Methyl Termination of Si(110) Surface for an Improved Stability Against Oxidation

by

Ankit Gupta

A Thesis submitted to the Faculty of Graduate Studies of

The University of Manitoba

in partial fulfilment of the requirements of the degree of

MASTER OF SCIENCE

Department of Electrical and Computer Engineering

University of Manitoba

Winnipeg

Copyright © 2015 by Ankit Gupta

ABSTRACT

Conversion and storage of solar energy in the form of hydrogen fuel using a solar water splitting device is one approach to meet increasing energy demands. Silicon microwires that serve as the light absorbing elements in the proposed design of the device, consist of different facets with an orientation along {110} direction. Oxidation of the microwire surface adversely affects the performance of the device by limiting the available photovoltage to drive the water splitting reactions. Functionalization of the silicon surface with an organic group can improve the oxidative stability of the surface. In this work, methyl substitution on a (110)-oriented monohydride terminated silicon surface using a chlorination/alkylation procedure was studied. Transmission infrared spectroscopy (TIRS), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) were used for characterizing different surfaces. TIRS observations indicated presence of coupled monohydride chains along [-1 1 0] direction on the hydrogen terminated silicon surface which was also supported by AFM images. XPS studies revealed a surface coverage of 0.83 ML for a methyl-terminated surface. The methyl-terminated surface was found to be stable when exposed to air, only 0.2 ML of surface oxide was observed even after a month from sample preparation. Thus, this surface preparation strategy can be implemented for the functionalization of the microwire surface.

Contents

Abstract ii

Acknowledgements v

List of Figures vii

List of Copyright Material for which Permission was Obtained ix

1. Introduction 1

1.1. Solar Energy and Hydrogen fuel……......1
1.2. Proposed Artificial Photosynthetic Device……..2
1.3. Surface Functionalization……4
1.4. Microwire Growth and Orientation……..5
1.5. Thesis Outline……...6

2 Background 7

2.1 Silicon Microstructure……...7
2.2 Wafer Cleaning……10
2.3 Hydrogen Termination and Anisotropic Etching……12
2.4 Functionalization……..14
2.5 Surface coverage……..16

3 Experimental Techniques 18

3.1 Sample Preparation……..18
3.2 Transmission Infrared Spectroscopy……...19
3.3 Atomic Force Microscopy……...22
3.4 X-ray Photoelectron Spectroscopy……..24
3.5 Surface Coverage……..…25

4 Results and Discussion 27

4.1 Results 27
4.1.1 Hydrogen Termination……27
4.1.2 Surface Functionalization…….....29
4.1.3 Surface coverage and Oxidative Stability……...32

4.2 Discussion 35
4.2.1 Functionalization and Surface Coverage…………………………………….....35
4.2.2 Oxidative Stability…………………………………………………………..36
4.2.3 Impact of Surface Roughness……………………………………………….37
4.2.4 Implications on Microwires…………………………………………………37

5 Conclusions and Future work 39

Appendix 41

References 45

ACKNOWLEDGEMENTS

I would like to thank University of Manitoba Faculty of Graduate Studies for their support and funding from Minister of Education and Advanced Learning, Manitoba. I am really grateful to my supervisors, Dr. Derek Oliver and Dr. Michael Freund for their guidance and support throughout my graduate program. I would not be able to complete my research without the support from my colleagues, namely Mahdi Nadimi, Megan McClarty, Elahe Asgari, Jared Bruce, Patrick Giesbrecht, Akin Iyogun, Kevin McEleney, Dwayne Chrusch and Onkar Singh Kang. It would have been really difficult to stay away from home if I hadn't met these wonderful friends who always supported and motivated me, namely Byoungyoul Park, Ashlesha Bhide, Ayesha Suboor, Sharmistha Bhadra, Janaranjana Sampath and Harshani Konara. I enjoyed working with some of the undergraduate students, Jordan Engel, Alvin Aliath and Ashish Kumar. Amy Dario from Department of Electrical and Computer Engineering has been a great support with her quick solutions to a lot of problems that students face during our graduate studies. I am really fortunate to have such wonderful parents and family who are always supportive in whatever I pursue in life. Veena Gupta, Abhinav Dadhich and Gautam Bajaj are a part of my extended family whom I can never thank enough for just being there whenever I need them. Finally, I would like to thank all my friends back home and IITJ family for making me what I am today.

To my parents

Anita and Shiv Prasad Gupta

List of Figures

1.1 The proposed design of a solar water splitting device. The semiconductor microwire arrays coated with catalysts will absorb sunlight and provide a surface for hydrogen evolution reactions. A polymer membrane provides mechanical support and facilitates charge transfer. Copyright: Megan McClarty. Reprinted with permission, from reference 2........ **3**

1.2 Model of silicon microwire with dominant crystal faces highlighted for a 6–sided wire. To the right is a scanning electron microscope image for an array of microwires that have 6–sided facets down the length of the wire. Copyright: Jared Bruce. Reprinted with permission, from reference 12........ **5**

2.1 A diamond cubic lattice structure........ **8**

2.2 Miller index representation of different crystal planes........ **8**

2.3 A simple representation of arrangement of silicon surface atoms with different orientations. Solid circles represent the top layer silicon atoms and the empty circles represent second layer of silicon atoms or silicon atoms that are directly connected to the body of the crystal. The dashed lines represent the dangling bonds........ **9**

2.4 Two-step chlorination/alkylation procedure used for attaching organic monolayers on hydrogen-terminated silicon surfaces........ **15**

2.5 A two-dimensional representation of monohydride-terminated silicon surfaces. The solid circles represent the surface silicon atoms attached to hydrogen and empty circles represent the second layer (bulk, below the plane of the page) of silicon atoms. For the Si(110) surface, only first layer of the silicon atoms is shown. Dashed lines represent the repeating unit (unit cell configuration)........ **16**

3.1 Wavelength and frequencies of different radiations in the electromagnetic spectrum...... **19**

3.2 Different vibration modes in a tri-atomic molecule........ **20**

3.3 Schematic representation of the set-up used for transmission infrared spectroscopy. The incident ray hits the sample at 74˚ to the surface normal (Brewster angle). The transmitted ray is detected by an MCT detector. The entire set-up is enclosed in an N_2(g)-purged chamber........ **21**

3.4 A tapping-mode atomic force microscopy set up. A resonating cantilever tip scans over the sample and the variation in the sample topography is detected by a laser beam-bouncing system with feedback controls........ **23**

4.1 TIRS spectrum of a hydrogen-terminated Si(110) surface. The peak at 2089 cm^{-1} corresponds to an in-phase coupled-monohydride stretching vibration and the peak at 2070 cm^{-1} corresponds to an out-of-phase stretching vibration (inset)..**27**

4.2 Tapping-mode AFM images of Si(110) surfaces. **a)** Before etching **b)** After FPM etch and treatment with deoxygenated water for 10 minutes, anisotropic etching by water results into terraces in [-1 1 0] direction producing a well ordered surface The horizontal streaking line at the bottom of image b) is most likely to be a result of topographic fluctuation that the tip couldn't recover from while scanning..**28**

4.3 XPS survey spectra of hydrogen-terminated (red), chlorinated (blue) and methylated (green) Si(110) surfaces. The spectra showed bulk silicon peaks along with C 1s and O 1s peaks. Chlorinated samples also showed Cl 2s and Cl 2p peaks that were absent in the other two spectra...**30**

4.4 High resolution XPS spectra of Si-2p region for a) H-terminated b) Cl-terminated and c) CH_3-terminated Si(110) surfaces. The spectra were fit to have two peaks (red) corresponding to the spin splits, Si-2$p_{3/2}$ and Si-2$p_{1/2}$. The Cl-terminated spectrum had an additional peak (blue) that is shifted in binding energy due to the surface overlayer. No silicon oxide peaks were observed in the 101 eV-103 eV region.....................................**31**

4.5 High resolution XPS spectra of C-1s region for a) H-terminated b) Cl-terminated and c) CH_3-terminated Si(110) surfaces. The spectra were fit to have two peaks (red) corresponding to the adventitious carbon. CH_3-terminated spectrum had a shoulder due to a shift in the binding energy for the carbon bonded to silicon which required an additional peak (blue)...**32**

4.6 High resolution XPS spectra of Si-2p region for H-Si(110) and CH_3-Si(110) surfaces. The peak between 101-105 eV represents surface silicon oxide. CH_3-Si(110) surface showed a greater oxidative stability even after a month of exposure to air......................................**34**

List of Copyrighted Material for Which Permission was Obtained

Figure 1.1: The proposed design of a solar water splitting device. The semiconductor microwire arrays coated with catalysts will absorb sunlight and provide a surface for hydrogen evolution reactions. A polymer membrane provides mechanical support and facilitates charge transfer. Copyright: Megan McClarty. Reprinted with permission, from reference 2……………………………………………………………………………..……...**3**

Figure 1.2: Model of silicon microwire with dominant crystal faces highlighted for a 6–sided wire. To the right is a scanning electron microscope image for an array of microwires that have 6–sided facets down the length of the wire. Copyright: Jared Bruce. Reprinted with permission, from reference 12…………………………………………………………………**5**

Chapter 1

Introduction

1.1 Solar Energy and Hydrogen fuel

The population around the globe is constantly increasing at an alarming rate. The world population is estimated to increase from 6 billion in 1999 to 9 billion in 2044.[1] This increase in the population in addition to an increased standard of living in the developing countries have raised the energy demands based on the per capita consumption.[2] The conventional energy resources are mostly based on non-renewable resources like fossil fuels. The rampant use of fossil fuels not only causes a scarcity of these resources but at the same time renders the environment in danger due to the emission of greenhouse gases. A sustainable development requires judicious use of these available resources keeping in mind the needs of future generations. This necessitates exploration of non-conventional, renewable and environmental friendly energy resources.

Sunlight is an enormous and inexhaustible source of energy that can help to mitigate the energy scarcity problems. The amount of solar energy falling on the earth surface is equivalent to 130 million 500 MW power plants.[3] The use of photovoltaic technology for the direct conversion of solar energy into electricity is an attractive scheme for energy harvesting. This technique however, faces the challenges of low efficiency, high cost and most

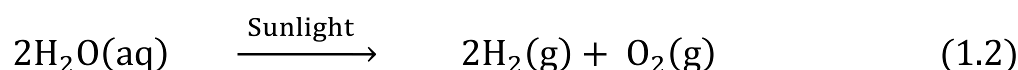
importantly, a consistent delivery of power due to the seasonal and daily variation of the available sunlight. Conversion of the solar energy in the form of chemical bonds seems to be a promising approach that will resolve the energy storage problems and will provide a clean path for harnessing energy.[3,4]

Hydrogen gas, when burned in presence of oxygen, produces water vapor with a release of energy as described in equation (1.1). The energy released in the reaction allows the use of hydrogen gas as a fuel with no carbon emissions. However, being a light gas, hydrogen is not freely available in the atmosphere and needs to be produced by other means. The fuel used in the process of production of hydrogen consumes more energy than what can be harnessed from H_2(g).[5] This causes the use of hydrogen gas as a fuel, highly unfavorable from an economic point of view. The use of sunlight to produce H_2(g) that can be stored and used as a fuel later on, can solve the aforementioned problem of fuel consumption.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \quad (1.1)$$

1.2 Proposed Artificial Photosynthetic Device

One of the proposed designs of an artificial photosynthetic device is based on conversion of solar energy into hydrogen fuel.[2-4,6,7] This device will use semiconductor materials to absorb sunlight to split water into hydrogen and oxygen gas.



$$2H_2O(aq) \xrightarrow{\text{Sunlight}} 2H_2(g) + O_2(g) \quad (1.2)$$

The device will consist of a dual array of high aspect ratio silicon microwire structures (Figure 1) that will increase the surface area available for light absorption. These microwires will be coated with suitable catalysts that will promote charge transfer at the semiconductor-liquid interface that will help in driving the water splitting reactions. One of the arrays that acts as photocathode will consist of p-type silicon that will drive the hydrogen evolution reaction (HER) whereas the n-type microwire array will drive the oxygen evolution reaction (OER).[3,4] The two microwire arrays will be embedded in a polymer membrane that will provide a mechanical support as well as a suitable medium for both electronic and ionic charge transfer to help separate both the hydrogen and oxygen evolving reactions.[8]

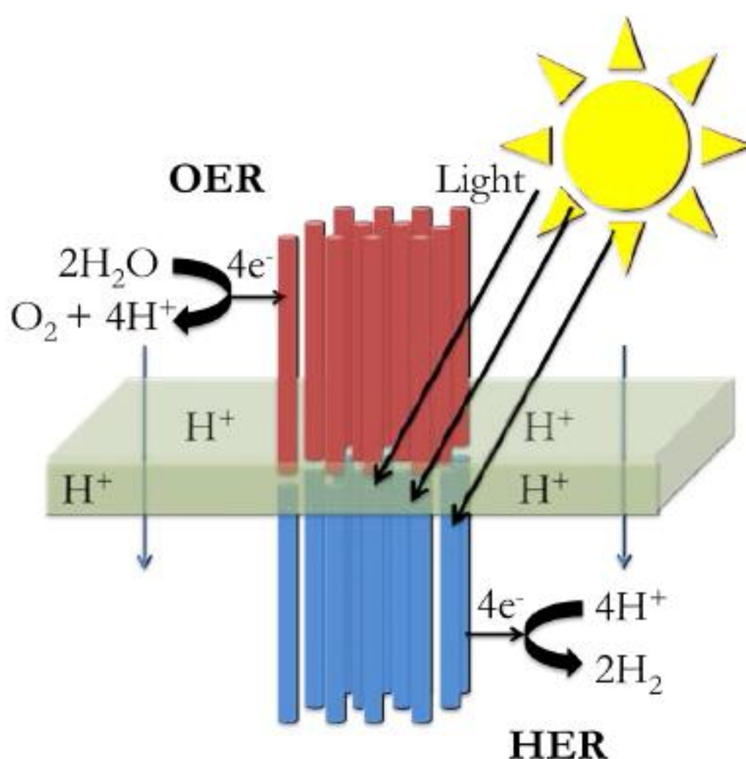


Figure 1.1 *The proposed design of a solar water splitting device. The semiconductor microwire arrays coated with catalysts will absorb sunlight and provide a surface for hydrogen evolution reactions. A polymer membrane provides mechanical support and facilitates charge transfer. Copyright: Megan McClarty. Reprinted with permission, from reference 2.*

1.3 Surface Functionalization

The efficiency of the proposed water splitting device is highly affected by the inherent losses in the device. The quality of the semiconductor surface is therefore very important for efficient charge transfer at the liquid-semiconductor interface and at the polymer-semiconductor junction. Silicon microwires are very sensitive towards oxidation when left in air or in an aqueous environment. Oxidation of these microwires increases the junction resistance at the polymer-semiconductor junction that can adversely affect the device performance.[6] To eliminate this problem, the silicon surface can be protected with a suitable overlayer that will prevent oxidation of the surface. Attaching hydrogen to silicon surface sites have shown to be an effective strategy as the hydrogen can provide a complete coverage to all the surface silicon sites with excellent electrical and chemical properties of the resulting surface. However, a hydrogen-terminated surface is only stable for a few minutes when left in air or in an aqueous environment and is not suitable as a long-term solution.

Functionalization of a silicon surface with an organic group had shown a better resistance towards oxidation.[9] The methyl ($-CH_3$) group, due to its small size, can also terminate all the available silicon sites on a Si(111) surface that makes it a suitable functional group that can protect the entire surface from oxidation to have a long term stability.[10,11] Therefore, attaching a methyl overlayer to the microwire surface seems to a suitable strategy for a long-term operation of the device.

1.4 Microwire Growth and Orientation

Silicon microwires are grown on a Si(111) wafer using a vapor-liquid-solid (VLS), bottom-up technique.[12] The wires grow vertically along the [111] direction (Figure 2) with a hexagonal cross section. The wires grown on a Si(111) wafer substrate using this technique have {110}-oriented facets along the longer dimension.[12-14] The edge joining the two consecutive {110}-facets may assume a different arrangement of atoms due to the irregularity in the symmetry. Some reports suggest that the atoms at these edges can have a {211}-orientation depending on the growth conditions.[12-14]

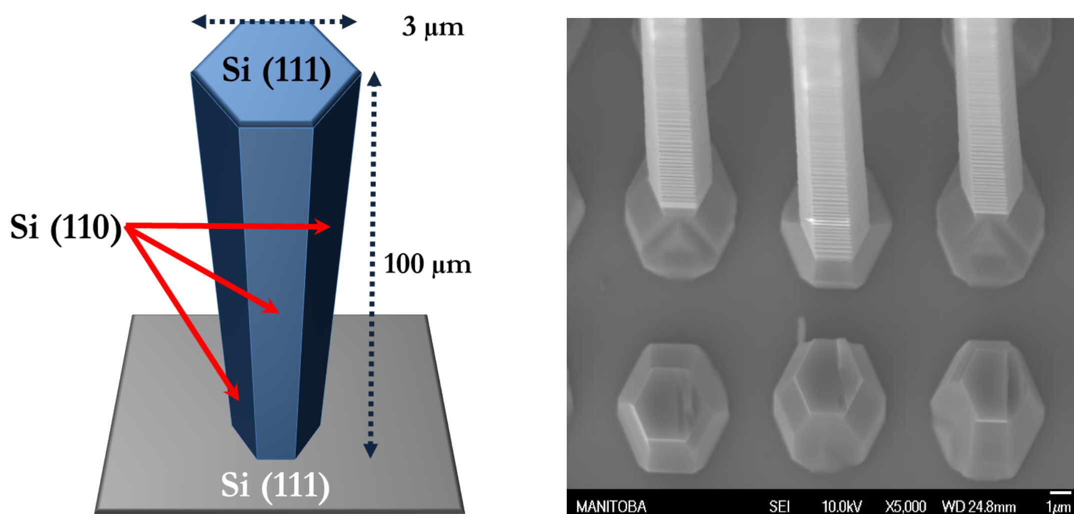


Figure 1.2 *Model of silicon microwire with dominant crystal faces highlighted for a 6–sided wire. To the right is a scanning electron microscope image for an array of microwires that have 6–sided facets down the length of the wire. Copyright: Jared Bruce. Reprinted with permission, from reference 12.*

Due to the complex three-dimensional structure of the microwires, it is difficult to use conventional spectroscopic techniques for surface characterization. Silicon surface functionalization techniques are well developed and studied for planar Si(111) surfaces.[9-11]

Therefore, to understand the chemical conditions required for chemical modification of silicon microwires, functionalization of a Si(111) surface is used as a reference.[13] {110}-oriented surfaces have a different bonding structure as compared to a (111)-oriented surface.[10,15] The difference in the bonding structure can directly impact the surface coverage and the chemical conditions required for surface preparation. Hence, {110}-oriented surfaces would be a better model for silicon microwire structure and it is important to investigate the functionalization techniques for these surfaces and the subsequent impact on the surface coverage.

1.5 Thesis Outline

This thesis provides a detailed background on different strategies that are being used for surface preparation and functionalization of silicon surfaces. Various experimental techniques like transmission infrared spectroscopy, X-ray photoelectron spectroscopy and atomic force microscopy are used to study a (110)-oriented planar silicon surface. Surface coverage after functionalization of a Si(110) surface with the methyl group is calculated. The effect of surface roughness on the oxidative stability of the surface is also discussed and a comparison is made with the previously attempted functionalization techniques for a Si(110) surface. The implications of these results on silicon microwires are also discussed.

Chapter 2

Background

2.1 Silicon Microstructure

Silicon is one of the most abundant elements found in the earth crust.[16] It is a group IV element in the periodic table with an atomic number 14. The element is the backbone of all the semiconductor devices operating today. A very high purity (99.999999999%) single-crystal silicon can be commercially produced that enables its use in microelectronic devices.[17] The semiconductor properties and abundance of the silicon also make it a suitable material for photovoltaic applications.[16] The silicon surface has a different structure when compared to bulk silicon. This facilitates the manipulation of the silicon surface for various applications. Thus, a thorough understanding of the silicon microstructure and different surface preparation strategies is of vital importance.

The crystal structure of silicon is proposed to be of diamond type (Figure 2.1) with a tetrahedral bonding arrangement in the bulk.[17-19] Different crystal faces of silicon can be obtained by cleaving the silicon crystal along a particular plane defined by their Miller indices. The three common silicon wafers with different orientations are along (100), (110) and (111) planes as shown in Figure 2.2.

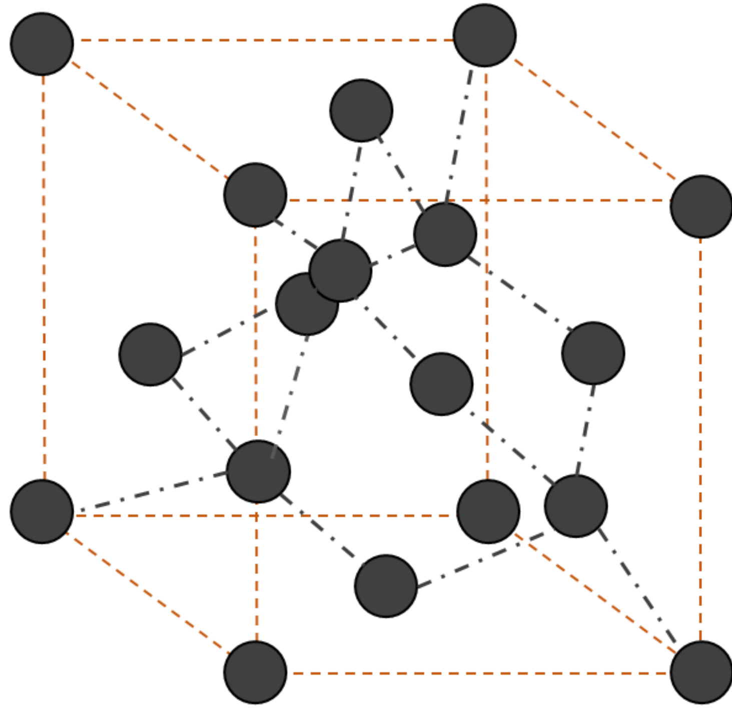


Figure 2.1 *A diamond cubic lattice structure.*

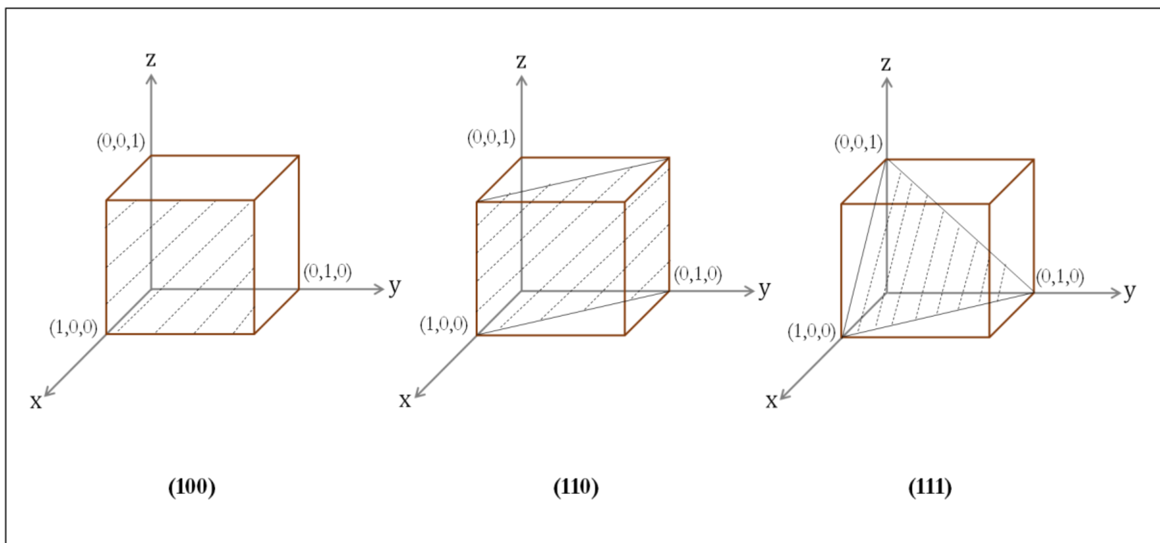


Figure 2.2 *Miller index representation of different crystal planes.*

The surface silicon atoms have unsatisfied valencies known as dangling bonds. A dangling bond contains only one electron unlike a regular bond that has a shared pair of electrons between two silicon atoms. An unreconstructed Si(100) surface has two dangling bonds per surface silicon atom (Figure 2.3). A Si(110) surface on the other hand, consists of a chain like structure that results into only one dangling bond per silicon site.[18] This makes the surface of a silicon wafer highly reactive and therefore, the preparation of the silicon surface is mostly done in vacuum to avoid instantaneous reactions with gases and adsorption of particles present in the atmosphere.[17,20]

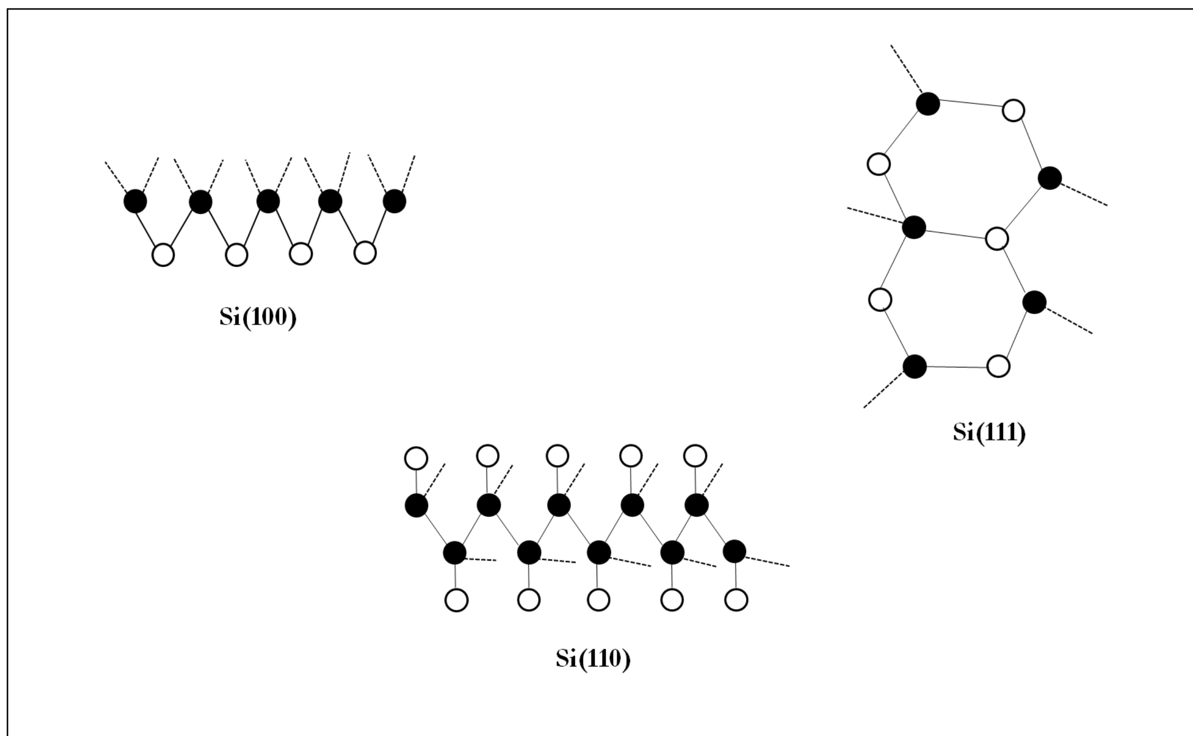


Figure 2.3 *A simple representation of arrangement of silicon surface atoms with different orientations. Solid circles represent the top layer silicon atoms and the empty circles represent second layer of silicon atoms or silicon atoms that are directly connected to the body of the crystal. The dashed lines represent the dangling bonds.*

When a bare silicon surface is exposed to air, the surface adsorbs the moisture present in atmosphere. The adsorbed moisture dissolves the atmospheric oxygen which then attacks the Si-Si back bonds to form a few nanometers thick native oxide layer. Ohmi predicted that if the silicon surface is exposed to an only moisture or only oxygen environment, it will never oxidize.[21] The oxidation of the silicon surface can be prevented or delayed by passivating it (terminating the surface silicon dangling bonds) with hydrogen using wet chemical processes. Different bonding structure of the silicon surfaces with different orientations requires a specific surface preparation strategy as discussed in the subsequent sections.

2.2 Wafer Cleaning

A silicon surface is often contaminated with particles adsorbed from the atmosphere, organic films, metallic impurities, etc. These impurities can adversely affect the device performance especially when the devices are of microscopic scale. For example, an impurity can act as an etching mask when a silicon surface is treated with HF-based solutions in various wet-chemical processes. The etching mask could preclude an effective passivation of the surface and hence can act as an active site for oxidation. Thus, an effective removal of any impurities present on the silicon surface is the first step for most surface preparation procedures.

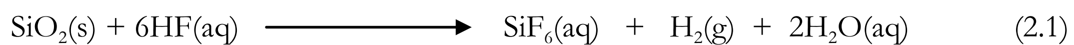
Various wafer cleaning procedures have been developed since the 1950s. Kern *et al.* provided a brief overview of the evolution of different technologies for wafer cleaning from 1950-1989.[22] The early silicon cleaning procedures include ultrasonic treatment for particle removal and boiling in hot concentrated nitric, sulphuric or hydrofluoric acids for removing

organic impurities. In 1970, Kern *et al.* at Radio Corporation of America (RCA) developed and published a very efficient peroxide based wafer cleaning procedure known as the RCA clean.[23] The RCA clean consists of two main steps: SC1 and SC2. In SC1, the wafer is treated with a 1:1:5 (v/v/v) solution of NH_4OH:H_2O_2:H_2O at about 80 ˚C for 10 minutes. The SC1 solution oxidizes the metallic and organic impurities present on the surface which then get dissolved in the solution. This step slightly etches the silicon surface and leaves a thin oxide layer.[24] An optional intermediate step between the SC1 and SC2 involves dipping the wafer in concentrated HF solution for few seconds to remove the oxide formed in the SC1 step. In the next step, known as SC2, the wafer is treated with a 1:1:6 (v/v/v) solution of HCl:H_2O_2:H_2O at about 80 ˚C for 10 minutes. The SC2 step removes all the inorganic impurities (like copper) that could not be removed in the SC1 step and also forms a protective oxide on the surface that prevents further contamination.

Teramoto *et al.* showed that (110)-oriented silicon surfaces are more sensitive towards surface roughening after the SC1 step as compared to a (100) or (111)-oriented surface.[25] This surface roughening could be attributed to the slight amount of etching during the SC1 process. Therefore, Si(110) wafers are cleaned with ozonized ultrapure water at room temperature or a 1:4 (v/v) solution of H_2SO_4:H_2O_2 at 95-100 ˚C (piranha clean) for 10 minutes.[15,25] Both cleaning procedures do not induce any surface roughness to the silicon surface. The inorganic impurities like copper are removed in the hydrogen-passivation step as discussed in the next section.

2.3 Hydrogen Termination and Anisotropic Etching

Cleaning with the piranha solution leads to formation of a protective oxide that needs to be etched away for H-termination of the surface. Etching with a concentrated or dilute hydrogen-fluoride (DHF) solution can be used for H-termination.[24,26,27] An HF solution selectively etches the silicon oxide on the surface leaving behind an H-terminated surface. The etching in an HF solution can be described by the following equation:



$$SiO_2(s) + 6HF(aq) \longrightarrow SiF_6(aq) + H_2(g) + 2H_2O(aq) \quad (2.1)$$

However, when etched with DHF, some of the silicon sites get attached to –OH groups that might lead to subsequent oxidation of the surface. Akahori *et al.* showed that when the Si(110) wafer is treated with a dilute hydrogen-fluoride solution mixed with a small amount of hydrogen-peroxide (H_2O_2), also known as a fluoride-peroxide mixture (FPM), a better H-terminated surface could be obtained.[15,28] The advantage of FPM etch is that if some of the sites get attached to the –OH group, the peroxide ions can completely oxidize those sites which is easier to remove by fluoride ions present in the solution. Therefore, the resulting surface is completely H-terminated and hydrophobic in nature in contrast to the oxidized surface which is hydrophilic. The H-terminated surface The FPM etch had also been shown to remove any inorganic impurities (like copper) present on the surface,[26] which facilitates in reducing the additional step of the SC2 process required in an RCA clean for the removal of inorganic impurities. On the silicon surface resulting from an FPM etch, silicon atoms at step edges and defect sites can have more than one unsatisfied valances i.e. the dangling bonds, which result into one or more hydrogen atoms attached to a single silicon atom and contain mono-, di- and tri-hydride terminated silicon sites.

The surface coverage after functionalization of an H-terminated silicon surface highly depends on the roughness of the H-terminated silicon surface.[29] A rough H-terminated silicon surface consists of mono-, di- and tri-hydride terminated silicon sites. An ideal H-terminated silicon surface only has monohydride-terminated silicon sites.[30] Steric hindrance due to the presence of di- and tri-hydride species results into an incomplete coverage after functionalization which may lead to a rapid oxidation over time.

The next step for an ideal H-terminated surface preparation is an anisotropic etching of the surface obtained after the FPM etch. The anisotropic etching preferentially etches the di- and tri-hydride species and produces a perfectly monohydride-terminated silicon surface. Higashi *et al.* showed that when a Si(111) surface is etched with an HF solution buffered with NH_4F at a controlled pH, anisotropic etching is observed.[30] This type of etching produced a perfectly mono-hydride terminated surface. Alternatively, instead of using a mixture of HF and NH_4F, first the silicon oxide can be etched by dipping the wafer into an HF or FPM solution and the anisotropic etching can be achieved by a subsequent etch in NH_4F solution. Jakob *et al.* found that when a buffered HF solution is used for etching a Si(110) surface, a rough surface is obtained with di- and tri-hydride species.[31] Ye *et al*. observed that the electrochemical etching of Si(110) surface in NH_4F solution requires a strict control of the electrode potential.[32] This precludes the use of an NH_4F for the anisotropic etching of (110)-oriented silicon surfaces.

Watanabe *et al.* (1991) first studied the anisotropic etching of a Si(111) surface by treating the surface with boiling water for 10 minutes after the HF etching.[33] However, the degree of anisotropy was lower than that for a NH_4F etch as observed by Pietsch *et al.* [34] Inspired by the anisotropic etching effect of water on Si(111) surfaces, Watanabe *et al.* (1996) first demonstrated that a monohydride-terminated Si(110) can be obtained by treating the surface with boiling water for 10 minutes after the HF etching.[35] Arima *et al.* found that if the FPM etched silicon surface is treated with water at room temperature for about 10 minutes, the OH^- ions anisotropically etch the di- and tri-hydride species leaving behind a completely monohydride-terminated surface.[15] The oxygen concentration in water needs to be controlled as it can oxidize the H-terminated silicon surface on a prolonged exposure.

2.4 Functionalization

Functionalization refers to the modification of the silicon surfaces by attachment of organic monolayers to impart desired chemical and electrical properties. Some organic films, when attached to a silicon surface form self-assembled monolayers (SAMs). Ulman[36] defined SAMs as "ordered molecular assemblies formed by the adsorption of an active surfactant on a solid surface." Bent *et al.* and Ciampi *et al.* provided a detailed overview of different dry and wet chemical preparation methods used for functionalization along with their potential applications.[17,37] Of these, the wet chemical surface functionalization approach for hydrogen terminated crystalline silicon surface is most attractive as all the reactions are carried out in chemical solutions and does not require a high temperature and low pressure requirement as observed for surface preparation procedures in vacuum.[9,17,37,38] The high temperature conditions may also degrade the microwire surface and may not be suitable for the polymer membrane.

Linford and Chidsey demonstrated that alkyl monolayers can be attached to hydrogen-terminated Si(100) and Si(111) surfaces by thermal decomposition of diacyl peroxides.[39] Following their work, several functionalization methods were proposed including two-step chlorination/alkylation, direct thermal attachment of alkyl Grignard reagent, UV-mediated hydrosilylation, electrochemical attachment of hydrocarbon monolayers, etc.[37] Of these, the two-step chlorination/alkylation method is the only wet chemical functionalization method that allows attachment of methyl monolayers on a hydrogen-terminated silicon surface. The other methods generally involve addition of larger organic groups containing double or triple bonds which can directly attach to the free radicals created due to the homolytic cleavage of Si-H bonds.[37] Thus, the two-step chlorination/alkylation is most suited functionalization procedure for the work presented in this thesis. The method consists of two steps: in the first step, an ideal hydrogen-terminated silicon surface is chlorinated in presence of a radical initiator (Figure 2.4). In the second step, the chlorinated surface is reacted with alkyl Grignard (RMgBr) or alkyl lithium (RLi) reagents to attach the required alkyl group to the silicon surface.[9] These reactions are needed to be carried out in an oxygen-limited environment (generally a N_2(g)-purged glove-box) as the intermediate products are susceptible towards oxidation.

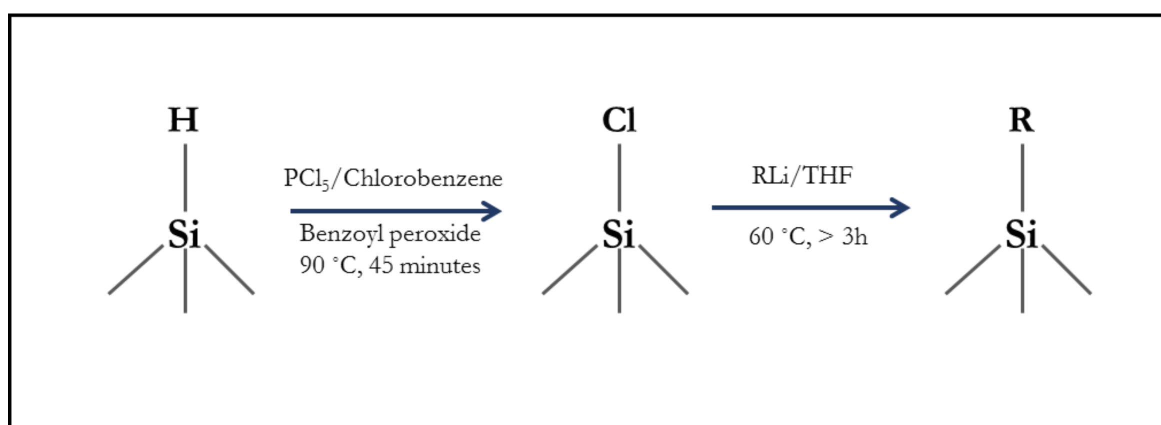


Figure 2.4 *Two-step chlorination/alkylation procedure used for attaching organic monolayers on hydrogen-terminated silicon surfaces.*

2.5 Surface coverage

An understanding of silicon microstructure as depicted in section 2.1 helps in estimating a possible surface coverage after functionalization for different surface orientation and organic groups. For instance, an ideal hydrogen-terminated Si(100) surface will have di-hydrides bonded to each of the surface silicon atoms. Therefore, to completely passivate the surface with an organic molecule, all the silicon atoms would have to be bonded to two functional groups. This will cause strong steric hindrance with the next neighborhood atom which is also bonded to two hydrocarbon atoms. Therefore, Si(100) surfaces can never be completely passivated with any of the functional groups.

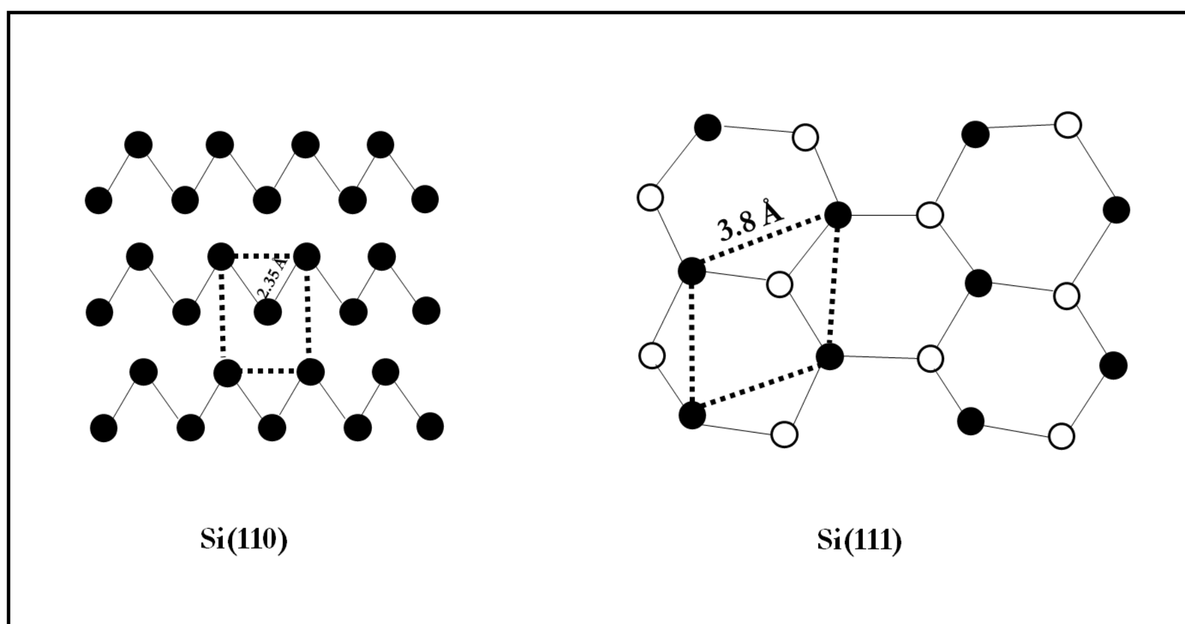


Figure 2.5 *A two-dimensional representation of monohydride-terminated silicon surfaces. The solid circles represent the surface silicon atoms attached to hydrogen and empty circles represent the second layer (bulk, below the plane of the page) of silicon atoms. For the Si(110) surface, only first layer of the silicon atoms is shown. Dashed lines represent the repeating unit (unit cell configuration).*

Figure 2.5 shows a unit cell (two-dimensional) representation of Si(111) and Si(110) surfaces. The inter-atomic distance between the surface silicon atoms on a (111)-oriented surface is 3.8 Å.[10] This provides sufficient space for the methyl group, with a Van-der-Waals diameter of 2.3-2.5 Å,[40,41] to passivate all the silicon sites on a (111)-oriented surface, without any steric hindrance. The ideal (110)-oriented surface can be represented as a rectangular unit cell with four of the silicon atoms occupying the corners of the rectangle and the fifth silicon atom is directly bonded to two of the corner atoms (Si-Si bond length ~2.35 Å).[32,35] The comparable size of the methyl group with the Si-Si bond length could hinder the complete passivation of a (110)-oriented surface. An incomplete surface coverage will lead to a relatively lower stability towards oxidation which can affect the device performance. It is therefore, important to explore the surface coverage possibilities for a (110)-oriented surface.

Chapter 3

Experimental Techniques

3.1 Sample Preparation

A double-side polished, boron-doped, p-type, (110)-oriented, silicon wafer (ρ > 60 Ω-cm, thickness 350 μm, *Virginia Semiconductor, Inc.*) was first cut into small rectangular pieces (~2 cm x 0.5 cm). The wafer was then cleaned with a 4:1 (v/v) H_2SO_4 (18 M):H_2O_2 (30 vol %), piranha solution that was kept at 95 ˚C -100 ˚C (*caution:* piranha solution can be extremely hot and dangerous, needs to be handled very carefully) for 10 minutes. The samples were then treated with deionized water (Millipore, 18.3 MΩ-cm) for 10 minutes, dried with Ar(g) and stored to be used later. The cleaned wafer was rinsed with methanol, acetonitrile and water sequentially and dried with Ar(g) before it was etched with a 1:1:98 (v/v/v) HF (49 vol %):H_2O_2 (30 vol %):H_2O solution for 5 minutes (*caution*: HF is a very dangerous acid, should only be handled in presence of a *safety-buddy* within 10 feet of the operator. MSDS* sheets for detailed safety precautions can be obtained from the University of Manitoba Clean-room). Finally, the sample was rinsed with deionized water (bubbled with Ar(g) for about 30 minutes to reduce the oxygen content) for 10 minutes and dried with Ar(g) to produce a monohydride terminated, H-Si(110) surface.[15]

---

*MSDS sheet can also be found at:
http://www.sigmaaldrich.com/catalog/product/sial/244279?lang=en®ion=CA

The monohydride-terminated sample was transferred to an N_2(g) purged glove box where it was reacted with a phosphorous pentachloride (PCl_5)-saturated, anhydrous chlorobenzene (99.8%, Sigma-Aldrich) solution with a small amount of benzoyl peroxide initiator at 90 ˚C for 45 minutes to obtain a chlorine-terminated, Cl-Si(110) surface. The sample was then rinsed with anhydrous chlorobenzene and anhydrous tertahydrofuran (THF, ≥99.9%, Sigma-Aldrich). The resulting Cl-Si(110) surface was reacted with 1.6 M methyl-lithium reagent (Sigma-Aldrich) in THF at 60 ˚C for a minimum of three hours to produce a methyl-terminated, CH_3-Si(110) surface.[9,10] The now-methylated sample was then cleaned with anhydrous THF followed by rinsing with anhydrous methanol (99.8%, Sigma-Aldrich) and removed from the chamber in the anhydrous methanol solution. The sample was then sonicated sequentially with methanol, acetonitrile and deionized water for five minutes each and finally dried with Ar(g).

3.2 Transmission Infrared Spectroscopy

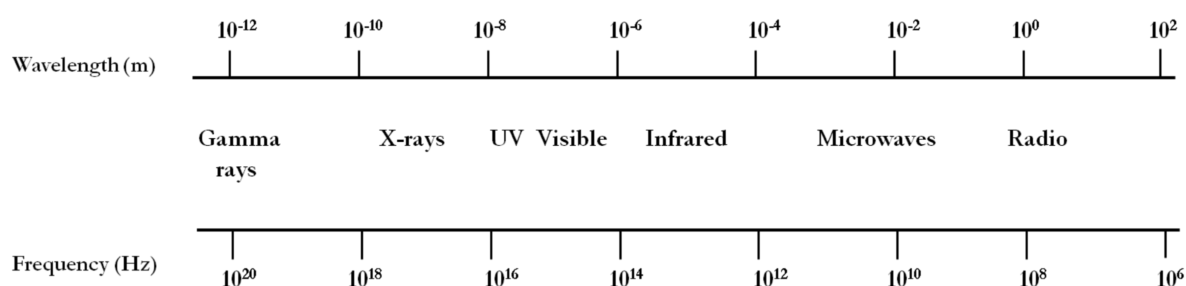


Figure 3.1 *Wavelength and frequencies of different radiations in the electromagnetic spectrum.*

Molecules in solids are continuously vibrating about their equilibrium positions above an absolute zero temperature (0 K). The associated vibration frequencies lie in the infrared region of the electromagnetic spectrum (Figure 3.1). When excited by an infrared light, the molecules can absorb the portion of the radiation corresponding to the difference between the consecutive vibrational states.[42] The absorbed vibrational frequency is a characteristic of a particular vibrational mode for a given molecule and hence can be used to identify the type of bonding between two different species.[43]

Different vibrational modes include stretching and bending modes. A stretching mode vibration changes the relative distance between two atoms but does not change the bond angle (Figure 3.2). Bending mode vibration in contrast changes the bond angle but does not change the bond length.[42] Stretching mode vibration can further be divided into symmetric and asymmetric stretch depending on the relative phase (stretch or compression) of different atoms vibrating in a molecule.

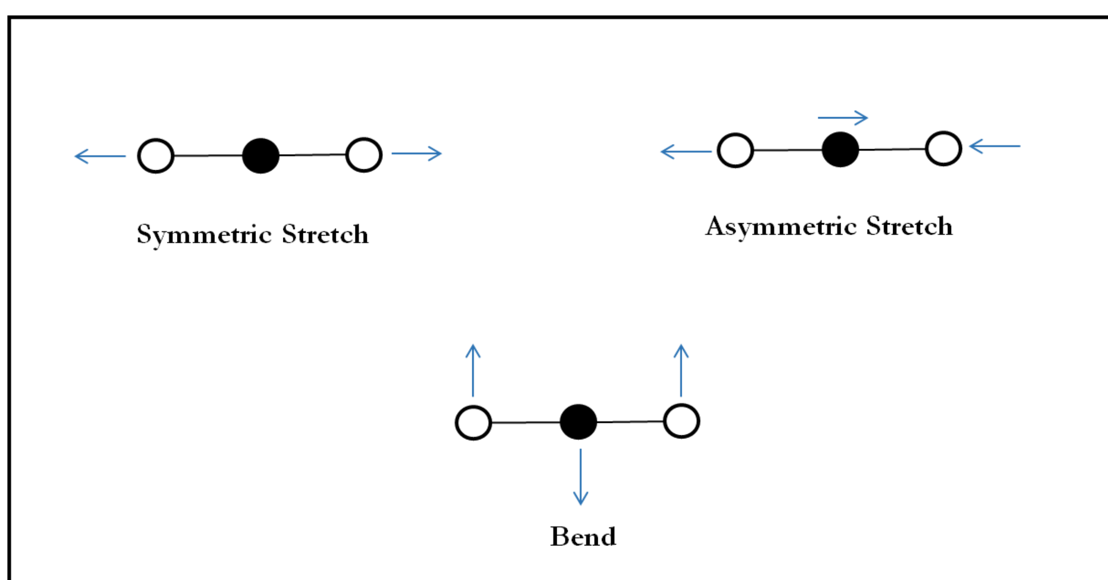


Figure 3.2 *Different vibration modes in a molecule.*

Different types of set-up used for infrared spectroscopy include a reflection, transmission and attenuated total reflectance (ATR) geometry. The absorbed signal in a single-reflection geometry is very weak and therefore difficult to detect. ATR geometry allows multiple reflection of the infrared ray passing through the sample and hence improves the signal obtained. However, this geometry requires a polarized infrared light incident on a silicon sample to detect the vibrational modes.[35,44] The transmission geometry allows the orientation of the sample with respect to the incident infrared light so that the signals corresponding to different polarizations can be obtained.[45-47]

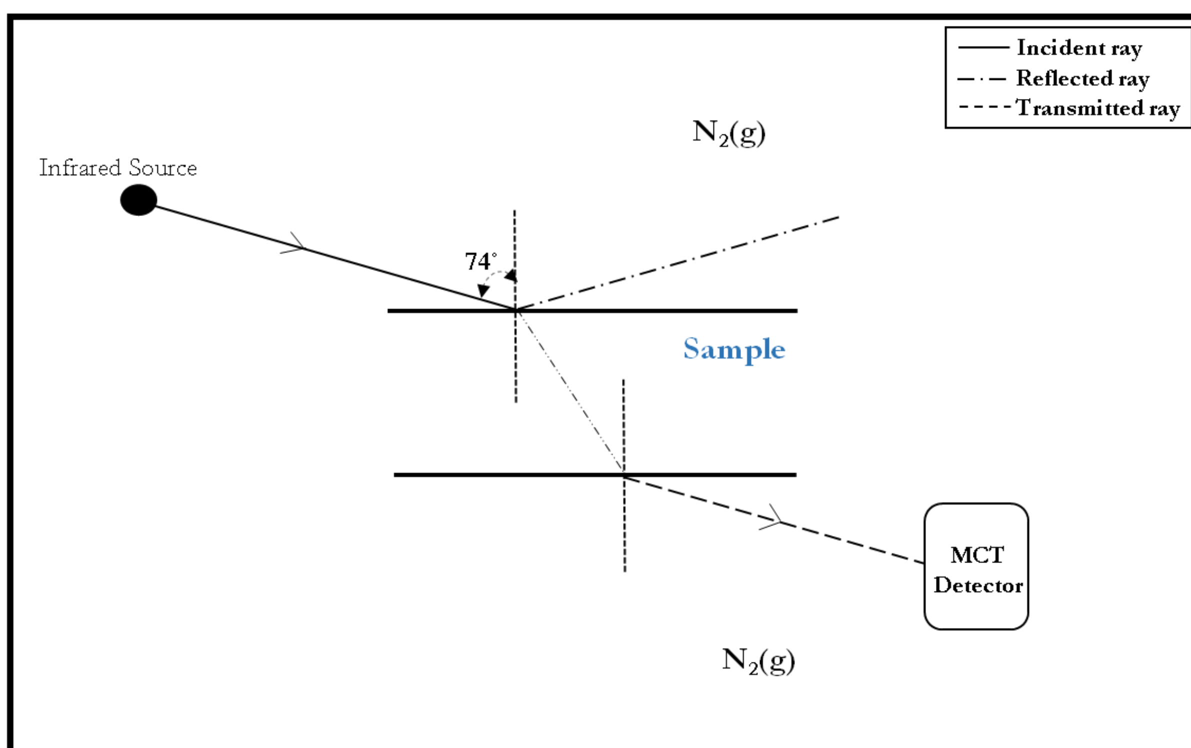


Figure 3.3 *Schematic representation of the set-up used for transmission infrared spectroscopy. The incident ray hits the sample at 74° to the surface normal (Brewster angle). The transmitted ray is detected by an MCT detector. The entire set-up is enclosed in an $N_2(g)$-purged chamber.*

A *Thermo Electron Nicolet 6700 FT-IR* spectrometer was used to collect all the infrared spectra. The set-up was enclosed in chamber that was continuously purged with N_2(g) to reduce the moisture and CO_2(g) content in the surrounding atmosphere. Polarization of the incident infrared light was not controlled and a transmission-geometry was used. The H-terminated Si(110) sample was placed in a sample-holder and the infrared light was incident at an angle of 74˚ (Brewster angle for silicon) with respect to the surface normal as shown in Figure 3.3. The Brewster angle was confirmed by rotating the sample on the sample holder at different angles and observing the signal. Maximum signal was obtained at an angle 74˚ measured from the surface normal. When the sample is oriented at Brewster angle, most of the s-polarized light is reflected off the surface.[45-47] The transmitted light consists mostly of p-polarized light with a small s-polarization component. Therefore, this geometry shows absorbed signal corresponding to vibrational modes that have dipoles oriented both parallel and perpendicular to the surface.[45] *OMNIC (Thermo Scientific)* software was used to collect the infrared spectrum with a resolution of 4 cm^{-1} (wavenumber) averaging over 1000 scans. A liquid-nitrogen cooled, mercury cadmium telluride (MCT) detector was used and all the spectra were referenced to a piranha-cleaned, oxidized Si(110) sample.

3.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is based on the relative motion between a cantilever tip and the given sample surface (Figure 3.4). The cantilever tip rasters over the sample surface and gets deflected as a result of variation in the sample topography. The deflection in the cantilever-deflection is detected by a beam-bouncing system consisting of a laser and a photodiode. This set up can be used to study the morphology of a sample surface at a sub-micron level.

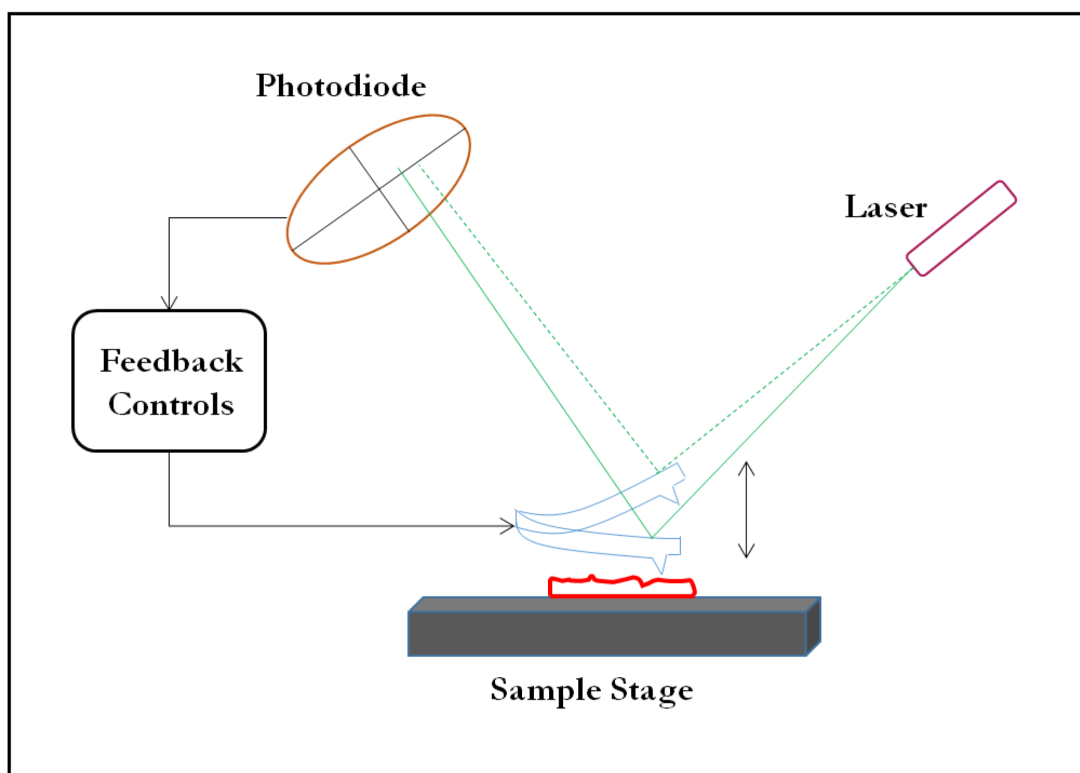


Figure 3.4 *A tapping-mode atomic force microscopy set up. A resonating cantilever tip scans over the sample and the variation in the sample topography is detected by a laser beam-bouncing system with feedback controls.*

A *di Dimension 3100* Scanning Probe Microscope (*Veeco Instruments Inc.*) was used for all the AFM measurements. The AFM was operated in tapping mode. In tapping-mode, a resonating cantilever is in intermittent contact with the sample surface. This mode allows reducing the possible vibrations while scanning and any damage to the tip/sample over time. The cantilever tip was first calibrated with a standard silicon grating sample. The height calibration was done using standard graphite (HOPG) sample. The calibration ensured that the tip was sharp and good for scanning (see Appendix B). After calibration, a freshly prepared Si(110) sample was scanned within an area of 2μm x 2μm and a scan rate of 0.2-0.5 Hz. The feedback gains, amplitude set point and drive amplitude were varied during the scan to improve the quality of the image. A *Nanoscope version 6.0* software was used for data collection.

3.4 X-ray Photoelectron Spectroscopy

X-rays are highly energetic electromagnetic waves with shorter wavelengths when compared to the infrared radiation as shown in Figure 3.1. These energetic x-rays can knock out core electrons orbiting around the nucleus when irradiated to a sample surface. These ejected electrons are known as photoelectrons and have characteristic binding energies given by[12]:

$$E_{BE} = h\upsilon - E_{KE} - w \qquad (3.1)$$

In the above equation, E_{BE} is the binding energy of an electron in the orbital, $h\upsilon$ is the energy of the incident x-rays, E_{KE} is the kinetic energy of the ejected photoelectron and w is the work function of the material.

X-rays can penetrate deep into a given material due to their high energy but the ejected photoelectrons undergo a strong scattering in the bulk of the material. This scattering results into a limited mean free path of the photoelectron of about few nanometers which makes X-ray photoelectron spectroscopy (XPS) a good surface sensitive technique. A different bonding environment on the surface due to the difference in the electronegativities of the overlayer atoms bonded to the silicon surface causes a shift in binding energy obtained in the high-resolution XPS spectrum. This shift in binding energy can be used to identify different surface overlayer atoms bonded to the silicon sites and the integrated intensities obtained from the peak-fitting can be used for a quantitative analysis of the surface coverage.[9,11,40,44,48,49]

XPS spectra were collected on a *Kratos Axis Ultra DLD XPS* spectrometer in vacuum environment with a base pressure of 10^{-9} Torr. Al K_α (1486.6 eV) monochromatic X-rays at 10 mA emission current and 15 kV anode voltage were used to excite the photoelectrons. Charge neutralization was not required as the samples were conductive enough that charge build-up was not an issue. All spectra were collected with a fixed analyzer transmission mode. Survey scans were collected with a pass-energy of 160 eV and high resolution scans were collected with a pass-energy of 20 eV. A high pass-energy allows larger number of electrons to pass through the analyzer which increases the window of electron-energy that could be observed but at the same time lowers the energy resolution. A low pass-energy restricts the energy window but improves the resolution and helps in quantification and deconvolution of individual peaks. Peak-fits for the high resolution XPS spectra were obtained using the CasaXPS software. A Shirley[50] procedure was used to first subtract the background from the spectra and then the spectra were decovolved into different peaks as found in the literature. The FWHMs of the constituent peaks were adjusted to achieve a best fit. Peak positions for the high-resolution XPS spectra of Si-2p region, were referenced to the bulk silicon peak (99 eV) and for the C-1s region, were referenced to the adventitious carbon peak (285 eV).

3.5 Surface Coverage

Surface coverage refers to the fraction of the available silicon surface sites that are attached to a given overlayer atom. The surface-overlayer model uses the ratio of the peak areas obtained from the high-resolution XPS spectrum to calculate the surface coverage for a given overlayer.[40,44,48] According to the model, an equivalent fractional monolayer, Φ_{ov} can be calculated as:

$$\Phi_{ov} = \left(\frac{\lambda \cos\theta}{a}\right)\left(\frac{SF_{Si}}{SF_{ov}}\right)\left(\frac{\rho_{Si}}{\rho_{ov}}\right)\left(\frac{I_{ov}}{I_{Si}}\right) \quad (3.2)$$

In the above equation, I_{ov}/I_{Si} is the intensity ratio of the peak areas of surface overlayer to the bulk silicon (Si 2p). θ is the angle used for the collection of the electrons which was 0° (with respect to the surface normal) for our set up. ρ_{Si} (2.328 g/cm^3) is the volumetric density of silicon and ρ_{ov} is the volumetric density of the overlayer (3 g/cm^3 for C).[40] SF_{Si} (0.328) and SF_{ov} (0.278 for C 1s) are the corresponding sensitivity factors (specific to the instrument) for silicon and the overlayer atoms respectively. a is the atomic diameter for the overlayer atoms (0.19 nm for C) and λ is the escape depth for the electrons through the overlayer with the assumption that $\lambda_{ov} = \lambda_{Si}$ for our calculations. The assumption holds valid as the calculated values for λ_{ov} for C 1s electrons was shown to be equal to the calculated value of λ_{Si} for Si 2p electrons.[44]

Chapter 4

Results and Discussion

4.1 Results

4.1.1 Hydrogen Termination

After the FPM etch and treatment with deoxygenated water, the hydrogen-terminated Si(110) sample was analyzed using TIRS with the set-up as described in section 3.2. Figure 4.1 shows the TIRS spectrum obtained with reference to the piranha-cleaned, oxidized Si(110) sample that was subsequently etched to produce a H-terminated Si(110) surface.

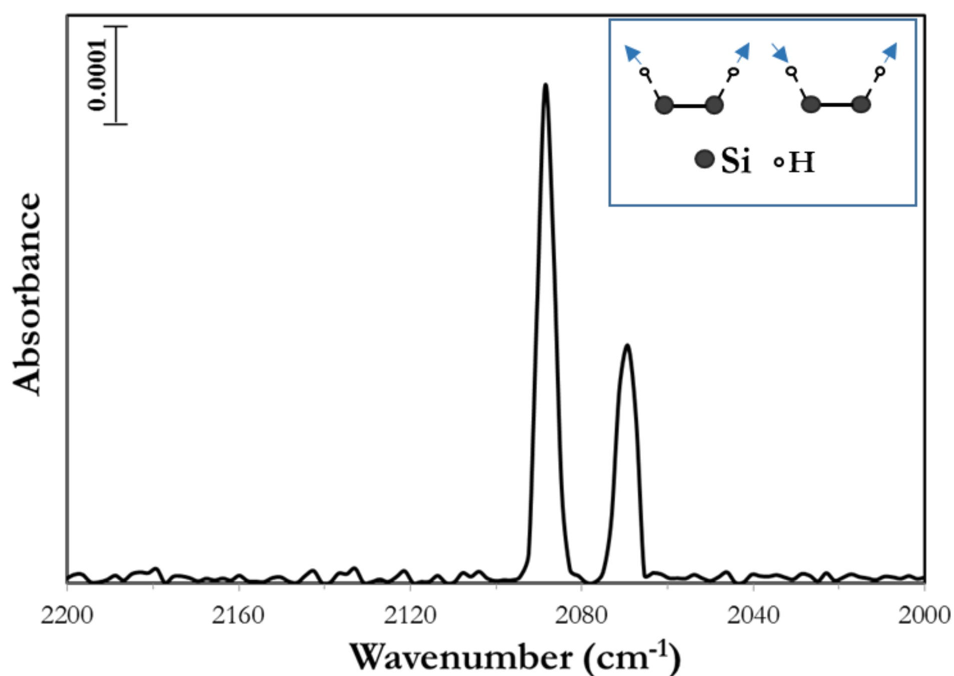


Figure 4.1 *TIRS spectrum of a hydrogen-terminated Si(110) surface. The peak at 2089 cm^{-1} corresponds to an in-phase coupled-monohydride stretching vibration and the peak at 2070 cm^{-1} corresponds to an out-of-phase stretching vibration (inset).*

TIRS spectrum showed two sharp peaks at wavenumbers 2089 cm^{-1} and 2070 cm^{-1}. The peak at 2089 cm^{-1} corresponds to an in-phase coupled-monohydride stretching vibration and the peak at 2070 cm^{-1} corresponds to an out-of-phase stretching vibration as shown in Figure 4.1 (inset). Both of these vibrational modes indicate a long chain monohydride structures along [-1 1 0] direction[15,35] on a (110)-oriented silicon wafer which was confirmed by the AFM scans as shown in Figure 4.2. The peaks associated with the initial oxidation of the H-terminated silicon surface were not observed in the region 2100-2200 cm^{-1} of the TIRS spectrum. The absence of these peaks suggested that there was no oxidation of the surface after the treatment with deoxygenated water which was also supported by the XPS measurements described in the next section (also see Appendix C).

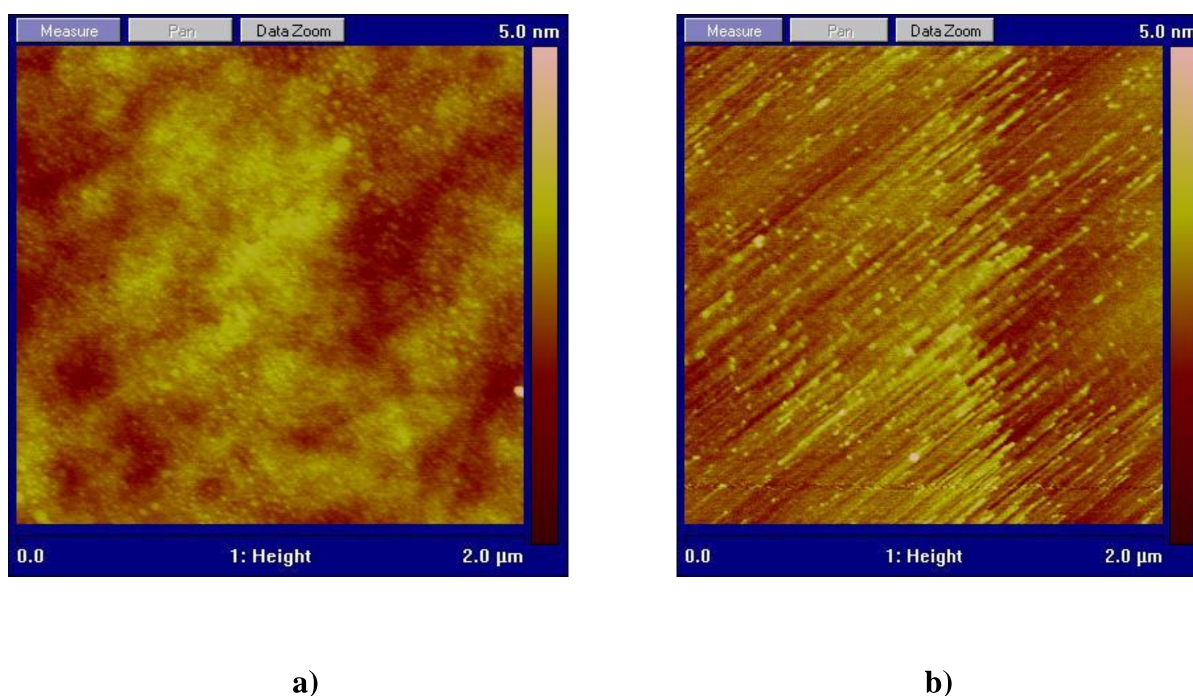


Figure 4.2 *Tapping-mode AFM images of Si(110) surfaces for a 2µm* x *2µm area. a) Before etching b) After FPM etch and treatment with deoxygenated water for 10 minutes, anisotropic etching by water results into terraces in [-1 1 0] direction producing a well ordered surface. The horizontal streaking line at the bottom of image b) is most likely to be a result of topographic fluctuation that the tip couldn't recover from while scanning.*

AFM measurements supported the TIRS observations for the H-terminated Si(110) surface. Figure 4.2 shows tapping-mode AFM scans of a 2µm x 2µm area of Si(110) surface before and after the hydrogen passivation. The surface before cleaning and etching (Figure 4.2a) showed an un-ordered surface with high and low lying areas. The variations in the topography can be attributed to the presence of different atomic layers of silicon atoms. The topographic features that appear higher (yellow region) are a few atomic layers high compared to the lower regions (brown).

After the piranha-clean and hydrogen-passivation, the topographic variations were still evident but an ordered arrangement was observed (Figure 4.2b). The anisotropic etching with water removes the di- and tri-hydride species that are present on the step-edges of the two atomic layers until a perfect monohydride surface is obtained. This anisotropic etching leads to a long coupled-monohydride chain structure along [-1 1 0] direction on a (110)-oriented silicon surface.[15,25,35]

4.1.2 Surface Functionalization

Functionalization and surface coverage of the Si(110) surface was studied with the survey and high-resolution XPS spectra. Samples were first analyzed with the XPS survey scan to identify all the elements present on the surface. Figure 4.3 shows XPS survey spectra of hydrogen-terminated, chlorinated and methylated Si(110) samples. The spectra showed peaks that correspond to O 1s (531 eV), C 1s (285 eV), Si 2s (149 eV) and Si 2p (99 eV) binding energies.[9,40,48] Peaks corresponding to Cl 2s (270 eV) and Cl 2p (200 eV) region appeared for the chlorinated surface confirming the presence of the chlorine overlayer. These chlorine peaks were absent in the survey spectrum for the methylated sample indicating that

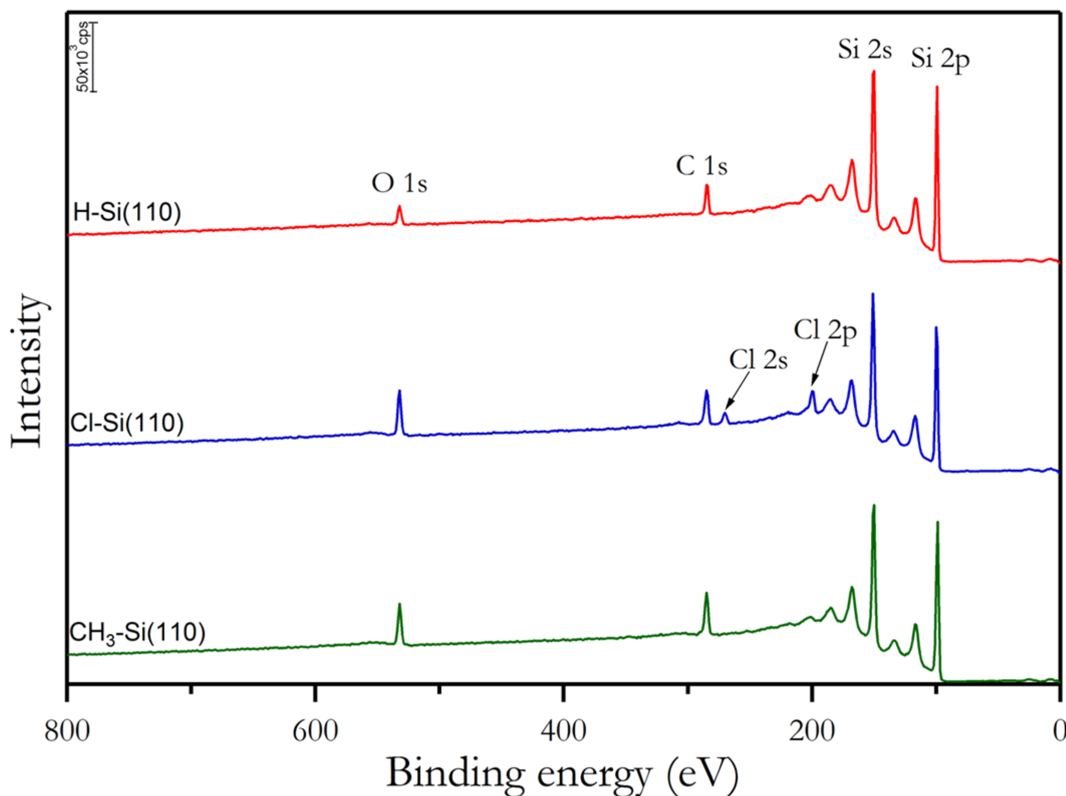


Figure 4.3 *XPS survey spectra of hydrogen-terminated (red), chlorinated (blue) and methylated (green) Si(110) surfaces. The spectra showed bulk silicon peaks along with C 1s and O 1s peaks. Chlorinated samples also showed Cl 2s and Cl 2p peaks that were absent in the other two spectra.*

the chlorine overlayer was completely removed after the methylation procedure. The presence of oxygen peaks may indicate oxidation of the surface but were associated with adventitious carbon based on the high resolution XPS observations. The spectra did not show a fluorine peak (686 eV) indicating that the samples were clean after the rinsing process, free of any residual impurities.

High resolution XPS spectra of Si 2p region as shown in Figure 4.4, were deconvoluted into two bulk silicon peaks corresponding to the spin splits,[48] Si-2$p_{3/2}$ and Si-2$p_{1/2}$. The spectrum for chlorine terminated sample was fit to have an additional peak that was associated with the surface overlayer. The shift in binding energy for the hydrogen and

methyl overlayer was not significant enough to distinguish between the surface and bulk silicon peaks.[9,48] This peak fitting was used to obtain the peak intensity areas for surface coverage calculations. The region between 101-103 eV showed no peaks that are associated with the surface silicon oxide indicating that there was no oxidation of the surface during treatment, within the detection layer of the instrument. This also confirmed that the O 1s peaks in the survey spectra (Figure 4.3) can be associated with the adventitious carbon.

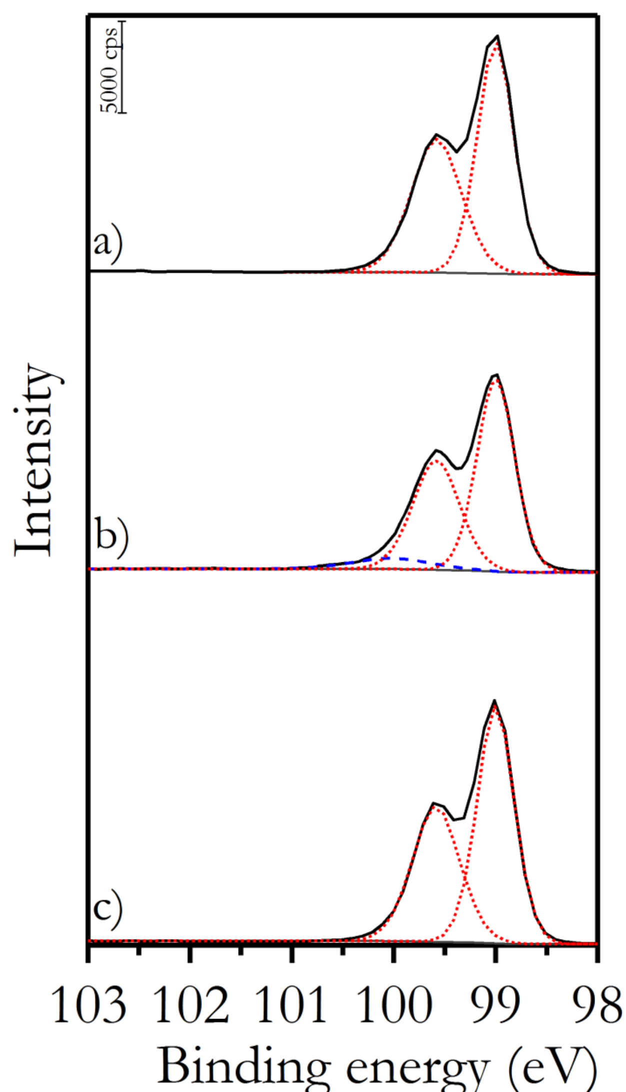


Figure 4.4 *High resolution XPS spectra of Si-2p region for a) H-terminated b) Cl-terminated and c) CH_3-terminated Si(110) surfaces. The spectra were fit to have two peaks (red) corresponding to the spin splits, Si-2$p_{3/2}$ and Si-2$p_{1/2}$. The Cl-terminated spectrum had an additional peak (blue) that is shifted in binding energy due to the surface overlayer. No silicon oxide peaks were observed in the 101 eV-103 eV region.*

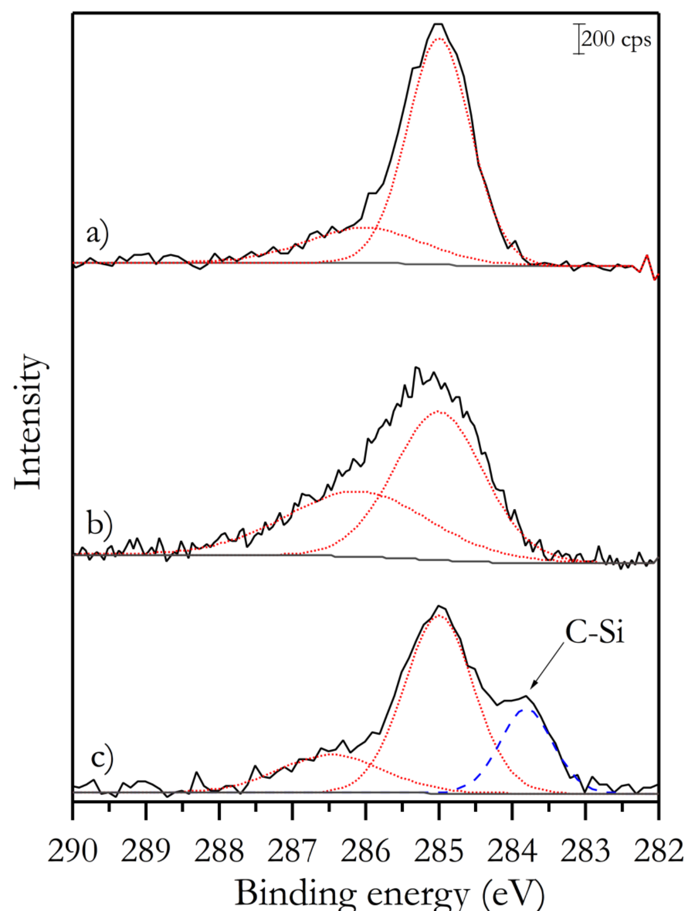


Figure 4.5 *High resolution XPS spectra of C-1s region for a) H-terminated b) Cl-terminated and c) CH_3-terminated Si(110) surfaces. The spectra were fit to have two peaks (red) corresponding to the adventitious carbon. CH_3-terminated spectrum had a shoulder due to a shift in the binding energy for the carbon bonded to silicon which required an additional peak (blue).*

High resolution XPS spectra of C 1s region for different Si(110) surfaces (Figure 4.5) confirmed the presence of adventitious carbon that is adsorbed from the atmosphere. For the case of methyl-terminated Si(110) surface, an additional peak was observed that corresponds to the carbon in the methyl group, bonded to the silicon atoms on the surface. The shift in binding energy for the carbon bonded to silicon can be attributed to the difference in the electronegativities of carbon, hydrogen, oxygen and silicon. Carbon bonded to silicon is more negative than the carbon bonded to hydrogen.[49] The intensity area for the C-Si peak was used to calculate the surface coverage for a methyl-terminated surface.

4.1.3 Surface coverage and Oxidative Stability

Surface coverage for the methyl-terminated Si(110) surfaces was calculated using the surface-overlayer model (equation 3.2). On average (6 different samples), a surface coverage of 0.83 of an equivalent monolayer (ML) of methyl overlayer was observed. Webb *et al.* observed a 0.85 ML of surface coverage on a methyl-terminated Si(111) surface based on the area ratios obtained from High-resolution XPS studies.[40] This ratio was correlated with a full monolayer coverage of methyl overlayer based on the low temperature STM measurements.[10]

The surface coverage can also be investigated by studying the oxidative stability of the methyl-terminated sample with time. A CH_3-Si(110) surface that is not fully passivated, will oxidize at a rapid rate when exposed to air in contrast to an ideal surface with a complete monolayer coverage. Figure 4.6 shows the high-resolution XPS spectra for H-terminated and methyl-terminated Si(110) surface, when exposed to air. An H-terminated surface got oxidized at a much faster rate compared to a methyl-terminated surface. The resulting surface oxide coverage was calculated by taking the ratio of the peak intensity areas associated with the surface oxide and bulk silicon. After 2 days of exposure to air in laboratory conditions, about 0.73 ML of surface oxide was detected for an H-terminated Si(110) surface, whereas only 0.20 ML of surface oxide was observed for a methyl-terminated surface even after a month of exposure to air. These observations are in excellent agreement with the oxidative stability studies of methyl-terminated Si(111) surfaces.[11] The relatively high oxidative stability of the methyl-terminated surface indicate a nearly full monolayer coverage of the

surface with the methyl groups.

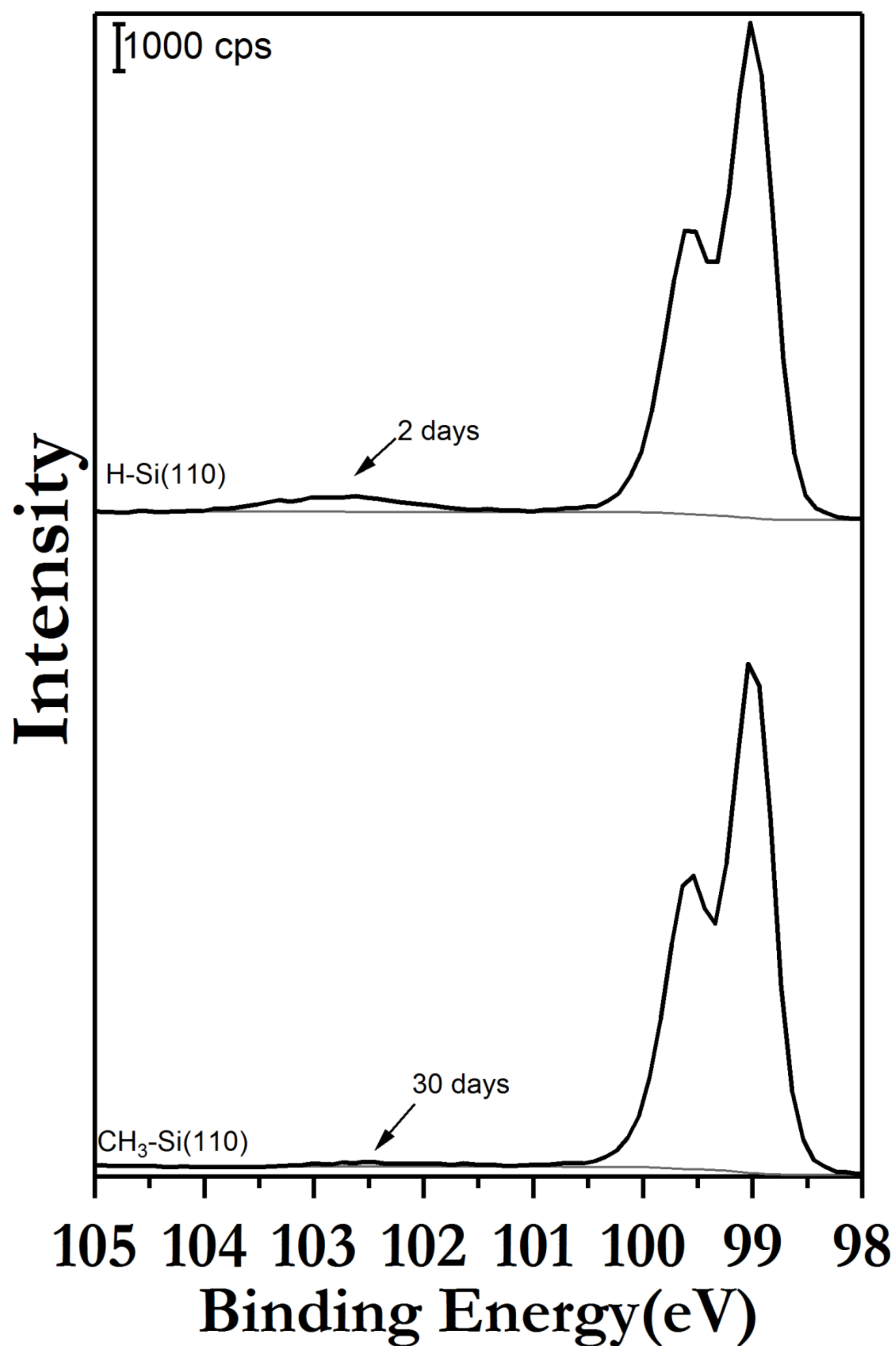


Figure 4.6 *High resolution XPS spectra of Si-2p region for H-Si(110) and CH_3-Si(110) surfaces. The peak between 101-105 eV represents surface silicon oxide. CH_3-Si(110) surface showed a greater oxidative stability even after a month of exposure to air.*

4.2 Discussion

4.2.1 Functionalization and Surface Coverage

XPS data showed that the Si(110) surface was successfully covered by a methyl overlayer after chlorination/alkylation procedure without any oxidation of the surface. The surface-overlayer model showed an average coverage of about 0.83 ML for six different samples with a standard deviation of 0.04 ML (See Appendix A). The statistical variation in the monolayer calculations for these six samples can be attributed to the uncertainties in the peak-fitting as the presence of adventitious carbon might affect the overall intensity variation for the peak-area associated with the C-Si peak as shown in Figure 4.5. The main contributing element that might vary the coverage values in equation 3.2 is the density term (ρ_{ov} = 3 g/cm^3) corresponding to carbon. The exact value associated density for carbon is uncertain with a variation (2.3-3.5 g/cm^3) in the reported values for different allotropic forms.[11,19,44] These variations combined with the instrumental accuracy will result into at least 10% of uncertainty in the measurement despite the high statistical accuracy.

The surface overlayer model assumes that the surface coverage should be calculated based on a close-packing arrangement of molecules on a given surface area. But, the methyl-molecules are actually placed according to the surface sites, which limit the close-packing arrangement of the methyl molecules as there are not enough surface silicon sites available. For example, for a 1 cm^2 area on a Si(110) surface, the total number of carbon atoms that can be closely packed (assuming circular cross-section) is about 3.5 x 10^{15} (atomic diameter for carbon = 0.19 nm). But the number of surface silicon sites available for the same area is only 1 x 10^{15}. Consequently, the surface coverage value as calculated from this model is an underestimation of what the correct value should be. A more appropriate conclusion could be

made by observing the CH_3-Si(110) surface with a scanning tunneling microscope as shown for the CH_3-Si(111) surface.[10,11]

The surface preparation plays a key role in determining the surface coverage for a Si(110) and Si(111) surfaces. As shown in this thesis, a Si(110) surface showed similar surface coverage as observed for a Si(111) surface after methylation using a chlorination/alkylation procedure.[11] The difference here lies in the monohydride-surface preparation for these two surfaces. For a Si(111) surface, the monohydride surface is obtained by etching the surface in a buffered HF solution in a oxygen-limited environment. The degree of anisotropy is lower when a Si(111) surface is treated with deoxygenated water unlike a Si(110) surface which results into a perfect monohydride surface. Therefore, a specific preparation procedure should be implemented for different surface orientations.

4.2.2 Oxidative Stability

Attaching organic groups to the silicon surface provides a greater stability towards oxidation due to the more stable Si-C bond compared to the Si-H bond for the case of a hydrogen-terminated surface.[9,11] Although a Si-C bond is strong enough to prevent the lateral extension of oxidation on a surface passivated with a sterically hindered organic group (eg, ethyl) that produces a lower coverage,[11] but the sites that are attached to hydrogen could quickly oxidize which may lead to a rapid deterioration of the surface. Therefore, passivating the surface with an organic group that can provide nearly full monolayer coverage seems to be a plausible strategy for long term stability. Methyl groups are smaller in size amongst all the alkyl groups and hence can provide best possible coverage for a given silicon surface as discussed in section 2.5. The oxidative stability of a methyl-terminated surface was also

evident even after a month of exposure to the atmosphere. Although the mechanism of oxidation of a methyl-terminated silicon surface is not well understood, but the small oxidation (0.2 ML of surface oxide) can be attributed to some defect sites or sites at the step edges as observed for the oxidation of methyl-terminated Si(111) surfaces.[11]

4.2.3 Impact of Surface Roughness

Unlike the silicon surfaces that are passivated with larger alkyl groups where the steric hindrance is due to the size of the alkyl groups, the functionalized surfaces that are prepared from a rough hydrogen-terminated surface face an inherent steric hindrance due to the presence of di- and tri-hydride species. In this case, even if the organic group is small enough to passivate all the silicon sites, the remaining Si-H bonds are still susceptible towards oxidation. Oxidative stability studies of methyl-terminated Si(110) surface that were prepared from a rough hydrogen-terminated surface (etched with 10% HF solution with no further treatment with water) reported that the surface had a complete monolayer of oxide only after a week of exposure to the atmosphere.[12] TIRS observations presented in this thesis showed that the hydrogen-terminated surface was ideal for functionalization with only monohydride-species present on the surface.

4.2.4 Implications on Microwires

Surfaces with different orientations require specific surface preparation strategies as discussed in Chapter 2. Silicon microwires consist of mainly {110}-oriented surfaces. Presently hydrogen-terminated microwires are prepared by etching the oxidized wires with a 10% HF solution, treating it with a KOH solution and/or etching with a NH_4F solution.[6] As

discussed in Chapter 2, these etching procedures do not produce a monohydride-terminated surface on a (110)-oriented surface. Presence of di- and tri-hydride species will lead to a rapid oxidation of the surface as discussed in section 5.2. The surface preparation strategy utilized in this thesis can be implemented on the microwire surface for long term stability.

The atoms present on the edge between two different facets of the microwire may have a different symmetry as discussed in section 1.4. On a hydrogen terminated microwire, such edges are likely to have some di-hydride species to satisfy all the dangling bonds.[51] The amount of steric hindrance due to this arrangement is difficult to predict because despite the presence of di-hydride elements, the deviation from the symmetrical arrangement may help in relaxing the stress between neighborhood molecules which is not possible in a continuous arrangement in case of an individual facet. Although the microwire facets mainly consists of {110} surfaces, the edge needs to be dealt with once such measurements are transferred to microwires to predict the complete passivation of the microwire surface.

Chapter 5

Conclusions and Future work

Methyl-terminated Si(110) surfaces prepared from the hydrogen terminated, H-Si(110) samples using chlorination/alkylation procedure, were investigated using XPS. These samples showed nearly full monolayer coverage of methyl groups on the surface. The oxidative stability studies revealed that the methyl-terminated Si(110) surface was stable when exposed to air even after a month from the sample preparation. TIRS observations showed monohydride peaks indicating that the H-Si(110) surface consisted of a coupled-monohydride chain structure which was ideal for subsequent functionalization. These observations were also supported by AFM images that showed an ordered topography of the H-Si(110) surface after the FPM etch and treatment with water. Planar silicon studies are very essential as the benchmark for the chemical and electrical behavior of silicon microwire arrays. This technique can be implemented for functionalization of microwire arrays.

Although the XPS observations indicated a full-monolayer coverage of methyl groups, it is still not clear how the molecules are arranged on the Si(110) surface to avoid the possible steric hindrance that may arise from the comparable size of methyl groups to that of the Si-Si bond length. As a future work, low-temperature tunneling microscopy studies of CH_3-Si(110) surfaces can provide an insight into the possible steric interaction between the methyl-molecules attached to silicon sites. A comparison between the density of states on

Si(111) and Si(110) surfaces will be helpful in understanding the electronic behavior of the two surfaces which is essential in understanding the junction behavior at the microwire-polymer junction.

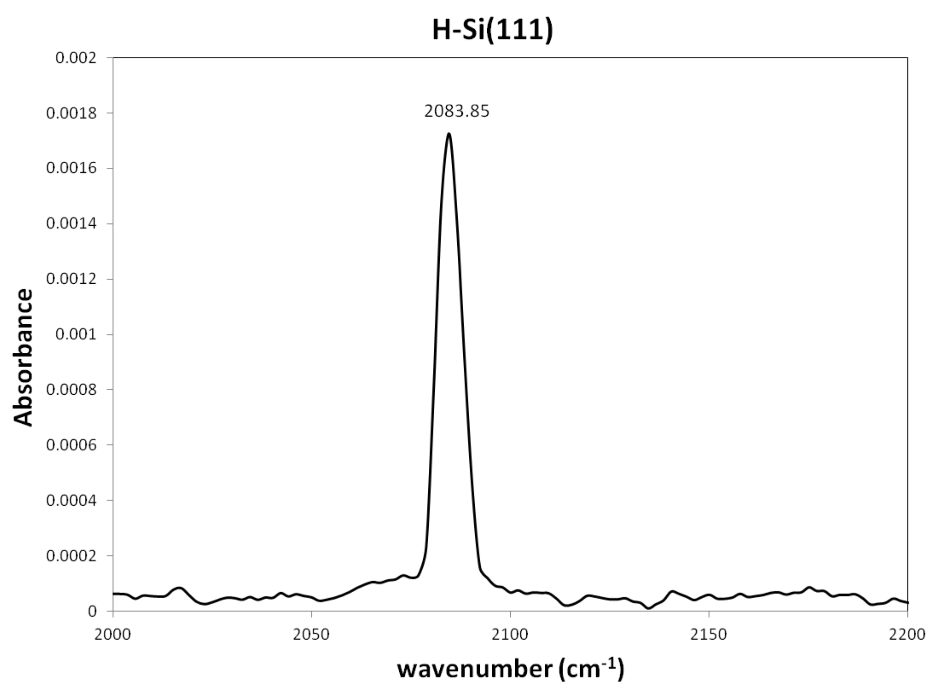
Appendix

A

A.1 Monolayer calculation for CH_3-Si(110) surfaces:

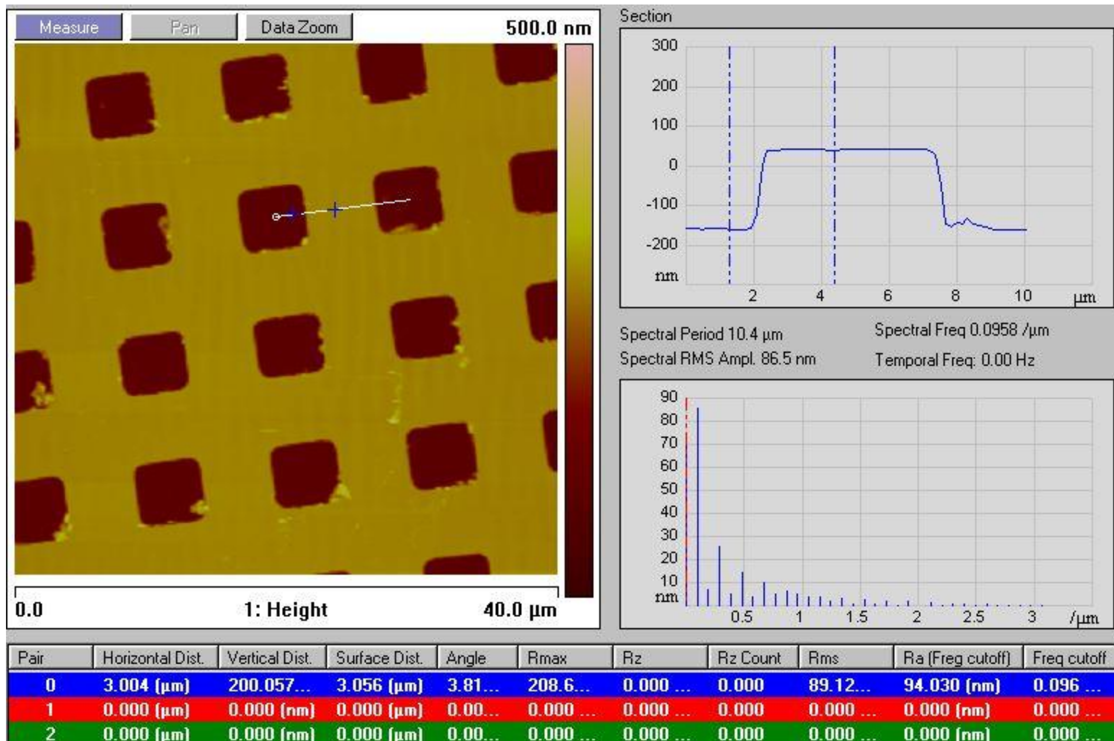
Sample #	Monolayer coverage (Surface overlayer model)
1	0.80
2	0.82
3	0.82
4	0.89
5	0.79
6	0.86
Average	**0.83**
Standard Deviation	0.04

A.2 TIRS Spectrum for monohydride terminated Si(111) surface:

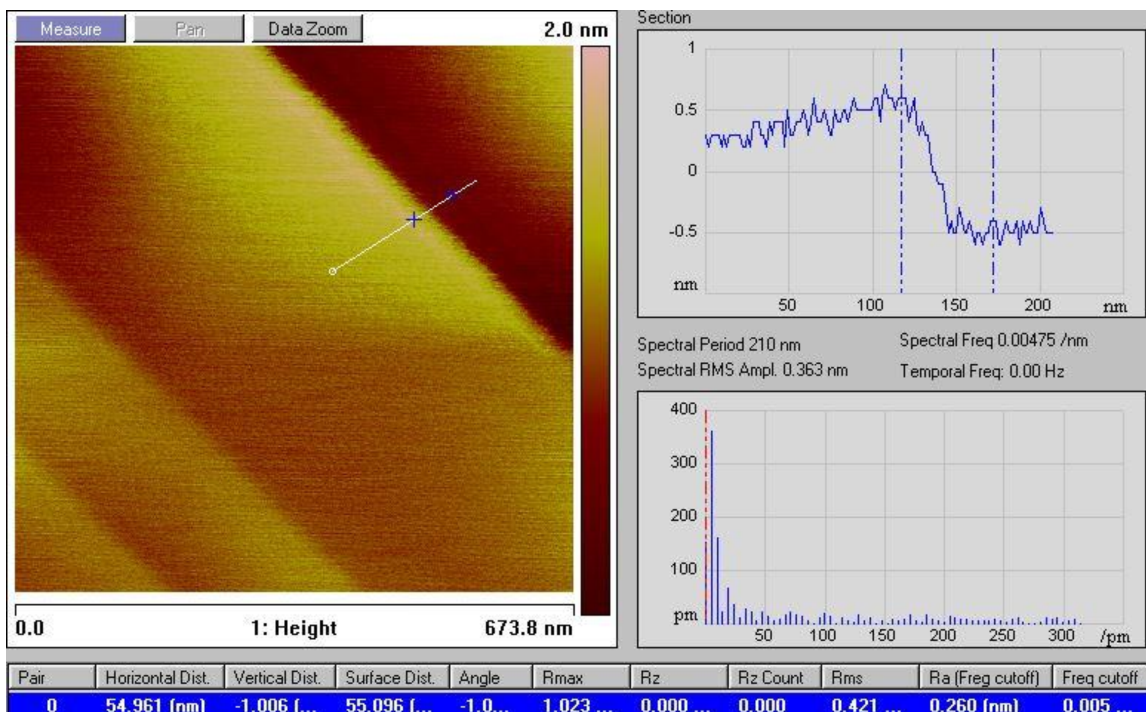


B

B.1 AFM-tip calibration:



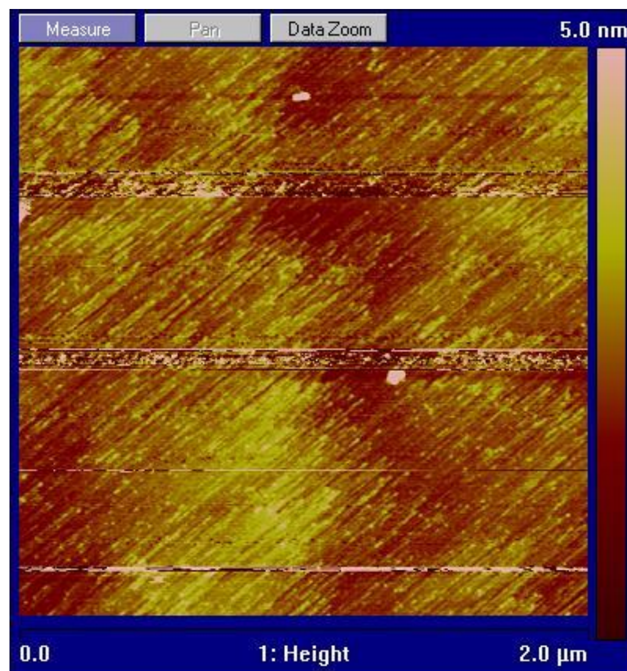
Silicon-grating



HOPG-sample

The tip calibration is first done by scanning a silicon grating sample. The grating features have a 10 μm pitch and are 200 nm deep. Once the scan is captured the distance between these features is measured along with the depth. The sample is then replaced with a standard HOPG surface. The sharpness of the tip can be examined by looking at the step edges between two atomic layers stacked on top of each other (three lines in the image shown). The step shown in the HOPG-scan is about 1 nm high which is equivalent to three atomic layers (1 layer ~0.3 nm). The tip is good for scanning if these terraces and step edges are clearly visible.

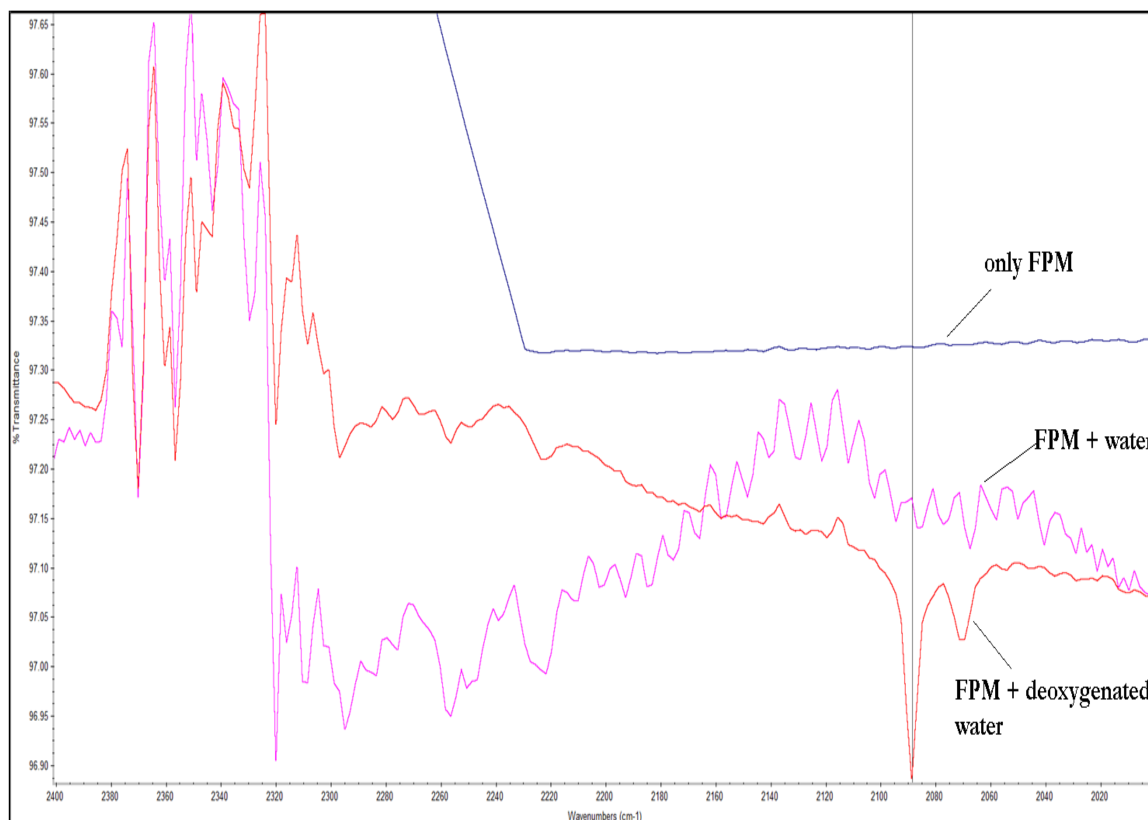
B.2 AFM-tip vibrations:



While scanning, the AFM-tip sometimes encounter sudden vibrations due to some topographic variations that degrades the image-quality. Varying the scan speed (0.2-0.4 Hz) and the amplitude-setpoint (0.2-0.4) can help in reducing these vibrations. In the above image for an H-Si(110) surface, the terrace lines are visible but the horizontal streaks are associated with the noise due to vibrations of the tip.

C

C.1 Effect of rinsing with deoxygenated water:



The figure shows the TIRS spectra (without baseline correction) for Si(110) surfaces after the FPM etch followed by treatment with normal DI water or deoxygenated DI water. Monohydride peaks (at 2089 cm^{-1}, marked with the vertical line) for a Si(110) surface were only observed when the surface was etched using FPM followed by rinsing with deoxygenated water for 10 minutes. To ensure success, the DI water used must have a low oxygen content. This was achieved by purging the DI water with argon or nitrogen gas for about 30 minutes. The monohydride signature peak was absent if the final deoxygenated rinse was not undertaken or undertaken with water that had not been fully purged.

References

1. International Database World Population: 1950-2050, *United States Census Bureau*, **2015**

2. McClarty, M. An Analysis of the Piezoresistive Response of n-type, Bottom-up, Functionalized Silicon Microwires. *M.Sc. Thesis, University of Manitoba,* **2014**

3. Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W. ; Mi, Q.; Santori, E. A.; Lewis, N. S. Solar Water Splitting Cells. *Chem. Rev.* **2010**, 110, 6446-6473.

4. Gray, H. B. Powering the planet with solar fuel. *Nature Chem.* **2009**, 1, 7.

5. Zehner, O. Green Illusions. *Lincoln and London: University of Nebraska Press*, **2012**

6.Yahyaie, I.; Ardo, S.; Oliver, D. R.; Thomson, D. J.; Freund, M. S.; Lewis, N. S. Comparison Between the Electrical Junction Properties of H-Terminated and Methyl-Terminated Individual Si Microwire/Polymer Assemblies for Photoelectrochemical Fuel Production. *Energy Environ. Sci.* **2012**, 5, 9789.

7. Bruce, J. P.; Asgari, S.; Ardo, S.; Lewis, N. S.; Oliver, D. R.; Freund, M. S. Measurement of the Electrical Resistance of n-Type Si Microwire/p-Type Conducting Polymer Junctions for Use in Artificial Photosynthesis. *J. Phys. Chem. C* **2014**, 118, 27742−27748.

8. Liu, J.; Davis, N. R.; Liu, D. S.; Hammond, P. T. Highly Transparent Mixed Electron and Proton Conducting Polymer Membranes. J. Mater. Chem., **2012**, 22, 15534-15539.

9. Bansal, A.; Li, X.; Lauermann, I.; Lewis, N. S.; Yi, S. I.; Weinberg, W. H. Alkylation of Si Surfaces Using a Two-Step Halogenation/Grignard Route. *J. Am. Chem. Soc.* **1996**, 118, 7225-7226.

10. Yu, H.; Webb, L. J.; Ries, R. S.; Solares, S. D.; Goddard, W. A. III; Heath, J. R.; Lewis, N. S. Low-Temperature STM images Methyl-Terminated Si(111) Surfaces. *J. Phy. Chem. B Lett.* **2005**, 109, 671-674.

11. Webb, L. J.; Michalak, D. J.; Biteen, J. S.; Brunschwig, B. S.; Chan, A. S. Y.; Knapp, D. W.; Meyer, J. M.; Nemanick, E. J.; Traub, M. C.; Lewis, N. S. "High-Resolution Soft X-ray Photoelectron Spectroscopic Studies and Scanning Auger Microscopy Studies of the Air Oxidation of Alkylated Silicon(111) Surfaces." *J. Phys. Chem. B* **2006**, *110*, 23450-23459.

12. Bruce, J. P. Surface Functionalization of Silicon Microwires for Use in Artificial Photosynthetic Devices. *M. Sc. Thesis, University of Manitoba,* **2015**.

13. Gallant, B. M.; Gu, X. W.; Chen, D. Z.; Greer, J. R.; Lewis, N. S. Tailoring of Interfacial Mechanical Shear Strength by Surface Chemical Modification of Silicon Microwires Embedded in Nafion Membranes. *ACS Nano,* **2015**, 9 (5), 5143–5153.

14. Wagner, R. S.; Ellis, W. C.; Jackson, K. A.; Arnold, S. M. Study of the Filamentary Growth of Silicon Crystals from Vapor. *J. Appl. Phys.* **1964,** 35, 2993-3000.

15. Arima, K.; Katoh, J.; Horie, S.; Endo, K.; Ono, T.; Sugawa, S.; Akahori, H.; Teramoto, A.; Ohmi T. Hydrogen Termination of Si(110) Surfaces upon Wet Cleaning Revealed by Highly Resolved Scanning Tunneling Microscopy. *J. Appl. Phys.* **2005**, 98, 103525(1)-103525(8).

16. Mazumder, B. Silicon and its Compounds, *Science Publishers Inc.* **2000**

17. Bent, S. F. Organic Functionalization of Group IV Semiconductor Surfaces: Principles, Examples, Applications and Prospects. *Surf. Sci.* **2002**, 500, 879-903.

18. Elwenspoek, M; Jansen, H. Silicon Micromachining. *Cambridge University Press*, **1998**

19. Sze, S. Physics of Semiconductor Devices. *John Wiley and Sons, Inc*. **1981**

20. Wolkow, R. A. Controlled Molecular Adsorption on Silicon: Laying a Foundation for Molecular Devices. *Annu. Rev. Phys. Chem.* **1999**, 50, 413-41.

21. Ohmi, T. Total Room Temperature Wet Cleaning for Si Substrate Surface. *J. Electrochem. Soc.* **1996**, 143, 2957-2964

22. Kern, W. The Evolution of Silicon Wafer Cleaning Technology. J. Electrochem. Soc. **1990**, 137, 1887-1892

23. Kern, W.; Puotinen, D. A. Cleaning Solutions Based on Hydrogen Peroxide for Use in Silicon Semiconductor Technology. *RCA Rev.* **1970**, 31, 187-206.

24. Okorn-Schmidt H. F. Characterization of Silicon Surface Preparation Processes for Advanced Gate Dielectrics. *IBM J. Res. Develop.* **1999**, 43, 351-365.

25. Teramoto, A.; Hamada, T.; Yamamoto, M.; Gaubert, P.; Akahori, H.; Nii, K.; Hirayama, M.; Arima, K.; Endo, K.; Sugawa, S.; Ohmi, T. Very High Carrier Mobility for High-Performance CMOS on a Si(110) Surface. *IEEE Trans. Elect. Dev.* **2007**, 54, 1438-1445.

26. Ohmi, T.; Imaoka, T.; Kezuka, T.; Takano, J.; Kogure, M. Segregation and Removal of Metallic Impurity at Interface of Silicon and Fluorine Etchant. *J. Electrochem. Soc.* **1993**, 140, 811-818.

27. Kurhekar, A. S.; Apte, P. R. Spectroscopic-ellipsometric study of native oxide removal by Liquid Phase HF Process. *International Nano Letters* **2013**, 3:10

28. Akahori, H. *Ph.D. Thesis*, *Tohoku University*, **2004**.

29. Tiana, F.; Yangb, D.; Opilab, R. L.; Teplyakova, A. V. Chemical and Electrical Passivation of Si(111) Surfaces. *App. Surf. Sci.* **2012**, 258, 3019-3026.

30. Higashi, G. S.; Chabal, Y. J.; Trucks, G. W.; Raghavachari, K. Ideal Hydrogen Termination of the Si (111) Surface. *App. Phys. Lett.* **1990**, 56, 656-658.

31. Jakob, P.; Chabal, Y. J.; Kuhnke, K.; Christman, S. B. Monohydride Structures on Chemically Prepared Silicon Surfaces. *Surf. Sci.* **1994**, 302, 49-56.

32. Ye, J. H.; Kaji, K.; Itaya, K. Atomic-Scale Elucidation of the Anisotropic Etching of (110) n-Si in Aqueous NH_4F: Studies by In Situ Scanning Tunneling Microscopy. *J. Electchem. Soc.* **1996**, 143, 4012-4019.

33. Watanabe, S.; Nakayama, N.; Ito T. Homogeneous Hydrogen-terminated Si(111) Surface Formed using Aqueous HF Solution and Water. *Appl. Phys. Lett.* **1991**, 59, 1458-1460.

34. Pietsch, G. J.; Köhler, U.; Henzler, M. Direct Observation of Silicon Surface Etching by Water with Scanning Tunneling Microscopy. *Chem. Phys. Lett.* **1992**, 197, 346-351.

35. Watanabe, S. Vibrational Study on Si(110) Surface Hydrogenated in Solutions. *Surf. Sci.* **1996**, 351, 149-155.

36. Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chem. Rev.* **1996**, 96, 1533-1554.

37. Ciampi, S.; Harper, J. B.; Gooding, J. J. Wet Chemical Routes to the Assembly of Organic Monolayers on Silicon Surfaces via the Formation of Si-C bonds: Surface Preparation, Passivation and Functionalization. *Chem. Soc. Rev.* **2010**, 39, 2158-2183.

38. Wolkow, R. A. Direct Observation of an Increase in Buckled Dimers on Si(001) at Low Temperature, *Phys. Rev. Lett.* **1992**, 68, 2636-2639

39. Linford, M. R.; Chidsey, C. E. D. Alkyl Monolayers Covalently Bonded to Silicon Surfaces. *J. Am. Chem. Soc.* **1993**,115, 12631-12632.

40. Webb, L. J.; Nemanick, E. J.; Biteen, J. S.; Knapp, D. W.; Michalak, D. J.; Traub, M. C.; Chan, A. S. Y.; Brunschwig, B. S.; Lewis, N. S. High-Resolution X-ray Photoelectron Spectroscopic Studies of Alkylated Silicon(111) Surfaces. *J. Phys. Chem. B* **2005,** *109,* 3930-3937.

41. Yu, H.; Webb, L. J.; Solares, S. D.; Cao, P.; Goddard, W. A.; Heath, J. R.; Lewis, N. S. Scanning Tunneling Microscopy of Ethylated Si(111) Surfaces Prepared by a Chlorination / Alkylation Process. *J. Phys. Chem. B* **2006**, *110*, 23898-23903.

42. Leng, Y. Materials Characterization. *John Wiley and Sons (Asia),* **2008**

43. Szymanski, H. A. Integrated Infrared Spectra Volume I. *Plenum Press*, **1964**

44. Haber, J. A.; Lewis, N. S. Infrared and X-ray Photoelectron Spectroscopic Studies of the Reactions of Hydrogen-Terminated Crystalline Si(111) and Si(100) Surfaces with Br_2, I_2 and Ferrocenium in Alcohol Solvents. *J. Phys. Chem. B* **2002**, 106, 3639-3656.

45. Webb, L. J.; Rivillon, S.; Michalak, D. J.; Chabal, Y. J.; Lewis, N. S. Transmission Infrared Spectroscopy of Methyl- and Ethyl-Terminated Silicon(111) Surfaces. *J. Phys. Chem. B* **2006,** 110, 7349-7356.

46. Michalak, D. J.; Rivillon, S.; Chabal, Y. J.; Estève A.; Lewis, N. S. Infrared Spectroscopic Investigation of the Reaction of Hydrogen-Terminated, (111)-Oriented, Silicon Surfaces with Liquid Methanol. *J. Phys. Chem. B* **2006**, 110, 20426-20434.

47. Rivillon, S. A.; Michalak, D. J.; Chabal, Y. J.; Wielunski, L.; Hurley, P. T.; Lewis, N. S. Investigation of the Reactions during Alkylation of Chlorine-Terminated Silicon (111) Surfaces. *J. Phys. Chem. C* **2007**, 111, 13053-13061.

48. Bansal, A.; Li, X.; Yi, S. I.; Weinberg, W. H.; Lewis, N. S. Spectroscopic Studies of the Modification of Crystalline Si(111) Surfaces with Covalently-Attached Alkyl Chains Using a Chlorination/Alkylation Method. *J. Phys. Chem. B* **2001,** 105, 10266-10277.

49. Nemanick, E. J.; Hurley, P. T.; Brunschwig, B. S.; Lewis, N. S. Chemical and Electrical Passivation of Silicon (111) Surfaces through Functionalization with Sterically Hindered Alkyl Groups. *J. Phys. Chem. B* **2006**, 110, 14800-14808.

50. Shirley, D. A. High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold. *Phys. Rev. B* **1972**, *5*, 4709-4714.

51. Migas, D. B.; Borisenko, V. E. The Role of Morphology in Stability of Si Nanowires. *J. App. Phys.* **2009**, 105, 104316(1)-104316(6).