6 Electrochemistry of Alkyl modified Si(111):

Few studies have been carried out on the electrical properties of these systems, and only within the last five to ten years have there been any papers published. One such study comes from Allongue *et al.* Phenyl monolayers were prepared by reduction of diazonium salts.²⁹ Capacitance measurements of the modified Si(111) surface reveal small defects at the interface. Measuring the capacitance over time tests the stability of the monolayer. The data implies that these organic films are quite robust. Oxide was found to slowly grow at defect sites beneath the monolayer and may be removed with little effect on the monolayer's electrical characteristics. Monolayer packing was found to be less than ideal and to depend on the molecular structure.

Characterization of organic monolayers on silicon is shown to be a function of alkyl chain length.³⁰ Monolayers formed from Grignard reagents were studied by electrochemical impedance measurements in an aqueous medium. Obtaining flatband measurements, while also studying the film thickness and contact angle provide a complete picture of the properties of the organic film. It is shown that such films demonstrate ideal behaviour at the electrode/solution interface in an aqueous medium. Modulating the dielectric constant of the film by varying the properties of the alkyl chain is suggested. An analogous report measures differential capacitance measurements and utilizes cyclic voltammetry in acetone to investigate the film.³¹ The measurements allow for determination of the dopant density and flatband of the system. It appears that the flatband does not change as a function of alkyl chain length. This is consistent with the apparent neutrality of the alkyl chain. Varying its length should not increase the

likelihood of polarizing the electrode surface. Again the packing of the system was shown to be less than ideal.

A related study targeted the distance dependence of electron transfer rates in alkyl chains by varying the chain length.³² The analysis including IR, XPS, ellipsometric and electrochemical measurements. The ability of the monolayer to limit electron-transfer was examined confirming the blocking ability of the alkyl chains. Electron transfer does not appear to be limited by the packing of the monolayers.

Examination of alkyl, fluorinated alkyl, and alkoxy monolayers yielded interesting results, and was characterized using ellipsometric, X-ray photoelectron spectroscopic and Atomic Force Microscopic (AFM) measurements.³³ Each of the monolayers was measured in methanol, acetonitrile and tetrahydrofuran (THF). THF provided the most reproducible electrochemical measurements. The insulating capacity of the monolayers was found to be greatest in alkyl modified Si(111) in THF. Methanol oxidized the electrode surface (aqueous solutions in general corrode the silicon surface). Surface states influenced electrochemical measurements limiting the reproducibility.

Defects or surface states are always a concern when dealing with silicon.³⁴ Particularly, oxidation of the surface by water and molecular oxygen is an issue. While it has been demonstrated that the H-Si(111) surface has very low recombination velocities, such measurements of alkyl modified silicon are rare. Recently it was reported that surface states on a Si(111) surface modified by alkyl chains were less than $3 \times 10^9 \text{ cm}^{-2}$. A typical surface has 1×10^{15} potential sites at which the chain can bind. That means that there is only one defect for approximately every 10^5 atoms. An interesting facet of the study is that this was found in samples that had been exposed to air for over four weeks.

The expected number of defect sites would be greater for a sample exposed for that length of time.

It is clear that organic monolayers on silicon have the potential for a great many applications. In order for these systems to be useful, full characterization of these thin films is required. Particularly, a full description of the electrical properties of these systems is necessary. The few studies that have been attempted to date have yet to clearly define the charge transfer properties of the interface. Further research into induced band bending as a function of different functional groups and the number of surface states at the interface is needed to understand the modified surface. A whole body of literature deals with these subjects for semiconductor devices. If organic monolayers are to be used as electronic components in such things as biochips and similar devices, a similar library of knowledge needs to be established.

2 Experimental

2.1 Sample Preparation

Single side polished, n-type, 1-5 Ω -cm resistivity, Silicon (111) wafers were obtained from Virginia Semiconductor Inc. Prior to modification, the silicon wafers were cut into 17 mm² samples. The samples were then cleaned in piranha, a 1:3 H₂O₂ (30%): H₂SO₄ (concentrated) ratio, at 100 °C for 30 minutes. The Teflon containers holding the samples had previously been cleaned in piranha. The samples were then repeatedly rinsed with Milli-Q water. Once the silicon was cleaned it was immersed, for 15 minutes, in argon deaerated NH₄F (40%) for preparation of the hydrogen terminated surface. Up to this point all chemicals used were HPLC grade.

Upon completion of the etching, the sample was taken out and rinsed with argon deaerated Milli-Q water and dried with N₂. It was then placed directly in a Schlenk tube for modification with undecylenic acid (UDA). The UDA was obtained from Sigma Aldrich and used as is. Hydrogen terminated samples being tested by Kelvin probe or electrochemical methods were measured immediately.

Neat UDA was placed in an Schlenk tube under argon purge at 100 °C for 1.5 hours to remove water and impurities. Once the sample was etched and in the Schlenk tube, the sample and solution were deaerated for 40 minutes to minimize the amount of contamination. The Schlenk tube was then sealed and irradiated for 3 hours using a Rayonet photochemical reactor (at 300nm wavelength). Once the samples were removed from the Schlenk tube they were copiously rinsed with tetrahydrofuran (THF), and trichloroethane (TCE). Again the samples were dried with inert gas.

Scheme 1

Figure 6. Reaction Scheme for the H-Si(111) Surface and Subsequent Modifications

Activation of the UDA was completed by submerging the silicon in a mixture of N-hydroxysuccinimide (NHS), (20mg/1.5mL) and 1-[3-(dimethylamin)propyl]-3-ethylcarbodiimide (EDC), (115mg/1.5mL). Figure 5 provides an overview of subsequent reactions.

The carbodiimide catalyzes the coupling of carboxyl groups with amines.³⁵ NHS is commonly used in the presence of EDC to create an active intermediate ester.³⁶

Following a thorough rinse with Milli-Q water, the samples were placed in this mixture for 20 minutes to initiate modification.

Subsequent hydrazide modifications followed the same procedural steps outlined by Mitchell *et al* and shown in Figure 5.²⁸ Phenylhydrazine (PH), and 4-nitrophenylhydrazine (NPH) were obtained by Aldrich and used as is. 2, 4-dinitrophenylhydrazine (DNPH) was obtained from Avocado Research Chemicals Ltd. Hydrazide modified silicon samples were created by placing the samples in a solution of 3.4mL of acetonitrile (ACN), and 0.8mL of triethylamine (TEA) and 2-propanol (IPA) with the hydrazide of interest. 250 μ L of PH and 250mg of NPH and DNPH were used for hydrazide modification. Modification was followed by a TCE rinse. Teflon containers under nitrogen purge were used for transport and temporary storage.

2.2 Ellipsometric Measurements

Ellipsometry is an optical reflection measurement that can be used to provide information about thickness, index of refraction, and the overall morphology of thin films and surfaces. It uses polarized light to probe the dielectric properties of a sample. The most common application of ellipsometry is the analysis of very thin films.

Light, like any other electromagnetic propagation, is a transverse wave. Because of this perpendicular component it can be polarized. Polarization is a manifestation of the orientation of the lines of electric flux in an electromagnetic field. Polarization can be constant, with a given shift, or it can rotate with each wave cycle.

An ellipsometer illuminates the surface of a sample with monochromatic light of known wavelength and polarization. The light source is separated into parallel and

perpendicular components (s and p respectively). A shift will occur upon reflection. This can be used to determine the thickness, among other properties, of the film. The ellipsometer essentially measures the change in the s and p polarized light using the light source as a reference. The phase shift in the perpendicular component is delta (Δ), and the change in the ratio of the amplitudes is psi (Ψ).

Figure 7. General Schematic for Ellipsometric Spectrometer

The figure above provides a general description of how the ellipsometer works. Psi and delta values are directly related to the index of refraction of the surface. Since the dielectric of the substrate is known, psi and delta can be found.

Modified silicon samples are taken directly from the lab to determine the thickness of the film. All measurements were performed with a Gaertner Scientific L116S ellipsometer. Each sample was measured eight times at random points to determine an average film thickness.

2.3 Attenuated Total Reflection (ATR) Fourier Transform

Infrared Spectroscopy (FTIR):

FTIR spectrometers measure the interaction of IR radiation with a sample, determining the frequencies at which the sample absorbs radiation and the intensities of

these absorptions. Finding these frequencies allows identification of the sample's chemical structure. This procedure works because particular elements and functional groups are known to absorb radiation at specific frequencies. The intensity of the absorption is related to the concentration of the sample. Intensity and frequency of sample absorption are the basis for the spectrum. Intensity is generally reported in terms of absorbance, the amount of light adsorbed by a sample, or percent transmittance, the amount of light that passes through it. Frequency is reported in terms of wavenumbers per cm.

An ATR crystal of silicon is used to measure the chemical composition of these thin films. When the light source hits the crystal, which is effectively a prism, the beam oscillates from front to back and is internally reflected.

The key components of a Fourier Transfer (FT) system are the source, the interferometer and the detector. In the interferometer the light beam strikes the beamsplitter. Approximately half the light is directed onto a fixed mirror. The remaining light is transmitted through the beamsplitter towards the moving mirror. When the beams recombine constructive or destructive interference will occur depending on mirror positions. When both mirrors are the same distance from the beamsplitter they are entirely in phase and the signal is maximized. This combined beam hits the sample and adsorption occurs. In the detector the beam is converted to an electrical signal. The interferometer is a way for the spectrometer to measure all optical frequencies simultaneously, modulating the intensity of individual frequencies of radiation before the detector picks up the signal.

The output of an interferometer is called an interferogram, a plot of intensity versus mirror position. The interferogram is a summation of all the wavelengths emitted by the sample. Using the mathematical process of FT, a computer converts the interferogram into a spectrum. The formula calculates the amplitude of each of the component signals. This is a measure of the intensity of the wavelength of light.

The ATR crystals measured by FTIR were modified in the same fashion as the silicon wafers. Each step of the modification was monitored to ensure reaction completion and elimination of the oxide. ATR crystals ($25 \times 5 \times 1 \text{ mm}^3$) were obtained from Harrick Scientific Corp. The spectra were measured using a Nicolet Magna-IR 860 spectrometer at 4 cm^{-1} resolution.

2.4 Electrochemical Measurements

The impedance of a circuit is its opposition to current. If a circuit is made up purely of resistors the impedance is the circuit resistance. However, when a sinusoidal voltage is applied to a circuit with capacitors and inductors, the current response is also sinusoidal but has a phase shift. The impedance has both magnitude and direction and can be represented by a phasor vector. The vector characteristics vary as a function of time. Because impedance is analogous to resistance in the imaginary number domain, rectangular forms for capacitors and inductors can readily be found using V-I relationships. Their relationships are listed below.

Z_R	R
Z_c	$1/j\omega C$

Z_L	$j\omega L$
-------	-------------

Table 2. Rectangular form of Impedance Circuit Elements.

The definitions of Table 2 represent the rectangular forms for the impedance of a resistor, capacitor, and inductor, and are their phasors where Z_R is the impedance of a resistor, Z_C is the total impedance of a capacitor and Z_L is the total impedance of an inductor. The symbol ω is the angular frequency, j is the imaginary root $1^{-1/2}$. These are the equations that the computer uses to determine discrete parameters.

The analysis of the signal is done by means of a Fast Fourier Transform. Both the potential and current signals in the time domain are converted to frequency domains. The cell impedance is calculated using.

$$Z = \frac{(E(f)(E^\circ(f)))}{I(f)(E^\circ(f))} \rightarrow \frac{V}{I} \quad \text{Equation 9}$$

Where E° and I° are the complex conjugates to their respective functions. Converting these quantities into polar co-ordinates would provide the impedance of the system. The ratio of the phasor voltage to the phasor current is the impedance of the circuit.

Impedance, differential capacitance and Mott-Schottky measurements were performed using an Autolab model PGSTAT30 electrochemical analyzer. The potentiostat was connected to a three-electrode Teflon circular cell. The electrolytes used for the measurements were 0.1M H_2SO_4 and distilled ACN with 0.1M tetrabutylammonium hexafluorophosphate (TBAPF₆). The solutions were deaerated with argon prior to measurement. While taking the measurements the cell was completely enclosed with an argon purge line running into the cell so as to allow minimum exposure to ambient air. The capacitance and Mott-Schottky measurements were performed at 5

kHz and 50 kHz respectively. Impedance plots were taken over a range of 500 kHz to 1Hz.

2.5 The Kelvin Probe

The Kelvin probe method measures the contact potential difference between the sample and a vibrating tip to measure the work function of the material. The work function of a substance is the least amount of energy required to remove an electron from its surface to a point where it has zero kinetic energy. In the case of a semiconductor the electron is removed from the conduction band.

The methodology behind the Kelvin probe is straightforward. By placing two materials with different work functions close enough together a capacitor is created. A schematic representation is given in Figure 8.

Figure 8. Kelvin Probe Schematic at Open Circuit

Once the two samples are brought into contact with one another the substance with the smaller work function (ϕ_1) will begin to lose electrons to the other (ϕ_2) until their Fermi levels are equal (Figure 9).

Figure 9. Kelvin Probe Schematic at Closed Circuit

The amount of charge is determined by vibrating the reference, which is compensated for by an external DC voltage.

Surface voltage (SV), is a measure of the amount of band bending in the light and dark. Illumination of the sample should free any charge that is in a trapped state at the surface. The voltage difference between dark and light is a measure of the band bending.

All samples were measured directly after thin film modification in ambient air. A 128mW white light optical fiber was used to illuminate the samples.

3 Results & Discussion:

Electrochemical Characterization of Modified Si(111) in an Aqueous Environment

The potential of a given system for use as or in electronic components requires a complete analysis of the electrical properties of the system. Organic thin films deposited on solid surfaces have been studied for quite some time.³⁷ The primary substrate for these modifications have been clean metallic, oxidized metallic, or oxidized semiconductor surfaces.^{38,39} In contrast, oxide free semiconductors modified with organic films are still in the preliminary stages of study.²⁹ Acquiring a fundamental understanding of these films requires a full electrical characterization of the system. The semiconductor-organic interface and organic-electrolyte interface are of particular interest. Following is a sequential analysis of the electronic properties of Si(111) modified by varying the trailing functional group.

3.1 Native Oxide

As mentioned previously, the generally accepted theory is that the oxidation of the hydrogen terminated surface occurs slowly in both aqueous environments as well as air.^{12,13,14} Because it is still difficult to know for certain to what extent oxidation of modified silicon occurs (or whether it occurs at all) a study of the charge transfer properties of the native oxide is necessary.

The determination of the Flatband potential for native oxide provides a measure of the inherent band bending of the semiconductor oxide. The data in Table 3 shows that in order to flatten the bands for silicon a negative potential needs to be applied. This simply means that the addition of electrons to the space charge region is required. The natural tendency of native oxide on n-type Si(111) is to be depleted of majority carriers (electrons).

Mott-Schottky plots were taken in depletion where the capacitance of the space charge region dominates. The Mott-Schottky equation (equation 7) was then used to extrapolate the E_{fb} (flatband potential) and N_d (dopant density). Madou *et al.* found the native oxide to have a flatband potential of -0.650 V vs. SCE.⁴⁰ This is in good agreement with the values obtained here. In Table 3 the open circuit potential is defined as the potential of the electrode at rest.

Sample	OCP (V) vs SCE	E_{fb} vs SCE (V)	N_d (cm ⁻³)	Band Bending at OCP (V)
1	-0.250	-0.665	$1.91 * 10^{15}$	-0.415
2	-0.352	-0.648	$1.84 * 10^{15}$	-0.296
3	-0.260	-0.670	$2.29 * 10^{15}$	-0.410
Measurement		-0.659	2.01	-0.374
Average		± 0.016	$\pm 0.24 * 10^{15}$	± 0.067

Table 3. Flatband, OCP potential and Dopant Densities for Native Oxide measured in 0.1M H₂SO₄

The extrapolated values for the dopant density correspond well with the 1 to 5 Ω -cm resistivity of the wafers provided by Virginia Semiconductor. A dopant density of

10^{15} cm^{-3} phosphorous doped silicon corresponds to a resistivity of $4.5 \text{ } \Omega\text{-cm}$.⁵ Measurement of the capacitance of the native oxide provides information about the voltage at which the sample moves from depletion to accumulation. If further modification or too long an exposure to an aqueous solution does indeed prompt the growth of oxide on a sample, this data would provide a reference. The samples appear to be fully in accumulation at approximately -0.200 V . (See Figure 10.) A similar peak appearing at the same voltage for subsequent modifications would be an indication of oxide growth.

The oxide capacitance curves are typical of the type obtained in sulfuric acid. Subsequent modifications may differ in reproducibility. The voltage range in which the sample moves into accumulation differs for each modification as well.

Figure 10. Capacitance Curves for Native Oxide on Si(111) in 0.1 M H₂SO₄ Measured in Accumulation. Fits are not shown

3.2 Hydrogen terminated Si(111):

Hydrogen terminated Si(111) serves as the starting point for subsequent modifications. The behaviour of these surfaces is important because the capacitance values found for the Si-H terminated surfaces are used to approximate the potential drop in the Helmholtz layer.²⁹ The measured value of the electrode is the total capacitance of the system. Broken down into individual components the capacitance can be expressed as:

$$\frac{1}{C_{total}} = \frac{1}{C_{sc}} + \frac{1}{C_H} \quad \text{Equation 10}$$

Where C_{Total} is the combined measured capacitance, C_{SC} is the capacitance of the space charge region and C_H is the Helmholtz capacitance. The circuit model that best describes this system is:

Figure 11. Circuit Model for the Solution/Semiconductor Interface

Where R_S is the series resistance due to the lack of a proper Ohmic contact. The Warburg impedance (the impedance as a result of diffusion) utilized in previous studies³¹ is replaced by the R_H circuit element. Warburg impedance has been proven in preceding reports to be an issue only at low frequencies.⁴¹ At 5kHz the circuit element can be ignored and treated simply as a resistance. In series with the Helmholtz capacitance is the

space charge capacitance. It is assumed that the capacitance of the space charge region can be neglected because, while the working electrode is in accumulation, majority carriers can readily compensate for any e^- field. This means the width of the space charge region is very small. The relationship

$$C = \frac{\varepsilon \varepsilon_o}{\ell} \quad \text{Equation 11.}$$

reflects this concept. Because of the small ℓ in equation 11 the capacitance of the space charge region is very big and can be neglected in equation 10. Voltages negative of the flatband cause the potential drop to occur in the Helmholtz layer. Further evidence of this comes from studies of the potential drops in both the space charge and Helmholtz layer versus applied bias.^{29,31,42}

Sample	Ocp (V) vs SCE	E_{fb} vs SCE (V)	N_d (cm ⁻³)	Band Bending at OCP (V)
1	-0.300	-0.432	$1.05 * 10^{15}$	-0.132
2	-0.190	-0.438	$9.89 * 10^{14}$	-0.248
3	-0.254	-0.318	$9.86 * 10^{14}$	-0.064
4	-0.367	-0.400	$1.31 * 10^{15}$	-0.033
5	-0.243	-0.412	$7.79 * 10^{14}$	-0.169
6	-0.334	-0.429	$1.75 * 10^{15}$	-0.095
Measurement		-0.405	1.14	-0.123
Average		± 0.045	$\pm 0.34 * 10^{15}$	± 0.078

Table 4. Flatband potential, OCP, and Dopant Densities for Hydrogen terminated Si(111) measured in 0.1M H₂SO₄

Determination of flatband potentials from Mott-Schottky plots provide an average E_{fb} of -0.405V vs. SCE. This value is comparable to -0.50V vs. SCE established by Yu *et al.*³¹, given that the dopant density was greater and the electrolyte used was $0.1\text{ M H}_2\text{SO}_4$ + 2% HF. Flatband potentials are known to be dependent on pH as well as on the dopant density of silicon.⁵ A similar result for the hydrogen terminated Si(111) measured in 5% HF was obtained by Mierry *et al.*⁴³ This study established a value of -0.45V vs. SCE for the Si-H surface. In addition, the dopant density established by Mierry *et al.*, approximately $1 \times 10^{15}\text{cm}^{-3}$ is comparable to the values obtained here. So this study likely serves as a better reference point.

There are other issues to note in the examination of Si-H as well. Much of the previous work has been measured in a mixture of acid and $0.1\text{ M H}_2\text{SO}_4$ and 2% HF.^{29, 31} The HF is added to prevent the growth of oxide on the samples. It etches the surface of the electrode and presumably etches the monolayer to some extent as well. If oxide were growing in the sulfuric acid, it would likely shift the flatband to a more negative potential. The capacitance curves are quite clean and show very few surface states. (Evidence of surface states will be presented in subsequent sections.)

Closer examination of the data prompts questions about the reproducibility of these measurements. Table 4 shows some variability from sample to sample. Adsorption, oxide growth and surface states are all phenomena that could potentially shift the flatband.⁵ These, and perhaps other unknowns, will all have minor effects on the state of the surface.

Figure 12. Capacitance Curves for Hydrogen terminated Si(111) in 0.1 M H₂SO₄ Measured in Accumulation. Fits are not shown

The capacitance curves for Si-H are reasonably reproducible. At negative voltages of the flatband a thin layer of majority carriers is present, on the order of a 100 Å thick.⁵ The maximum value of the accumulation layer, or the plateau region, is the total capacitance of the system.

Capacitance curves for Si-H illustrate a Helmholtz value of 3.65 versus 3.5 and 3.7 μF respectively evaluated in previous studies.^{31,29} The data taken in both previous studies was measured at 1kHz.^{31,29} The differential capacitance measurements taken throughout this study were taken at 5kHz.

The circuit model put forward for these structures in conjunction with impedance measurements can verify parameters such as the capacitance in accumulation and provide additional insights about the system like its parallel resistance. It should be noted that

experimental impedance data is very difficult to correlate.^{44,45} Common issues include the arc not passing through the origin, the semi-circle being depressed below the real axis, and arcs with substantial distortions. Figure 13 below is typical of impedance arcs. Any distortions may be a result of overlapping time constants, electrode roughness or poor choice in circuit models.

Figure 13. Complex Impedance plot for the Si-H surface in 0.1M H₂SO₄, where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element. Measurements are taken 0.4V in accumulation

Analysis of single impedance arcs provides a relatively simple and good first approximation as to whether a circuit model is plausible as well as discrete values for the parallel resistance and capacitance.

Assuming that the potential drop is almost entirely in the Helmholtz layer, from the circuit model in Figure 11 it would be reasonable to expect a single arc. That is in fact what is seen for the majority of these systems.

Figure 14. Simple RC circuit model representing the Dashed Lines in all Impedance Arcs

The total impedance of the system for circuit elements in series can be calculated by:⁴⁶

$$Z_{total} = Z_1 + Z_2 + \dots + Z_n \quad \text{Equation 12}$$

The total impedance of units in parallel is:

$$\frac{1}{Z_{total}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \dots + \frac{1}{Z_n} \quad \text{Equation 13}$$

The components for the circuit model (excluding the impedance of the space charge layer in Figure 15) can be simplified into their rectangular coordinates.

$$\frac{1}{Z_{Parallel}} = \frac{1}{R_p} + j\omega C \quad \text{Equation 14}$$

Where R_p is the parallel resistance, ω is the angular frequency, and j is the imaginary component $(-1)^{1/2}$.

With some algebraic manipulation the total impedance becomes:

$$Z_{total} = R_s + \frac{R_p - j\omega C R_p^2}{1 + \omega^2 C^2 R_p^2} \quad \text{Equation 15}$$

for a simple RC circuit.

This expression can be further reduced into the real and imaginary components of the total impedance. From equation 15 it is also clear that the imaginary component of the circuit is frequency dependent.

As mentioned earlier, impedance arcs are typically difficult to interpret and correlate.^{44,45} To compensate for real world systems where depressed complex impedance plots are common, a non-intuitive circuit element was proposed. This Constant Phase Element (CPE) can be used in systems where some property is not homogeneous. Physical causes of CPE behaviour can be electrode roughness or inhomogeneous reaction rates at the surface, or even perhaps variations in the thickness of the monolayer on an electrode.^{44, 47}

Figure 15. Simple CPE circuit model representing the Solid Lines in all Impedance Arcs

To achieve the best possible correlation between experimental and theoretical results, Naumann *et al.* chose to fit both the single capacitor in parallel with a resistor as well as a CPE in parallel with a resistor.⁴⁷ The same procedure has been used in this study. The equation that fits $\text{Re}(Z)$ or the real component of the data is:^{44, 47}

$$\frac{R [1 + (\omega Tc)^{1-\alpha} \cos \frac{\pi}{2}(1-\alpha)]}{[1 + \omega Tc)^{1-\alpha} \cos \frac{\pi}{2}(1-\alpha)]^2 + [(\omega Tc)^{1-\alpha} \sin \frac{\pi}{2}(1-\alpha)]^2} \quad \text{Equation 16}$$

When alpha is zero, the expression simply becomes that of the real component of equation 15. From the fit and the experimental values for the total impedance, the

imaginary component can be calculated. The time constant, T_c , was calculated by using the relationship.

$$\omega_p T_c = 1. \quad \text{Equation 17}$$

R_p and C were calculated using

$$R_p C = T_c. \quad \text{Equation 18}$$

It is important to note that this relationship only holds true for the case when α is zero and the CPE acts as a capacitor.⁴⁷ Because data fits both models reasonably well, these equations are used as an approximation for the capacitance in accumulation and to determine the resistance of the monolayer.

The impedance plot, Figure 12, shows that the capacitance value is somewhat higher but in agreement with the values determined from Figure 12. The expectation of the Si-H terminated surface is that the parallel resistance should be small. Therefore it is basically the solution resistance or R_s that is measured in this case.

The complex impedance plot for the Si-H surface, Figure 12, is slightly distorted but it is clear that both the CPE and the capacitor fit the data reasonably well. The tail end of the graph appears, at first glance, to be the beginning of a Warburg or diffusional impedance, which can be recognized by its linearity and that it has a slope of 1. The slope of the tail in this graph is 0.35. It is difficult to determine whether this is due to the Warburg impedance or due to the beginning of another arc. The difference in the slope would suggest that this is the start of another impedance arc.

3.3 Undecylenic Acid modified Si(111)

Figure 16. FTIR Spectrum for UDA Modified Si(111)

Confirmation of the UDA modification is achieved by FTIR measurements. The peaks of significance are observed at 2933, 2854, 1714 cm⁻¹. These values are virtually identical to those established by Mitchell *et al* in a recent article.²⁸ The peaks correlate with a methylene symmetric and asymmetric stretch and the carbonyl group of the acid group.

Flatband potential measurements for the undecylenic modified surface in Table 5 show slightly smaller variability with respect to SCE than the Si-H electrode. The net change in voltage for both the acid and Si-H is largely a function of the open circuit potential (OCP). The OCP of the electrode can be regarded as the potential of the substance at rest. There is no net current flowing in or out of the electrode. This means that the OCP is a measure of the state of the modified semiconductor. It cannot necessarily be relied upon as a discrete measurement because it is not known if the

electrode/electrolyte interface is at equilibrium. Changes to the surface such as adsorption of species and formation of native oxide may influence the OCP.⁵ The Mott-Schottky plots are typically recorded after measuring the capacitance of the electrode so that the system has had at least a few minutes to sit in the solution. With the exception of samples 2 & 6, in Table 5 the open circuit potential of the acid modified surface is relatively stable and hovers close to zero with respect to the original reference electrode. This is true of the Si-H surface with the exception of one or two outlying pieces of data. The open circuit potential can also be used to gauge the reproducibility of the measurements, and the stability of a sample. It can be used as a guide to pinpoint changes, likely due to adsorption and oxide growth, on the surface. The open circuit potential should be consistent from sample to sample assuming that the treatment and modification are identical. This therefore means that processes at the surface are causing the differences in the measurements.

Another important trend is the increase in flatband potential from the Si-H surface to undecylenic acid. This implies that more electrons are needed to flatten the bands, meaning that the surface is further in depletion. This is consistent with the introduction of impurities and an increased number of surface states that trap negative charge at the interface. The treatment of the sample after removal from the Schlenk tube should be considered. It is likely that ambient air still gets trapped in the tube regardless of the amount of time the sample is purged. Under irradiation, surface reactions are likely to occur. This was made clear by Cicero *et al.* in an examination of the photoreactivity of H-Si(111) with dioxygen and terminally unsaturated hydrocarbons.⁴⁸ Surface states can be introduced at any step of the process.

Sample	OCP (V)	E_{fb} vs SCE (V)	N_d (cm ⁻³)	Band Bending at OCP (V)
1	-0.230	-0.652	$9.68 * 10^{14}$	-0.422
2	-0.127	-0.610	$7.49 * 10^{14}$	-0.483
3	-0.298	-0.623	$1.39 * 10^{15}$	-0.325
4	-0.288	-0.603	$9.70 * 10^{14}$	-0.315
5	-0.247	-0.662	$1.10 * 10^{15}$	-0.415
6	-0.287	-0.589	$1.21 * 10^{15}$	-0.302
7	-0.319	-0.607	$1.17 * 10^{15}$	-0.288
Measurement		-0.621	1.08	-0.364
Average		± 0.027	$\pm 0.21 * 10^{15}$	± 0.075

Table 5. Flatband potential, OCP, and Dopant Densities the UDA Modified Si(111) measured in 0.1M H_2SO_4

Mott-Schottky plots typical of each of these modified surfaces are shown in Figure 17. The linearity is generally consistent from sample to sample but the slope, which is used to determine the dopant density, varies to some extent.

Figure 17. Mott-Schottky plot for Undecylenic Acid in 0.1M H₂SO₄ Measured in the Depletion Region at 50 kHz. Fits are not shown.

The acid film, in contrast to the Si-H, is thick enough that ellipsometric measurements can be made. From the capacitance and the film thickness the dielectric of the material can be extrapolated.

$$\frac{1}{C_{total}} = \frac{1}{C_{sc}} + \frac{1}{C_H} + \frac{1}{C_m} \quad \text{Equation 19}$$

Where C_m is the Monolayer capacitance.

Just as Equation 10 was used to determine the value of the Helmholtz layer, Equation 19 in conjunction with Equation 11 is used to calculate the results in Table 6.

Sample	C_{total} (μF)/cm ²	C_m (μF)/cm ²	$\epsilon_{effective}$ (F/cm)	l (Å)
1	1.50	2.55	4.63	15.5 ± 0.5

Sample	C_{total} (μF)/ cm^2	C_m (μF)/ cm^2	$\epsilon_{\text{effective}}$ (F/cm)	l ($\text{\AA}$)
2	1.18	1.74	3.10	15.2 ± 0.2
3	1.45	2.41	4.09	14.5 ± 1.2

Table 6. Total and Monolayer Capacitance, Effective dielectric and Thicknesses for UDA modified Si(111) in 0.1 M H_2SO_4

The effective dielectric constant of the system falls between 3 and 4 F/cm, and is slightly higher than the dielectric constants for comparable organic liquids.⁴⁹

The equivalent circuit model that best describes this system is the same as Figure 11, except that another capacitor C_M in parallel with a resistor R_M have been added to represent the monolayer.

Figure 18. Equivalent Circuit Model for an Alkyl Modified Si(111) Electrode

By looking at the circuit model, it would appear that there are two clear time constants, and potentially two arcs for the monolayer and the Helmholtz capacitance under accumulation.⁴⁵ The capacitance of the monolayer can be difficult to differentiate from the Helmholtz capacitance. Uncertainties for Impedance Spectra (IS) are common. Fitting the data can be difficult because although the circuit elements of an equivalent circuit may be correct, their geometric configurations may be out of order. Different

connectivity of various circuit elements leads to different spectra.⁴⁵ There are also interface processes like monolayer-solution interactions that may skew the data.

Figure 19. Complex Impedance plot for the UDA surface in 0.1M H₂SO₄, where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element.

Measurements are taken 0.35 V in accumulation

The 200Ω resistance of the acid monolayer appears to be small for a well formed film on silicon. It is barely twice that of the H-terminated surface.

Impedance characterizations of self-assembled monolayers (4'-Hydroxy-4-mercaptobiphenyl, HMB) on gold have yielded comparable results.⁵⁰ The majority of systems tested in this study yielded parallel resistances on the order of 10kΩ.⁵⁰ While the organic structure is entirely different from the molecules studied here, the important similarity is that the monolayer is acting as a poor insulator. The author suggests that HMB is a poor barrier to electron transfer, i.e. the monolayer is leaky. From the number of surface Si atom sites available it is already known that a uniform monolayer could not possibly be formed.^{15,16} It is likely that some parallel can be drawn between these alkyl

modified Si(111) and the thiols and golds. Questions are certainly raised about the packing and the order of the monolayer. It is reassuring that because the insulator is leaky, the surface oxidation may not be occurring to an appreciable extent, since oxide is a good insulating layer and would increase the R_p value.

The time constant, τ , or T_c , which is a measure of the relaxation time of the capacitor of the circuit, is smaller than the Si-H surface. This behaviour is contrary to the expected trend of an insulating layer. Capacitance values determined from impedance measurements are in accord with those evaluated from Capacitance vs. Voltage curves.

In the UDA, Figure 18, at very high frequencies a linear region is evident (towards the origin). This could be a result of the penetration into the film. It corresponds with the small R_p values as well. Because the electrolyte (or other species) takes much longer to diffuse across a thin layer than the period of the AC stimulus, the measurement is distorted. The electrode does not behave as though the coating has a finite thickness.⁵¹ It behaves as though the thin film is infinite. This is characteristic behaviour of thin films.

Kelvin Probe measurements of the surface were also performed in order to verify the amount of band bending. These measured the difference in the work function between a sample and a reference electrode. The sample may have localized states that extract charge from the bulk of the electrode, thus trapping carriers. These create surface charge which gives rise to a field that penetrates into the semiconductor. In reality the Kelvin probe provides a measure of band bending in the electrode, caused by these surface states. Along with this bending is the potential for the creation of surface dipoles.⁵² This may be the result of a surface defects, adsorbed species, or deliberate introduction of a dipole by way of modification.

Under illumination, a redistribution of charge occurs. Photogenerated electron hole pairs can screen the charge that creates the band bending. The difference between the values measured in the light and dark provide a measure of the band bending. It is important to note that the illumination will affect states in the gap but not the dipole at the surface.⁵² The latter will instead cause a vertical shift. If there is a dipole pulling electrons away from the surface, a more negative shift should be seen for an n-type material w.r.t a gold electrode. This would mean that there is a large electron density at the surface and that it is easier to pull an electron off the surface.

The relative positions of the semiconductor with respect to gold electrode can readily be found. The position of the Fermi level can be calculated using the dopant density of silicon:

$$n = N_c e^{(E_f - E_c)/kT}$$

where n is the dopant density, N_c is the effective density of conduction band states, E_f is the Fermi level, E_c is the conduction band edge, k is the Boltzmann constant.

Figure 20. Band Representation Kelvin Probe Measurements

Figure 20 implies that the Fermi level should be approximately 0.7eV from that of gold. That is what is seen from the Kelvin probe measurements of the acid surface. Figure 21 shows some vertical or dipole change from sample to sample but the effect is small. Because the measurements are taken in air this change in dipole could easily be a result of adsorbed impurities. The sample itself is depleted by approximately -200mV. Similar measurements made by Hartig *et al*, examined p-type chemical oxide and the Si-H surface.⁵³ The chemical oxide showed no band bending and the Si-H surface showed a 75mV change. This is consistent with measurements made on n-type silicon. Kelvin probe measurements reveal a surface photovoltage of approximately -50mV. Goldstein *et al* also performed photovoltage measurements on p-type Si-H surface to determine similar parameters and discovered a 50mV difference.⁵⁴ The reference for the Kelvin probe vibrating capacitor was a pure gold wire.

Figure 21. Surface Voltage for independent samples of UDA modified Si(111) in Dark and under Illumination. Higher Plateaus are Measured in the Dark and Lower Values Correspond with Light.

The eleven carbon alkyl chain preceding the acid group would function as a good insulator to a dipole of the carboxyl group. However, that does not mean that there is no dipole effect from the acid group. It is clear from Figure 21 that the Fermi level at about 0.7eV from Gold is shifted to more negative values. This would correspond with a negative dipole on the surface. This could be a result of film penetration or perhaps the electron withdrawing nature of the carboxyl group. The dipole effect corresponds with effective dielectric values of the UDA samples as well.

3.4 N-Hydroxysuccinimide modified Si(111):

Figure 22. FTIR Spectrum of NHS modified Si(111)

Activation of the UDA group by NHS is confirmed by Figure 22. The FTIR spectra for the NHS group is virtually identical to that published by Mitchell *et al.*²⁸ Peaks of interest appear at 2923, 2853, 1815, 1787, and 1742 cm^{-1} . The two additional peaks appear in the region characteristic of carbonyls. Imides often have weak companion bands to the strong carbonyl band.⁵⁵

Further modification of the UDA required soaking the sample in an aqueous mixture of EDC and NHS for approximately 30 minutes. (See section 2.1 to view the molecules and their reaction scheme.) Thus far the samples had only been exposed to organic solvents. Although Milli-Q water was used, any impurity in the chemicals and the length of exposure in the medium could have introduced more surface states. This is reflected in the flatband measurements. Table 7 shows the flatband with respect to SCE has decreased by approximately -0.1V and the net change by -0.2V.

A perplexing behaviour is the change of polarity of the open circuit potential. There appears to be a shift in voltage of the system at rest. This may a reflection of the surface treatment of the NHS.

Sample	OCP (V) vs SCE	E_{fb} vs SCE (V)	N_d (cm ⁻³)	Band Bending at OCP (V)
1	-0.166	-.0703	$1.59 * 10^{15}$	-0.537
2	-0.092	-0.730	$9.98 * 10^{14}$	-0.638
3	-0.167	-0.684	$7.20 * 10^{14}$	-0.517
4	-0.057	-0.677	$6.75 * 10^{14}$	-0.620
5	-0.123	-0.721	$9.73 * 10^{14}$	-0.598
6	-0.126	-0.790	$1.03 * 10^{15}$	-0.664
Measurement		-0.718	9.98	-0.596
Average		± 0.041	$\pm 0.32 * 10^{14}$	± 0.058

Table 7. Flatband potential, OCP, and Dopant Densities the NHS Modified Si(111) measured in 0.1M H_2SO_4

Dopant densities are consistent with both the UDA and the Si-H surface hovering around $1 * 10^{15} \text{cm}^{-3}$. The effective dielectric constant again ranges between 4 and 5. The latter is indicative of a molecule's ability to separate charge. It is a measure of how well a material acts as an electrical insulator. The NHS group has polar groups on it but the net dipole should be in the opposite direction.

Table 8 shows that the capacitance values are somewhat lower than that of the acid but these do not reflect the increase in chain length. The carbonyl groups should pull

electron density towards the surface of the electrode.⁴⁹ This is contrary behaviour to that of the acid group.

Sample	$C_{\text{total}} (\mu\text{F})/\text{cm}^2$	$C_m (\mu\text{F})/\text{cm}^2$	$\epsilon_{\text{effective}}$	$l (\text{\AA})$
1	1.14	1.68	3.97	20.2 ± 0.6
2	1.21	1.81	4.05	19.1 ± 1.2
3	1.35	2.14	5.01	20.0 ± 0.7

Table 8. Monolayer Capacitance, Effective Dielectric constant, and Monolayer thickness of N-Hydroxysuccinimide modified Si(111) measured in 0.1M H₂SO₄

The change in the flatband potential is reflected in the Kelvin Probe measurements. The surface voltage difference is more variable for the NHS surface ranging from -425 to -280mV . The magnitude is certainly greater than the acid modified surface, but there is considerably more fluctuation in the data. Sample number three appears to show some charge trapping by shifting both the dark and light voltages to more and more negative values over time. Kronik *et al.* attribute this behaviour to adsorbed species.⁵² This is likely the case here as well. Some variation in the samples should be expected because of the sensitivity to adsorption and the difficulty in knowing whether a monolayer modification has been successful. The general trend however, is an increased tendency of the sample to be depleted of majority carriers.

The surface voltage (SV) shifts considerably between UDA and NHS samples. The increase in the amount of the band bending matches the Mott-Schottky measurements. Again the increase is likely due to the actual surface treatment of the

sample. Although the growth of the surface oxide is assumed to be slow in an aqueous environment, it appears to cause an increased number of surface states.

Sample	Illuminated Potential (mV)	Dark surface Potential (mV)
1	-875	-450
2	-840	-560
3	-1150	-730

Table 9. Surface voltage measurements for N-Hydroxysuccinimide modified Si(111) in 0.1M H₂SO₄

The impedance data for the NHS is virtually ideal in its fit with a simple RC circuit. The CPE component has a relatively small α of 0.01. Towards the origin in Figure 23, the beginnings of a small curve can be seen. This may be due to surface states that have not fully charged because the electrode was not driven far enough into accumulation.

Figure 23. Complex Impedance plot for the NHS surface in 0.1M H₂SO₄, where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element.

Measurements are taken 0.3V in accumulation

A marked increase in the parallel resistance suggests that modification of the undecylenic acid by NHS makes a better insulator and creates a more densely packed monolayer. The capacitance extracted from the impedance data is somewhat larger than that from the plateau region in Capacitance vs. Voltage curves, but still comparable at a first approximation. The time constant has increased as well, and coincides with an increased R_p .

3.5 Phenylhydrazine Modified Si(111)

Sample	Ocp vs SCE (V)	E_{fb} vs SCE (V)	N_d (cm ⁻³)	Band Bending at OCP (V)
1	-0.281	-0.8560	$1.25 * 10^{15}$	-0.575
2	-0.369	-0.905	$9.22 * 10^{14}$	-0.536
3	-0.340	-0.923	$1.12 * 10^{15}$	-0.583
4	-0.276	-0.883	$1.19 * 10^{15}$	-0.607
5	-0.388	-0.860	$1.14 * 10^{15}$	-0.472
6	-0.327	-0.857	$1.168 * 10^{15}$	-0.530
Measurement		-0.881	1.13	-0.551
Average		± 0.028	$\pm 0.11 * 10^{15}$	± 0.048

Table 10. Flatband potential, OCP, and Dopant Densities the PH Modified Si(111) measured in 0.1M H_2SO_4

With respect to SCE, the E_{fb} values of the phenylhydrazide (PH) are increasingly negative in comparison with NHS. However, the net difference from OCP is the true measure of the flatband. Since the net potential is less negative, the semiconductor is not as depleted. The phenyl ring, which has a strong electron affinity, is the likely cause of this change. Electron density is concentrated around the ring and that causes a net dipole on the surface. The nitrogen groups may be acting as donors as well.⁴⁹ Charge in the semiconductor would redistribute accordingly if the dipole permeated the electrode.

An item of note is the change in the open circuit potential with the subsequent modifications. An extensive literature search provided little insight into this phenomenon. However, this trend is so consistent that the behaviour must be a function of the modification. It may be a measure of the dipole of the tail group.

The Kelvin probe measurements reflect the decreased change in band bending that is seen from the Mott-Schottky plots. The $-0.3V$ potential difference between the sample in the dark and under illumination is less than that of the NHS modified surface. This is important because the band bending has increased with each modification thus far. With the phenylhydrazide it decreases.

Figure 24. Surface Voltage for PH modified Si(111) in Dark and under Illumination. Higher Plateaus are Measured in the Dark and Lower Values Correspond with Light.

The Kelvin Probe data shows a time-variant change in the surface dipole. Toward the right in Figure 24, two of the measurements show considerable variability. There is also a net change in the amount of band bending from one cycle of light to dark to the next. These samples appear to adsorb/trap species, affecting the surface properties of the film. This was also suggested in a recent paper by Mitchell *et al.*²⁸ Hydrazide surfaces were found to trap charge at the interface. The charging capabilities were reversible and could be modulated by controlling O₂ and water vapor. Further mention is made of the hydrazide group possibly being ionized as an electron donor.²⁸

The NHS sample had a similar effect while the acid sample showed very little of this behavior. In addition, the surface has become less and less like gold, due to a higher electron density at the surface. The surface dipole shows a vertical shift away from the reference electrode. It becomes easier to remove an electron from the surface, when compared to gold.

Sample	$C_{\text{total}} (\mu\text{F})/\text{cm}^2$	$C_m (\mu\text{F})/\text{cm}^2$	$\epsilon_{\text{effective}}$	$L (\text{\AA})$
1	1.21	1.81	4.30	20.3 ± 0.9
2	1.27	1.95	4.54	19.9 ± 0.6
3	1.38	2.22	5.15	19.8 ± 0.6

Table 11. Monolayer Capacitance, Effective Dielectric constant, and Monolayer thicknesses for PH modified Si(111) measured in 0.1M H_2SO_4

The impedance data for the cell in accumulation reveals an arc that is considerably depressed (see Figure 25). A simple RC circuit cannot be used to model this data. In contrast, a CPE circuit with an α of 0.18 matches the data quite well. The resistance is similar to that of the NHS sample. The time constant has also increased implying the relaxation time of the circuit has decreased. It takes less time for the capacitor to discharge. This might indicate a measure of the uniformity of the monolayer. The capacitance values in Table 11 are slightly lower than the values extracted from the time constant. This is likely due to the fact that evaluation of the time constant only holds for a simple RC circuit. Upon closer examination of Figure 25, it is clear that there are actually two impedance arcs. The first few data points do not show the peak required to extract a time constant from the data. This initial arc could be a result of increased introduction of defects on the surface. The parallel resistance has also increased slightly which means the NHS and PH surfaces are better insulators than the UDA samples. This could be because the groups are larger and are better able to protect the surface from permeation and surface trapping.

Figure 25. Complex Impedance plot for the PH surface in 0.1M H₂SO₄, where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element.

Measurements are taken 0.3V in accumulation

3.6 Nitrophenylhydrazine Modified Si(111)

Figure 26. FTIR Spectrum of NPH

The FTIR spectra of NPH is slightly more complicated than the NHS surface. The characteristic peaks at 2923 and 2853 cm^{-1} represent the methylene groups of the alkyl chain. IR Peaks also appear in the carbonyl region at 1733, 1716, and 1700 cm^{-1} . These are more difficult to explain. Aryl overtones are broader and span longer scales so this cannot be the cause of such peaks. There are very few functional groups absorbing at this energy. Unreacted NHS would be shifted to higher frequencies and be represented by a stronger carbonyl stretch.⁵⁵ It is likely that these bands can be explained by solvent effects or introduction of impurities. The chemistry for modification is well established and utilized previously.^{28,35,36} This spectra was taken after 10 minutes in the NPH solution. To ensure maximum coverage and elimination of side reactions it has been recommended that the sample be allowed a minimum of twenty minutes. This was the procedure followed for all subsequent modifications.

The aromatic peak at 1636 cm^{-1} is characteristic of the carbon double bond, which confirms the presence of a phenyl ring. The quartet of peaks between 1580-1550 is characteristic of an aromatic nitro group in the para position and confirms the modification of the NHS to NPH.⁵⁵ The characteristic amide stretch at 1652 cm^{-1} provides additional evidence. The phenylhydrazide surface was also measured and revealed identical peaks with exception to the nitro group. The peaks at 1734 and 1717 cm^{-1} were still present at the same intensity. Because of the treatment of these surfaces with several solvents and the trapping capability of the surface these peaks could be present for a variety of reasons.

The open circuit potential of the nitrophenylhydrazide is somewhat more variable than previous modifications. However, the general trend seems to imply a shift back to a

more positive potential. The potential shift with respect to SCE is more negative compared to NHS and less negative than the phenylhydrazine. This must be a reflection of the larger dipole effect of the nitro group. Because the OCP has shifted in a positive direction, the net difference is about -0.2V larger than the phenylhydrazide.

Sample	OCP (v)	E_{fb} vs SCE (v)	N_d (cm^{-3})	Band Bending at OCP (V)
1	-0.068	-.876	$4.60 * 10^{14}$	-0.808
2	-0.108	-.799	$1.03 * 10^{15}$	-0.691
3	-0.278	-.858	$4.39 * 10^{14}$	-0.580
4	-0.160	-.773	$9.80 * 10^{14}$	-0.613
5	-0.212	-.882	$1.03 * 10^{15}$	-0.670
Measurement		-0.838	$7.88 \pm .31$	-0.672
Average		± 0.049	$* 10^{15}$	± 0.088

Table 12. Flatband potential, OCP, and Dopant Densities the NPH Modified Si(111) measured in $0.1\text{M H}_2\text{SO}_4$

There is a clear increase in the effective dielectric of the monolayer that previous modifications have not shown. This change is likely due to the nitro group withdrawing electron density from the phenyl ring and alkyl chains. This diminishing of electron density should cause the semiconductor to be less depleted. The measurement of the net change of the Mott-Schottky data shows this but not to the same extent seen in PH surfaces. The net change, -0.67V , is larger than both the NHS and PH modifications. It should be noted that two measurements hover at 0.6V and the other two at 0.7V . It is

difficult to determine which set of measurements is representative of the NPH surface. A possible explanation could be the problems that arose during the modification of the samples. The NPH was difficult to dissolve and often left visible residue on the samples. This residue could not be removed with either sonication in TCE or rinsing with THF.

Sample	$C_{\text{total}} (\mu\text{F})/\text{cm}^2$	$C_{\text{m}} (\mu\text{F})/\text{cm}^2$	$\epsilon_{\text{effective}}$	$l (\text{\AA})$
1	1.41	2.29	5.87	21.9 ± 0.9
2	1.50	2.54	6.78	22.8 ± 0.3
3	1.40	2.27	6.06	22.8 ± 2.0

Table 13. Monolayer Capacitance, Effective Dielectric constant, and Monolayer thickness for Nitrophenylhydrazide modified Si(111) measured in 0.1M H_2SO_4

Kelvin probe measurements show a net shift in the positive direction, which matches the OCP. The net band bending is smaller at about -0.25V . This clearly shows a discrepancy between the Kelvin Probe and Mott-Schottky measurements. The positive open circuit potential may be explained by the positive vertical shift in the Kelvin Probe. The surface dipole has become more positive, meaning it is more difficult to take electrons away from the surface. An increased effective dielectric constant should create a greater dipole. The pull is away from the semiconductor with the nitro group attracting electron density away from the interface. This is indicative of an overall negative dipole. A possible explanation is that the sample has a strong ability to attract ambient substances to it, thereby effectively adjusting the surface dipole. Perhaps the electron density is attracting positively charged species towards it to create a layer of adsorbed charge. If this occurred prior to immersion into the electrochemical cell, that would account for the

electrode being further depleted. Again this would coincide with the behaviour shown by Mitchell *et al.*²⁸

Figure 27. Surface Voltage for NPH modified Si(111) in Dark and under Illumination. Higher Plateaus are Measured in the Dark and Lower Values Correspond with Light.

The impedance arc in Figure 28 shows some uncharacteristic behaviour. The film resistance has greatly increased supporting the idea that charge is trapped in or on the film. There is probably some electrode interaction in this system that is not immediately obvious. The time constant for the system is not unusual showing similar relaxation times to the NHS and NPH surfaces. The small initial distortions in the impedance arcs that are visible in the UDA, NHS and PH are not seen in NPH. It is important to note that, in the case of NHS and PH the distortions are the beginnings of small impedance arcs that cannot be resolved. With the UDA surface it is a linear region which is characteristic of thin film penetration.

Figure 28. Complex Impedance plot for the NPH surface in 0.1M H₂SO₄, where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element.

Measurements are taken 0.3V in accumulation

3.7 Dinitrophenylhydrazine Modified Si(111)

The dinitrophenylhydrazide (DNPH) modified silicon samples reveal the same trend as the phenyl modified substrate. The surface is less depleted of majority carriers, likely due to the large capability to withdraw electrons that the nitro groups have. The magnitude of the change shows a shift further into depletion compared to the PH. While puzzling, closer examination of the data reveals more variability in the NPH and DNPH measurements than the PH surfaces. Outlying data points such as sample 3 and 4 could potentially be skewing the data as was the case for the NPH surface.

Sample	Ocp (v)	E _{fb} vs SCE (v)	N _d (cm ⁻³)	Band Bending at OCP (V)
1	-0.301	-.9489	1.184 * 10 ¹⁵	-0.6479
2	-0.442	-.942	1.07 * 10 ¹⁵	-0.500
3	-0.302	-1.025	9.53 * 10 ¹⁴	-0.722
4	-0.335	-1.066	1.71 * 10 ¹⁵	-0.731
5	-0.400	-.940	1.29 * 10 ¹⁵	-0.540
6	-0.320	-.873	9.49 * 10 ¹⁴	-0.553
Measurement		-0.966	1.19 ± .29 *	-0.616
Average		±0.069	10 ¹⁵	±0.099

Table 14. Flatband potential, OCP, and Dopant Densities the DNPH Modified Si(111) measured in 0.1M H₂SO₄

Even with the polar end groups the effective dielectric constant has not changed appreciably. This is unusual considering the larger values found in the NPH samples. Capacitance values for each modification, with the exception of the unusual behaviour of the NPH impedance data, have all been quite similar.

Sample	C _{total} (μF)/cm ²	C _m (μF)/cm ²	ε _{effective}	l (Å)
1	1.27	1.95	4.59	20.1 ± 0.7
2	1.08	1.53	3.57	19.9 ± 0.8
3	1.05	1.29	3.01	19.9 ± 0.5

Table 15. Monolayer Capacitance, Effective Dielectric constant, and Monolayer thickness of Dinitrophenylhydrazide modified Si(111) measured in 0.1M H₂SO₄

The surface photovoltage, Figure 28, shows a decrease in band bending. There is also a dipole shift, further away from the gold reference, probably due to the polar nitro groups. It is difficult to quantify the vertical shift due to what looks like the charge/discharge behaviour of the surface over time. The second curve drifts in a positive direction and shifts to a position parallel to the initial measurement. This drift is also seen under illumination, which implies that states that are deeply trapped are not released by the absorbed photons at the given light intensity. The overall positive shift over time further supports the theory that the NPH and DNPH trap potential charge.

Figure 29. Surface Voltage for DN PH modified Si(111) in Dark and under Illumination. Higher Plateaus are Measured in the Dark and Lower Values Correspond with Light.

The Impedance arc of Figure 30, derived under accumulation, yields two distinct time constants. The first arc could be due to surface states on the sample. If the sample was not driven far enough into accumulation two distinct arcs should be visible. The

capacitance $2.35\mu\text{F}$ value for the large arc is considerably larger than the measured values. If this is indeed the correct capacitance, that would mean the effective dipole on the surface is larger than the calculated value.

Figure 30. Complex Impedance plot for the NPH surface in $0.1\text{M H}_2\text{SO}_4$, where the dashed lines represent the fit from a Simple RC circuit and the solid line is the fit the CPE element.

Measurements are taken 0.35V in accumulation. Where $R_{p1} = 320$, $T_{c1} = 4.63\text{E-}6$, $C_1 = 0.021\text{ uF}$ are the values for the first arc and $R_{p2} = 780$, $T_{c2} = 1.28\text{E-}3$, $C_2 = 2.35\text{uF}$ represent the second arc.

3.8 Substrate Quality and Surface States

An interesting feature of the capacitance curves is the growth of a small arc in the depletion region with subsequent modifications. The reason for this additional capacitive component is likely the presence of surface states. Capacitance and impedance measurements provide the tools to study the interface capacity. A low interface density (less than 10^{11} cm^{-2}) is the goal of all surface chemists and is indicative of a well-packed, uniform monolayer⁵. Lewis *et al.* exhibited a surface trap density of 3

$\times 10^9 \text{ cm}^{-2}$ on alkylated silicon samples.³⁴ The number seems small considering that the samples have the same packing issues as the ones considered here. It should be noted that the experiment examined the methyl terminated surface to ensure maximum coverage and the surface trap density was determined by measuring the surface recombination velocity. It may be less sensitive than electrochemical measurements. Permeation into the film would almost certainly cause these monolayers to illustrate a much larger number of surface states. The extra capacitance of these samples is a reflection of this.

Figure 31. Capacitance curves of the UDA, NHS, and DNPH measured in 0.1 M H_2SO_4 . Fits not shown.

Figure 31 shows the capacitance curves of three modified electrodes. The PH curve is omitted because it is virtually identical to the NHS. The NPH is omitted because the curve is on the same order of magnitude as the DNPH. Careful examination of the region around -0.4V reveals an increase in capacitance. A closer look at the curves, Figure 32, allows examination of the growth of the additional capacitance.

Figure 32. Capacitance curves of the UDA, NHS, and DNPH. In order of increasing surface state Capacitance.

The impedance measurements are used to extract the number of interface states when the applied bias is approximately at flatband. The capacitance of the monolayer, which is largely due to dipole contributions, should not be greatly affected at this voltage level. At flatband, the redox potential of the electrolyte is the same as the Fermi level. Therefore, there is no need to be concerned about the capacitance of the space charge layer, and the Helmholtz capacitance is negligible. Impedance data can then be used to determine the total capacitance of the monolayer, plus the contribution of the surface states. The number of interface states is equivalent to Equation 8. Typical impedance arcs at flatband are seen in Figure 33.

Figure 33. Complex Impedance Arcs for PH in 0.1M H₂SO₄ at E_{fb} where the Solid Line Represents the Fit of a simple RC circuit.

Using Equation 20 for the total capacitance of the electrode taken at flatband allows the number of surface defects to be quantified.

$$\frac{1}{C_{total}} = \frac{1}{C_m} + \frac{1}{C_{ss}} \quad \text{Equation 20}$$

There was considerable difficulty in obtaining impedance curves for the DNPH data. As a result, the NPH results will be representative of the DNPH samples since the growth curves are virtually identical.

	C_{total} (μF)	C_m (μF)	C_{ss} (μF)	N_{it} * 10¹¹/cm²
UDA	0.15	2.23	0.16	1.03
NHS	0.39	1.88	0.49	3.16
PH	1.69	1.99	11.21	72.4

	$C_{\text{total}} (\mu\text{F})$	$C_{\text{m}} (\mu\text{F})$	$C_{\text{ss}} (\mu\text{F})$	$N_{\text{it}} * 10^{11}/\text{cm}^2$
NPH	1.15	2.37	2.23	14.4

Table 16. The Number of Surface states, Monolayer & Surface State Capacitance for Modified Si(111)

Clearly, Table 16 shows that the increase of defects from one modification to the next makes these systems problematic for potential device applications. More complete coverage or passivation of unreacted sites on the silicon would greatly enhance the accuracy of the electrochemical measurements. Only general trends can be discerned at present. Because of the difficulty in differentiating between monolayer characteristics and impurities or defects it is hard to quantify values like capacitance.

	Band Bending in Solution (V)	Band Bending in Ambient Air (V)	Effective Dielectric F/cm	Monolayer Capacitance (μF)
Si-H	-0.123	-0.050	N/A	N/A
UDA	-0.364	-0.230	3.94	2.23
NHS	-0.596	<-0.350	4.34	1.88
PH	-0.551	-0.280	4.66	1.99
NPH	-0.672	~ -0.200	6.24	2.34
DNPH	-0.616	~ -0.200	3.72	1.59

Table 17. Summary of Electrical Properties of modified Silicon(111) in Sulfuric Acid

A summary of the band bending can be found in Table 17 to view the difference from one modification to the next. A measurable increase in band bending pushing the semiconductor electrode is seen from Si-H to UDA and then to the NHS

surface. The trend is confirmed with by Kelvin probe measurements. The PH modification appears to pull electron density away from the semiconductor indicated by a decrease in band bending. This means that the semiconductor is able to feel the effect of the electric field that results from the dipole. The NPH surface shows this trend in the Kelvin probe data but not in aqueous measurements. The DNPH is quite similar to the PH data.

Capacitance values for each surface are comparable with a slight decrease with the DNPH sample. This is a reflection of the dielectric constant. The decreased band bending should coincide with a greater monolayer capacitance and greater dielectric constant. The changes are small enough from one monolayer to the next that deviations can be attributed to solvent interaction, surface states, or contact issues.

4 Results & Discussion:

A Study of Modified Si(111) in ACN/0.1 M TBAPF₆

The measured electrochemical behaviour of silicon samples modified in organics should be reproducible in other solvents. The following is an examination of the electrochemical measurements completed in acetonitrile utilizing TBAPF₆ as the electrolyte. The entire sequence of measurements is not complete due to the difficulty in working with this particularly solvent. It will become clear that measurements in ACN can be used to substantiate trends observed in aqueous solutions but prove difficult to interpret and often lead to ambiguous results.

4.1 UDA modified Si(111):

Mott-Schottky measurements of the acid modified surface in acetonitrile serves as the reference for successive modifications. The hydrogen terminated surface was not measured in ACN due to the difficulty in obtaining duplicate measurements.

The flatband potentials for the UDA modified surface in Table 18 yield some interesting results. In comparison to measurements taken in an aqueous environment, the E_{fb} vs. SCE is similar and highly reproducible. The OCP with respect to SCE has shifted to a more negative potential for the UDA samples in the organic solvent. The resultant amount of band bending has increased as well. An ideal surface would produce virtually identical results regardless of solvent if it were a uniform monolayer. Some deviations may occur because of the ability of an electrolyte to compensate for an electric field but should be small. If there is substantial solvent interaction with the electrode, the OCP and flatband values could potentially be shifted. In an aqueous environment the alkyl chains

would prevent water permeation to any large extent. Acetonitrile is a hydrophobic, smaller molecule that could penetrate the thin film more effectively at sites where coverage was minimized. This was suggested by Yu *et al.* in a study of electron transfer through modified silicon in ACN.³⁰

Previous studies performed in ACN have shown that this particular solvent has a tendency to pin the Fermi level and increase the number of surface states in the gap.^{56,57} The surface states, which may initially be absent, seem to grow over time.^{56,57} This behaviour is seen clearly in the measurements of differential capacitance.

The net difference, approximately -660mV in ACN, corresponds to the amount of band bending for the UDA surface. Compared to the aqueous solvent, the electrode is further depleted of majority carriers. This would also agree with film permeation of the alkyl chains.

Sample	Ocp (v) vs SCE	E _{fb} vs SCE (v)	N _d (cm ⁻³)	Band Bending at OCP (V)
1	-0.016	-0.697	1.59 * 10 ¹⁵	-0.681
2	-0.021	-0.689	1.85 * 10 ¹⁵	-0.668
3	-0.027	-0.757	1.76 * 10 ¹⁵	-0.730
4	-0.050	-0.748	1.78 * 10 ¹⁵	-0.698
5	-0.132	-0.661	1.51 * 10 ¹⁵	-0.529
Measurement		-0.710	1.69 ± .14 *	-0.661
Average		±0.041	10 ¹⁵	±0.077

Table 18. Flatband potential, OCP, and Dopant Densities for UDA terminated Si(111) measured in ACN/0.1M TBAPF₆

An obvious inconsistency in measurements between the two solvents is the slope of the Mott-Schottky curve that yields the dopant density. The dopant density (N_d) derived in ACN is larger than the values found in an aqueous environment. Very little information regarding such behaviour is addressed in the literature. Because the procedure was systematic and the only factor varied was the solvent, this behaviour must be attributed to the solvent and electrolyte. The two values are on the same order of magnitude so there is no real cause for concern.

Figure 34 shows various capacitance curves for UDA samples measured in ACN. It is clear that the data is reproducible. The plateau region, where the capacitance in accumulation is at a maximum, is similar from sample to sample. It should be noted that it took several more trials to obtain valid results in ACN than in an aqueous solution. In the sulfuric acid solution, measurements were much more reproducible than in organic solvent.

Figure 34. Capacitance curves measured in Accumulation of UDA modified Si (111) in ACN/0.1 M TBAPF₆. Fits are not shown.

The capacitance of the acid and NHS samples in ACN are similar to the measured values in sulfuric acid. Because of the similarity of the data, the Helmholtz capacitance value, 3.56 μF , established in the aqueous solution will be used to estimate values in the organic solvent. Particularly, the monolayer capacitance, and effective dielectric constant in ACN will be determined.

Sample	$C_{\text{total}} (\mu\text{F})/\text{cm}^2$	$C_m (\mu\text{F})/\text{cm}^2$	$\epsilon_{\text{effective}} (\text{F}/\text{cm})$	$l (\text{\AA})$
1	1.82	3.64	5.29	12.4 ± 1.3
2	1.61	2.88	4.82	14.3 ± 0.3
3	1.64	2.99	5.32	15.2 ± 0.8

Table 19. Capacitance, Effective dielectric and Thicknesses for UDA modified Si(111)

The total capacitance of the system is slightly higher in ACN than previously measured values obtained in sulfuric acid. This causes the monolayer capacitance to become greater. The effective dielectric constant is proportional to the monolayer capacitance so this also increases. Overall, the data is quite similar to the values established in sulfuric acid. It is a reassuring indication with regard to the state of the thin film.

Figure 35. Complex Impedance Arcs for UDA in 0.1M ACN/0.1 M TBAPF₆ 0.4V in accumulation, where the Solid Line Represents the Fit of a simple RC circuit.

The impedance data for the film in organic solvent measured in accumulation yields an overall capacitance similar to that of the aqueous measurements. However, the resistance of the monolayer greatly increased. This would be indicative of a well-packed monolayer. The resistances for both the UDA and NHS surfaces were considerably smaller in the sulfuric acid solution than ACN. These results coincide with the theory that

ACN is permeating the thin film. The increase in resistivity must be a result of the surface having vacant sites filled with ACN.

Trying to measure the impedance of these samples in ACN has proven difficult, particularly at flatband. Measuring the number of surface states in organic solvent would have been very useful as a guide to the measure of film penetration over time. However, none of the modified silicon samples produced any relevant data because the curve never reaches a plateau within the frequency range. The potentiostat would freeze up and be unable to complete the cycle of measurements at low frequencies.

4.2 NHS Modified Si(111)

The NHS modified Si(111) shows similar results to the UDA surface. Although the flatband with respect to SCE becomes increasingly negative, the OCP shows a fair amount of variation. As a result the change in band bending in ACN from UDA to NHS does not show the same push into depletion that is seen in sulfuric acid. The semiconductor is not as depleted as the acid samples in ACN. The net difference is comparable to the aqueous solution measurements for the NHS surface. The contrary behaviour of the NHS samples could again be a result of film penetration. If ACN is inserting itself into the film it could be inducing an electric field causing the semiconductor to react in kind. The error in this set of data has also increased.

Sample	Ocp (v) vs SCE	E_{fb} vs SCE (v)	N_d (cm ⁻³)	Band Bending at OCP (V)
1	-0.387	-0.778	$1.55 * 10^{15}$	-0.391

Sample	Ocp (v) vs SCE	E _{fb} vs SCE (v)	N _d (cm ⁻³)	Band Bending at OCP (V)
2	-0.124	-0.808	1.52 * 10 ¹⁵	-0.684
3	-0.301	-0.863	1.76 * 10 ¹⁵	-0.562
4	-0.099	-0.7561	1.59 * 10 ¹⁵	-0.657
Measurement		-0.801	1.60 ± .11*	-0.574
Average		±0.046	10 ¹⁵	±0.133

Table 20. Flatband potential, OCP, and Dopant Densities for NHS terminated Si(111) measured in ACN/0.1M TBAPF₆

The variability of the OCP could be a result of several issues. Dissolved oxygen in the solution can strongly affect the OCP of silicon electrodes.^{58,59} The resultant shift may be as much as 100-150mV. Bertanga *et al* suggest a positive shift in OCP may occur with an oxygenated solution.^{58,59} The solvent used for the study was HF so it is difficult to say what electrode behaviour would result from the organic solvent. The acetonitrile was taken freshly distilled but it is plausible that during preparation of the solution and electrode the solvent could have been contaminated whereas the aqueous solution was under purge continuously. In conjunction with this, the Fermi level may be pinned. Chazalviel *et al.* suggest that in acetonitrile this may occur as a result of adsorbed electrolyte species and the beginning of the oxidation of silicon.⁵⁶ Fermi level pinning would mean that the potential drop in depletion is in the Helmholtz layer instead of the space charge region. This would cause obvious shifts in flatband.

The difficulty in reproducing the Mott-Schottky data should be reflected in the capacitance measurements. It is clear from Figure 36, that this is not the case. The capacitance curves for NHS are reproducible and have comparable values to the acid modified surface. Whatever electrode processes are occurring at the surface affecting the Mott-Schottky do not seem to be affecting the total capacitance. However, the curves for the NHS surface do show some unusual characteristics. The second curve in Figure 36 reveals two humps prior to reaching the plateau region. This is common of measurements in acetonitrile and becomes more apparent with subsequent modifications.

Another interesting facet of the capacitance curves is the growth of surface states with time. Figure 36 shows a small curve very similar to those examined in Section 3.8. These curves are representative of the more reproducible samples that have been measured. If the sample is left too long in ACN, this curve, which is presumably a result of surface states, will increase dramatically. This behaviour must be a result of permeation into the thin film.

Figure 36. Capacitance curves measured in Accumulation of NHS modified Si (111) in ACN/0.1 M TBAPF₆. Fits are not shown.

Sample	$C_{\text{total}} (\mu\text{F})/\text{cm}^2$	$C_{\text{m}} (\mu\text{F})/\text{cm}^2$	$\epsilon_{\text{effective}} (\text{F}/\text{cm})$	$l (\text{\AA})$
1	1.74	2.99	6.26	17.9 ± 1.5
2	1.47	2.45	5.71	19.9 ± 0.7
3	1.42	2.32	4.94	18.2 ± 0.9

Table 21. Capacitance, Effective dielectric and thicknesses for NHS modified Si(111)

Table 21 reveals a surface characterized with a greater dielectric constant than the UDA surface. This behaviour was not evident in the aqueous measurements. It could be a result of film permeation or perhaps the fact that the cumulative dipoles on the NHS surface are better able to pull electron density away from the tail group. The dielectric is not a reflection of the orientation of the dipole, just the magnitude of it.

4.3 Phenylhydrazide Modified Si(111)

The data in Table 22 follows a similar trend to the measurements performed in aqueous solution. The E_{fb} with respect to the saturated calomel electrode is similar to NHS. The OCP has shifted further negative and as a result the net difference is smaller. This indicates that the phenylhydrazide surface is not as far in depletion as the NHS modified electrode. There is some amount of variability in the OCP measurements but the overall trend is quite apparent. Dopant densities are similar for each of the modified samples measured in acetonitrile. Having the PH surface less depleted is the same trend as that observed in an aqueous solution.

Sample	Ocp (V) vs SCE	E_{fb} vs SCE (V)	N_d (cm ⁻³)	Band Bending at OCP (V)
1	-0.329	-0.750	$1.52 * 10^{15}$	-0.421
2	-0.527	-0.716	$1.42 * 10^{15}$	-0.189
3	-0.559	-0.821	$1.76 * 10^{15}$	-0.262
4	-0.437	-0.707	$1.53 * 10^{15}$	-0.270
5	-0.597	-0.794	$1.65 * 10^{15}$	-0.197
6	-0.341	-0.801	$1.70 * 10^{15}$	-0.460
Measurement		-0.405	$1.14 \pm .34$	-0.300
Average		± 0.045	$* 10^{15}$	± 0.114

Table 22. Flatband potential, OCP, and Dopant Densities for PH terminated Si(111) measured in ACN/0.1M TBAPF₆

The phenylhydrazide modified surface is where the difficulty in taking measurements in ACN became obvious. Capacitance curves rendered highly erratic results. This occurred even when the ellipsometry measurements show data typical of the surface. There seems to be very little lateral shift in the measurements, which seemed to be common among all the other sets of data. The depressed capacitance values and unusual plateau regions make it impossible to determine any information regarding the nature of the insulating layer.

Figure 37. Capacitance curves measured in Accumulation of PH modified Si (111) in ACN/0.1 M TBAPF₆. Fits are not shown.

If the ACN is able to infiltrate the surface, it would have an influence on both the flatband and capacitance measurements. The effect could present itself as a flatband or OCP shift. It is difficult to determine how Fermi level pinning would affect capacitance measurements. The simplest picture of pinning is purely having the Fermi level fixed

with no potential drop occurring in the space charge region. However, capacitance is measured in accumulation and the potential drop should be across the Helmholtz layer. It is difficult to interpret such curves except to realize that there is a clearly a surface interaction occurring that hasn't been accounted for. In contrast, the capacitance curves are quite reproducible in H_2SO_4 . There should be little deviation between the two sets of measurements except for small solvent effects. The UDA and NHS surface are somewhat reproducible.

It could very well be the nature of the hydrazide structure that is the cause for the unusual surface interactions. The Kelvin probe measurements of the hydrazides show distinct potential shifts with time and potential charge trapping behaviour. Perhaps it is the ACN/Hydrazide interaction that is causing shifts in capacitance. A uniform monolayer would just have the tail groups interacting with the solvent and electrolyte.

4.4 Nitrophenylhydrazide Modified Si(111)

The NPH silicon electrodes displayed some variability with respect to OCP and flatband. The band bending however, showed smaller variation with the fourth sample having the smallest change. The net change of both the PH and NPH have shown that the polarity of the surfaces have driven the electrode to be less depleted. The dipole of the monolayer is compensating for the band bending. It is difficult to determine whether the flatband with respect to SCE is less depleted than the PH surface. Two of the samples show the semiconductor follow this trend and the others imply that the modification is further depleted. The variations are likely a result of the Fermi level pinning discussed in previous sections.

Sample	Ocp (V) vs SCE	E _{fb} vs SCE (v)	N _d (cm ⁻³)	Band Bending at OCP (V)
1	-0.237	-0.657	1.62 * 10 ¹⁵	-0.420
2	-0.509	-0.899	1.61 * 10 ¹⁵	-0.390
3	-0.337	-0.657	1.82 * 10 ¹⁵	-0.320
4	-0.703	-0.881	1.66 * 10 ¹⁵	-0.178
Measurement		-0.405	1.14 ± .34 *	-0.327 ± 0.108
Average		±0.045	10 ¹⁵	

Table 23. Flatband potential, OCP, and Dopant Densities for NPH terminated Si(111) measured in ACN/0.1M TBAPF₆

The impedance measurements for the NHP surface reveal a faster time constant and very large parallel resistance. An R_p value of 14k Ω is quite large and similar to the value obtained in the sulfuric acid solution. It's curious that the NPH surface should show the largest insulator resistance. The shape, size and polarity of the molecule are so similar to the DNPH surface that analogous results would be expected for both modifications. Unfortunately, the DNPH surface was not examined in organic solvent.

Figure 38. Complex Impedance Arcs for NPH in 0.1M ACN/0.1 M TBAPF₆ 0.4V in accumulation, where the Solid Line Represents the Fit of a simple RC circuit.

Capacitance values for the NPH modification are slightly higher than the values obtained in aqueous measurements. The results cannot be cross-referenced with direct capacitance measurements because of the difficulty in obtaining consistent data. Sample variations occurred regularly for the NPH surface.

Figure 39. Capacitance curves measured in Accumulation of NPH modified Si (111) in ACN/0.1 M TBAPF₆. Fits are not shown

The capacitance curves for the NPH surfaces are variable with a tendency of having a confusing plateau region. Some curves may plateau, while other will start to increase by very small increments. A decreased capacitance in the accumulation region has even been observed.

The task of producing reliable results in ACN has proven to be a daunting one. Although general behaviour for a data set can be found, extracting discrete values for the modified silicon samples is not possible. A tool that could provide information key to understanding the surface/solvent interaction would be further impedance measurements. Further experimentation is required to develop a greater understanding of interactions at the interface.

4.5 Electrical Properties of modified Silicon(111) in Acetonitrile

	Band Bending in Solution (V)	Band Bending in Ambient Air (V)	Effective Dielectric F/cm	Monolayer Capacitance (μF)
UDA	-0.661	-0.230	5.14	3.17
NHS	-0.574	<-0.350	5.63	2.60
PH	-0.300	-0.280	N/A	N/A
NPH	-0.327	$\sim$ -0.200	N/A	N/A

Table 24. Summary of Electrical Properties of modified Silicon(111) in Acetonitrile

A snapshot of the data for measurements in acetonitrile is provided in Table 24. Effective dielectric constants for the UDA and NHS surface are larger than values determined in sulfuric acid. This is likely because the monolayer capacitance is larger. The discrepancy could be a result of the fact that the values were determined by the Helmholtz capacitance determined in an aqueous environment. Perhaps the solvent effect is larger than originally suggested. The decreased band bending of the PH and NPH surfaces in ACN corresponds nicely with the KP data and aqueous measurements. Note the exception discussed in Section 3.6 with respect to the NPH data in sulfuric acid.

5 Conclusions:

Modification of semiconductors is an emerging field of study that appears to hold great promise. From the resultant data of this report it appears that several issues still need closer examination before potential device applications can be realized. These include the reproducibility of the OCP, surface states and monolayer density, as well as 2nd order circuit models.

It is clear from the data that surface modifications can be correlated with the OCP. The measured potential of the silicon electrodes at rest provides a gauge of how each successive modifications are affecting the electrode. In an aqueous environment the OCP values are similar for both the hydrogen terminated and UDA surfaces. With the NHS modification the OCP shifts to a more positive potential implying that the electrode is more insulating to current flow in the solution. Phenylhydrazine and Dinitrophenylhydrazine reveal similar behaviours with OCP shifts to negative potentials whereas the Nitrophenylhydrazide surface shifts to slightly more positive values as well.

Further investigation into the exact nature of the OCP shift is required in order to determine the exact cause. Comparisons of the open circuit potential in the dark and under illumination may shed light on the issue. Determining whether there is a correlation between dipole shifts in Kelvin probe measurements and OCP shifts is worth investigation.

A relationship between the flatband and OCP shifts and the dipole on the molecule is apparent. The amount of band bending in both the Kelvin probe measurements and the Mott-Schottky data is consistent with one another. It is small for the H-Si surface and increases with successive modifications. The difference between the

acid modified sample and the NHS is substantial, leaving the electrode depleted of majority carriers. However, as the silicon is modified with end groups having large dipole moments, the amount of band bending decreases.

Dipole shifts measured in the Kelvin probe correspond with the expected dipole shifts due to monolayer modification. Shorter chained alkyls would have a stronger impact on the space charge region because the electric field would penetrate the electrode from a shorter distance. Future considerations into varying the type of molecules used for the end group should also be considered in order to effectively observe the dipole effect. Strong electron withdrawing agents like halides on short chains may suffice to clearly display this trend.

The density of surface states, $10^{11-12}/\text{cm}^2$, reveals that it is premature to consider these surfaces for practical applications. Further investigations into creating more densely packed monolayers and better quality surfaces is required before such a function can be considered. Further characterization needs to be completed before this question can be addressed. Additional impedance spectroscopy is one way in which this can be done.

The impedance measurements for the thin films in both solvents display somewhat contrary results. The resistances of the insulating layers in aqueous solution are considerably smaller than those in ACN. This can be explained by penetration of the thin film by acetonitrile. Both cases reveal that the surfaces are not optimally packed. This is indicative of a inhomogeneous monolayer. Impedance curves at flatband in ACN would have provided a measure of the permeability of the film by extracting the number of surface states from the thin film. Confirming the capacitance values of the Si-H

surface that is used to estimate the Helmholtz layer in ACN would also provide information about the nature of the interaction of the surface with solvent.

The capacitance values obtained from impedance measurements are consistent with the values measured directly. The values don't change with the addition of polar groups at the tip of the chain. This is contrary to the Kelvin probe measurements and flatband data. A large dipole moment should increase the dielectric constant of a material. The monolayer capacitance values do not reflect this, and should be the subject of further studies. Molecular modeling of these systems could shed light on the subject.

Circuit models used to fit the impedance arcs match the data well. The occasional need to fit a CPE element to the data implies that there is surface inhomogeneity. This is yet another indication of poor packing. Information about the packing/permeability of the monolayer needs refining before device applications can be considered. Simply stated, more solid-state measurements in conjunction with solution electrochemistry is required in order to paint a complete picture of these surfaces.

References

1. A. Vilan and D. Cahen, *Trends in Biotechnology*, 2002, **20**, 22.
 2. M. Ratner, *Materials Today*, 2002, **5**, 20.
 3. H. O. Finklea, *Semiconductor Electrodes*, Elsevier, Amsterdam, 1988.
 4. R. Pieret, *Volume 1: Semiconductor fundamentals*, 2nd Ed., Addison-Wesley Publishing Co. Reading, 1988.
 5. X. G. Zhang, *Electrochemistry of Silicon and Its Oxide*, KluwerAcademic/Plenum Publishers, New York, 2001.
 6. G. S. Higashi, Y. J. Chabal, G. W. Trucks and K. Raghavachari, *Appl. Phys. Lett.*, 1990, **12**, 656.
 7. Jakob and Y. J. Chabal, *J. Chem. Phys.*, 1991, **95**, 2897.
 8. C. P. Wade and C. E. D. Chidsey, *Appl. Phys. Lett.*, 1998, **71**, 1679.
 9. P. Allongue, V. Kieling and H. Gerischer, *Electrochimica. Acta*, 1995, **40**, 1353.
 10. D. D. M. Wayner and R. A. Wolkow, *J. Chem. Soc Perkin Trans. 2*, 2002, **1**, 23.
 11. M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami and M. Ohwada, *J. Appl. Phys.*, 1990, **68**, 1272.
 12. D. Graf, M. Grudner and R. Schulz, *J. Vac. Sci. Technol.*, 1989, **A**, **7**, 808.
 13. D. Graf, M. Grudner and R. Schulz, *J. Appl. Phys.*, 1990, **68**, 5155.
 14. T. Miura, M. Niwano, D. Shoji and N. Miyamoto, *J. Appl. Phys.*, 1996, **79**, 4373.
 15. M. R. Linford and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 1993, **115**, 12631.
 16. M. R. Linford, P. Fenter, P. M. Eisenberger and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 1995, **117**, 3145.
-

-
17. J. Terry, M. R. Linford, C. Wirgen, R. Cao, P. Pianetta and C. E. D. Chidsey, *Appl. Phys. Lett.*, 1997, **71**, 1056.
 18. J. E. Bateman, R. D. Eagling, B. R. Horrocks and A. Houlton, *J. Phys. Chem. B.*, 2000, **104**, 5557.
 19. G. P. Lopinski, D. D. M. Wayner and R. A. Wolkow, *Nature*, 2000, **406**, 48.
 20. R. L. Cicero, C. E. D. Chidsey, G. P. Lopinski, D. D. M. Wayner and R. A. Wolkow, *Langmuir*, 2001, **18**, 305.
 21. A. Bansal, X. Li, I. Lauerman and N. S. Lewis, *J. Am. Chem. Soc.*, 1996, **118**, 7225.
 22. He, S. N. Patitsas, K. F. Preston, R. A. Wolkow and D. D. M. Wayner, *Chem. Phys. Lett.*, 1998, **286**, 508.
 23. R. Boukherroub, F. Bensebaa, S. Morin and D. D. M. Wayner, *Langmuir*, 1999, **15**, 3831.
 24. P. Allongue, C. Henry de Villeneuve, J. Pinson, F. Ozanam, J. N. Chazalviel and X. Wallart, *Electrochimica. Acta*, 1998, **43**, 2791.
 25. A. Fidelis, F. Ozanam and J.N. Chazalviel, *Surf. Sci.*, 2000, **444**, L7.
 26. A. B. Sieval, A. L. Demirel, J. W. M. Nissink, M. R. Linford, J. H. v. d. Maas, W. H. d. Jeu, H. Zuilhof and E. J. R. Sudholter, *Langmuir*, 1998, **14**, 1759.
 27. R. Boukherroub and D. D. M. Wayner, *J. Am. Chem. Soc.*, 1999, **121**, 11513.
 28. S. A. Mitchell, T. R. Ward, D. D. M. Wayner, and G. P. Lopinski, *J. Phys. Chem. B*, 2002, **106**, 9873.
 29. P. Allongue, C. Henry de Villeneuve, and J. Pinson, *Electrochimica Acta*, 2000, **45**, 3241.
-

-
30. H.-Z. Yu, R. Boukherroub, S. Morin and D. D. M. Wayner, *Electrochem. Commun.*, 2000, **2**, 562.
31. H.-Z. Yu, S. Morin, D. D. M. Wayner, P. Allongue and C. Henry de Villeneuve, *J. Phys. Chem. B.*, 2000, **104**, 11157.
32. J. Cheng, D. B. Robinson, R. L. Cicero, T. Eberspacher, C. J. Barrelet and C. E. D. Chidsey, *J. Phys. Chem. B.*, 2001, **105**, 10900.
33. C. J. Barrelet, D. B. Robinson, J. Cheng, T. P. Hunt, C. F. Quate and C. E. D. Chidsey, *Langmuir*, 2001, **17**, 3460.
34. W. J. Royea, A. Juang and N. S. Lewis, *Appl. Phys. Lett.*, 2000, **77**, 1988.
35. J.M. Tedder, A. Nechvatal, A.W. Murray, et al. *Amino-acids and proteins. In: Basic organic chemistry*. London: John Wiley & Sons, 1972.
36. J.V. Staros, R.W. Wright, D.M. Swingle, *Anal. Biochem.* 1986, **156**, 220.
37. A. Ulmann, *An Introduction to Ultrathin Organic Films*, Academic Press, San Diego, 1991.
38. A. Ulmann, *Chem. Rev.* 1996, **96**, 1533.
39. A. Ulmann, *Adv. Mater.* 1990, **2**, 573.
40. M.J. Madou, B.H. Loo, K.W. Frese, S.R. Morrison, *Surface Science*, 1980, **107**, 135.
41. J.L. Diot, J. Joseph, J.R. Martin, and P. Clechet, *J. Electroanal. Chem.*, 1985, **193**, 75.
42. G. Oskam, J.G. Long, A. Natarajan, and P.C. Searson, *J. Phys. D.*, 1998, **31**, 1927.
43. P. De Mierry, D. Ballutaud, and M. Aucouturier, *J. Electrochem. Soc.* 1990, **137**, 2966
44. J. R. Macdonald, *Impedance Spectroscopy Emphasizing Solid Materials and Systems*, John Wiley & Sons, New York, 1987.
-

-
45. J.R. Macdonald, *Electrochimica Acta*, 1990, **35**, 1483.
 46. D. E. Johnson, J. R. Johnson, and J. L Hilburn, *Electric Circuit Analysis*, 2nd Ed., Prentice Hall, New Jersey, 1992.
 47. R. Naumann, E.K. Schmidt, A. Jonczyk, K. Fendler, B. Kadenbach, T. Liebermann, A. Offenhausser, and W. Knoll, *Biosensors & Bioelectronics*, 1999, **4**, 651.
 48. R.L Cicero and C.E.D. Chidsey, *Langmuir*, 2000, **16**, 5688.
 49. A. Streitweiser, C. H. Heathcock, *Introduction to Organic Chemistry*, Macmillan Publishing Co., Inc., New York, 1976.
 50. R.P. Janek, W.R. Fawcett, and A. Ulman, *Langmuir*, 1998, **14**, 3011.
 51. B. Boukamp, *Equivalent Circuit (EQUIVCRT.PAS) Users Manual*, Univ. Twente, Enschede, the Netherlands, 1989.
 52. L. Kronik, Y. Shapira, *Surface and Interface Analysis*, 2001, **31**, 954.
 53. P. Hartig and J. Rappich, *App. Physics Letters*, 2002, **80**, 67.
 54. B. Goldstein and D. J. Szostak, *Surface Science*, 1980, **99**, 235.
 55. N.B. Colthup, L.H. Daly, and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1975.
 56. J.-N. Chazalviel and T.B. Truong, *J. Am. Chem. Soc.*, 1981, **103**, 7447.
 57. D. Laser and A. J. Bard, *The J. Phys. Chem.*, 1976, **80**, 459.
 58. V. Bertanga, C Plorgonven, F. Rouelle, and M. Chemla, *J. Electrochem. Soc.*, 1995, **142**, 3532.
 59. V. Bertanga, C Plorgonven, F. Rouelle, and M. Chemla, *J. Electrochem. Soc.*, 1997, **422**, 114.
-