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Manipulation of surface chemistry and nanostructure in porous silicon-based chemical sensors

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MANIPULATION OF SURFACE CHEMISTRY AND NANOSTRUCTURE IN POROUS SILICON-BASED CHEMICAL SENSORS

A Dissertation submitted in partial satisfaction of the requirements for the degree

Doctor of Philosophy

in

Chemistry

by

Anne Marie Ruminski

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Professor William C. Trogler

2009
The dissertation of Anne Marie Ruminski is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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Chair

University of California, San Diego

2009
DEDICATION

In memory of my Dad, Lawrence, who passed away during all of this. He used to watch me via the webcam that once was in lab, and would excitedly question me later what exactly it was that he saw me doing. Dad was always interested in what I was up to in my life. He along with my mother Mary, brother Mike, and fiancé Dan have been crucial to my success through the years, always being very supportive and encouraging. It has been hard losing my #1 fan, but I am very fortunate to have such wonderful people in my life.
# Table of Contents

- **Signature Page** .................................................................................. iii
- **Dedication** ......................................................................................... iv
- **Table of Contents** ............................................................................... v
- **List of Figures** .................................................................................... ix
- **List of Tables** ..................................................................................... xiv
- **Acknowledgements** ............................................................................ xvi
- **Vita** .................................................................................................... xix
- **Publications** ....................................................................................... xx
- **Abstract of Dissertation** ..................................................................... xxi

## Chapter One

**Introduction** ................................................................................................. 1
1.1 Abstract .................................................................................................. 2
1.2 Introduction ............................................................................................. 4
1.3 Preparation of Porous Silicon ................................................................. 5
1.4 Sensing with Porous Silicon .................................................................. 9
  1.4.1 Sensing Mechanism ...................................................................... 9
  1.4.2 Sensor Challenges: Background Interference and Analyte Specificity ........................................... 12
1.5 Approaches for Improving Sensor Stability, Selectivity, and Sensitivity .... 18
  1.5.1 Sensing Enhancement Through Covalently Attached Surface Chemistry ........................................... 18
  1.5.2 Sensing Enhancement Through Physical Adsorption of Molecules in the Porous Layer ................... 22
  1.5.3 Sensing Enhancement Through Designed Porous Layer Structure ................................................ 25
  1.5.4 Sensing Enhancement by Combining Pore-Size Tailoring and Chemical or Molecular Surface Modifications ................................................................. 29
1.6 Conclusions ........................................................................................... 34
CHAPTER TWO

REMOTE SENSING OF VOCs WITH AN ARRAY OF OPTICAL FIBERS CAPPED WITH CHEMICALLY MODIFIED POROUS SILICON.........................................................36
2.1 Abstract ........................................................................................................37
2.2 Introduction ....................................................................................................37
2.3 Experimental ..................................................................................................42
  2.3.1 Sensor Construction ..................................................................................42
  2.3.2 Gravimetric Determination of Porosity ....................................................43
  2.3.3 Scanning Electron Microscopy ..................................................................44
  2.3.4 Surface Chemical Modification ................................................................44
  2.3.5 Infrared Spectroscopy ..............................................................................45
  2.3.6 Water Contact Angle Measurements ....................................................45
  2.3.7 Vapor Dosing Measurements ...................................................................46
2.4 Results and Discussion ..................................................................................47
  2.4.1 Preparation and Characterization of Porous Si Photonic Crystals............47
  2.4.2 Effect of Chemical Modification on Analyte Response.............................56
  2.4.3 Stability of Chemically Modified Porous Si Sensors ...............................60
  2.4.4 Free Standing Porous Si Films Combined with Optical Fibers for Remote Sensing .................................................................63
  2.4.5 Calibration of Porous Si Tipped Fibers with Isopropanol, Heptane, and Relative Humidity .................................................................66
  2.4.6 Remote Sensing Application: Detection of Analyte Breakthrough in Activated Carbon Respiratory Cartridges .........................................70
2.5 Conclusions ...................................................................................................80

CHAPTER THREE

HUMIDITY-COMPENSATING SENSOR FOR VOLATILE ORGANIC COMPOUNDS USING STACKED POROUS SILICON PHOTONIC CRYSTALS............................................83
3.1 Abstract .........................................................................................................84
3.2 Introduction ....................................................................................................85
3.3 Experimental ..................................................................................................86
  3.3.1 Sample Preparation ..................................................................................87
  3.3.2 Infrared Spectroscopy ..............................................................................89
  3.3.3 Scanning Electron Microscopy ..................................................................89
  3.3.4 Gravimetric Determination of Porosity ....................................................89
  3.3.5 Water Contact Angle Measurements ....................................................90
  3.3.6 Vapor Dosing Experiments ...................................................................91
  3.3.7 Reflectance Spectra ...............................................................................91
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3.1</td>
<td>Preparation of Porous Si Photonic Crystal Diffraction Gratings</td>
<td>159</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Infrared Spectroscopy</td>
<td>161</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Scanning Electron Microscopy</td>
<td>161</td>
</tr>
<tr>
<td>5.3.4</td>
<td>Light Diffraction Imaging</td>
<td>161</td>
</tr>
<tr>
<td>5.4</td>
<td>Results and Discussion</td>
<td>161</td>
</tr>
<tr>
<td>5.4.1</td>
<td>Patterning Porous Silicon</td>
<td>161</td>
</tr>
<tr>
<td>5.4.2</td>
<td>Generations of Porous Si Patterning</td>
<td>168</td>
</tr>
<tr>
<td>5.4.3</td>
<td>Additional Patterning of Porous Si</td>
<td>174</td>
</tr>
<tr>
<td>5.4.4</td>
<td>Sensing Application for Porous Si Diffraction Gratings</td>
<td>177</td>
</tr>
<tr>
<td>5.5</td>
<td>Conclusions</td>
<td>178</td>
</tr>
</tbody>
</table>

### APPENDIX A

**SURFACE CHEMISTRY GRADIENT THROUGH A LIGHT-MEDIATED CHEMICAL REACTION**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.1</td>
<td>Introduction</td>
<td>180</td>
</tr>
<tr>
<td>A.2</td>
<td>Porous Silicon Fabrication and Light Mediated Chemical Modification</td>
<td>181</td>
</tr>
<tr>
<td>A.3</td>
<td>FTIR and Elemental Analysis SEM Characterization of Chemically Modified Porous Silicon</td>
<td>182</td>
</tr>
<tr>
<td>A.4</td>
<td>Surface Chemical Gradient Functionalization</td>
<td>183</td>
</tr>
</tbody>
</table>

**REFERENCES**                                                                 | 194  |
LIST OF FIGURES

CHAPTER ONE

Figure 1.1 Si anodization mechanism and pore formation schematic……..8
Figure 1.2 Photographs of porous Si rugate filters exposed to analyte…..11
Figure 1.3 Analyte detection methods.............................................17
Figure 1.4 Amine terminated porous Si interacting with CO₂………….21
Figure 1.5 Photograph of zein coated porous Si spotted with an active protease..........................................................24
Figure 1.6 Cross sectional scanning electron microscope image of a porous Si double layer.................................................27
Figure 1.7 Change in EOT of a double layer sample upon introduction of sucrose and BSA.........................................................28
Figure 1.8 Schematic of a porous Si double layer containing protease, protein, and subsequent digested protein fragments............32
Figure 1.9 Porous Si ammonia sensor...............................................33

CHAPTER TWO

Figure 2.1 Photograph of optical fibers capped with porous Si.........41
Figure 2.2 Reflectivity spectrum of a porous Si rugate.......................51
Figure 2.3 Attenuated total reflectance Fourier transform infrared spectra of chemically modified porous Si..........................54
Figure 2.4 Change in reflectivity peak position of chemically modified porous Si to 500 ppm isopropanol and heptane vapors........59
| Figure 2.5 | Change in reflectivity peak position of chemically modified porous Si to isopropanol and heptane vapors after 1, 8, and 15 days since chemical modification........................62 |
| Figure 2.6 | Scanning electron microscope image of porous Si capped optical fiber; vapor dosing schematic..........................65 |
| Figure 2.7 | Isopropanol and heptane response curves of porous Si capped optical fibers........................................68 |
| Figure 2.8 | Relative humidity response curves of porous Si capped optical fibers..................................................69 |
| Figure 2.9 | Respiratory cartridge simulator..........................................76 |
| Figure 2.10 | Isopropanol carbon bed breakthrough monitored by an optical fiber capped with as etched porous Si......................77 |
| Figure 2.11 | Isopropanol, heptane, and relative humidity carbon bed breakthrough monitored by optical fibers capped with thermally oxidized porous Si........................................78 |
| Figure 2.12 | Isopropanol, heptane, and relative humidity carbon bed breakthrough monitored by optical fibers capped with thermally reacted with acetylene porous Si........................................79 |

**CHAPTER THREE**

| Figure 3.1 | Diffuse reflectance FTIR spectra of porous silicon photonic crystal films.........................................................93 |
| Figure 3.2 | Fabrication of porous silicon double stack photonic crystals.................................................................97 |
| Figure 3.3 | Reflectivity spectrum of a sample containing two photonic crystals, and a cross-sectional SEM image of a double stack.................................................................98 |
| Figure 3.4 | Frequency shift of the photonic peak corresponding to the indicated chemically modified porous Si rugate filter in response to water vapor.........................................104 |
Figure 3.5  Dose-response curves for a double stack sensor to toluene, showing the ability of Equation 3.2 to compensate for RH...105

Figure 3.6  Dose-response curves for a double stack sensor to DMMP, showing the ability of Equation 3.2 to compensate for RH...109

Figure 3.7  Dose-response curves for a double stack sensor to heptane, showing the ability of Equation 3.2 to compensate for RH...110

Figure 3.8  Dose-response curves for a double stack sensor to ethanol, showing the ability of Equation 3.2 to compensate for RH...111

Figure 3.9  Frequency shift of hydrophobic and hydrophilic porous Si stacks as a function of analyte vapor concentration............115

Figure 3.10 Dose-response curves for a double stack sensor after RH interference has been removed using Equation 3.2.............116

CHAPTER FOUR

Figure 4.1  ATR-FTIR spectra.............................................................132

Figure 4.2  Shift in porous Si reflectivity peak position after 10 minute exposure to aqueous HF.............................................137

Figure 4.3  ATR-FTIR spectra of ozone oxidized porous Si after 10 minute exposure to aqueous Si.............................................138

Figure 4.4  ATR-FTIR spectra of furnace oxidized porous Si after 10 minute exposure to aqueous HF.........................139

Figure 4.5  Relative shift in wavelength of the main reflectivity peak from ozone oxidized porous Si rugate filters upon exposure to various concentrations of aqueous HF as a function of time.................................................................140

Figure 4.6  Reflectivity spectra of an ozone oxidized porous Si sample containing an impregnated polystyrene fiducial marker, before and during exposure to aqueous HF............................144

Figure 4.7  Reflectivity spectra of a porous Si sample containing a fiducial maker at normal incidence and at 8, 17, 27, and 37 degrees off normal.................................................................147
Figure 4.8  Photographs of a porous Si sample containing a fiducial marker before and after exposure to HF.................................148

Figure 4.9  Comparison of sample response to HF measured at normal incidence, 9, and 40 degrees off normal.................................149

Figure 4.10  Relative shift in reflectivity peak position of ozone oxidized porous Si to 0.4 %HF as a function of time, measured at normal incidence, 9, and 40 degrees off normal.................................150

Figure 4.11  Relative shift in reflectivity peak position of porous Si after 30 minute exposure to Cl2 gas in relative humidity....................153

Figure 4.12  ATR-FTIR spectra of porous Si samples after exposure to chlorine gas for 30 minutes.........................................................154

CHAPTER FIVE

Figure 5.1  Fabrication schematic of porous Si diffraction gratings........164

Figure 5.2  ATR-FTIR spectrum of PDMS microcontact patterned Si....165

Figure 5.3  Photographs taken under a microscope of patterned PDMS, microcontact printed Si, and patterned bulk Si.......................166

Figure 5.4  SEM images of diffraction grating patterned bulk and porous Si.................................................................167

Figure 5.5  SEM images of 1st and 6th generation patterned porous Si....171

Figure 5.6  Photographs of light diffracted by patterned porous Si..........172

Figure 5.7  Photographs taken under a microscope of patterned PDMS, microcontact printed Si, and patterned bulk Si with circular features.................................................................175

Figure 5.8  SEM images of bulk and porous Si patterned with circular features.................................................................176

APPENDIX A
Figure A.1  FTIR spectra of a light-mediated 1-decene hydrosilylated porous Si sample.................................................................187

Figure A.2  Gradient filter used to modify light intensity....................191

Figure A.3  Transmission mode FTIR spectra of a light-mediated 1-decene hydrosilylated sample using a light intensity gradient .................................................................192

Figure A.4  Transmission mode FTIR spectra of a light-mediated undecylenic acid hydrosilylated sample using a light intensity gradient .................................................................193
LIST OF TABLES

CHAPTER ONE
Table 1.1 Chemicals and biomolecules detected with porous Si ..............15

CHAPTER TWO
Table 2.1 Porosity and thickness of porous Si samples ....................52
Table 2.2 Surface chemistries prepared on porous Si samples ..........53

CHAPTER THREE
Table 3.1 Slope of response curves and properties of analytes ....117

CHAPTER FOUR
Table 4.1 Porosity and thickness of porous Si samples .................133
Table 4.2 Porosity of ozone oxidized rugate samples before and after exposure to aqueous HF for 10 minutes .................141
Table 4.3 Reflectivity peak position of empty ozone oxidized porous Si and its polystyrene filled porous Si fiducial marker as a function of probing angle .................145

CHAPTER FIVE
Table 5.1 Calculated and measured distance between diffracted light orders and direct transmission of light (order = 0) through a porous Si diffraction grating .........................173

APPENDIX A

xiv
<table>
<thead>
<tr>
<th>Table A.1</th>
<th>Ratio of Element Atomic % / Si Atomic % measured by SEM-EDX for porous silicon modified with 3,3,4,4,5,5,6,6,6-nonafluoro hexane</th>
<th>188</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table A.2</td>
<td>Ratio of Element Atomic % / Si Atomic % measured by SEM-EDX for porous silicon modified with 5-bromo-1-pentene</td>
<td>189</td>
</tr>
<tr>
<td>Table A.3</td>
<td>Ratio of Element Atomic % / Si Atomic % measured by SEM-EDX for porous silicon modified with 1-decene</td>
<td>190</td>
</tr>
</tbody>
</table>
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The author of this dissertation was one of the primary authors or co-author on all publications.
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ABSTRACT OF THE DISSERTATION

MANIPULATION OF SURFACE CHEMISTRY AND NANOSTRUCTURE IN
POROUS SILICON-BASED CHEMICAL SENSORS

by

Anne Marie Ruminski

Doctor of Philosophy in Chemistry

University of California, San Diego, 2009

Professor Michael J. Sailor, Chair

An ideal environmental sensor has zero baseline drift, a fast response time, is sensitive and selective to the analyte of interest, and has the ability to be miniaturized. Porous silicon is an attractive material for sensing applications due to its high surface area, readily modified surface chemistry, and optical signal transduction capability. This thesis describes the construction and chemical
modification of porous silicon photonic crystals for use in chemical sensing. The specific aims of this work were to develop new methods to maximize sensor stability, remove background signal interference, and to induce chemical specificity into the sensor.

This thesis begins with an introduction on porous silicon preparation methods and its sensing mechanisms, as well as different chemicals and biomolecules that have been detected and their detection limit. We show a multitude of chemical modifications of the porous silicon surface that produce long-term stability and induce analyte class specificity to the sensor.

Next, a method to remove interfering effects of changing relative humidity from the response of porous silicon is developed. Two porous silicon films are separately etched and chemically modified into silicon, one on top of the other. The response of each film is measured simultaneously. Each film has a characteristic response towards water vapor. The effect of changing humidity can then be accounted for by calculating the weighted difference between the two layer responses. Thereby, building an internal reference into the sensor.

A second type of internal spectral reference to eliminate artifacts associated with varying angle of incidence of an optical probing detector relative to a one-dimensional photonic crystal sensor was developed. The chemically non-
responsive internal spectral reference was built into a photonic crystal sensor chemically modified to respond specifically to hydrofluoric acid.

Lastly, a simple and inexpensive method to etch patterns into porous silicon was developed. A masking layer was imprinted onto a silicon surface through microcontact printing, followed by an electrochemical etch. The imprinted residue reduces the etching rate of the bulk silicon below, while unmasked silicon etches normally. The resulting inhomogeneous etching rate of silicon transfers the pattern into the bulk silicon.
CHAPTER ONE

INTRODUCTION
1.1 Abstract

Porous silicon nanostructures attract much interest for chemical and biological sensing due to their unique properties which include flexible pore size, tailorable surface chemistry, and optical reflectivity and photoluminescence spectra. Small pore diameters allow pre-concentration of gaseous analytes for lower detection limits while large pore diameters allow for the capturing of high molecular weight biomolecules. Detection of molecules entering the porous layer is achieved by monitoring the optical spectrum (in reflectivity based sensors) of the sample. The presence of molecules causes the refractive index of the porous layer to increase, resulting in a spectral red shift.

Like their contemporaries, porous silicon based sensors face several key challenges: signal drift, background interference and chemical specificity. Harsh environmental conditions can degrade the sensor leading to signal drift. Interfering molecules present in large concentrations relative to the analyte of interest can saturate the sensor, making it difficult to selectively identify the analyte of interest. This chapter gives an overview of methods employed to overcome these challenges. Methods include surface chemistry modification through covalent attachment, adsorption of reactants to the porous surface, tailoring pore diameter and porous layer structure.

The concepts of surface chemistry, porosity, molecular interaction, diffusion, and optics as it is studied in the porous Si system can provide insight into related porous materials and applications. Characterizations such as FTIR,
SEM, water contact angle measurement and BET are essential for understanding these materials. The methods and results detailed in this chapter can be applied to related materials and applications.

### 1.2 Introduction

Uhlir at Bell Laboratories accidentally discovered porous silicon in the mid 1950s while attempting to electrochemically machine silicon wafers for use in microelectronic circuits.\(^1\) Intense interest in porous silicon did not develop until 1990 when efficient room temperature photoluminescence was discovered.\(^2,3\) Initially, reports focused on understanding the photoluminescent properties and examining pore formation. A variety of pore shapes, dimensions, and porosity were studied in detail. Since then, the chemical, physical, and optical properties of the material have been extensively studied. Various optical structures such as Fabry-Perot layers and Bragg stacks were constructed. Porous silicon was first used as an environmental sensor by Tobias in the late 1980s for humidity sensing.\(^4\) Developments in the sensor field over the past 20 years have produced sensors for chemical and biological applications. The detection of volatile organic compounds (VOCs),\(^5-8\) toxins,\(^9\) explosives,\(^10\) polycyclic aromatic hydrocarbons,\(^11\) proteins,\(^12\) DNA\(^13\) and enzyme activity\(^14\) have all been reported.

Many application areas exist for environmental and biomedical sensors. Potential environmental sensors include air quality, water quality and industrial process monitoring, remote sensing, residual life indicators for personal protection probes, and many more.
equipment, on-body chemical exposure monitors and homeland security. Uses for biomedical sensors include point-of-care diagnostics, medical research instrumentation, clinical diagnostics, and in-vivo sensors.

Porous silicon has many advantageous properties for sensing applications. The porous structure possesses a high surface area for analyte adsorption/reaction (typically several hundred m² per cm³). Pore dimensions are tunable between 1 nm – 100 µm, accommodating species ranging from small molecules to cells. Sophisticated nanostructures such as photonic crystals are easy to manufacture and can be prepared with distinct spectral signatures to allow multiplexing. Surface chemistry is tailorable through an extensive library of modifications, imparting stability to the sensor. And the optics and electronics that are used in porous silicon sensors can be miniaturized into low-power units.

Multiple sensing mechanisms are available to porous silicon based sensors. The presence of molecules in the pores affects the refractive index, photoluminescence and dielectric constant of the porous layer. Capacitance, resistance, diode, photoluminescence, optical interference, elipsometry, MALDI, and resonance raman based sensing have all been reported. Chapter 1 focuses on using porous Si for optical interference based sensing of chemical and biological agents.

1.3 Preparation of porous silicon
Porous silicon is produced by stain etching, electrochemical or photoelectrochemical etching of silicon wafers. The most commonly used method is electrochemical etching, in which an anodic current is applied to a single crystal silicon wafer (p- or n-type) in the presence of aqueous hydrofluoric acid (HF) electrolyte solution. Pore size, morphology and porosity are controlled by the electrolyte solution concentration, applied current density, crystal orientation of the wafer, and dopant concentration and type. Porous silicon is classified according to the pore diameter ($d$) as microporous ($d < 10$ nm), mesoporous ($10$ nm $< d < 50$ nm) and macroporous ($d > 50$ nm).\textsuperscript{28}

The mechanism of porous Si formation has been debated in the literature and there are many articles that study the possible mechanisms.\textsuperscript{3,15,28-31} One proposed reaction scheme is depicted stepwise in Figure 1.1. Silicon etching is initialized when a current applied to the wafer causes hole ($h^+$) carriers to migrate to the Si/electrolyte interface.\textsuperscript{3} The positive charge on the surface allows nucleophilic attack by a fluoride ion on a Si-H bond resulting in a Si-F bond. The polarizing effect of the bonded fluorine allows another fluoride ion to attack the Si atom which generates a molecule of H$_2$ and injects one electron into the electrode. The polarizing effect of the two F atoms bonded to the Si atom reduces the electron density of the Si-Si backbond, weakening the bond, and allowing for attack by HF or H$_2$O. Si is thereby removed from the surface in the form of SiF$_4$. The remaining Si atoms on the surface are hydride terminated. Removal of the SiF$_4$ species produces a dip in the silicon surface. Migrating hole carriers will
preferentially travel to lower surface points, resulting in pore formation (Figure 1.1). Hole carriers become depleted from the pore walls, protecting the walls from further dissolution.

Various structures can be electrochemically etched into silicon including Fabry-Perot layers, multilayers, Bragg mirrors, rugate filters and microcavities. Silicon etched at a constant current produces straight pores that behave as Fabry-Perot interferometers. Optical interference patterns result from the Fabry-Perot layers due to incident light reflecting as an interference pattern as waves reflecting from the air/porous silicon and porous silicon/bulk silicon interfaces combine constructively and destructively. Multilayered porous Si is formed when the applied current density is abruptly changed causing a change in pore diameter. The resulting optical reflectivity spectrum superimposes the interference patterns reflecting from the additional porous layers. Bragg mirrors, which behave as a high reflectivity stop band, consist of a stack of thin porous layers etched with alternating low and high current density, producing layers with high and low refractive indices, respectively. A rugate filter consists of a similar layered structure with alternating refractive indices, however, it is prepared by electrochemically etching the Si wafer with a periodic current waveform. Rugates behave as photonic crystals, reflecting specific wavelengths of light determined by the periodicity of the porous layers. Microcavity structures consist of two Bragg mirrors that are separated by a defect layer, resulting in a high reflectivity stop band containing a resonant dip.
Porous silicon films can be removed from the bulk Si substrate and broken into small particles by ultrasonic fracture to prepare ultraminiature sensors. Removal of the porous Si film is performed after etching the porous layer by using a low concentration of HF electrolyte and applying a current pulse. The lower HF concentration removes silicon from the porous silicon/bulk silicon interface faster than pores can propagate, undercutting the porous film and removing it from the bulk silicon substrate.
Figure 1.1 Silicon anodization reaction steps and pore formation schematic. (Adapted from references 3, 29.)
1.4 Sensing with porous silicon

1.4.1 Sensing Mechanism

Reflectivity spectra from the structures described above are related to the index of refraction of the porous silicon films. Any change in the refractive index is observed as a wavelength shift in the reflectivity spectrum. A change in refractive index of the porous Si layer is induced by entrance of analyte entering the pores and replacing air or buffer. This optical property is harnessed for sensing applications. In Figure 1.2, the admission of toluene liquid or vapor into a porous silicon rugate filter causes a distinguishable color change from green to red. With porous Si Fabry-Perot interferometers, etched at a constant current, a change in refractive index is monitored by the optical thickness (OT) of the film which is obtained from a fast Fourier transform (FFT) of the interferogram. Optical thickness is defined as the product $nd$, where $n$ and $d$ are the refractive index and thickness of the porous layer, respectively.

A standard approach for detecting low concentrations of analyte is to pre-concentrate the sample. Materials with high surface area can be expected to collect a large number of molecules per unit volume based solely on surface adsorption effects (e.g. Langmuir adsorption, etc.). Nanoscale pores possess an additional capability to concentrate a vapor via micocapillary condensation. $^{36}$ The smaller the pore radius, the lower the partial pressure at which condensation can occur at a given temperature. $^{37}$ The extent of both monolayer adsorption and
capillary condensation are influenced by the surface properties of the porous matrix, which can be tailored using chemical modifications.¹⁸
Figure 1.2 Porous Si rugate filters display a spectral shift in the presence of chemical agents. The material contains a layered nanostructure that imparts a unique optical reflectivity spectrum. Replacement of the air in the pores with an organic liquid (top image) or vapor (bottom two images) causes a shift in the photonic resonance from green to red.
1.4.2 Sensor challenges: background interference and analyte specificity

Table 1.1 presents a list of selected chemicals and biomolecules detected with porous Si and Figure 1.3 shows analyte detection methods. One of the largest problems with point sensors is not their ability to respond to various agents of interest, but their lack of ability to identify a specific agent in the presence of a large background of other compounds. Porous Si-based sensors are no exception. The key parameter is discrimination – eliminating the effects of non-specific interactions from other molecules that can blind the sensor to its intended target. The problem of interference often overwhelms a sensor well before it hits its ultimate detection limit. Interfering molecules, even those with a relatively weak affinity for the sensor’s recognition elements, are usually present at higher concentrations relative to the analyte of interest that they saturate the sensor. A common example is the interference exhibited by water vapor. The concentration of water vapor in normal air is usually measured in terms of relative humidity (RH). As a point of reference, the concentration of water vapor in a typical office (60% RH, room temperature) corresponds to 8000 mg/m$^3$. Chemical toxins illicit their effects when the toxin is at the ppm level, or around 1 mg/m$^3$. Thus a chemical sensor must be able to detect its target in the presence of a water background that is several thousand times larger than the concentration of the target. To complicate matters, RH can change substantially within a few minutes,
producing a false response from the sensor. There are five approaches that have been used to improve specificity:

1. **Use a chemical or catalytic reaction** that is specific for the analyte of interest. Examples include copper ion catalyst for the detection of fluorophosphonate nerve agents with porous SiO$_2$ films,$^9$ or palladium nanoparticles that have been used to detect hydrogen gas.$^{38}$ An example of a biosensor that harnesses a catalytic reaction is an ELISA (Enzyme Linked Immunosorbent Assay); the catalyst in this case is an enzyme such as horseradish peroxidase cross-linked to a selective antibody.

2. **Make a cross-reactive array of many sensor elements.** So-called the “dog’s nose” approach because it mimics the mammalian olfactory system.

3. **Add a specific recognition element.** Very commonly employed in biosensors, using an antibody,$^{39}$ aptamer,$^{40}$ or complementary DNA strand.$^{13}$ A typical example is the home pregnancy test, which uses antibodies.

4. **Apply a time-resolved physical method.** Examples include chromatography, mass spectroscopy, or temperature programmed desorption. This method operates on small differences in the physical properties of molecules to distinguish
an analyte, for example: size, mass, and heat of vaporization.

5. **Apply a spectroscopic technique**, such as infrared, Raman, or fluorescence spectroscopy. These are referred to as “signature” or “fingerprint” methods because they identify molecules based on a diversity of spectral peaks (vibrational modes in the case of infrared or Raman). A very high sensitivity variant of Raman is surface-enhanced raman spectroscopy (SERS), which uses gold or silver nanoparticles as an absorbent.41

Discrimination also has a time component to it. Thermal or chemical fluctuations in the sample matrix can cause a sensor to drift, giving differing responses on different days or even from minute to minute. Ideally, the operational mechanism of the sensor must provide a low detection limit with high discrimination and no drift. The discrimination problem is particularly challenging for portable sensors. A sensor used outside of the clinical or analytical laboratory setting does not have the luxury of near-infinite supplies of reagents, power, and space. In this chapter, we will detail work using porous silicon sensors that strive to minimize drift and maximize sensitivity and selectivity.
## Table 1.1 Chemicals and biomolecules detected with porous silicon.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Detection Level</th>
<th>Method</th>
<th>Reversible?</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohols</td>
<td>250 ppb</td>
<td>Interference, gas phase</td>
<td>Y</td>
<td>42 43 44</td>
</tr>
<tr>
<td>Alkanes</td>
<td>ppm</td>
<td>Interference, gas phase</td>
<td>Y</td>
<td>42 43 44</td>
</tr>
<tr>
<td>Aromatic molecules</td>
<td>0.06 mM</td>
<td>PL quenching, liquid phase</td>
<td>Y</td>
<td>11,45</td>
</tr>
<tr>
<td>Amines</td>
<td>0.25 µM</td>
<td>PL quenching, liquid phase</td>
<td>N</td>
<td>46-48</td>
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<tr>
<td>SO₂</td>
<td>440 ppb</td>
<td>PL quenching</td>
<td>Y</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>&lt;1 ppm</td>
<td>conductivity</td>
<td>Y</td>
<td>50</td>
</tr>
<tr>
<td>CO₂</td>
<td>ppth</td>
<td>Interference</td>
<td>Y</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>ppm</td>
<td>Conductivity</td>
<td>Y</td>
<td>52</td>
</tr>
<tr>
<td>NO₂</td>
<td>100 ppb</td>
<td>FET</td>
<td>Y</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>ppb</td>
<td>Conductivity</td>
<td>Y</td>
<td>54,55</td>
</tr>
<tr>
<td></td>
<td>70 ppb</td>
<td>PL quenching</td>
<td>Y</td>
<td>56</td>
</tr>
<tr>
<td>NO</td>
<td>2 ppm</td>
<td>PL quenching</td>
<td>Y</td>
<td>56</td>
</tr>
<tr>
<td>O₂</td>
<td>62 torr</td>
<td>PL quenching</td>
<td>Y</td>
<td>57</td>
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<tr>
<td></td>
<td>100 ppm</td>
<td>conductivity</td>
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<td>Interference</td>
<td>Y</td>
<td>38</td>
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<tr>
<td></td>
<td>ppm</td>
<td>Conductivity</td>
<td>Y</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>5800 ppm</td>
<td>resistivity</td>
<td>Y</td>
<td>59,60</td>
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<tr>
<td>Proteins</td>
<td>1 pM</td>
<td>Interference</td>
<td>Y/N</td>
<td>12,61</td>
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<tr>
<td>DNA</td>
<td>2 fM</td>
<td>Interference</td>
<td>Not addressed</td>
<td>12,13,61</td>
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<tr>
<td>Gram negative bacteria</td>
<td>1.7 µg</td>
<td>Interference</td>
<td>N</td>
<td>62</td>
</tr>
<tr>
<td>Molecule</td>
<td>Detection Level</td>
<td>Method</td>
<td>Reversible?</td>
<td>Reference</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------</td>
<td>----------------------</td>
<td>-------------</td>
<td>-----------</td>
</tr>
<tr>
<td>TNT</td>
<td>1 ppb</td>
<td>PL quenching,</td>
<td>N</td>
<td>10</td>
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<tr>
<td></td>
<td></td>
<td>interference</td>
<td></td>
<td>63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not addressed</td>
<td></td>
<td>9,64,65</td>
</tr>
<tr>
<td>Sarin simulant:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DFP</td>
<td>800 ppm</td>
<td>Interference</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>DMMP</td>
<td>ppm</td>
<td>Interference</td>
<td>Y</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1.3 Analyte detection methods.


1.5 Approaches for Improving Sensor Stability, Selectivity, and Sensitivity

1.5.1 Sensing enhancement through covalently attached surface chemistry

As etched porous Si is hydride terminated, however the surface Si-H bonds are not stable and are susceptible to oxidation when exposed to air. Oxidation of the surface will result in a decrease in the refractive index of the porous layer over time, and hence a drift in the reflectivity spectrum. Stability of the porous layer can be greatly improved through chemical modification of the surface chemistry. The simplest porous Si chemical modification is a hydrophilic surface oxide, prepared by thermal oxidation in air or with ozone. This surface readily reacts with hydrofluoric acid (HF). HF attacks Si-O bonds, resulting in degradation of the porous surface and an observable blue shift in the optical spectrum. An oxidized porous Si film will react specifically to HF and not to other acids such as HCl. Therefore, the selectivity for HF has been utilized for HF sensing and a porous Si oxide sensor capable of detecting 30 ppm HF$_{(g)}$ in 10 minutes has been demonstrated.\(^{56}\)

A multitude of other chemical modifications may also be applied to porous silicon to achieve stability and selectivity in sensing, which is the subject of Chapter 2. Gao and coworkers studied the stability and sensitivity of four different surface types: as etched hydride terminated, ozone treated,
electrochemically methylated, and thermally oxidized porous Si. Samples were exposed to ethanol, methyl ethyl ketone, and \( n \)-hexane vapors in nitrogen. They found that surface modification had a pronounced effect on specificity and stability. Hydride terminated and electrochemically methylated samples were more sensitive to the hydrophobic analyte in comparison to the thermally oxidized and ozone oxidized surfaces. Electrochemically methylated samples were also found to be much more stable than the hydride terminated samples.

Rocchia and coworkers utilized surface chemistry to construct a CO\(_2\) sensitive porous silicon sensor by modifying ozone oxidized samples with 3-amino-1-propanol. CO\(_2\) interacts with amine groups to form carbamate species (Figure 1.4). Upon CO\(_2\) exposure, optical reflectivity spectra displayed reversible red shifts (from short to longer wavelengths) that scaled with concentration presumably due to an increase in the refractive index of the film when the new carbamate species formed. A detection of 5 ppth CO\(_2\) was achieved.

The chemically modified porous silicon environmental sensors described above are good examples of sensors that could be combined in a cross-reactive array of many sensor elements to mimic the mammalian olfactory system. Modification of the surface chemistry helps to stabilize the sensor and minimize drift, while adding specificity to the sensing array due to selective chemistry in the porous matrix that reacts with particular analytes of interest.

Chemical modification of porous silicon has also proven to be very important for biological sensors. Surface chemistry is crucial for producing
sensors that are resistant to degradation in aqueous media, have selectivity towards a molecule of interest, and can prevent non-specific binding.

Dancil and coworkers developed a chemical modification scheme that covalently attached protein to the surface of porous silicon. Ultimately, biotinylated protein A was attached to the porous film via a multi step process in order to specifically detect an antibody, human Immunoglobulin G (IgG). The chemical modification scheme is as follows: First, ozone oxidized porous silicon was treated with a sulfur containing silane which was reduced to generate an S-H species and further reacted to create a NHS-modified surface. Next, the sample was rinsed with a solution containing biotinylated bovine-serum albumin (BSA), which couples to the NHS-modified porous Si surface, and exposed to streptavidin, which has an extraordinary affinity for biotin. Lastly, biotinylated protein A was added to the sample. Protein A selectively binds only the Fc portion of certain antibodies while not having affinity to the other portions of the antibody, F(ab’)2 or F(ab). When a solution containing 2.5 mg/mL of Human IgG was introduced, an increase in the optical thickness of the porous film was observed. The interaction between protein A and the antibody was reversible through the addition of 0.1 M acetic acid. Nonspecific interactions were prevented by the design of the surface chemistry and this was demonstrated by exposing the protein A modified porous Si surface to the F(ab’)2 fragments of the antibody. The F(ab’)2 exposed protein A terminated samples did not show any increase in OT, indicating that nonspecific interactions were not occurring.
Figure 1.4 Amine terminated porous silicon interacting with CO\(_2\) to form a carbamate species.
1.5.2 Sensing enhancement through physical adsorption of molecules in the porous layer

Much work has been published on porous silicon sensors modified through physical adsorption or capping with molecules to impart selectivity to the sensor. However, a simple covalent modification of the porous film is also necessary to stabilize the sensor against degradation from environmental conditions.

Perelman and coworkers described a simplified biomolecule attachment strategy for sensing peptide/drug binding. BSA was non-covalently adsorbed to the pore walls of thermally oxidized porous silicon. The BSA layer was used as a linker for bioconjugate attachment of a tripeptide Ac-L-Lysine-D-Alanine-D-Alanine (KAA). The KAA peptide specifically binds to the antibiotic drug vancomycin. Drug binding was measured by monitoring changes in the optical thickness of the sample film, and 16 µM of vancomycin was detected.

Orosco and coworkers published a paper detailing protein-coated porous silicon for amplified optical detection of protease activity. In this study, a porous Si photonic crystal was electrochemically methylated followed by coating with a hydrophobic zein protein. Methylation of the surface had two purposes - to stabilize the porous layer from degradation over time, and to add hydrophobic groups to exclude buffer solution. Introduction of pure buffer produced no optical response of the porous layer spectrum. When a buffer solution containing active pepsin protease was spotted onto the zein-coated film, proteolytic digestion of the
zein protein layer occurred and proteolytic cleavage products infiltrated into the
photonic crystal layer. This resulted in an increase in refractive index of the film
and an observable color change from the original green to red (Figure 1.5). Using
this sensor design, protease concentrations as low as 7 pmol were detected.
Inspired by this work, Gao and coworkers designed a similar porous Si sensor and
demonstrated sensitive detection (0.1 ng/mL in a 1 µL sample) of matrix
metalloproteinase-2 (MMP-2), a protein closely associated with tumor aggression
and metastatic potential.⁷⁰
Figure 1.5 Dilution series for active protease pepsin, showing the effect of the concentration of pepsin on the observed color change in a zein covered porous Si photonic crystal. The sample was spotted with one microliter aliquots of buffer solution containing active pepsin in the concentration listed (in picomoles) and allowed to react for 1 hour.
1.5.3 Sensing enhancement through controlling the porous layer structure

Controlling pore diameter can be used to enhance selectivity, especially in biosensors where a wide range of sizes exist between biomolecules, viruses, and cells. Porous silicon with a lateral pore diameter gradient was produced to separate molecules based on size. The pores size gradient was achieved using an asymmetric electrode configuration during the electrochemical etching process, and pore sizes ranged from >500 nm down to <10 nm, the further the distance from the electrode. BSA, the test molecule, was introduced to the sample and produced a measured change in the reflectivity spectrum only in regions in which the pore size was large enough to admit the protein.

Etching a second porous layer beneath an existing layer can be utilized to add additional sensing channels within a porous Si film. If one applies a current step, the diameter of the pores abruptly changes as shown in the cross sectional scanning electron microscope image of Figure 1.6 where the current step transitioned from high to low. The ability to tune the pore diameter through the etching process provides a convenient method to build porous structures that can act as reservoirs or size exclusion membranes.

The application of double layers of porous Si structures to the problem of drift reduction in a biochemical assay has been demonstrated. The method extracts a differential signal from the optical signature from both layers
simultaneously. It provides a sensitive means to detect analyte binding at the solution/film interface and significantly reduces the effect of fluctuations in lamp intensity and other experimental variables that lead to noise or baseline drift in biosensors. A double porous layer consisting of large diameter pores on top of small diameter pores was used to detect the protein, BSA, when in a large (100-fold by mass) excess of a small molecule, sucrose. Sucrose penetrated into both porous layers whereas BSA only entered the large pores. Detection was accomplished by computing the weighted difference in the frequencies of two peaks in the FFT spectrum (Figure 1.7).
Figure 1.6 A scanning electron microscope cross-sectional view of a porous silicon nanostructure containing a built-in size separation membrane. The diameter of the pores are controlled by the current density applied during the electrochemical etching process.
Figure 1.7 Change in EOT (effective OT, 2nd) of a double layer porous silicon sample upon introduction of sucrose, BSA, and the combination of sucrose + BSA. In the figure, layer 2 represents the peak in the FFT spectrum due to the small pore diameter layer and layer 3 represents the peak due to the combination of the large and small pore diameter layers. The top difference trace represents the weighted difference of the EOT layers, with a weighting factor $\gamma = 1.58$, which eliminates the effect of sucrose and allows the selective detection of BSA. This method effectively eliminates background signal interference.
1.5.4 Sensing enhancement by combining pore-size tailoring and chemical or molecular surface modifications

Additional selectivity can be added and sensor drift eliminated by combining tailored porous structure design and chemical modification. One example is a sensor built to compensate for changing relative humidity. Although RH could be measured independently of the sensor, such a function can be designed into a porous Si double-layer nanostructure.\textsuperscript{64} The advantage of this approach is that it can also be used to discriminate between different agents of interest. In this approach, a double stack photonic crystal was prepared where one stack was hydrophobic-functionalized and the second stack was hydrophilic-functionalized. The result showed that one layer displayed a greater response to a given agent than the other due to the hydrophilicity discrimination, and the relative responses of the two layers provided the information needed to identify the agent. Obtaining agent selection while subtracting interference from relative humidity using a double-layer nanostructure will be discussed in greater detail in Chapter 3.

Double layers can also be harnessed to act as nano-reactors, which process very small (nanoliter) quantities of material.\textsuperscript{72} In this method, the top porous stack is etched with large pore diameters (~100 nm) to trap protease molecules, forming a sensitive reacting layer. The bottom porous layer has smaller pore diameters (~6 nm), which excludes protease and other large proteins but captures
the protease digestion products. Digested protein fragments that infiltrate the bottom porous layer produce a measurable change in the optical reflectivity spectrum allowing for label-free quantification of enzyme kinetics in real-time (Figure 1.8).

This type of nanoreactor has been demonstrated to quantify protease activity, but the approach is applicable to a range of reactions of interest to the high-throughput analytical and synthetic communities, such as DNA amplification, polymerization, enzyme-linked assays, and protein purification. The most important advance represented by this work is the demonstration that a multifunctional nanostructure can be used to immobilize, separate, and detect products of a biological reaction.

Specific chemical recognition elements can be incorporated into porous Si that will provide improved capability to identify targeted chemical agents. The fabrication process used to prepare porous Si can be modified to allow the incorporation of an internal reference signal. For example, the pH-responsive indicator dye bromothymol blue was incorporated into the material, providing specific detection of ammonia, Figure 1.9. To correct for the effects of zero-point drift, “Signal” and “Reference” channels were incorporated into the photonic crystal in the form of two separate spectral reflectance peaks. The wavelength of the “Signal” peak coincides with the absorption maximum of the deprotonated bromothymol blue pH indicator dye, and the wavelength of the “Reference” peak appears in a region of the spectrum where no protonated or
deprotonated dye absorbances occur. The ratio of the intensities of the two peaks in the reflectivity spectrum provides an accurate measure of ammonia vapor concentration in the range 15–1300 mg/m$^3$. The ratiometric method is insensitive to large fluctuations in probe light intensity.
Figure 1.8 A double layer nanoreactor consisting of a top porous layer with large diameter pores to hold an active protease (pepsin, green) and a bottom porous layer with small pore diameters to capture digested protein fragments (red). The assay was carried out by adding the protein substrate α-casein (blue) and monitoring the reflectivity spectrum of the sample to detect enzymatic reaction in real time.
Figure 1.9 Porous Si can be prepared to display two reflectance peaks. When this type of sample is infused with bromothymol blue, a pH-responsive ammonia vapor sensor results. One reflectance peak overlaps the absorbance band of the deprotonated dye while the other appears in a “clear” spectral region.
1.6 Conclusions

Porous silicon provides a fascinating matrix for chemical and biological sensing systems. The high surface area, ease at which it can be produced and chemically modified makes it an advantageous material for vapor and biomolecular sensing. This chapter described properties of porous Si that can be tailored for selective and stable detection of analytes. Sensitivity and stability can be enhanced through chemical modifications of the Si surface species for detection of small molecules and biomolecules. Further sensitivity can be achieved by controlling pore size and shape for developing reference layers that will normalize for signal drift, humidity interferents, and interferents in complex biomolecules matrices. The tailorability of chemical modification and porous layer structure make porous silicon a promising platform for achieving better, selective sensors.
Chapter one, in part, is a reprint (with co-author permission) of the material as it appears in the following publication: Ruminski, A.M., Sailor, M.J., Porous Silicon Optical Reflectors for Chemical and Biological Sensing (Manuscript in preparation). The author of this dissertation is a co-author of this manuscript.
CHAPTER TWO

REMOTE SENSING OF VOCs WITH AN ARRAY OF OPTICAL FIBERS CAPPED WITH CHEMICALLY MODIFIED POROUS SILICON
2.1 Abstract

Sensing of the volatile organic compounds (VOCs) isopropyl alcohol (IPA) and heptane in air using a collection of sub-mm porous silicon-based sensor elements is demonstrated. The sensor elements are prepared as one-dimensional photonic crystals (rugate filters) by programmed electrochemical etch of highly doped p-type silicon, removed from the bulk silicon substrate and affixed to the end of optical fibers. The stability and response of the sensors is tested as a function of surface chemistry, using the following modification methods: ozone oxidation, thermal oxidation, thermal hydrosilylation with 1-dodecene, electrochemical methylation, thermal reaction with dichlorodimethylsilane and thermal carbonization with acetylene. The acetylated porous Si microsensor displays a greater response to heptane than to IPA, whereas the other chemical modifications display a greater response to IPA than to heptane. This work is focused on the thermally oxidized and thermally acetylated microsensors. The thermal oxide sensor displays a strong response to water vapor, while the acetylated material response is minimized. Application of the miniature sensors to the detection of VOC breakthrough in a full-scale activated carbon respirator cartridge simulator is demonstrated. The potential of an array of multiple sensor types to improve analyte specificity is discussed.

2.2 Introduction
The use of porous Si has been explored for various environmental sensing applications. The photoluminescence\textsuperscript{6,23,74} refractive index\textsuperscript{5,25} and dielectric constant\textsuperscript{4,75} of porous Si are very sensitive to the presence of molecules in the pores. Volatile organic compounds\textsuperscript{5-7} explosives\textsuperscript{10} and polycyclic aromatic hydrocarbons\textsuperscript{11} have all been detected, with detection limits of a few ppb reported for some of these compounds\textsuperscript{76}.

Porous Si offers many advantages as a chemical sensing platform. The porous layer contains a high specific surface area for analyte adsorption (on the range of a few hundred m\textsuperscript{2} per cm\textsuperscript{3})\textsuperscript{15}. The surface chemistry is tailorable\textsuperscript{18}, and the porous layer is easy to produce.

Porous Si photonic crystals can be fabricated from highly doped p-type silicon by applying a sinusoidal anodic current during an electrochemical etch. This etching waveform produces a porous film with a periodic modulation in porosity and refractive index in the \textit{<100>} direction of the silicon wafer, resulting in an optical structure known as a rugate reflector\textsuperscript{34}. The reflectivity spectrum contains a sharp spectral peak at a wavelength corresponding to the period of the sinusoidal etching waveform. Reflectivity peak wavelengths are also dependent on the refractive index of the porous film. When a substance enters the pores the refractive index of the porous layer increases, producing a red shift in the reflectivity peak. The shift of the reflectivity peak provides a means to quantify the amount of chemical in an analyte matrix.
The chemical functionality of the surface species dictates the response and the stability of the porous Si sensor.\textsuperscript{18,77,78} In particular, grafting of chemical functionalities via formation of Si-C bonds has been found to be a convenient reaction to prepare stable sensors that display a degree of chemical selectivity. Grafting can be achieved by electrochemical reduction of alkyl halides\textsuperscript{79} or by hydrosilylation of terminal alkenes.\textsuperscript{80-82} Whereas the surface of native surface porous Si contains hydrophobic, air-reactive Si-H species, grafting of aliphatic hydrocarbons generates a similarly hydrophobic but significantly more stable surface. Using aliphatic compounds that contain specific functional groups such as carboxylate provides a means to incorporate different surface affinity properties while retaining the chemical stability of the Si-C bonded sensor surface.\textsuperscript{64}

In this work, we prepare porous Si surfaces with different chemical modifications, and quantify the response of the materials to hydrophilic (isopropanol) and hydrophobic (heptane) analytes. The stability of each sensor type is quantified for a period of 15 days. From this screen, two sensor chemistries with acceptable stability and displaying significantly different analyte responses are incorporated into porous Si microparticles that are then attached to the tips of optical fibers (Figure 2.1). The suitability of the fiber-based microsensors in a remote sensing application—as end-of-service life indicators for activated carbon beds—is demonstrated. We find that the combined response from the two fiber sensors is able to discriminate between the hydrophobic and
hydrophilic analytes. Microsensors modified with acetylene minimizes but not completely removes interference from relative humidity.
Figure 2.1 Optical fibers capped with chemically modified porous silicon.
2.3 Experimental

Single-crystalline highly doped p-type Si (0.0008-0.0012 Ω–cm resistivity, (100) polished, B-doped) was purchased from Siltronix Corp. All reagents were used as received unless otherwise noted. Aqueous HF (49%), isopropanol, acetic acid, undecylenic acid and lithium iodide were purchased from VWR International. Heptane, dodecene, iodomethane and silanization solution I (~5% dichlorodimethylsilane in heptane) were purchased from Sigma-Aldrich, Inc. Ethanol was purchased from Rossville Gold Shield Chemical Company. Acetonitrile was purchased from EM Science, purified using a two-column solid-state purification system (Glasscontour System, Irvine, CA), transferred to a glovebox (Vacuum Atmospheres Company, Hawthorne, CA) without exposure to air, and stored over molecular sieves. Oxygen was purchased from Westair Gases & Equipment, acetylene from Airgas, Inc., and nitrogen from Praxair, Inc. Optical fiber (600 micron silica core, low O.H.) was purchased from Thorlabs, Inc. Liquid epoxy resin (Epotuf 37-140, diglycidyl ether of bisphenol-A) was provided by Reichhold, Inc. Curing agent (Ancamine 2432) was provided by Air Products and Chemicals, Inc. Activated carbon (type RV6 12x20) was purchased from Calgon.

2.3.1 Sensor Construction

Porous Si samples containing a single spectral reflectance peak were prepared by anodization of highly doped p-type Si wafers in a 3:1 v:v solution of
aqueous hydrofluoric acid:ethanol in a two-electrode configuration using a platinum ring counter-electrode. Etching was performed in a Teflon etching cell using a galvanostat (Princeton Applied Research Model 363) under computer control (LabView, National Instruments). The porous layer was etched using a sinusoidal current density waveform varying between 13.3 and 66.4 mA cm\(^{-2}\) with a period ranging between 8 and 11.5 seconds for an etch duration ~10 minutes. The electrolyte solution was mixed during the etching process to minimize hydrogen bubble formation on the sample surface and to encourage etchant solution exchange in the porous film. \(^{34}\) Fiber sensors required the detachment of the porous layer from the bulk Si. The porous layer was detached by applying a current of 3.8 mA cm\(^{-2}\) for 8 minutes in a 3.3% hydrofluoric acid in ethanol solution. Free standing porous Si was attached to optical fiber with partially cured mixture of bisphenol A epoxy and modified aliphatic amine curing agent and allowed to cure for two days before use.

### 2.3.2 Gravimetric Determination of Porosity

Five repetitions of each sample etch type were prepared. Samples were weighed before etching \((m_1)\), after etching \((m_2)\), and after dissolving the porous layer with a 0.1M basic solution of KOH in water and ethanol \((m_3)\). The following equation was used to determine the porosity: \(^{83}\)

\[
Porosity = \frac{m_1 - m_2}{m_1 - m_3}
\]  

(2.1)
2.3.3 Scanning Electron Microscopy

Porous layer thickness was examined with a Phillips XL30 environmental SEM operating in secondary electron mode. An accelerating voltage of 10 keV was used. Porous Si tipped optical fibers were sputter-coated with chromium prior to acquisition to avoid sample charging.

2.3.4 Surface Chemical Modification

Surface functionalized samples were chemically modified according to the following procedures. Thermally oxidized samples were prepared by inserting as-prepared H-terminated porous Si samples in a tube furnace (Lindberg/Blue M) under air at 600 °C for 90 minutes. Ozone oxidation was achieved by placing as-prepared H-terminated porous Si samples in a flowing stream of ozone (Ozone Solutions, product ID OZV-8, flux of 8 g h⁻¹) for 4 minutes. Silanization of samples was performed by the submersion of ozone oxidized samples in ~5% dichlorodimethylsilane in heptane under inert conditions on a Schlenk line. The samples were heated to 105 °C for 8.5 hours, cooled, and rinsed with dichloromethane and ethanol. Porous samples were functionalized with dodecene through a hydrosilylation reaction. Samples were placed in a flask and covered with alkene. The flask was brought through three freeze-pump-thaw cycles on a Schlenk line. Samples were heated to 150 °C under nitrogen for 3 hours, then cooled and rinsed with dichloromethane and ethanol. Hydrogen terminated porous Si samples were methylated via an electrochemical reaction. A sample
was placed in an etching cell with a glass cap fitted with a stopcock and a counter electrode feed through. The vessel was attached to a Schlenk line, evacuated and filled with nitrogen three times. The sample (working electrode) and the Pt counter electrode was then covered with 4 mL of a 0.2 M iodomethane and 0.2 M lithium iodide in acetonitrile solution. A cathodic current of 5 mA cm\(^{-2}\) was applied for 2 minutes while under white light illumination. Samples were acetylated at various temperatures. Porous Si samples were placed in a ceramic boat and inserted into a tube furnace under a nitrogen flow of 2 L min\(^{-1}\). After ten minutes the furnace was set to the desired temperature (150, 300, 485 or 500 °C). Once the furnace temperature reached the set point, acetylene gas was introduced to the samples at a flow rate of 1 L min\(^{-1}\). After 30 minutes the acetylene flow was stopped and the temperature turned down.

### 2.3.5 Infrared Spectroscopy

Surface modification was verified through ATR-FTIR spectroscopy. Spectra were recorded with a Thermo Scientific Nicolet 6700 FTIR with a Smart iTR diamond ATR attachment using a resolution of 4 cm\(^{-1}\) and an average of 64 scans.

### 2.3.6 Water Contact Angle Measurements

Sessile drop contact angle measurements were collected on three samples of each surface chemistry using a digital camera and Adobe Photoshop CS2 for
analysis. Using a glass syringe, a 5 µL drop of Millipore water was delivered to the chip surface to form a water droplet. Contact angles were measured on both sides of the droplet and averaged.

### 2.3.7 Vapor Dosing Measurements

Reflectance spectra of porous Si were collected with an Ocean Optics USB2000 spectrometer coupled to a bifurcated fiber optic cable. Porous Si chips were probed with a microscope objective lens coupled to the bifurcated cable. Porous Si films attached to the tip of a fiber optic cable were coupled to the bifurcated cable with a fiber coupler. Samples were illuminated with a tungsten halogen (Ocean Optics LS-1) light source. Porous Si chips were exposed to 500 ppm IPA and heptane using a computer-controlled gas dosing system. Nitrogen carrier gas was set to a flow rate of 1.5 L min\(^{-1}\) using a mass flow controller (Alicat Scientific). Analyte was injected with a low-volume liquid flow pump (Valco M6) into a brass block heated to ~45 °C. Porous silicon tipped optical fibers were exposed to solvent under a flow of air. Air flow rate was set at 32 L min\(^{-1}\) using a Miller Nelson HCS-401 air conditioning system (Miller Nelson Instruments, a unit of assay technology). Analyte was injected as described above. Carbon filtration pack simulation breakthroughs were performed with a custom built simulator consisting of a stainless steel box with an inlet and outlet hole on opposite ends of the box for air flow. Inside the box was a small cylinder large enough to contain 50 grams of carbon. The air flow rate through the
chamber was 32 L min⁻¹. Note that in Figure 2.11C the periodic dips beginning at ~190 minutes in the oxidized trace are due to a water pump injecting cool water into the Miller Nelson air conditioning system. Each time the pump turned on, the relative humidity dropped briefly.

2.4 Results and Discussion

2.4.1 Preparation and Characterization of Porous Si Photonic Crystals

Porous Si samples were prepared by electrochemical etch of highly doped p-type silicon in an ethanolic HF solution. The current was varied sinusoidally, producing a film containing layers with gradually modulated porosity.³⁴ The layered structure acts as a one-dimensional photonic crystal known as a rugate filter, displaying a peak in the reflectance spectrum whose wavelength is determined by the wavelength of the sine wave used in the etch. All samples were etched with the same minimum and maximum current density, HF concentration and etch duration, and the current periodicity was adjusted in order to produce a reflectance peak located at ~650 nm after chemical modification (Figure 2.2).

Sample porosity was determined by gravimetric analysis.³³ Samples were weighed before etching, after etching and after dissolution of the porous layer with a 0.1M KOH solution in water and ethanol. Four sample etch types were prepared for porosity analysis: a rugate reflector etched with a period of 10
seconds, a rugate reflector etched with a period of 11.5 seconds, a single stack etched at the lowest current density value used for the rugate reflectors, and a single stack etched at the highest current density value used for the rugate reflectors. Porous layer thickness was measured by cross-sectional scanning electron microscopy (SEM). The average porosity and thickness of each sample is given in Table 2.1.

The various chemical modification reactions were performed immediately after etching the samples. Nine different chemical reactions from the literature were employed to generate distinct surface functionalities. Table 2.2 summarizes the chemical reaction chemistries, the idealized type of surface it generates, and the measured sessile drop contact angles. Representative attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra are given in Figure 2.3. The oxidation methods all tend to generate hydrophilic surfaces. Ozone oxidation produces a more hydrophilic surface than thermal oxidation, presumably due to the presence of a larger amount of surface Si-OH species. The ATR-FTIR spectra support this interpretation; along with the asymmetric Si-O-Si and Si-O stretching vibrations at 1025 cm\(^{-1}\) and 780 cm\(^{-1}\), respectively, a strong band assigned to \(\nu\) O-H is observed at 3350 cm\(^{-1}\) for the ozone-oxidized material. This species is detected as a minor component in the ATR-FTIR spectrum of the thermally treated material. At the temperature used in the thermal oxidation reaction, hydroxylated (Si-OH) surfaces are known to undergo dehydration to generate the more hydrophobic Si-O-Si surface.\(^{85-87}\) The asymmetric Si-O-Si and
Si-O stretching vibrations for the thermally oxidized material appeared in the FTIR spectrum at 1033 and 808 cm\(^{-1}\), respectively.

Several of the chemical modification methods of Table 2.2 result in hydrophobic material, by placing either aliphatic hydrocarbons or silicon carbide-like species on the surface. The silicon carbide-like species are generated by pyrolysis of acetylene on the surface of a porous Si chip. Previous studies report that the temperature of the pyrolysis reaction plays a key role in determining the degree of hydrophobicity or hydrophilicity of the resulting “hydrocarbonized” porous film\(^{88,89}\). In this study, four different pyrolysis temperatures (150, 300, 485 and 500 °C) were used to prepare hydrocarbonized samples. For all of the preparations, ATR-FTIR spectra display a prominent broad band at 1000 cm\(^{-1}\). This band appears in a region of the FTIR spectrum (1050-1150 cm\(^{-1}\)) that is generally associated with silicon oxides. However, the band remained after samples were soaked in an ethanolic solution of HF, suggesting that the band cannot be due to oxide (silicon oxides rapidly dissolve in HF solutions). On the basis of density functional theory calculations, Salonen and coworkers assigned the 1000 cm\(^{-1}\) band of thermally carbonized porous Si to C-H stretching vibrations from a species in which the carbon atom is back-bonded to Si atoms\(^{90}\). This assignment is consistent with the other bands observed in the FTIR spectrum, which include C-H stretching (~2900 cm\(^{-1}\)) and bending (~1385 cm\(^{-1}\)) vibrations\(^{91}\).
Contact angle measurements of the acetylene-treated, hydrocarbonized samples were less consistent than with the other chemical modifications. The water contact angle was observed to decrease as a function of time, and the footprint of the drop on the sample was often not round. We ascribe this to surface heterogeneity; presumably the acetylation chemistry produces a mixture of hydrophobic and hydrophilic domains.

Three chemical modification methods were used to place aliphatic hydrocarbon species on the porous Si surface: a long hydrocarbon chain was bonded to the surface through a thermal hydrosilylation reaction with 1-dodecene, a methyl group was attached by electrochemical reduction of methyl iodide, and a dimethylsiloxy group was attached by thermal reaction of an ozone-oxidized sample with dichlorodimethylsilane. ATR-FTIR spectra confirmed the presence of the aliphatic or methyl species. The aliphatic species displayed bands assigned to C-H stretching and deformation modes at 2966, 2926, 2858 and 1469 cm\(^{-1}\), and the methyl-capped surfaces displayed a distinctive band associated with the methyl rocking mode at 769 cm\(^{-1}\). Both of the surface preparations that produce surface-bound methyl species (electrochemical reduction of CH\(_3\)I or reaction with dichlorodimethylsilane) generate material that displays the same contact angle.
Figure 2.2  Typical reflectance spectrum of the porous Si rugate filters used in this study. The sample is etched using a sine wave that generates a one-dimensional photonic crystal. This spectrum is of a native surface (Si-H terminated) sample. The reflectance spectrum is acquired at normal incidence, as indicated in the inset.
### Table 2.1 Porosity and Thickness of Porous Si Samples[a]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity (%)[b]</th>
<th>Thickness (µm)[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rugate, 10s period</td>
<td>74.2 ± 0.6</td>
<td>13.27 ± 0.06</td>
</tr>
<tr>
<td>Rugate, 11.5s period</td>
<td>75.6 ± 0.7</td>
<td>13.5 ± 0.1</td>
</tr>
<tr>
<td>Single layer, 13.3 mA/cm²</td>
<td>66 ± 2</td>
<td>--</td>
</tr>
<tr>
<td>Single layer, 66.4 mA/cm²</td>
<td>76.9 ± 0.6</td>
<td>--</td>
</tr>
</tbody>
</table>

[a] All samples prepared using a 3:1 v:v solution of aqueous hydrofluoric acid:ethanol. Rugate layers were etched using a sinusoidal current density waveform varying between 13.3 and 66.4 mA/cm². All layers were etched for a duration of 10 minutes.

[b] Gravimetric measurement. Errors represent 1 standard deviation from 5 measurements.

[c] Cross-sectional SEM measurement of cleaved samples. Errors represent 1 standard deviation from 3 measurements.
Table 2.2 Surface Chemistries Prepared on Porous Si Samples[a]

<table>
<thead>
<tr>
<th>Process</th>
<th>Chemical Reaction</th>
<th>Surface Species</th>
<th>Contact Angle (°)[b]</th>
<th>$r = \Delta \lambda$(Heptane)/$\Delta \lambda$(Isopropanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native surface</td>
<td>Si-H</td>
<td>Si-H</td>
<td>102 ± 3</td>
<td>0.74</td>
</tr>
<tr>
<td>Ozone oxidation$^{93}$</td>
<td>Si-H + O$_2$ =&gt; Si-O-Si, Si-OH</td>
<td>Si-O-Si, Si-OH</td>
<td>11 ± 1</td>
<td>0.053</td>
</tr>
<tr>
<td>Thermal oxidation (600 °C, 90 m)$^{44}$</td>
<td>Si-H + O$_2$ =&gt; Si-O-Si</td>
<td>Si-O-Si</td>
<td>20 ± 1</td>
<td>0.11</td>
</tr>
<tr>
<td>Hydrosilylation with 1-dodecene$^{92}$</td>
<td>Si-H + CH$_3$CH$_2$(CH$_3$)$_2$ =&gt; Si-(CH$_2$)$_3$CH$_3$</td>
<td>Si-(CH$_2$)$_3$CH$_3$</td>
<td>119 ± 2</td>
<td>0.69</td>
</tr>
<tr>
<td>Electrochemical methylation$^{79}$</td>
<td>Si-H + CH$_3$I =&gt; Si-CH$_3$</td>
<td>Si-CH$_3$</td>
<td>102 ± 3</td>
<td>0.92</td>
</tr>
<tr>
<td>Ozone oxidation + dichlorodimethylsilane$^{78}$</td>
<td>(1) Si-H + O$_3$ =&gt; Si-O-Si =&gt; Si-O-Si(CH$_3$)$_2$ =&gt;</td>
<td>Si-O-Si(CH$_3$)$_2$-O-Si</td>
<td>101 ± 1</td>
<td>0.49</td>
</tr>
<tr>
<td>Thermal acetylation (150 °C, 30 m)$^{90}$</td>
<td>Si-H + H-C $\equiv$ C-H =&gt; “Si-C”</td>
<td>“Si-C”</td>
<td>112 ± 3</td>
<td>0.36</td>
</tr>
<tr>
<td>Thermal acetylation (300 °C, 30 m)$^{90}$</td>
<td>Si-H + H-C $\equiv$ C-H =&gt; “Si-C”</td>
<td>“Si-C”</td>
<td>53 ± 3</td>
<td>0.75</td>
</tr>
<tr>
<td>Thermal acetylation (485 °C, 30 m)$^{90}$</td>
<td>Si-H + H-C $\equiv$ C-H =&gt; “Si-C”</td>
<td>“Si-C”</td>
<td>80 ± 3</td>
<td>5.0</td>
</tr>
<tr>
<td>Thermal acetylation (500 °C, 30 m)$^{90}$</td>
<td>Si-H + H-C $\equiv$ C-H =&gt; “Si-C”</td>
<td>“Si-C”</td>
<td>76 ± 7</td>
<td>2.9</td>
</tr>
</tbody>
</table>

[a] Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of all samples are included in Figure 2.3. Surface species shown in the table are meant to represent idealized surface chemistry. Many of the reactions also generate oxide concomitant with the modification reaction.

[b] Contact angle measurements were performed on the same day as chemical functionalization.
Figure 2.3 Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of porous Si samples containing the different chemical modifications used in this study. Top to bottom: native surface (Si-H); ozone oxidized (Si-OH); thermally oxidized at 600 °C for 90 min (Si-O-Si); thermally hydrosilylated with 1-dodecene (Si-(CH₂)₁₁-CH₃); electrochemically methylated (Si-CH₃); ozone oxidized followed by thermal reaction with dichlorodimethylsilane (Si-O-Si(CH₃)₂-O-Si); thermally reacted with acetylene at 150 °C (Si-C (150)); thermally reacted with acetylene at 300 °C (Si-C (300)); thermally reacted with acetylene at 485 °C (Si-C (485)); and thermally reacted with acetylene at 500 °C (Si-C (500)). Full scale spectra are shown in black. A portion of the spectrum (>1300 cm⁻¹), shown in grey, is multiplied by 10 and offset along the y-axis for clarity. Native surface silicon displays features characteristic of Si-H bonds, at 2120 and 2088 cm⁻¹ (ν Si-H), 910 cm⁻¹ (δ SiH₂) and 623 cm⁻¹ (δ SiH₃). The hydrosilylated material contains features at 2966, 2926, 2858 and 1469 cm⁻¹ (C-H stretching and deformation modes). The electrochemically methylated sample contains one main feature at 769 cm⁻¹ (ρ CH₃). Material that is ozone-oxidized and then subsequently reacted with dichlorodimethylsilane contains features at 2963 cm⁻¹ (C-H), 1261 cm⁻¹ (δ CH₂R), 1012 cm⁻¹ (Si-O), and 790 cm⁻¹ (ρ CH₃). Thermally acetylated samples contain features associated with C-H stretching and bending vibrations at ~2900 and 1385 cm⁻¹, respectively. The band at ~1000 cm⁻¹ is due to C-H stretching vibrations from a species in which the carbon atom is backbonded to Si atoms.
2.4.2 Effect of Chemical Modification on Analyte Response

The relative hydrophobicity of chemically modified porous Si chips was evaluated by comparing the optical response of each sample to isopropanol and to heptane vapors. The analytes were individually vaporized in a nitrogen stream at a concentration of 500 ppm. The reflectivity peak maximum of the porous Si photonic crystal was recorded while the sample was exposed to nitrogen and nitrogen containing analyte vapor (Figure 2.4). The shift in the reflectivity peak maximum of a given sample to heptane is divided by the response to isopropanol, producing a response factor “r” as defined in eq. 2.2.

\[
r = \frac{\Delta \lambda_{\text{heptane}}}{\Delta \lambda_{\text{isopropanol}}} \tag{2.2}
\]

Calculated r values of the chemically modified porous Si chips are listed in Table 2.2. Larger values of r indicate a greater degree of hydrophobicity. As might be expected from the relatively large quantity of surface Si-OH species, ozone-oxidized samples display the smallest r value (0.053), followed closely by thermally oxidized samples (0.11). This result is in agreement with water contact angles, where ozone-oxidized samples had the smallest contact angle followed by thermally oxidized (Table 2.2).

Other samples with r values less than 1.0 include chips that were: acetylated at 150 °C or at 300 °C; reacted with dichlorodimethylsilane; functionalized with dodecene; electrochemically methylated; or unmodified, native surface porous Si. Water contact angle measurements on native surface
hydride terminated porous Si indicate a relatively hydrophobic surface, however
the surface hydrides oxidize slowly in air, producing hydrophilic Si-O groups and
a corresponding decrease in the value of the contact angle. Samples that were
electrochemically methylated displayed the same water contact angle, and
surfaces modified with 1-dodecene had a larger contact angle than the native
surface Si-H samples. However ATR-FTIR spectra of these samples show that
there are also residual Si-H sites on these surfaces. As with native surface porous
Si, air oxidation of Si-H species present in these samples is expected to generate
surfaces that are less hydrophobic than expected.

Although the samples reacted with dichlorodimethylsilane and the
electrochemically methylated samples displayed the same water contact angle, the
dimethylsiloxy terminated samples exhibit a significantly smaller r value than the
methyl terminated samples. We attribute this difference to the presence of the Si-
O bonds attaching the dimethylsilyl species to the surface and the underlying
oxidized porous Si material. Liquid water only probes the hydrophobic methyl
groups on the outermost layer, whereas water vapor can penetrate to the more
hydrophilic oxides. The electrochemically methylated material has much less
oxide and so is expected to exhibit hydrophobic characteristics to both liquid and
gas phase water. The water contact angles of the thermally acetylated samples
showed no obvious correlation with the measured r value, most likely due to a
high degree of surface heterogeneity produced by the acetylation reaction.
Only two samples exhibited $r$ values greater than 1.0: the acetylated samples prepared at 500°C ($r = 2.9$) and at 485°C ($r = 5.0$). The ATR-FTIR spectra of the samples prepared at 485 °C displayed more intense C-H stretches at 3055 and 2900 cm$^{-1}$ than samples prepared at 500 °C, indicative of a greater degree of hydrophobicity that is consistent with the relative $r$ values measured. Acetylated samples prepared at temperatures $> 500$ °C have a blackened appearance. Salonen and coworkers have suggested that the reaction of acetylene with porous Si leads to significant carbonization at temperatures $> 500$ °C. 90
Figure 2.4 Response of chemically modified porous Si photonic crystal samples to isopropanol (IPA) and heptane vapors. Vertical bars indicate the increase in wavelength ($\Delta \lambda$) of the resonant spectral peak of the photonic crystal relative to the sample in pure N$_2$, for the indicated surface chemistries. Simplified surface chemistries are described in Table 2.2: Si-H (native surface porous Si); Si-OH (ozone oxidized); Si-O-Si (thermally oxidized at 600 °C); Si-(CH$_2$)$_{11}$CH$_3$ (hydrosilylated with dodecene); Si-CH$_3$ (electrochemically methylated); Si-O-Si(CH$_3$)$_2$-O-Si (modified with dimethylsiloxane); Si-C (N) (acetylated at N °C). Analyte concentrations are 500 ppm isopropanol and 500 ppm heptane. Values are the average of 5 samples; error bars represent one standard deviation.
2.4.3 Stability of Chemically Modified Porous Si Sensors

The reproducibility of the vapor response of the chemically modified porous Si wafers was examined over a period of 15 days. Seven of the ten surface types were studied: native surface (Si-H), ozone oxidized (Si-OH), thermally oxidized (Si-O-Si), dodecyl terminated (Si-(CH$_2$)$_{11}$CH$_3$), methyl terminated (Si-CH$_3$), dimethylsiloxy terminated (Si-O-Si(CH$_3$)$_2$-O-Si), and acetylated at 485°C (Si-C). Samples were stored in the open laboratory atmosphere and then challenged with 500 ppm of isopropanol and heptane vapors 1, 8 and 15 days after chemical modification. Figure 2.5 displays the average responses and r value of each chemically modified sample. ATR-FTIR spectra were acquired for every sample on each of the three sampling days.

Native surface samples displayed no significant change in their response to isopropanol or heptane over the 15 day period. ATR-FTIR spectra of native surface samples displayed a slight increase in the band associated with Si-O-Si stretching vibrations at 1050 cm$^{-1}$. Ozone oxidized samples displayed no change in analyte response or in the ATR-FTIR spectrum, within the error limits of the experiments. Thermally oxidized samples displayed an increase in response to isopropanol during the first 8 days, though no significant change in the heptane response. No detectable changes were apparent in the ATR-FTIR spectra during the 15 days.

Samples modified with dodecyl, methyl and dimethylsiloxy groups retained the same response to heptane and isopropanol vapors within the error
limits for the duration of the 15 day test. However ATR-FTIR spectra of dodecyl modified samples displayed prominent Si-O-Si and C-H bands at day 1, which decreased in intensity by day 8. No further changes in the ATR-FTIR spectra were noted at day 15. ATR-FTIR spectra of electrochemically methylated samples showed a slight growth of the oxide band at 1050 cm$^{-1}$, while spectra of the dimethylsiloxy modified samples remained the same over 15 days.

Overall the average heptane and isopropanol response of samples reacted with acetylene at 485°C remained the same within the error limits throughout the 15 day study. However there was a large variation in analyte response between individual samples and between each day. We attribute this variation to surface heterogeneity, which was also evident in the water contact angle measurements.
Figure 2.5 Response of chemically modified porous Si photonic crystal samples to isopropanol and heptane vapors as a function of storage time (in air). Top and Middle: Vertical bars indicate the increase in wavelength ($\Delta\lambda$) of the resonant spectral peak of the photonic crystal upon exposure to 500 ppm isopropanol (Top) or 500 ppm heptane (Middle), for the indicated surface chemistries. Responses measured on day 1 (black bar), day 8 (grey bar) and day 15 (white bar). Bottom: $r$ value (see eq. 2.2). Horizontal dashed line at $r = 1.0$ separates samples that display a greater response to heptane ($r > 1$) from those that display a greater response to isopropanol ($r < 1$). Values are the average of 5-6 samples; error bars represent one standard deviation. Simplified surface chemistries are described in Table 2.2: Si-H (native surface porous Si); Si-OH (ozone oxidized); Si-O-Si (thermally oxidized at 600 °C); Si-(CH$_2$)$_n$CH$_3$ (hydrosilylated with dodecene); Si-CH$_3$ (electrochemically methylated); Si-O-Si(CH$_3$)$_n$-O-Si (modified with dimethylsiloxane); Si-C (485) (acetylated at 485 °C).
2.4.4 Free Standing Porous Si Films Combined with Optical Fibers for Remote Sensing

The interior of a carbon filter cartridge is one example of a volume-constrained sensing environment; there are many other instances in which a small sensor form factor is required. The chip-based porous Si sensors discussed so far have a diameter of ~ 1.2 cm. Previous work has shown that the active porous sensing layer can be removed from the Si substrate and fractured into particles of ~ 50 µm diameter.\textsuperscript{8,94} Referred to as “smart dust,” the small particles retain the gas absorption properties and sensing capability of the original chip-mounted films.\textsuperscript{84} In this work, such freestanding porous Si particles were attached to the tip of 600 micron diameter optical fibers (Figure 2.6) as previously demonstrated.\textsuperscript{95} The process produces no significant change in the reflectivity spectrum relative to the original chip-based sensors. The small size of the optical fibers allows multiple sensor probes to be placed in a remote location of limited space.

To better differentiate between classes of environmental toxins, three porous Si surface chemistries covering a range of hydrophobic/hydrophilic characteristics were chosen. Chemical modifications that displayed large differences in their relative analyte responses, based on r values, were used in the fiber-based sensor experiments: native surface porous Si (Si-H, r = 0.74), thermally oxidized (Si-O-Si, r = 0.11), and thermal acetylation at 485 °C (Si-C, r
= 5.0). Because the acetylation chemistry was highly variable, a single batch of acetylated porous Si films were used for all the fibers in this study.

Porous Si photonic crystals were etched as described in section 2.4.1. After etching, the porous layer was removed from the bulk Si using an electropolishing etch. The free-standing porous Si films were then immediately functionalized by a thermal treatment in either air (Si-O-Si) or acetylene (Si-C) as described in section 2.4.2, or they were left unmodified (Si-H). Optical fiber was cleaved to a desired length, stripped partially of the outer cladding layer, and polished on aluminum oxide lapping film to provide a smooth tip for optimal light coupling. The free-standing porous Si particles were attached to the tips of the fibers using a partially cured bisphenol A epoxy/modified aliphatic amine curing agent mixture and allowed to cure at room temperature for two days before use.
Figure 2.6 (A) Scanning electron microscope (SEM) image of an optical fiber capped with a porous Si vapor sensor (rugate filter). The porous Si layer was prepared as a freestanding film and attached to the glass fiber with epoxy. (B) Schematic depicting the optical configuration used for remote sensing.
2.4.5 Calibration of Porous Silicon Tipped Fibers with Isopropanol, Heptane, and Relative Humidity

The distal end of each porous Si-tipped optical fiber was fed into a splitter, where one arm went to a light source and the other to a CCD spectrometer. Thus the spectrum of light reflected from the porous Si sensor could be monitored from the backside of the particle, leaving the other end open to access of analyte vapors (Figure 2.6.B). The sensors were calibrated with isopropanol and heptane vapors in an air ambient. Reflectivity peak maxima were recorded in air at ~36% relative humidity and room temperature. Then, analyte concentrations of 50, 100, 200, 400, 500, 600 and 700 ppm were introduced sequentially, with an air purge in between each dose to return the sensor response to the initial baseline reading. Results are displayed in Figure 2.7. As expected, exposure to isopropanol produces the largest wavelength shift in the Si-O-Si sample, followed by Si-H and lastly Si-C. The wavelength shift measured for the Si-H and Si-C samples is linear with analyte concentration. The Si-O-Si sample response curve increases sharply at lower concentrations, but the slope decreases at higher concentrations. All three surface chemistry types display a relatively linear response to heptane vapor. Si-C samples display the greatest change in reflectivity peak wavelength upon exposure to heptane, followed by Si-H and then Si-O-Si.

The permissible exposure limits (PEL) for volatile organic compounds published by the Occupational Safety and Health Administration (OSHA) is generally reported as a time weighted average (TWA), where the value is the
average VOC exposure limit over a set time (usually eight hours). The OSHA PEL (TWA) for isopropanol is 500 ppm,\textsuperscript{96} and for heptane it is 500 ppm.\textsuperscript{96} As shown in Figure 2.7, the fiber-mounted porous Si sensors are capable of detecting these analytes at lower concentrations than the OSHA PEL.

To probe the effects relative humidity (RH) has on the porous Si capped fiber sensors, samples were exposed to stepped increments of \sim 5\% RH beginning at a RH \sim 41.5\% (Figure 2.8) in air. The response curves are similar to the isopropanol curves: the oxidized Si-O-Si sample displays the largest response. Si-H samples display the next largest response, followed by Si-C samples. The dose-response curves of Si-H and Si-C samples are approximately linear; Si-O-Si exhibits a decrease in sensitivity with increasing concentration. Figure 2.8 (top) compares the response of the 3 surface chemistries. Relative humidity exerts a large effect on the reflectivity peak position of the oxidized sample, producing a total wavelength shift of 30 nm when relative humidity changes from 41.5\% to 99\%. By comparison, the more hydrophobic Si-H and Si-C samples display relatively minor responses of < 0.8 nm over the same relative humidity change. The results are consistent with the measured sessile drop water contact angle measurements, where thermally oxidized (Si-O-Si) chips show a small contact angle of 20\°, while the corresponding value for Si-H is 102\°.
Figure 2.7 Dose-response curves for fiber-mounted optical porous Si sensors exposed to the analytes isopropanol (top plot) and heptane (bottom plot). Surface chemistries on the porous Si samples were: hydrogen-terminated (Si-H, circles), thermally oxidized (Si-O-Si, squares) or thermally reacted with acetylene at 485 °C (Si-C, diamonds). Lines are included as a guide to the eye. Values displayed represent an average of 6-9 samples, error bars correspond to 1 standard deviation.
Figure 2.8  Response of fiber-mounted optical porous Si sensors to relative humidity (RH). Samples are: native surface porous Si (Si-H, gray circles), thermally oxidized (Si-O-Si, black squares) and thermally reacted with acetylene at 485 °C (Si-C, black diamonds). All data points represent the change in wavelength of the reflectivity peak as a function of RH, relative to the wavelength value at RH = 41.5%. Data from 9 samples are shown, representing 3 samples for each of the 3 different surface chemistries. (Top) Chart comparing all three sample types. (Bottom) Plot expanded along the y-axis, showing only the Si-H and the Si-C samples. Lines are added to each sample as a guide to the eye.
2.4.6. Remote Sensing Application: Detection of Analyte Breakthrough in Activated Carbon Respiratory Cartridges

There is a significant need for small remote sensors, and optical fibers are widely used for this purpose.\textsuperscript{97-100} With a diameter of only a few tens to hundreds of microns, fiber optic-based chemical sensors have been used to detect volatile organic compounds,\textsuperscript{98,101} relative humidity\textsuperscript{101} and aqueous biomolecules.\textsuperscript{102-104} Optical fibers have been used to detect analyte breakthrough in activated carbon filtration cartridges in gas masks.\textsuperscript{95,105} End-of-service life indicators for filtration packs are greatly needed to improve the safety of gas mask users.\textsuperscript{95} Health and safety regulations in the United States require the use of end-of-service life indicators on gas masks, however these regulations are not enforced due to the lack of capable sensors. Instead, a systematic filtration pack change-out schedule is followed.\textsuperscript{106,107} This method is not reliable because the highly variable environment of the workplace greatly affects the lifespan of a carbon filtration cartridge.

Porous Si capped fibers were used to detect analyte breakthrough in an activated carbon respiratory cartridge simulator (Figure 2.9). The simulator chamber was constructed to hold 50 grams of activated carbon, the amount used in a typical personal respirator cartridge. The cartridge contained two sampling ports for a conventional gas chromatograph (GC), one at the middle of the bed of activated carbon (mid bed) and a second located at the air outlet of the box (end bed). Three holes were included in the cartridge chamber to accommodate the
fiber sensors, and the entire assembly was placed in a stainless steel containment vessel.

Three capped fibers containing Si-H, Si-O-Si and Si-C terminated porous Si were positioned at the middle of a bed of activated carbon and reflectivity spectra were recorded for several minutes without air flow to achieve a baseline. Conditioned air was initiated at a flow rate of 32 L min\(^{-1}\), reflectivity spectra were recorded for several minutes to obtain a new baseline, and lastly analyte flow was begun.

Figure 2.10 displays the response of a native surface porous Si sensor to the breakthrough of 500 ppm isopropanol in a carrier gas of air at 36% relative humidity. After ~75 minutes of isopropanol vapor flow, the porous Si sensor displayed a red shift of the reflectivity peak indicating the presence of isopropanol (breaking through the carbon bed). The native surface porous Si sensor displays a significant blue shift throughout the experiment. This is attributed to the unstable hydride surface, which oxidizes over time. Silicon oxides possess a smaller refractive index than Si, hence a blue shift in the spectral peak. Thus the Si-H particles are not particularly appropriate for monitoring vapor breakthrough in a carbon filter.

Figure 2.11 displays the response of Si-O-Si modified porous Si to analyte breakthrough in a carbon bed. Samples were separately exposed to 500 ppm of isopropanol (Figure 2.11.A) or heptane (Figure 2.11.B) vapor in conditioned air carrier gas at 36% relative humidity in the same procedure as described above.
The reflectivity peak position of the sensors remained constant during the first few minutes when there is no air flow. Upon initiation of air flow, the reflectivity peak in each sample displays a blue shift. The blue shift is attributed to a decrease in relative humidity as the ambient laboratory air is purged from the chamber and replaced by conditioned air. Air drawn from the mid bed access port (normally used to draw air samples into the GC) under a zero flow condition was measured with a chilled mirror hygrometer (Dewmaster). The relative humidity was 42%, several percent larger than the conditioned air. After 10 minutes of air flow, the relative humidity measured in the bed matched the RH of the carrier gas. The Si-O-Si samples continued to blue shift due to water vapor having a high affinity towards the hydrophilic porous Si, resulting in a slower desorption rate of water from the film. This effect was also observed after RH calibrations of the fibers (Figure 2.8) when RH was decreased. Analyte flow was introduced at time $t = 0$. As expected from the modified fiber calibrations to analyte (Figure 2.7), the Si-O-Si fiber displayed a greater response upon the breakthrough of isopropanol in the carbon bed versus heptane.

To examine the effects of changing RH, a Si-O-Si modified sample monitored the breakthrough of heptane vapor when in a carrier gas of air at 80% RH (Figure 2.11.C). Spectra were recorded for 5 minutes in the carbon bed with no air flow, followed by 5 minutes of 80% RH air flow. Heptane vapor was introduced at time $t = 0$. The reflectivity spectrum immediately began to red shift upon initiation of the carrier gas at 80% RH due to water adsorption in the
hydrophilic porous layer. The Si-O-Si modified sample continued to red shift, with an increase in signal response as heptane broke through the bed, followed by a blue shift in the reflectivity peak position, finally leveling off at the reflectivity peak shift range recorded in the RH calibrations in Figure 2.8. This response was reproducible. In an attempt to clarify the results, Si-O-Si modified samples monitored the breakthrough of 80% RH without heptane through a carbon bed (Figure 2.11.D). A slow continuous red shift in the reflectivity peak was observed over 10 hours, different from the RH calibrations in Figure 2.8 which leveled off within 3 minutes. Comparing this result to the heptane at 80% RH breakthrough explains the initial gradual red shift of the reflectivity peak. However the reason for the red shift at heptane breakthrough is unclear since heptane induced a much smaller response at 36% RH from the sample (Figure 2.11.B) than was observed in 80% RH. One possibility is that water breaks through the carbon bed first, adsorbing preferentially to hydrophilic sites in the porous layer and forming three dimensional clusters. As heptane later breaks through the carbon bed it adsorbs slowly due to the interaction with the surface, then once a monolayer has been adsorbed proceeds more quickly from stronger heptane-heptane interactions, leading to the increase in red shift of the reflectivity peak. Continued water adsorption displaces heptane resulting in the blue shift in the reflectivity peak due to the lower refractive index of water than heptane. Another possible factor influencing the sensor response may be displacement of water molecules from the
carbon surrounding the sensor as heptane breaks through the bed. The displaced water results in a temporary increase in RH and resulting sensor response.

Si-C terminated porous silicon fiber sensor response to analyte breakthrough in a carbon bed is displayed in Figure 2.12. Fibers were exposed to analyte and relative humidity as described above. The fibers proved to be less sensitive to changes in RH in the carbon bed than the Si-O-Si modified fibers. The blue shift in reflectivity peak position upon introduction of 36% RH conditioned air to the initial 42% RH carbon bed produced a much smaller shift than was observed for the Si-O-Si samples. Again, as expected from Figure 2.7, the Si-C terminated porous Si sensors displayed a greater signal response upon the carbon bed breakthrough of heptane versus isopropanol vapor in a RH of 36%. Carbon bed breakthrough of heptane vapor in 80% RH carrier gas produced a similar but slightly larger red shift than heptane breakthrough at 36% RH, although the amount of shift was within the heptane calibration error bar of Figure 2.7. Spectra from breakthrough of 80% RH only (Figure 2.12.D) displays a small, sharp initial red shift when the high RH air flow begins due to water entering the porous layer. This sharp shift was also observed upon air flow start in the heptane at 80% RH breakthrough.

The carbon bed breakthrough data show that porous Si capped optical fibers are susceptible to signal drift due to changing RH. A large increase in RH produces a large shift in the signal of Si-O-Si material. The Si-C modified porous
Si has a much smaller signal response to changes in RH, but is not completely unaffected by RH. RH response is a limitation of this system.
Figure 2.9 Respiratory cartridge simulator. (A) Simulator box containing air inlet and outlet, GC probe ports at mid carbon bed and air outlet, and holes for the porous Si tipped optical fibers. (B) Inside the simulator box is a smaller chamber that holds 50 grams of activated carbon. The carbon is kept in place by filter paper placed on the bottom and top of the chamber. Optical fibers and the mid bed GC probe are visible. (C) The smaller chamber partially filled with activated carbon. (D) An opened commercial activated carbon respiratory filtration pack for comparison.
Figure 2.10 Response of native surface (Si-H) porous Si optical sensor embedded in a carbon bed, demonstrating the detection of breakthrough of the analyte. Breakthrough is also monitored by gas chromatograph (GC) probes (right y-axis) at mid bed (gray long dash) and at the outlet of the bed (gray short dash). Lines are added as a guide to the eye. Optical sensor data points were obtained every 20 sec. GC data points were obtained every 4 min. Analyte flow was initiated at time = 0, and contained 500 ppm isopropanol in a carrier gas of air at 36% relative humidity.
Figure 2.11  Response of thermally oxidized (Si-O-Si) porous Si optical sensors embedded in a carbon bed, demonstrating the detection of breakthrough of (A) 500 ppm isopropanol in a carrier gas of air at 36% RH, (B) 500 ppm heptane in a carrier gas of air at 36% RH, (C) 500 ppm heptane in a carrier gas of air at 80% RH and (D) 80% RH. The GC is not able to detect water vapor. Experimental format is identical to that of Figure 2.10. Breakthrough is also monitored by gas chromatograph (GC) probes (right, y-axis) at mid bed (gray long dash) and at the outlet of the bed (gray short dash).
Figure 2.12  Response of thermally reacted with acetylene at 485 °C (Si-C) porous Si optical sensors embedded in a carbon bed, demonstrating the detection of breakthrough of (A) 500 ppm isopropanol in a carrier gas of air at 36% RH, (B) 500 ppm heptane in a carrier gas of air at 36% RH, (C) 500 ppm heptane in a carrier gas of air at 80% RH and (D) 80% RH. The GC is not able to detect water vapor. Experimental format is identical to that of Figure 2.10. Breakthrough is also monitored by gas chromatograph (GC) probes (right, y-axis) at mid bed (gray long dash) and at the outlet of the bed (gray short dash).
2.5 Conclusions

The surface chemistry has a pronounced effect on analyte response in porous Si-based optical sensors. Native surface Si-H porous Si is hydrophobic but does not have a stable reflectivity peak wavelength over time as was reported in Figure 2.10 (top). Acetylated samples showed VOC response variation between sample, and the acetylation process would need to be refined to produce a more reliable sensor. An ideal chemical modification would keep response to VOC fairly similar between samples and between days. This was true for ozone oxidized (Si-OH), methyl (Si-CH₃) and dimethylsilox terminated samples (Si-O-Si(CH₃)₂-O-Si). Additionally, porous Si tipped fiber sensors could be further reduced in size by using a smaller diameter optical fiber.

This work displayed that analyte discrimination can be added to a porous Si photonic crystal sensor through surface chemistry modification. Several chemical modifications were performed, resulting in sensors with various degrees of affinity towards hydrophobic and hydrophilic analytes. Porous Si chip based sensors were reduced to a smaller form factor size. Free standing chemically modified porous Si films were attached to the tip of 600 micron diameter optical fibers. Porous Si tipped optical fibers were used to detect analyte breakthrough in an activated carbon bed. A bundle of 3 fibers with different chemical modifications were inserted into a carbon bed. Each fiber surface chemistry had a unique response to the isopropanol and heptane analytes used. By monitoring the response of the three chemically modified porous Si capped fibers, a better
classification of the analyte breaking through the carbon bed can be achieved. A limitation of this system is the porous Si signal response to changes in RH. Si-C modified porous Si reduced response to RH in comparison to Si-O-Si material, yet was not a complete solution to the problem as signal response to changing RH was still present. RH calibrations of the materials produced a repeatable response. Including a separate RH detector in addition to the porous Si capped fiber sensors would allow the precise measurement of RH which could then be used to calculate the change in porous Si reflectivity peak due to RH.

For general environmental remote sensing, a bundle of chemically modified porous Si tipped optical fibers could be used as an electronic nose. The individual response of each fiber in the sensor array towards analytes could be recorded and compared, producing a unique response pattern for different analytes which could then be used to identify unknown environmental contaminants.
This chapter, in part, is a reprint (with co-author permission) of the material as it appears in the following manuscript submitted for publication: Ruminski, A.M., King, B.H., Snyder, J.L., Sailor, M.J., Remote sensing of VOCs with an array of optical fibers capped with chemically modified porous silicon. (Manuscript in preparation). The author of this dissertation is the one of the primary authors of this publication.
CHAPTER THREE

HUMIDITY-COMPENSATING SENSOR FOR VOLATILE ORGANIC COMPOUNDS USING STACKED POROUS SILICON PHOTONIC CRYSTALS
3.1 Abstract

One-dimensional photonic crystals constructed from multilayered stacks of porous Si are used as sensors for gas phase volatile organic compounds (VOCs). The ability of a double-stack structure to provide compensation for drift due to changing relative humidity (RH) is investigated. In this approach, two separate photonic crystals (dielectric stacks) are etched into a crystalline Si substrate, one on top of the other. The top stack is chemically modified to be hydrophobic (by hydrosilylation with dodecene) and the bottom stack is made hydrophilic (by hydrosilylation with undecylenic acid). It is shown that the optical spectrum of the double stack structure provides an effective means to discriminate VOCs from water vapor. In this approach, shifts in the peak frequencies from both photonic crystals are measured simultaneously. Because the two stacks respond differently to water and to VOC, the effect of changing humidity can be nulled by calculating the weighted difference between the two peak frequencies. Reliable determination of the concentration of VOC vapor in nitrogen over a range of relative humidity values (25% < RH < 75%) is demonstrated. The ability of the double-stack structure to discriminate between water vapor and VOCs is quantified for four different VOCs: toluene, dimethyl methylphosphonate (DMMP), heptane and ethanol.
3.2 Introduction

Most sensors for vapors in the environment are limited by zero-point drift caused by fluctuations in temperature or relative humidity. Changes in relative humidity are particularly problematic for sensors that operate on the basis of a measured change in conductivity or capacitance. The large dielectric constant of water leads to large changes in capacitance or parasitic surface conductivity for small changes in relative humidity. Optical sensors that measure changes in refractive index are not as susceptible to such effects. Regardless of the transduction mechanism, most point sensors can benefit from chemical modification that imparts a hydrophobic nature to the sensor element. If the target analyte is a VOC, such an approach can be used to minimize the effects of water vapor, while enhancing the adsorption of the organic compounds of interest. In general the effects of relative humidity are minimized but not completely eliminated. Ideally one would like to incorporate compensation for zero-point drift into the physical design of the sensor.

In this work a combination of chemistry and materials design is used to improve the ability of a porous Si-based VOC sensor to operate in the presence of a widely fluctuating humidity background. The first part of the approach involves chemical modification of a porous Si layer with a hydrophobic dodecyl group in order to minimize its affinity for water vapor. The second part involves electrochemical fabrication of a second photonic crystal directly beneath the dodecyl-grafted surface. This new photonic crystal is modified with a carboxylic
acid functionality, creating a more hydrophilic sensor layer. This tandem etch-modification method produces two multilayered stacks (photonic crystals) with differing chemical affinities, one on top of the other. The combined structure is probed with a single beam of white light, and the reflectivity spectrum of each stack is monitored simultaneously as the sensor is challenged with VOC/water vapor mixtures. The change in the spectral peak positions gives an indication of the quantity of analyte in each of the porous photonic crystals. Due to the differing chemical functionalities, the two photonic crystals respond differently to analytes, with a significant difference exhibited towards water vapor. It is found that the effect of fluctuations in relative humidity is effectively removed by subtracting the scaled response of the hydrophilic stack from the response of the hydrophobic stack.

3.3 Experimental Methods

All reagents were used as received unless otherwise noted. Aqueous HF (49%) and ethanol (200 proof) were purchased from Fisher Scientific and Rossville Gold Shield Chemical Company, respectively. Dodecene, undecylenic acid, heptane (99%), and iodomethane (99%) were purchased from Sigma-Aldrich Inc. Dimethyl methylphosphonate was purchased from Strem Chemicals. Toluene and ultra dry lithium iodide (99%) were purchased from VWR International. Acetonitrile was purchased from EM Science, purified using a two-
column solid-state purification system (Glasscontour System, Irvine, CA),
transferred to a glovebox (Vacuum Atmospheres Company, Hawthorne, CA)
without exposure to air and stored over molecular sieves. Ultra high purity
nitrogen was purchased from Westair Gases & Equipment. Porous Si samples
were prepared from single-crystalline highly doped p-type Si (0.0008-0.0012 Ω-
cm resistivity, (100) polished, B-doped) purchased from Siltronix Corp.

3.3.1 Sample Preparation

Porous Si samples were prepared by anodization of the highly doped p-
type Si wafers in ethanolic HF solution (3:1 v/v 49% aqueous HF:ethanol) in a
two-electrode configuration using a platinum mesh or ring counter-electrode. Si
wafers with an exposed area of 1.3 cm² were contacted on the back side with a
strip of aluminum foil and mounted in a Teflon etching cell. Double stack
samples were prepared as follows: First a top porous stack was etched using a
sinusoidal current density waveform, varying between 11.5 mA cm⁻² and 34.6 mA
cm⁻², with a period of 10 s, and with 34 repeats. The electrolyte solution was
manually mixed with a pipette during the etching process in order to prevent
hydrogen bubbles from forming on the porous surface and to encourage etchant
solution exchange in the porous film. The sample was rinsed with pure ethanol,
removed from the etch cell, rinsed with ethanol again, and then dried in a stream
of N₂ gas. The sample was then chemically modified by hydrosilylation with neat
1-dodecene: the chip was placed in a small flask and completely covered with the
alkene, the flask was brought through three freeze-pump-thaw cycles on a Schlenk line, placed under a N₂ atmosphere, and heated to 130 °C in a silicone oil bath. After two h the samples were cooled, removed from the reaction chamber and rinsed with dichloromethane and ethanol. The second photonic stack was then prepared using the same etch conditions, except the period was 11.63 s, and 60 repeats were applied. Next, the sample was hydrosilylated with neat undecylenic acid following the same procedure used for 1-dodecene. Samples were then soaked in a 3:1 HF:ethanol solution that was mechanically mixed for 20 min, and immediately electrochemically methylated in an acetonitrile solution containing 0.2 M methyl iodide and 0.2 M lithium iodide. Manipulation of the methyl iodide solution was performed under a controlled dry N₂ atmosphere using standard Schlenk-line techniques. The sample was placed in an etching cell with a glass cap fitted with a stopcock and a counter electrode feed-through, and the apparatus was attached to a Schlenk line. After evacuating the system and backfilling with dry N₂ three times, 4 mL of 0.2 M methyl iodide solution was added into the vessel, submerging the sample (working electrode) and the Pt counter electrode. A cathodic current of 5 mA cm⁻² was applied for 2 min under white light illumination.

To fabricate single-stack samples, a Si wafer was etched with the same conditions as stack 1. The samples were either left unmodified, or hydrosilylated with alkene followed by methylation as described above. The samples were stored under vacuum in a desiccator until needed for gas dosing tests. Samples for
the lowest/highest porosity measurements in section 3.4.2 were prepared by etching a Si wafer at 11.5 mA cm$^{-2}$ (lowest porosity) or 34.6 mA cm$^{-2}$ (highest porosity) for 10 minutes.

### 3.3.2 Infrared Spectroscopy

Dodecyl, undecylenic acid, and methyl chain attachment was verified through diffuse reflectance infrared spectroscopy (Figure 3.1). Diffuse reflectance infrared spectra were recorded with a Nicolet MAGNA 550 spectrometer equipped with a CsI beam splitter, using a spectral resolution of 4 cm$^{-1}$ and an average of 128 scans. The sample chamber was purged with nitrogen during spectral acquisition. The porous layer was mechanically removed from the bulk Si substrate for IR analysis.

### 3.3.3 Scanning Electron Microscopy

Individual stacks and double stack samples were examined with a Phillips XL30 environmental scanning electron microscope operating in secondary electron mode. An accelerating voltage of 20 keV was used. Samples were sputter coated with ~30 nm of chromium prior to acquisition to avoid sample charging.

### 3.3.4 Gravimetric Determination of Porosity
Triplicates of all samples were prepared: porous Si double photonic stack samples, samples consisting of only the top photonic stack or the bottom photonic stack of the double stack, and samples prepared by etching at a constant current density, where the current density value was equal to either the minimum current density or the maximum current density used in the sinusoidal current density waveform used in preparation of the photonic stacks. Samples were weighed before etching (m₁) and after etching (m₂). A dilute basic solution of KOH in water and ethanol was used to dissolve the porous film. Samples were weighed after the porous film was removed (m₃). The porosity of the sample was determined using the equation:\(^8^3\)

\[
\text{Porosity} = \frac{m_1 - m_2}{m_1 - m_3}
\]  

(3.1)

3.3.5 Water Contact Angle Measurements

Porous Si chips were viewed along an edge with a digital camera. Using a glass syringe, a 5 \(\mu\)L drop of deionized (DI) water was delivered to the chip surface to form a water droplet. The contact angles formed at the interface of the DI water drop and the porous Si surface were measured using Adobe Photoshop CS2. Contact angles measure the wetting of a solid by a liquid. Small angle values indicate that water wets the surface well, characteristic of a hydrophilic surface. A large contact angle indicates poor wetting, or a more hydrophobic surface.
3.3.6 Vapor Dosing Experiments

A computer-controlled gas dosing system was employed. The system consists of four interchangeable analyte-filled bubblers maintained at 15 °C in a constant temperature bath and connected to 10 cm³ min⁻¹ or 1000 cm³ min⁻¹ mass flow controllers. All RH values reported correspond to a temperature of 15 °C. Nitrogen carrier gas is regulated by a 1000 cm³ min⁻¹ mass flow controller and nitrogen purge gas is regulated by a 2000 cm³ min⁻¹ mass flow controller. Solenoid valves downstream of the bubblers prevent any detectable leakage of the analyte gases. A four-way valve before the test chamber ensures that the analytes delivered are pre-mixed before delivery. The test chamber is at room temperature, nominally 21 °C. Dosing experiments were computer-automated. A second computer with a CCD spectrometer was used to collect optical reflectance spectra from the porous Si samples.

3.3.7 Reflectance Spectra

Reflectance spectra of porous Si were collected with an Ocean Optics USB2000 CCD spectrometer fitted with a microscope objective lens coupled to a bifurcated fiber optic cable. A tungsten halogen (Ocean Optics LS-1) light source was focused onto the center of a porous Si surface with a spot size of approximately 1-2 mm². Reflectivity data were recorded in the wavelength range
of 400-1000 nm. Both the illumination of the surface and the detection of the reflected light were performed along an axis coincident with the surface normal.
Figure 3.1 Diffuse reflectance FTIR spectra of porous silicon photonic crystal films with key bands labeled. (A) A porous silicon sample after etching. The surface is hydride-terminated. (B) A dodecyl-terminated, methyl-endcapped single stack film. (C) A single stack film reacted with undecylenic acid, followed by methyl endcapping. (D) A porous silicon double stack that was chemically reacted with 1-dodecene, undecylenic acid, and methyl iodide.
3.4 Results and Discussion

3.4.1 Synthesis of Stacked Photonic Crystals of Porous Si

Each photonic crystal stack was prepared by an anodic electrochemical etch of a silicon wafer in ethanolic HF solution.\(^9\) The applied current was varied sinusoidally, producing photonic crystals with reflectance spectra whose peak maxima appear in the visible spectral range.\(^8\) The electrochemical etching reaction generates a hydrogen-terminated surface that can be hydrosilylated by heating in neat alkene. The hydrosilylation reaction stabilizes the etched surface by replacing reactive Si-H species with an aliphatic group, grafted to the surface via Si-C bonds.\(^18\)

To create a double stack sensor, electrochemical etching and chemical modification steps are performed in tandem (Figure 3.2).\(^9\) The chemistry relies on the fact that the Si-C bonds formed in the hydrosilylation step are not removed by HF-containing electrolytes. Etch conditions are chosen such that the reflectivity peak maximum from one photonic crystal stack is adequately separated from the other in the spectral domain (Figure 3.3.A). Although porous Si is not completely transparent in the near IR spectral range, stack 1 (the top layer) is sufficiently transparent to allow observation of the peak originating from stack 2. Each photonic crystal was etched using a sinusoidal current waveform. The same maximum and minimum current densities were used for both photonic stacks, while the period of each waveform was different in order to separate the spectral reflectance peaks.
Two distinct surface chemical modifications provide the double-stack sensor with a differential response towards water vapor. In this study, the first stack ($\lambda_{\text{max}} = 515$ nm) is thermally hydrosilylated with 1-dodecene. The hydrosilylation reaction stabilizes the etched surface and increases the hydrophobicity of the porous Si film.

A second stack ($\lambda_{\text{max}} = 669$ nm) is then etched beneath the first, and this second photonic crystal is subsequently hydrosilylated with undecylenic acid. Undecylenic acid contains a carboxylic acid group that imparts a more hydrophilic nature to the stack. The entire structure is then electrochemically methylated with a solution of 0.2 M methyl iodide and 0.2 M lithium iodide in acetonitrile. This “endcapping” procedure attaches methyl species to residual reactive Si-H sites on the surface, and it has been shown to significantly stabilize modified porous Si surfaces.

Diffuse reflectance infrared spectroscopy confirms the presence of the dodecyl functionality (Figure 3.1). Samples modified with 1-dodecene display bands in the infrared spectrum characteristic of C-H stretching and deformation modes at $\sim$2930 cm$^{-1}$, 2860 cm$^{-1}$, and 1465 cm$^{-1}$, respectively. These features remain after the samples are treated with an ethanolic HF solution, confirming the presence of the Si-C linkage (the Si-O bond is removed by treatment with ethanolic HF). Samples modified with undecylenic acid have an additional peak at 1710 cm$^{-1}$ due to a C=O stretch. A methyl rocking mode band is observed at 768 cm$^{-1}$ from the methyl endcapping reaction.
Water contact angles were measured on the double stack and on each individual stack (fabricated separately). The water contact angle for a dodecyl/methyl-modified stack was 93° ± 2°, and for an undecylenic acid/methyl stack it was 87° ± 2° (errors are two standard deviations). The slightly larger contact angle for the dodecyl/methyl-modified stack indicates a more hydrophobic surface. The water contact angle for the double stack was 92° ± 2°, consistent with the dodecyl/methyl-modified single stack (the dodecyl/methyl-modified stack is the top stack in the double stack structure). The contact angle measurements indicate that the hydrophobicity of the top layer is not significantly altered by the subsequent electrochemical etching and modification chemistries used to form the bottom layer. During the hydrosilylation reaction used to modify the bottom stack of a double stack, the entire structure is exposed to undecylenic acid. However, at this point in the synthesis the top stack has already been hydrosilylated with dodecene, and there are few accessible Si-H species remaining in that stack. The grafting reaction of undecylenic acid is thus restricted to the lower stack.
Figure 3.2 Fabrication of porous Si double stack photonic crystals. A silicon wafer is electrochemically etched and then chemically modified via hydrosilylation with 1-dodecene. A second porous stack is etched beneath the first stack and is subsequently modified with undecylenic acid. The entire structure is then stabilized by electrochemical grafting of -CH₃ groups. The end result is a double stack porous Si sample with a top hydrophobic layer and a bottom hydrophilic layer.
Figure 3.3 (A) Reflectivity spectrum of a sample containing two photonic crystals, one on top of the other (double stack). A cross-sectional schematic of the structure is shown in the inset. The reflectivity spectrum shown is acquired at normal incidence. (B) Cross-sectional secondary electron scanning electron micrograph of the double stack porous silicon photonic crystal.
3.4.2 Determination of Porosity and Thickness of Double Stacks

Porosities were measured by gravimetric analysis. Samples were weighed before etching, after etching, and after removal of the porous Si film by chemical dissolution with an aqueous solution of KOH and ethanol. Since hydrosilylated films are too stable to dissolve in basic solutions, the gravimetric determinations were performed on freshly-etched samples that were not chemically modified. Three types of samples were prepared to characterize the layer properties: one type contained only stack 1, the second type contained only stack 2, and the third type contained stack 1 on top of stack 2. Average porosity measured was 68 ± 1% for stack 1, 69 ± 1% for stack 2, and the double stack was 68 ± 1% (from replicate measurements on 3 samples, values given with two standard deviations). The minimum and maximum porosity within a given stack was also determined. Two types of samples were prepared: one type was etched at the lowest current density value used in the preparation of a stack, and the second was etched at the highest current density value. Both of the sample types were etched at their respective current density values for 10 min. The minimum and maximum porosity values were determined by gravimetry to be 63 ± 2% and 69 ± 1%, respectively. The thickness of the porous Si stacks was determined by cross-sectional scanning electron microscopy. The average of four SEM measurements (of chemically modified films) yielded a thickness of 4990 ± 80 nm
for stack 1, 10,800 ± 400 nm for stack 2, and 16,000 ± 300 nm for the double stack (Figure 3.3.B).

3.4.3 Response of Chemically Modified Photonic Crystals to Water Vapor

Adsorption of a vapor onto the inner pore surfaces of a porous Si photonic crystal film causes a change in the total refractive index that can be quantified in the reflectivity spectrum. The frequency of a spectral peak from a porous Si photonic crystal decreases upon introduction of any analyte with a refractive index larger than air, and the magnitude of the red shift scales with the amount of analyte present.

First, the responses of chemically modified single photonic crystal stacks of porous Si to water vapor were characterized. The single stacks were etched and hydrosilylated with either dodecene or undecylenic acid, and the films were then endcapped via methylation. An unmodified ‘freshly etched’ stack was also prepared for comparison. The response of the three types of porous Si films to water vapor was investigated with a computer-controlled gas dosing system, using ultra high purity nitrogen as a carrier gas. Samples were dosed with water vapor concentrations ranging from 0 mg m⁻³ (0% RH) to 11230 mg m⁻³ (87.5% RH at 15 °C). A plot of the frequency shift of the photonic feature vs. water vapor concentration (Figure 3.4) displays a red-shift of the films with increasing water concentration. As expected, the film modified with the carboxylic acid-
terminated surface species displays a greater affinity for water vapor than the
dodecyl-terminated stack. The freshly etched stack displays the largest response
to water vapor. Freshly etched porous silicon is hydride-terminated and quite
hydrophobic; however the Si-H bond is susceptible to oxidation in atmospheric
conditions. Slow oxidation of the freshly etched stack by air reduces the
hydrophobicity of the porous layer, increasing the response to water vapor. The
oxidation reaction thus leads to significant zero point drift. The hydrosilylated,
methyl end-capped material is much less susceptible to air oxidation, providing a
more stable and reproducible sensor response.

Next, a chemically modified porous double stack structure was exposed to
water vapor in the same concentration range as the single stacks. The stack with
the hydrophobic chemistry was fabricated on top of the hydrophilic stack in these
experiments. The water responses of the hydrophobic and hydrophilic layers of
the double stack are generally within 2σ error of the water response of the
respective single photonic stacks. However, the hydrophobic stack of the double
stack structure typically displays a slightly smaller response to a given
concentration of water vapor than the hydrophobic single stack. The opposite is
true for the hydrophilic film; the hydrophilic portion of the double stack generally
displays a slightly larger shift when exposed to water vapor than the hydrophilic
single stack. The results of Figure 3.4 indicate that either stack in the double stack
structure does not display a significant difference in its response to water vapor
relative to the response of the corresponding single stack sample. The sensor
response of the hydrophilic lower layer of the stack thus does not appear to be
greatly affected by the presence of the hydrophobic top layer and vice versa.

3.4.4 Elimination of the Effects of Relative Humidity in the Sensing of

Toluene with a Double Stack

The double stack was exposed to concentrations of 510, 1020, and 1530
mg m\(^{-3}\) toluene vapor at relative humidity (RH) values of 0, 25, 50, and 75%
(Figure 3.5). The spectral peaks of both stacks red shift with increasing relative
humidity or with increasing toluene concentration, but the relative magnitude of
the frequency shifts differ between stacks 1 and 2. Both stacks respond to toluene
within seconds of the initial exposure, and the signal stabilizes within 2-3 min. A
purge of pure N\(_2\) restores the original signal within 1-2 min. Although the
hydrophobic and hydrophilic stacks display a similar response to toluene, each
displays a significantly different response to water as shown in Figure 3.5.A. The
frequency shift data from the double stack can be used to provide a humidity-
independent measurement of toluene concentration. The response parameter \(R\) is
defined as:

\[
R = \Delta f_1 - \gamma \Delta f_2
\]  

(3.2)

where the frequency shift of stacks 1 (hydrophobic stack) and 2 (hydrophilic
stack) are \(\Delta f_1\) and \(\Delta f_2\), respectively, and \(\gamma\) is a constant weighting factor. With the
appropriate weighting factor, subtraction of \(\Delta f_1\) from \(\Delta f_2\) effectively nulls the
response to water vapor. The result of application of Equation 3.2 to the data of
Figure 3.5.A is presented in Figure 3.5.B. A value of 0.47 was used for the weighting factor $\gamma$. This value is related to the chemical nature of the two stacks, and it was found that it is generally applicable to the double layer stack for exposure to all the organic vapors tested.

Signal to noise ratios (S/N) were evaluated to determine the effect of application of Equation 3.2 to the sensor data. S/N was calculated using the following equation:

$$
\frac{S}{N} = \frac{\bar{x}}{3 \times \text{std}(B)}
$$

(3.3)

where $\bar{x}$ is the average signal change upon exposure to analyte ($\Delta f_1$, $\Delta f_2$ or $R$) and $B$ is the baseline value (signal in absence of analyte) immediately prior to introduction of the analyte dose. The 3$\sigma$ value calculated for the noise includes 99.7% of the baseline values. Calculations indicated that the S/N for $R$ is not much different compared to the S/N for the individual stacks $\Delta f_1$ and $\Delta f_2$. 
Figure 3.4 Frequency shift ($\Delta f$) of the photonic peak corresponding to the indicated chemically modified porous Si rugate filter stack in response to water vapor concentrations ranging from 0 mg m$^{-3}$ (0% RH) to 11230 mg m$^{-3}$ (87.5% RH at 15 °C). Five samples are presented: 3 single stacks and 2 double stacks. The single stacks are: freshly etched hydride-terminated Si (black triangles), dodecene-modified methyl-endcapped Si (hydrophobic, black circles), and undecylenic acid-modified methyl-endcapped Si (hydrophilic, black squares). Chemically modified hydrophobic and hydrophilic stacks of a double stack are plotted with gray circles and gray squares, respectively. 2σ error bars are included. The lines are added as a guide to the eye.
Figure 3.5 Dose-response curves for a double stack sensor, showing the ability of Equation 3.2 to compensate for changes in relative humidity (RH). Toluene vapor is used as the analyte. (A) Frequency shift of the individual resonances arising from each layer in the double stack. Sample was exposed to three concentrations of toluene (510, 1020 and 1530 mg m$^{-3}$) at increasing values of relative humidity (RH = 0, 25, 50 and 75%). The gray solid line corresponds to the hydrophobic, dodecyl-terminated stack response ($\Delta f_1$); the black dashed line represents the hydrophilic, undecylenic acid-modified stack ($\Delta f_2$). (B) Response of the double stack represented as the quantity $\Delta f_1 - \gamma \Delta f_2$ (after Equation 3.2), which removes effects of changing relative humidity. The weighting factor $\gamma = 0.47$ was applied. (C) Toluene dose concentration profile.
3.4.5 Response of the Double Stack Sensor to Nerve Agent Simulant

Detection of organic analytes with a low vapor pressure is a particular challenge for point sensors operating in an environment in which the humidity is changing. Porous Si double stacks were tested with the nerve agent simulant dimethyl methylphosphonate (DMMP) over a range of RH values. The hydrophilic film (stack 2) displays a larger frequency shift ($\Delta f_2$) upon exposure to the analyte than the hydrophobic film (stack 1, $\Delta f_1$), Figure 3.6. Stack 1 responds within seconds to DMMP, while stack 2 requires an additional minute to register an initial response. The values of both $\Delta f_1$ and $\Delta f_2$ reach steady state after $\sim$50 min. Upon purging with pure N$_2$, 90% of the original signal is recovered after $\sim$60 min. The low volatility of DMMP results in much slower responses for both layers. Exposure of the sensor element used in Figure 3.5 to DMMP, and using the same weighting factor ($\gamma$) of 0.47, yields a satisfactory correction for the RH response for DMMP at concentrations as low as 19 mg m$^{-3}$. Whereas the sensor displays a significant response to DMMP at a concentration of 9.3 mg m$^{-3}$, this response is comparable to the noise level when the humidity correction algorithm is applied. Incomplete purging of DMMP from the sensor is thought to contribute to the noise.

The 19 mg m$^{-3}$ (4 ppm) limit of detection (LOD) of DMMP is larger than other published results. For example, a poly (vinylidene fluoride) (PVDF) coated quartz crystal microbalance sensor has a calculated LOD of 0.94 ppm; a
A chemicapacitor filled with siloxane-fluoro alcohol (SXFA) has demonstrated a lowest detected concentration of 0.18 ppm and a calculated LOD of 2 ppb, and the calculated LOD for a single walled carbon nanotube capacitor coated with a thin polycarbosilane coating is 0.5 ppb.

### 3.4.6 Response of the Double Stack Sensor to Ethanol and Heptane Vapors

In order to determine if the method is generally applicable to a range of VOC analytes, the sensor element was challenged with heptane and ethanol vapors. These experiments were carried out with the same sample used for Figures 3.5 and 3.6. The sample was exposed to heptane vapor at concentrations of 910, 1820 and 2730 mg m$^{-3}$; each vapor concentration was tested at RH values of 0, 25, 50 and 75% (Figure 3.7). Upon exposure to heptane, the hydrophobic film (stack 1) displays a larger frequency shift than the hydrophilic film (stack 2), attributed to the hydrophobic nature of heptane. Both stacks display a response to heptane within 10 s of analyte introduction, reaching a steady state response within 3 min. N$_2$ purge recovers the original signal within 2 min. Application of Equation 3.2 with the same weighting factor ($\gamma = 0.47$) successfully removes RH interference from the heptane sensing data. The S/N of the response parameter $R$ is somewhat improved relative to the S/N of $\Delta f_1$ and $\Delta f_2$ for the individual stacks.

Similar results are obtained using ethanol as an analyte. Ethanol was introduced to the double stack sample at concentrations of 490, 980 and 1470 mg
m$^3$ and RH values of 0, 25, 50 and 75% (Figure 3.8). In the case of ethanol, the hydrophilic film (stack 2) displays a larger frequency shift ($\Delta f_2$) than the hydrophobic film (stack 1, $\Delta f_1$), attributed to the hydrophilic nature of ethanol. Each stack responds to ethanol within 10 s of analyte introduction, reaching steady-state within 4 min. N$_2$ purge recovers the original signal within 3-4 min. Again, applying a weighting factor ($\gamma$) of 0.47 in Equation 3.2 successfully eliminates interference in the sensor data due to changing RH in the range 25% < RH < 75%. For ethanol analyte, application of Equation 3.2 produces a smaller S/N in the response factor $R$ than is observed for either $\Delta f_1$ or $\Delta f_2$.

The response parameter $R$ of Equation 3.2 provides a good correction for RH in the range RH = 25-75% for all analytes studied. For the more hydrophobic analytes (toluene, heptane), the correction also provides reliable responses at lower humidity (in the range RH = 0-25%, Figure 3.5, Figure 3.7). As might be expected, the correction is not as effective at low humidity for the more hydrophilic analytes ethanol and DMMP. Presumably these analytes are more effective at competing with water for the hydrophilic surface sites in the stacks, as discussed in the next Section.
Figure 3.6 Dose-response curves for a double stack sensor as in Figure 3.5, using DMMP as the analyte. (A) Frequency shift of the individual resonances from the double stack, exposed to three concentrations of DMMP at sequential RH values of 25, 50 and 75%. The response of the hydrophobic, dodecyl-terminated stack ($\Delta f_1$) is indicated with the gray solid line; the hydrophilic, undecylenic acid-modified stack ($\Delta f_2$) is indicated with the black dashed line. (B) A plot of the quantity ($\Delta f_1 - \gamma \Delta f_2$) from Equation 3.2, using the same weighting factor of $\gamma = 0.47$ as in Figure 3.5. (C) DMMP dose concentration profile.
Figure 3.7 Response of a double stack sensor to heptane. (A) The double stack was exposed to three concentrations of heptane (910, 1820 and 2730 mg m\(^{-3}\)) at sequential relative humidity values of 0, 25, 50 and 75%. The hydrophobic, dodecyl-terminated stack response is shown with the gray solid line; the hydrophilic, undecylenic acid-modified stack is shown with the black dashed line. (B) Heptane response of a double stack after removing effects of relative humidity through application of Equation 3.2. A weighting factor \(\gamma = 0.47\) is used. (C) Heptane dose concentration profile.
Figure 3.8 Response of a double stack sensor to ethanol vapor. (A) The double stack was exposed to three concentrations of ethanol (490, 980 and 1470 mg m\(^{-3}\)) at sequential relative humidities of 0, 25, 50 and 75%. The hydrophobic, dodecyl-terminated stack response is shown with the gray solid line; the hydrophilic, undecylenic acid-modified stack is shown with the black dashed line. (B) Ethanol response of a double stack after removing effects of relative humidity through application of Equation 3.2. A weighting factor $\gamma = 0.47$ is used. (C) Ethanol dose concentration profile.
3.4.7 Interpretation of Analyte Interactions with Individual Layers of the Double Stack

The relative analyte responses of the two types of surface chemistries incorporated into stacks 1 and 2 can be interpreted in terms of surface adsorption properties: hydrogen bonding, van der Waals forces, and dipolar interactions. The VOC concentration levels introduced to the double stacks in this study are too low for microcapillary condensation to play a significant role; the largest relative pressure was less than 0.02 P/P_S, where P is the analyte partial pressure and P_S is the saturation vapor pressure of the analyte. Analytes that contain proton acceptors and/or donors (water, DMMP, and ethanol) produce a greater response from the carboxylic acid-containing hydrophilic stack. The hydrophobic stack 1 has no similar functional groups, although small amounts of residual oxides present on the surface may provide some affinity for proton donors or acceptors.

The other two analytes (heptane and toluene) do not contain proton acceptors/donors. Heptane exhibits a slightly greater affinity towards the hydrophobic stack relative to the hydrophilic stack, and toluene shows almost no preference. Both stacks are expected to display some affinity for heptane based on van der Waals interactions with the long, saturated hydrocarbon chains (> 9 CH₂) which comprise a large part of the surface modification of each stack. In the case of toluene, the hydrophobic and hydrophilic stacks display identical responses within the error limits of the measurements. Presumably, the small
dipole moment of toluene (0.38 Debye) provides it with comparable affinity for the two types of surface chemistries.

Figure 3.9 displays the responses of each stack to all of the analytes measured in this study. The data are presented as the frequency shift ($\Delta f$) of either the hydrophobic or the hydrophilic stack of a double stack as a function of analyte concentration. The data represent average frequency shifts of each layer when exposed to a given concentration of analyte, measured at 25% RH. There is a linear dependence of the frequency shift on analyte concentration for both the hydrophobic and the hydrophilic stacks for all analytes studied in the dose concentration range, with $R^2$ values greater than or equal to 0.987. The slope of the linear responses (listed in Table 3.1) and the frequency shifts in Figure 3.9 can be used to compare the affinity of individual stacks towards the analytes examined. The absolute magnitude of the slope and the response of the hydrophobic stack are largest for DMMP, followed by toluene and heptane (similar values), ethanol and lastly water. Analyte response of the hydrophilic stack is very similar to that of the hydrophobic stack, showing the largest response to DMMP, followed by toluene, heptane, ethanol and lastly water. With one exception (DMMP), the value of the shift at a given concentration of analyte scales with the refractive index of the analyte (Table 3.1). Although DMMP possesses a smaller refractive index, it displays a much larger response than toluene. This is attributed to the much lower saturation vapor pressure of DMMP compared with the other analytes. In general, molecules with lower saturation
vapor pressures partition more effectively to a solid phase. Figure 3.10 summarizes the sensitivity of the combined sensor after the effect of humidity has been removed by application of Equation 3.2.
Figure 3.9 Frequency shift of hydrophobic ($\Delta f_1$) and hydrophilic ($\Delta f_2$) porous Si stacks as a function of analyte vapor concentrations: water (gray circles), toluene (black boxes), DMMP (gray diamonds), heptane (gray triangles), and ethanol (black inverted triangles). The data represent average analyte responses obtained in the presence of 25\% RH (except for the water trace). 2σ error bars are included. Data is presented using a logarithmic concentration scale to allow comparison. (Top) Dodecyl-terminated, methyl-endcapped hydrophobic stack response and (Bottom) undecylenic acid-terminated, methyl endcapped hydrophilic stack response.
Figure 3.10 Dose-response curves for a double stack sensor after relative humidity interference has been removed using Equation 3.2. The quantity ($\Delta f_1 - \gamma \Delta f_2$) from Equation 3.2 has been applied to the data from Figures 3.5, 3.6, 3.7, and 3.8 using a weighting factor of $\gamma = 0.47$. The plot represents double stacks exposed to toluene (black squares), DMMP (gray diamonds), heptane (gray triangles) and ethanol (black inverted triangles). Average sensor response at 0 (toluene and heptane only), 25, 50 and 75% RH for each analyte are pooled, with $2\sigma$ error bars.
Table 3.1 Slope of response curves and properties of analytes used in this study.[a]

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Slope of response curve [m²·mg⁻¹·cm⁻¹]</th>
<th>Vapor pressure [Torr][b]</th>
<th>Dipole moment [Debye][c]</th>
<th>Refractive index[d]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si-(CH₂)₅-CH₃ hydrophobic surface</td>
<td>Si-(CH₂)₆-C(O)OH hydrophilic surface</td>
<td></td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>-5.4 x 10⁻⁴</td>
<td>-1.3 x 10⁻³</td>
<td>23.8</td>
<td>1.85</td>
</tr>
<tr>
<td>toluene</td>
<td>-8.2 x 10⁻³</td>
<td>-9.0 x 10⁻³</td>
<td>28.4</td>
<td>0.38</td>
</tr>
<tr>
<td>DMMP</td>
<td>-9.5 x 10⁻³</td>
<td>-1.6</td>
<td>1.2</td>
<td>3.62</td>
</tr>
<tr>
<td>heptane</td>
<td>-7.9 x 10⁻³</td>
<td>-7.0 x 10⁻³</td>
<td>45.7</td>
<td>0</td>
</tr>
<tr>
<td>ethanol</td>
<td>-3.5 x 10⁻³</td>
<td>-5.4 x 10⁻³</td>
<td>59.0</td>
<td>1.69</td>
</tr>
</tbody>
</table>

[a] Both surface types are methyl end-capped. Slope of the dose-response curve at 25% RH from Figure 3.9, frequency shift vs. concentration in mg m⁻³. The slope includes all dose concentrations for a given analyte, but excludes zero. DMMP = Dimethyl methylphosphonate.


[c] Taken from ¹²⁰.

[d] Refractive index at λ=589.3 nm, 20°C.
3.5 Conclusions

Porous Si photonic crystals were modified by hydrosilylation with a hydrophobic (dodecene) or a hydrophilic (undecylenic acid) alkene. The amount of water or VOC vapors admitted into the pores can be monitored by measurement of the frequency of the photonic peak in the visible reflectivity spectrum. The frequency of the spectral peak displays a linear dependence on VOC concentration within the range tested; the peak red-shifts with increasing analyte concentration. Analyte detection relies on physisorption in the high surface area porous matrix, which is dependant on the chemical nature of the surface and analyte properties such as polarity and saturation vapor pressure.

When fabricated such that the hydrophobic stack lies on top of the hydrophilic stack, the optical response from the two layers can be monitored simultaneously with a single spectrometer probe. The hydrophobic stack shows a smaller frequency shift in the presence of water vapor compared to the hydrophilic stack. When the hydrophilic stack response is multiplied by a weighting factor and subsequently subtracted from the hydrophobic stack response (eq. 3.2), interference from fluctuations in relative humidity in the analyte stream is removed. Reliable detection of the VOC analytes toluene, DMMP, heptane and ethanol is achieved over a wide humidity range (25-75% RH), and the measured frequency shift is linear with analyte concentration. The weighting factor is independent of the four analytes. The sensor cannot discriminate between different VOC analytes. Although the analyte sensitivity
reported in this work is not as high as with some methods, the ability to eliminate the effects of relative humidity is a key factor in the minimization of false alarms in remote sensing applications.
Chapter three, in part, is a reprint (with co-author permission) of the material as it appears in the following publication: Ruminski, A.M., Moore, M.M., Sailor, M.J., Humidity-Compensating Sensor for Volatile Organic Compounds Using Stacked Porous Silicon Photonic Crystals. *Advanced Functional Materials*, (2008) 18, 3418-3426. The author of this dissertation is the primary author of this manuscript.
CHAPTER FOUR

INTERNALLY REFERENCED REMOTE SENSOR FOR HF

USING A REACTIVE POROUS SILICON PHOTONIC CRYSTAL
4.1 Abstract

A sensor for aqueous HF is constructed from an oxidized, chemically reactive porous Si-based photonic crystal. HF dissolves silicon oxide from the porous matrix, causing an irreversible change in refractive index of the film that is monitored as a blue-shift in the resonance peak of the photonic crystal. A portion of the porous nanostructure is filled with inert polystyrene that protects the oxide from attack by HF, acting as an internal spectral reference. The polystyrene fiducial marker also allows elimination of artifacts associated with the shift of the one-dimensional photonic crystal resonance peak with changing probing angle. The porous Si samples are produced by a time-modulated anodic electrochemical etch of crystalline silicon. High-temperature air or room-temperature ozone oxidation reactions are used to prepare the HF-reactive surface, and it is found that the ozone oxidation reaction produces a more sensitive HF sensor. Reflectance spectra from both the polymer-filled and the unfilled, reactive porous layers are acquired simultaneously using a CCD-based spectrometer.

4.2 Introduction

Many physical properties of porous Si have been harnessed to make chemical sensors, including capacitance,\textsuperscript{4,20} resistance,\textsuperscript{21} photoluminescence,\textsuperscript{6,23} and optical reflectivity.\textsuperscript{12,14} An attractive feature of porous Si is that the electrochemical process used to prepare it allows the fabrication of more complex functional nanostructures that can incorporate sample filtration,\textsuperscript{71,72,122,123}
concentration,\textsuperscript{84} signal amplification,\textsuperscript{69,124,125} or drift compensation\textsuperscript{32,73,126,127} features into the sensor.\textsuperscript{128} Optical reflectivity is the most common property used to probe and quantify these features.

The optical reflectivity characteristics of porous Si-based photonic structures allows their incorporation into remote sensing systems ("Smart Dust") in which molecules adsorbed in the porous matrix are detected using a free-space optical laser probe.\textsuperscript{8,84,94} This work focuses on two significant problems associated with remote detection of chemicals in the environment using porous Si photonic materials; in particular zero point drift and dependence of returned signal on the probe-sample angle. We find that both of these limitations can be mitigated by incorporation of a stable, fiducial spectral feature in the nanostructure. The detection of HF in aqueous media is used as a benchmark in this study.

The detection of HF gas with oxidized porous Si films is an example of an irreversible, reactive chemical sensor. Porous Si chemical sensors that have been modified to undergo specific, irreversible chemical reactions with the analyte have been employed to provide a degree of chemical selectivity for various detection problems;\textsuperscript{9,125} in some cases these irreversible reactions provide very high sensitivity as well.\textsuperscript{40,61,69} Previous HF sensor work used a thin Fabry-Perot film of porous SiO\textsubscript{2} that was prepared by oxidation of porous Si with ozone.\textsuperscript{66} Exposure to HF gas converted the oxide to volatile SiF\textsubscript{4}, reducing the net refractive index of the porous layer. The change in refractive index was measured by optical
reflectivity, and a detection limit of 30 ppm in 10 min was achieved. A sensor for fluorophosphonate nerve agents such as Sarin was subsequently prepared by combining this HF sensor with a molecular catalyst that selectively hydrolyzes the P-F bond to HF. The catalyst was incorporated within the porous nanostructure, providing a relatively rapid and selective response.

HF is a toxic compound that is commonly used to etch glass or metal parts. It is used in numerous other industrial processes, such as the production of refrigerants, herbicides, pharmaceuticals, high-octane gasoline, electrical components and plastics. The toxicity of HF derives from its ability to quickly penetrate the skin and react with calcium ions, leading to slow-healing burns and bone loss. OSHA has set the permissible exposure limit (PEL) at 3.0 ppm (8-hour time-weighted average, TWA).

Detection of HF in environmental samples is commonly accomplished using a collection agent that is exposed for a prescribed period of time and subsequently subjected to a laboratory-based analysis. For example, filter paper impregnated with K₂HPO₄ can be used as a collection agent; after exposure the sample is eluted with 0.1 M sodium citrate and the fluoride concentration is determined potentiometrically. This method can detect HF gas in the concentration range 0.68-5.45 ppm, over a period of 48 hours. Polymer-based collection agents have also been employed; an alkaline impregnated polypropylene film detects HF gas in the concentration range 0.1-387 ppm in 4 hours when subjected to electrochemical analysis using a fluoride selective-ion
These dosimeters are designed to respond to HF in the gas phase only, and cannot detect aqueous hydrofluoric acid. Also, the methods do not monitor HF in real time, but must be analyzed after exposure. The device reported in this work uses a porous SiO$_2$ matrix as both the collection agent and the sensing element, allowing continuous monitoring of the presence of HF. A major advantage of the sensor developed in this study over the previously reported porous SiO$_2$-based HF sensor is the inclusion of a fiducial marker to reduce zero point drift and probing angle limitations, which enables remote monitoring applications.

### 4.3 Experimental

Single-crystalline highly doped p-type Si (0.0008-0.0012 Ω-cm resistivity, (100) polished, B-doped) was purchased from Siltronix Corp. All reagents were used as received. Aqueous HF (49%), hydrochloric acid, methanol and hexane were purchased from VWR International. Ethanol was purchased from Rossville Gold Shield Chemical Company. Oxygen was purchased from Westair Gases & Equipment.

#### 4.3.1 Sample Preparation

Porous silicon photonic crystals containing a single spectral reflectance peak were formed by anodization of highly doped p-type silicon wafers in a 3:1 v:v solution of aqueous hydrofluoric acid:ethanol in a two-electrode configuration.
using a platinum ring counter-electrode. Etching was performed in a Teflon etching cell using a galvanostat (Princeton Applied Research Model 363) under computer control (LabVIEW, National Instruments). The hydrofluoric acid solution was mixed during the etching process to minimize hydrogen bubble formation on the sample surface and to encourage etchant solution exchange. A cosine current density waveform varying between 13.3 and 39.8 mA cm\(^{-1}\) with a period of 12 seconds and 100 repeats was used to etch the porous layer. Samples were etched on the polished side of the silicon wafer except for samples probed at an angle of 40°, these samples were etched on the non-polished side for increased scattering of light. Sets of samples were then placed through an oxidation process. Ozone oxidation was achieved by placing as-prepared H-terminated porous silicon samples in a flowing stream of ozone (Ozone Solutions, product ID OZV-8, flux of 8 g h\(^{-1}\)) for 4 minutes followed by heating at 180 °C for 30 minutes. Thermally oxidized samples were prepared by etching silicon with the same current density minimum and maximum, but with a period of 14 seconds and 86 repeats. Samples were then inserted into a tube furnace (Lindberg/Blue M) under air at 600 °C for 90 minutes. A fiducial marker consisting of polystyrene was added by pipeting 1 µL of 12% wt/wt polystyrene in toluene on to the porous film followed by heating in an oven at 180 °C for 30 minutes.

4.3.2 Gravimetric Determination of Porosity
Five repetitions of each sample etch type were prepared. Samples were weighed before etching ($m_1$), after etching and subsequent surface modification if any ($m_2$), and after dissolving the porous layer with first ethanolic HF (if ozone oxidized) followed by a 0.1M basic solution of KOH in water and ethanol ($m_3$). The following equation was used to determine the porosity: \(^8\)

$$\text{Porosity} = \frac{m_1 - m_2}{m_1 - m_3} \quad (4.1)$$

Furnace oxidized at 600 °C samples were measured following a separate procedure. \(^{132}\) Furnace oxidized samples were weighed after etching and oxidation ($m_1$). The oxidized porous layer was then dissolved in ethanolic HF and the sample was weighed again ($m_2$). The sample was further dissolved in a 0.1 M basic solution of KOH in water and ethanol ($m_3$) and weighed again. Porosity was calculated using the equation:

$$P = \frac{V_{\text{total}} - V_{\text{SiO}_2} - V_{\text{Si}}}{V_{\text{total}}} \quad (4.2)$$

where $V_{\text{total}}$ is the total volume of the porous oxide layer and was calculated by the equation:

$$V_{\text{total}} = St \quad (4.3)$$

where $S$ is the wafer surface area exposed to HF during etching of the porous film, and $t$ is the thickness of the porous layer which was determined by cross-sectional SEM measurements. $V_{\text{SiO}_2}$ is the volume of the SiO$_2$ fraction in the porous oxide layer and was calculated from the equation:
\[ V_{\text{SiO}_2} = \frac{m_1 - m_2}{d_{\text{SiO}_2}} \]  

(4.4)

where \( d_{\text{SiO}_2} \) is the density of bulk SiO\(_2\), using a value of 2.21 g cm\(^{-3}\). \( V_\text{Si} \) is the volume of remaining Si in the porous layer and was calculated from the equation:

\[ V_\text{Si} = \frac{m_2 - m_3}{d_\text{Si}} \]  

(4.5)

where \( d_\text{Si} \) is the density of Si, using a value of 2.33 g cm\(^{-3}\).

### 4.3.3 Scanning Electron Microscopy

Porous layer thickness was examined with a Phillips XL30 environmental SEM operating in secondary electron mode. Accelerating voltages of 10 and 20 keV was used.

### 4.3.4 Infrared Spectroscopy

Surface modification was verified through ATR-FTIR spectroscopy. Spectra were recorded with a Thermo Scientific Nicolet 6700 FTIR with a Smart iTR diamond ATR attachment using a resolution of 4 cm\(^{-1}\) and an average of 128 scans.

### 4.3.5 Dosing Measurements

Reflectance spectra of porous silicon were collected with an Ocean Optics USB4000 CCD spectrometer coupled to a bifurcated fiber optic cable. Porous silicon chips were probed with a microscope objective lens coupled to the
bifurcated cable. Samples were secured in a teflon cell. For HF exposure experiments, samples were immersed in 1 mL deionized water for 3 minutes. The water was removed, the sample was dried, and 1 mL of aqueous HF was added. The solution was mixed every minute to remove bubbles from the porous silicon surface. Samples were exposed to the HF solution for 10 minutes. Samples probed at an angle were illuminated by a second lamp at a complimentary angle. Chlorine was produced by acidification of sodium hypochlorite solutions as described by Mattson et al. followed by a rinse with water to remove HCl. Porous silicon samples were contained in a teflon cell fitted with a glass top (20 mL volume) containing a septum under ambient air. Chlorine (30 mL) was injected into the cell.

4.4 Results and Discussion

4.4.1 Preparation and Characterization of Porous Si Photonic Crystals

Porous silicon photonic crystals were prepared by electrochemically etching boron-doped p++ type crystalline silicon in a solution of aqueous hydrofluoric acid and ethanol. A computer-controlled cosine current density waveform was applied to the silicon anode, resulting in a multilayered porous silicon film containing a pseudo-sinusoidal porosity gradient. The reflectance spectrum of the resulting material approximates a rugate filter, displaying a peak corresponding to the stop band of the photonic crystal. The wavelength of the
reflectivity peak is controlled by the period and average value of the current density waveform used in the electrochemical etch. The as-etched material possesses a hydrogen-terminated Si surface. Chemical modification of the surface is required to produce a HF reactive sensor. HF reactive, oxide-terminated surfaces were prepared by two methods. Porous silicon samples were either thermally oxidized at 600 °C,\textsuperscript{44} or ozone oxidized followed\textsuperscript{93} by heating at 180 °C for 30 minutes. (This second step was included to match the surface chemistry to samples containing a fiducial marker which must be heated when adding the marker). Surface modification was examined with attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Figure 4.1). Spectra display strong Si-O bands around 1020 \text{cm}^{-1} for both oxidation methods, and an additional OH stretch around 3300 \text{cm}^{-1} for the ozone oxidized sample.

The thickness of porous Si photonic crystals was determined by cross-sectional scanning electron microscopy (SEM) observation. The average value of three SEM measurements (with one standard deviation) yielded a thickness of 17.1 ± 0.2 \text{µm}, 18.3 ± 0.3 \text{µm} and 18.7 ± 0.1 \text{µm} for as-etched, ozone oxidized and furnace oxidized porous silicon, respectively (Table 4.1).

Gravimetric analysis was used to measure % porosity of the etched films.\textsuperscript{83,132} Three etch types of samples were prepared to characterize the layer properties of each surface chemistry type: samples etched with a cosine varying current, samples etched at the lowest current density of the cosine waveform for 10 minutes and samples etched at the highest current density for ten minutes.
Results are shown in Table 4.1. Porosity of the as-etched rugate structures decreased during oxidation. Oxidation of porous silicon causes a volume expansion which shrinks pore diameters producing a drop in porosity.\textsuperscript{134}
Figure 4.1 ATR-FTIR spectra of porous Si samples before and after oxidation: as-etched, hydride terminated material (top); ozone-oxidized (middle); furnace-oxidized (bottom). Ozone oxidation produces a more hydrophilic, hydroxylated surface, whereas thermal oxidation generates a dehydrated silicon oxide. The black traces represent full scale spectra, and the portion of the spectrum shown in gray (> 1300 cm\(^{-1}\)) is multiplied by 10 and offset along the y-axis for clarity.
Table 4.1  Porosity of as etched, ozone oxidized, and furnace oxidized at 600 °C porous silicon films.

<table>
<thead>
<tr>
<th>Surface Chemistry, Sample Layer</th>
<th>Thickness (µm)[a]</th>
<th>Porosity (%) avg[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Etched</td>
<td>13.3 mA cm⁻¹</td>
<td>4.7 ± 0.1</td>
</tr>
<tr>
<td>Si-H</td>
<td>39.8 mA cm⁻¹</td>
<td>13.6 ± 0.2</td>
</tr>
<tr>
<td>Rugate</td>
<td>17.7 ± 0.2</td>
<td>67 ± 1</td>
</tr>
<tr>
<td>Ozone Oxidized</td>
<td>13.3 mA cm⁻¹</td>
<td>4.59 ± 0.08</td>
</tr>
<tr>
<td>Si-OH</td>
<td>39.8 mA cm⁻¹</td>
<td>13.6 ± 0.4</td>
</tr>
<tr>
<td>Rugate</td>
<td>18.3 ± 0.3</td>
<td>59 ± 1</td>
</tr>
<tr>
<td>Furnace Oxidized</td>
<td>13.3 mA cm⁻¹</td>
<td>4.57 ± 0.07</td>
</tr>
<tr>
<td>Si-O-Si</td>
<td>39.8 mA cm⁻¹</td>
<td>14.0 ± 0.3</td>
</tr>
<tr>
<td>Rugate</td>
<td>18.7 ± 0.1</td>
<td></td>
</tr>
</tbody>
</table>

[a] Cross-sectional SEM measurement of cleaved samples. Errors represent 1 standard deviation from 3 measurements.

[b] Gravimetric measurement. As etched and ozone oxidized porosities were calculated differently than furnace oxidized samples. See section 4.3.2 for details. Errors represent 1 standard deviation from 4-5 measurements.
4.4.2 Porous Si Exposure to Aqueous Hydrofluoric Acid

Oxidized porous silicon rugate samples were exposed to aqueous hydrofluoric acid solutions. Reaction of hydrofluoric acid with oxide is detailed in Equation 4.6:

\[ SiO_2 + 4HF \rightarrow SiF_4(g) + 2H_2O \]  

Equation 4.6

The reactivity of the sample towards HF was examined by monitoring the position of the reflectivity peak maximum. Hydride terminated porous samples were subjected to the same solutions for comparison. HF concentrations used in this study were 12, 6, 3, 1.5, 0.75, 0.4, 0.2 and 0.1 %HF (287500, 143750, 71875, 35938, 17969, 9583, 4792 and 2396 ppm, respectively). Samples were submerged in deionized water for 3 minutes, followed by removal of water and drying of the sample, and lastly immersion in an HF solution. The shift of the reflectivity peak maximum after 10 minutes of HF solution exposure is presented in Figure 4.2. At the higher HF concentrations (> 1.5%), furnace oxidized samples displayed the largest change in reflectivity peak position of the 3 surface chemistry types. At HF concentrations < 1.5% ozone oxidized samples displayed the largest change in reflectivity peak wavelength. The ozone oxidized samples had the best dynamic range, successfully displaying a significant peak shift at concentrations as low as 0.1 %HF. Therefore, ozone oxidation is deemed the better oxidation method of the ozone and furnace oxidation methods used in this study. As expected, as-etched samples incurred a significantly smaller wavelength change when exposed to HF. This response to HF is due to the
unstable Si-H species oxidizing in the presence of water and dissolved oxygen followed by degradation by HF.

Ozone oxidized samples were re-examined by ATR-FTIR after being submerged in aqueous HF solutions for 10 minutes (Figure 4.3, furnace oxidized ATR-FTIR spectra are shown in Figure 4.4). Samples exposed to HF solutions of 1.5% and greater no longer contained Si-O and Si-OH stretches, but had a spectrum characteristic of as etched hydride terminated porous silicon (Figure 4.1 top), indicating that the oxide species were completely removed by the HF in the solution. Samples submerged in solutions containing less than 1.5 %HF had increasing amounts of oxide present in ATR-FTIR spectrum, indicating incomplete removal of oxide by HF. An examination of the reflectivity peak position vs. time of samples subjected to aqueous HF shows that rate of removal of the oxide species is dependent on HF concentration (Figure 4.5). Samples exposed to HF concentrations 1.5% and greater display two different slopes. The first sharp initial decrease in slope is contributed to the removal of oxide species. The second less steep slope can be linked to the slow continued oxidation of the porous layer by water and dissolved oxygen followed by removal of the oxide species with HF. Samples were kept in HF solutions for longer than 10 minutes. Samples submerged in HF solutions in the concentration range 0.2 – 1.5 %HF for time periods greater than 10 minutes did experience an equivalent change in wavelength shift as was obtained by samples submerged in 12 %HF for 10 minutes. For example, samples submerged in 0.75 %HF shifted 63 nm in 32
minutes, samples submerged in 0.4 %HF shifted 63 nm in 69 minutes. Therefore, lower concentrations of HF may be detected if sample exposure time was increased to durations greater than the 10 minutes used in this study.

Porosity of ozone oxidized samples before and after exposure to 6, 1.5, 0.4 and 0.1 %HF for 10 minutes was determined by the gravimetric method (Table 4.2). An increase in % porosity is observed after exposure to HF. The porosity of samples exposed to 6 and 1.5 %HF are almost identical. Examination of Figure 4.5 shows the two HF concentrations have similar reflectivity peak position vs. time traces such that the entire oxide component is removed within the first few minutes of HF exposure followed by slower oxidation and removal. The wavelength position vs. time trace for 0.4 %HF is much different, with a single lower angled slope indicating a slower removal of the oxide component, which leads to a % porosity after HF exposure to be considerably smaller than 1.5 and 6 %HF samples.
**Figure 4.2** Shift in porous silicon reflectivity peak position after 10 min exposure to various concentrations of HF in water. Three sample types are presented: ozone-oxidized (white bar), furnace-oxidized at 600 °C (gray bar) and as-etched, hydride-terminated porous Si (black bar). Data are the average of 5 samples each, with error bars representing 1 standard deviation.
Figure 4.3  ATR-FTIR spectra of ozone oxidized samples after 10 minute exposure to various concentrations of HF in water. From top to bottom: 0.1, 0.2, 0.4, 0.75, 1.5, 3, 6, 12 %HF. Full scale spectra are shown in black. A portion of the spectrum (> 1300 cm$^{-1}$), shown in grey, is multiplied by 10 and offset along the y-axis for better clarity.
Figure 4.4 ATR-FTIR spectra of furnace oxidized at 600 °C samples after 10 minute exposure to various concentrations of HF in water. From top to bottom: 0.1, 0.2, 0.4, 0.75, 1.5, 3, 6, 12 %HF. Full scale spectra are shown in black. A portion of the spectrum (> 1300 cm⁻¹), shown in grey, is multiplied by 10 and offset along the y-axis for better clarity.
Figure 4.5 Relative shift in wavelength of the main reflectivity peak from ozone-oxidized porous Si rugate filters upon exposure to various concentrations of aqueous HF, as a function of time. Samples were submerged in deionized water followed by replacement with HF solution at time = 0. From bottom to top: 0.1, 0.4, 1.5 and 6 % HF. The data are presented as the measured wavelength maximum at the given time subtracted from the wavelength maximum at time = 0 for each sample. All spectra were obtained from samples submerged in water (time < 0) or the aqueous HF solution at the indicated concentrations (time > 0). Individual data points are plotted, a line is added to guide the eye.
Table 4.2 Porosity of ozone oxidized rugate samples before and after exposure to HF solutions for 10 minutes.

<table>
<thead>
<tr>
<th>HF Exposure</th>
<th>Porosity (%) avg[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 %HF (Un-exposed)</td>
<td>59.8 ± 0.6</td>
</tr>
<tr>
<td>6 %HF</td>
<td>84.4 ± 0.9</td>
</tr>
<tr>
<td>1.5 %HF</td>
<td>83.1 ± 0.4</td>
</tr>
<tr>
<td>0.4 %HF</td>
<td>76.6 ± 0.8</td>
</tr>
<tr>
<td>0.1 %HF</td>
<td>63 ± 1</td>
</tr>
</tbody>
</table>

[a] Gravimetric measurement. Errors represent 1 standard deviation from 3 measurements.
4.4.3 Building an Internal Reference in Porous Si Remote Sensors

A reference channel can be added to a sensor as a way to incorporate a constant signal for comparison against a changing sensing signal, or as a means to remove interferants (such as relative humidity) from a chemical sensing response. Another motivation for incorporating a reference channel in porous silicon is as a means of removing probing angle of incidence dependency. Wavelength position of a porous Si interference spectrum is correlated to the angle at which the spectrum is acquired, as described by the Bragg equation (Equation 4.7)

\[ n\lambda = 2Nd\sin\theta \]  

(Equation 4.7)

where \( n \) is the order of reflection, \( \lambda \) is the incident wavelength, \( N \) is the refractive index at \( \lambda \), \( d \) is the optical thickness of each layer, and \( \theta \) is the probing angle (90° for normal incidence). The interference fringe position shifts to higher frequencies at probing angles off of normal incidence. This property adds an extra variable which must be considered when analyzing sensor response. The rigid sensing set up used in the laboratory setting consisting of a mounted sample and locked down sensor is not practical for remote sensing applications, thus making probing angle dependency particularly problematic. Therefore it is essential that the porous Si sensors placed out in the environment and probed remotely must have a means to compensate for reflectivity spectrum fluctuation due to a variable sensor probing angle. A porous Si sensor incorporating a fiducial marker with a separate reflectivity peak position than the analyte sensing
signal and where both the fiducial and sensing signal reflectivity peak position fluctuate by the same amount when probing angle is changed would effectively solve the problem.

A HF non-reactive fiducial marker was added to ozone oxidized samples by spotting a small area of the surface with a solution of polystyrene in toluene, followed by 30 minutes of heating at 180 °C to fully infiltrate the depth of the pores with polystyrene. The reflectivity peak position of polystyrene-filled porous Si red shifts by approximately 100 nm. An example of a reflectivity spectrum taken at normal incidence and acquired at the porous Si/polystyrene-filled porous Si border is displayed in Figure 4.6. To test the reflectivity peak position of porous silicon and polystyrene filled porous Si as a function of probing angle, three samples were probed in air at normal incidence and 8, 14, 17, 27 and 37 degrees off normal incidence. The reflectivity peak position of both empty porous Si and polystyrene filled porous Si blue shifted by similar amounts at each probing angle. The results of one sample are given in Figure 4.6 and Table 4.3.
Figure 4.6  Reflectivity spectra of an ozone oxidized sample with a polystyrene fiducial marker at (from top to bottom): normal incidence (0 degrees), 8, 17, 27 and 37 degrees off normal. Spectra were acquired in air at the empty ozone oxidized porous Si/polystyrene infused porous Si interface as shown in the schematic. Δ indicates the difference in reflectivity peak maximum of the porous Si + polystyrene and empty porous Si peaks. Reflectivity peak maxima are listed in Table 4.3. Peak intensities are scaled.
Table 4.3 Reflectivity peak position of empty ozone oxidized porous Si and its polystyrene filled porous Si fiducial marker as a function of probing angle, and difference between the two reflectivity peak wavelengths.

<table>
<thead>
<tr>
<th>Probing Angle</th>
<th>Empty pSi (nm)</th>
<th>pSi + polystyrene (nm)</th>
<th>Difference (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>560</td>
<td>659</td>
<td>99</td>
</tr>
<tr>
<td>8 Degrees</td>
<td>558</td>
<td>658</td>
<td>100</td>
</tr>
<tr>
<td>14 Degrees</td>
<td>557</td>
<td>657</td>
<td>100</td>
</tr>
<tr>
<td>17 Degrees</td>
<td>554</td>
<td>654</td>
<td>100</td>
</tr>
<tr>
<td>27 Degrees</td>
<td>545</td>
<td>645</td>
<td>100</td>
</tr>
<tr>
<td>37 Degrees</td>
<td>531</td>
<td>631</td>
<td>100</td>
</tr>
</tbody>
</table>
4.4.4 Exposure of Internally Referenced Porous Si Sensors to HF

Ozone oxidized samples containing a polystyrene filled fiducial marker were exposed to aqueous HF solutions at concentrations of 6, 1.5, 0.4 and 0.1 %HF for 10 minutes. The reflectivity peak maximum position of empty porous Si and polystyrene filled porous Si was monitored over time (Figure 4.7), and color change of the surface was visible to the eye at some HF concentrations (Figure 4.8). Reflectivity peak positions were monitored at 3 probing angles: 0, 9 and 40 degrees off normal incidence. Samples probed at 40 degrees were etched on the roughened side of the silicon wafer to promote scattering of light. The change in reflectivity peak position of the oxidized porous silicon during HF exposure was the same within error bars at each of the probing angles (Figure 4.9). Traces of the ozone oxidized and polystyrene-filled porous Si peak positions vs. exposure time are displayed in Figure 4.10. The traces at the 3 angles of probing incidence are identical. The results show that polystyrene infused porous Si can successfully be used as a fiducial marker to remove probing angle limitations, that a porous silicon sensor containing a fiducial marker can be probed at angles off of normal incidence and still achieve accurate results by comparing the reactive porous Si reflectivity peak wavelength position with that of the fiducial marker. Subtraction of the ozone oxidized, water-filled porous Si reflectivity peak position from the polystyrene infused non hydrofluoric acid reactive porous Si reflectivity peak position results in a difference of ~40 nm at all probing angles before HF exposure. An increase in the difference indicates hydrofluoric acid detection.
Figure 4.7 Reflectivity spectra of an ozone-oxidized porous Si sample containing an impregnated polystyrene fiducial marker, before and during exposure to aqueous HF at a concentration of 1.5%. Spectra were acquired at the ozone oxidized porous silicon/polystyrene infused porous silicon interface. A cross-sectional schematic of the structure containing the polystyrene fiducial marker is shown in the inset. From top to bottom: reflectivity peak of sample in deionized water, after 1 minute, 2 minutes and 10 minutes exposure to 1.5% HF. All spectra were taken of samples submerged in water or 1.5% aqueous HF.
Figure 4.8  A simple visual sensor for HF is constructed from a chemically reactive porous silicon-based photonic crystal. A portion of the porous nanostructure is filled with an inert polymer that acts as an internal reference. After submersion in 1.5% aqueous HF for ten minutes, a distinctive color change is visible to the eye.
Figure 4.9  Shift in ozone oxidized porous silicon reflectivity peak position after 10 minute exposures to various concentrations of HF in water.  Samples were probed at 3 different angles to the surface normal: 0° (white bar), 9° (grey bar) and 40° (black bar).  Data represents the average of 5 samples with one standard deviation error bars.
Figure 4.10  Reflectivity peak position at different sample probing angles of ozone oxidized (black diamond) and polystyrene filled (grey square) porous silicon during exposure to 0.4 %HF. Samples were submerged in deionized water followed by replacement with HF solution at time = 0. Spectrometer probe was located at (top) 0°, (middle) 9° and (bottom) 40° off normal incidence. Results indicate that the angle of incidence does not significantly effect the separation between the reflectivity peak maximum of porous silicon and the polystyrene filled fiducial marker. For comparison between the 3 samples, the reflectivity peak is displayed as the measured wavelength minus the initial wavelength of the ozone oxidized sample. All spectra were taken of samples submerged in water (time < 0 minutes) or in aqueous HF (time > 0 minutes).
4.4.5 Exposure of Porous Si to Chlorine Gas

The specificity of the HF responsive sensors was challenged with exposures to chlorine gas. The same three surface chemistry types (as-etched, ozone oxidized and furnace oxidized at 600 °C) were exposed to chlorine gas for 30 minutes. Chlorine was produced by acidification of sodium hypochlorite solutions as described by Mattson et al. followed by washing with deionized water to remove HCl. Reflectivity peak position of the samples in an air tight vessel filled with laboratory air was recorded for ten minutes, followed by injection of an excess of chlorine. All surface chemistry types experienced a sharp several nm red shift in reflectivity peak position as chlorine containing relative humidity exchanged with air in the porous layer, changing the index of refraction of the porous film. The ozone oxidized and furnace oxidized samples retained this change in reflectivity peak position. As-etched samples however saw an immediate blue shift in reflectivity peak position, indicating oxidation of the film by chlorine and water (Equations 4.8 and 4.9). A summary of the results is given in Figure 4.11. An ATR-FTIR spectrum of as etched porous silicon after exposure to chlorine for 30 minutes displays Si-O and Si-OH peaks, further proving oxidation of the film (Figure 4.12). ATR-FTIR spectra of ozone and furnace oxidized samples show no change after chlorine exposure.

\[
\text{(4.8)}
\]
Samples were further exposed to chlorine gas in a nitrogen atmosphere. Reflectivity peak spectra were acquired while samples were filled with nitrogen. Chlorine from a lecture bottle was then introduced. All samples experienced an immediate red shift in reflectivity peak position by several nanometers. Chlorine was then purged from the sample holder with nitrogen. The ozone and furnace oxidized samples blue shifted to the initial reflectivity peak position. The as-etched samples blue shifted, but not completely to the starting reflectivity peak position. We attribute this to the Si-H species reacting with chlorine to form Si-Cl (Equation 4.8).\(^74,78\) This experiment was repeated, this time bubbling nitrogen and chlorine gases through water. The presence of relative humidity with chlorine when exposed to as etched samples produced a greater blue shifting reflectivity peak position, exactly as was seen with the as-etched samples dosed with the wet chlorine produced by the acidification of hypochlorite solutions described above. We attribute this increase in degradation to the presence of water which replaces Si-Cl with Si-OH, reducing the index of refraction of the film (Equation 4.9).\(^78\) In summary, exposure of as etched, ozone oxidized, and furnace oxidized at 600 °C to chlorine gas in addition to the previous HF studies shows that we can construct porous silicon sensors initially responsive to either chlorine or HF analytes, but not to both analytes, producing a level of selectivity to the sensors.
Figure 4.11  Shift in porous silicon reflectivity peak position after 30 minute exposure to Cl₂ gas in relative humidity, samples had not been removed from the Cl₂/RH environment. Three sample types are presented: ozone oxidized (white bar), furnace oxidized at 600 °C (grey bar) and as etched hydride terminated porous silicon (black bar). Data represents the average of 5 samples with one standard deviation error bars.
Figure 4.12  ATR-FTIR spectra of porous silicon samples exposed to chlorine gas/relative humidity for 30 minutes.  (Top) As etched hydride terminated (Middle) ozone oxidized and (Bottom) furnace oxidized porous silicon.  Full scale spectra are shown in black.  A portion of the spectrum (> 1300 cm$^{-1}$), shown in grey, is multiplied by 10 and offset along the y-axis for better clarity.
4.5 Conclusions

This work has demonstrated that the surface chemistry of porous Si can be modified so that a sensor is reactive to specific analytes. A fiducial marker consisting of polystyrene was added to porous Si sensors to produce a reference channel and also to remove probing angle limitations that plague porous Si sensors. Errors in sensing responses exist when the reflectivity peak position of the reactive signal taken at an angle is compared to the original position taken at normal incidence. When probed at an angle, the fiducial marker reflectivity peak wavelength shifts by the same nm amount as the reactive porous Si reflectivity peak. Thus by comparing the wavelength position of both signals before and after a sensing event, we were able to eliminate errors in signal response resulting from changes in probing angle.
This chapter, in part, is a reprint (with co-author permission) of the material as it appears in the following publication: Ruminski, A.M., Barillaro, G., Chaffin, C., Sailor, M.J., Internally referenced remote sensor for HF using a reactive porous silicon photonic crystal. (Manuscript in preparation). The author of this dissertation is one of the primary authors of this manuscript.
CHAPTER FIVE

MICROCONTACT PRINTING FOR THE GENERATION OF
DIFFRACTION GRATINGS IN POROUS SILICON
5.1 Abstract

A porous silicon two-dimensional photonic crystal was prepared in porous silicon by an electrochemical etch of a silicon wafer that had first been imprinted to produce a one-dimensional diffraction grating pattern. The mask consisted of polydimethylsiloxane (PDMS) polymer residue, which was transferred to a silicon surface via microcontact printing at elevated temperatures with a PDMS stamp. An electrochemical etch of the imprinted wafer, followed by an electropolishing reaction to remove the porous layer, allowed the transfer of the pattern to the silicon. Subsequent etching using a sinusoidal current density waveform followed by an electropolishing reaction produced the two-dimensional freestanding porous silicon photonic crystal. Up to 6 patterned freestanding porous Si photonic crystals were etched from the same silicon chip.

5.2 Introduction

Patterns have been produced in porous Si by reactive ion etching of a photolithographic pattern, pulsed UV laser ablation, ion implantation of a holographic pattern, and dry removal soft lithography. The interference of two beams of a frequency doubled Nd:YAG laser have been used to prepare permanent relief holographic gratings in porous Si. Microcontact printing is a simple method that has been used to create patterns on a variety of surfaces.

Using microcontact patterning or other lithographic methods can produce a number of 2- and 3-dimensional structures. The drawback however is that the
procedures tend to be complicated and time-consuming for most materials.\textsuperscript{147} By contrast, porous Si is a material that has strong potential in the field of 3-dimensional structures. The porous Si system provides the ability to electrochemically etch structures whose porosity is modulated in the z-direction (normal to the wafer surface). Selective masking of the Si surface prior to etching allows the convenient generation of 3-dimensional structures.\textsuperscript{148} In this work we use microcontact printing to generate a patterned polymer layer on a Si wafer surface, which is then electrochemically etched. Due to the inhibition of the silicon dissolution in the masked region the etch gives rise to a thicker porous layer in the unmasked areas than the masked areas, thereby resulting in the pattern being transferred to the bulk Si. The porous layer is then removed, and the patterned Si wafer is etched with a photonic crystal (rugate filter), providing an inexpensive and quick procedure to prepare porous 2- and 3-dimensional structures in silicon.

5.3 Experimental

Silicon was purchased from Silitronix. Poly dimethyl siloxane (PDMS) stamps were prepared with Sylgard 184 elastomer (Dow Corning). Aqueous hydrofluoric acid (HF, 49\%) and all solvents were purchased from Fisher and used as received.

5.3.1 Preparation of Porous Si Photonic Crystal Diffraction Gratings
A grating was patterned onto p-type Si (boron doped, 0.0005-0.0012 Ω–cm resistivity, polished on the (100) face) by first applying a 3 second anodic current at 442 mA/cm$^2$ to a wafer in 3:1 v/v 49% aqueous hydrofluoric acid: ethanol which produced a roughened surface. The wafer was immediately placed in contact with a poly dimethyl siloxane (PDMS) stamp, weighed down with a 100 g (238 g/cm$^2$) weight, and heated at 150 °C for 3 hours. The PDMS stamp contained a diffraction grating pattern that was molded from a master grating consisting of 4.8 µm wide lines spaced 3.2 µm apart and 6 µm deep. Next, the diffraction pattern was etched into the Si wafer by applying an anodic current at 88 mA/cm$^2$ for 2 minutes in a 3:1 v/v HF:ethanol electrolyte solution. The porous layer was removed through an electropolishing reaction where a current density of 4.2 mA/cm$^2$ was applied for 10 minutes in a 3.3 % aqueous HF (49%) in ethanol solution. A photonic crystal was etched in the resulting patterned silicon wafer by the application of a sinusoidal current-time waveform varying between 11.5 and 34.6 mA/cm$^2$, with a period 12.7 seconds, and 100 repetitions, and in an 3:1 v/v HF:ethanol solution. The porous layer was removed through the previously mentioned electropolishing reaction, and was immediately placed in contact with a glass slide that was soaked in base, followed by heating in an oven at 70 °C for 1 hour. Circles were patterned in Si through the same method. PDMS was molded from a master pattern consisting of circular pillars that were 22 µm in diameter, 42 µm spacing between hole edges, and 40 µm tall.
5.3.2 Infrared Spectroscopy

Microcontact printing of PDMS to the Si surface was verified through ATR-FTIR spectroscopy. Spectra were recorded with a Thermo Scientific Nicolet 6700 FTIR with a Smart iTR diamond ATR attachment using a resolution of 4 cm\(^{-1}\) and an average of 128 scans.

5.3.4 Scanning Electron Microscopy

Grating patterns and porous layer thickness were examined with a Phillips XL30 environmental SEM operating in secondary electron mode. Accelerating voltages of 10 and 20 keV were used.

5.3.5 Light Diffraction Imaging

Diffracted light was imaged using a Canon EOS Digital Rebel XTi camera, set at an aperture value of 4, and a 1/13 second exposure time. A diode laser source (OZ Optics), at 641 nm wavelength, 2 mW output, and with a 2 mm\(^2\) spot sized was used to illuminate the samples.

5.4 Results and Discussion

5.4.1 Patterning Porous Si

Porous Si films containing a pattern in the x-y plane were prepared from a pre-patterned bulk Si wafer (Figure 5.1). The bulk Si wafer was patterned through microcontact printing with a polydimethylsiloxane (PDMS) polymer stamp. The
silicon wafer surface was first roughened by creating a thin porous layer using an electrochemical etch consisting of a 3 second current pulse at 442 mA cm$^{-2}$ while in an electrolyte solution containing hydrofluoric acid. The thickness of the roughened layer, measured by cross sectional scanning electron microscopy (SEM), was $0.60 \pm 0.02 \mu m$. The roughened Si surface was then imprinted by heating the sample at 150 °C on a hotplate while in contact with a patterned PDMS stamp for 3 hours. A weight was placed on top of the sample to insure a good contact between the stamp and the Si surface. The process results in oligomeric silicone residues from the PDMS stamp partially infiltrating into the roughened surface.

The transfer of PDMS from the stamp onto the roughened Si surface was confirmed using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. ATR-FTIR spectra (Figure 5.2) of microcontact printed Si samples displayed peaks characteristic of pristine PDMS$^{149}$: a methyl CH stretching band at 2970 cm$^{-1}$, a CH$_3$ symmetric deformation band at 1261 cm$^{-1}$, Si-O-Si band at 1100 cm$^{-1}$, Si-C at 864 cm$^{-1}$, and Si-(CH$_3$)$_2$ at 808 cm$^{-1}$. Optical microscope images of the imprinted Si samples reveal lines of PDMS residue, Figure 5.3.

The PDMS masked Si sample was etched with a current of 88 mA/cm$^2$ for 2 minutes. The electrochemical etch produces pores that propagate primarily in the <100> direction, perpendicular to the polished (100) original surface of the Si wafer. This is true for the portions of the Si surface that are freely open to HF.
The Si areas masked off by PDMS undergo an undercutting etch of the masked area that produces slower pore formation in the z-direction than the unmasked areas of Si resulting in a pattern being transferred to the bulk Si. The thickness of the porous layer, measured by cross sectional SEM, at the deepest etched non-imprinted Si areas was $5.8 \pm 0.1 \, \mu\text{m}$ and $5.11 \pm 0.06 \, \mu\text{m}$ at the thinnest etched imprinted Si areas. An electropolishing reaction removes the porous layer, leaving behind the patterned bulk Si. The surfaces were examined by scanning electron microscopy (SEM). Cross-sectional SEM images of the etched masked sample, and the patterned bulk Si after the porous layer was removed (Figure 5.4) show a profile of hills and valleys in the Si wafer. Subsequent etching of the patterned bulk Si with a sinusoidal varying current produces a rugate filter.\textsuperscript{34} Cross-sectional SEM image of a rugate filter displays the porosity bands oscillating with the surface contours of the bulk Si (Figure 5.4). The thickness of the rugate etch porous layer was $19.2 \pm 0.3 \, \mu\text{m}$.
Figure 5.1  Fabrication of a Si diffraction grating. A roughened Si surface is formed by applying a short, high current etch, and immediately placed in contact with a patterned PDMS stamp at an elevated temperature which transfers the pattern to the Si surface. The masked Si wafer is etched, an undercutting etch takes place under the masked areas which etch at a slower rate in the z-direction than the unmasked areas, producing a pattern in the bulk silicon. After removing the porous layer, the patterned bulk Si can subsequently be etched with a sinusoidal waveform, producing a photonic crystal. Additional patterned porous Si films can be produced from one Si sample.
Figure 5.2 Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrum of a roughed Si surface after thermal microcontact printing with PDMS. The spectrum displays peaks characteristic of pristine PDMS: C-H stretching band at 2970 cm$^{-1}$, a CH$_3$ symmetric deformation band at 1261 cm$^{-1}$, Si-O-Si at 1100 cm$^{-1}$, Si-C at 864 cm$^{-1}$, and Si-(CH$_3$)$_2$ at 808 cm$^{-1}$.\textsuperscript{149}
Figure 5.3  Images taken through an optical microscope of (A) a patterned PDMS stamp, (B) a PDMS imprinted Si sample, and (C) resulting patterned bulk Si when a PDMS imprinted Si sample is etched and the porous layer is removed.
Figure 5.4 Scanning electron microscopy cross-sectional images of (A) a roughened Si surface patterned via thermal microcontact printing with a PDMS stamp, (B) the porous layer resulting from etching a PDMS masked Si wafer, (C) bulk Si after the porous layer was removed through an electropolishing etch, and (D) a rugate structure etched into a patterned bulk Si wafer.
5.4.2 Generations of Porous Si Patterning

The patterned rugate filter was removed from the bulk Si through an electropolishing etch. The freestanding porous film retained the diffraction grating pattern, as verified through optical microscopy and the observation of diffracted light when a laser was directed at the film. Additional patterned films were produced from the same patterned bulk Si wafer. Up to 6 generations, i.e. subsequent etches on the same wafer, of patterned porous films were etched, while still retaining the diffraction pattern. As the patterned bulk Si wafer is re-etched, the patterned features become less pronounced as viewed through cross-sectional SEM (Figure 5.5). This indicates that there are a finite number of porous films that can be produced from a single patterned piece of Si. The decrease in height contrast of the hills and valleys in the silicon after repeated etching could be due to a different HF concentration in the two areas that results in a different etch rate. The hills have a higher HF concentration and in turn a higher etching rate with respect to the valleys.

The fidelity of the five generations of porous Si diffraction grating films was tested by illuminating the samples with a diode laser (2 mW power, 2 mm² spot size) and imaging their resulting diffraction patterns (Figure 5.6). Nine orders of diffraction were observed by eye from the first generation film. In general, the intensity of higher order diffracted light decreased as the generation number of the porous Si sample increased, where only 7 orders of diffraction were visible by eye for the fifth generation film. The decrease in light intensity
corresponds to the decrease in feature size of the bulk and porous Si, which was observed in the SEM micrographs (Figure 5.5).

The distance, $x$, of each of the 9 orders of diffracted light in Figure 5.6 from the directly transmitted light (order $m = 0$) was calculated using equations 4.1 and 4.2. First, the angle at which an order of diffracted light varies from direct transmission, $\theta$, was calculated by:

$$d \sin \theta = m \lambda$$

(4.1)

where $d$ is the spacing between the raised features in the porous Si diffraction grating (8 $\mu$m), $m$ is the diffraction order number, and $\lambda$ is the wavelength of the incident laser (641 nm). Next, the distance, $x$, was calculated by inserting $\theta$ into the equation:

$$\tan \theta = \frac{x}{y}$$

(4.2)

where $y$ is the distance between the porous Si sample and where the surface the diffracted light is captured on (9.2 cm). The calculated $x$ values for the 9 orders of diffracted light are displayed in Table 1. Additionally, the distance of each beam of diffracted light from the transmitted light was measured for the five generations of porous Si films. The measured values are in good agreement with the calculated values for the first 3 orders of diffracted light, then the measured values become increasingly greater than calculated. This is apparent in Figure 5.6, as the spacing between orders of diffracted light becomes greater at higher orders instead of retaining even spacing. In addition, the spot size of diffracted light becomes
wider at the higher diffraction orders, indicating the porous Si grating is not a perfect grating consisting of infinitely narrow features.
Figure 5.5 Cross-sectional scanning electron microscopy images of porous Si rugate structures etched into a patterned Si wafer. (A) 1st generation etch and (B) 6th generation etch.
Figure 5.6 Images of the diffraction pattern generated by free standing patterned porous Si films, using the transmission mode set up detailed in the schematic. Up to 9 orders of diffraction was observed. Multiple generations of porous Si free standing films were etched from a single patterned Si wafer. Probing the films with a laser produced the light diffraction patterns: chronologically numbered generation one (1, top) through generation five (5, bottom). The zero order light spot, which corresponds to direct transmission of light, is marked in the images by the number 0.
Table 5.1  The distance of diffracted light from directly transmitted light (m = 0) as a function of diffraction order (m). Distances were calculated using equations 1 and 2. Additionally, distances were measured for each generation of patterned porous Si films. Values are listed in centimeters.

<table>
<thead>
<tr>
<th>Diffraction Order (m)</th>
<th>Calculated, cm</th>
<th>Gen. 1, cm</th>
<th>Gen. 2, cm</th>
<th>Gen. 3, cm</th>
<th>Gen. 4, cm</th>
<th>Gen. 5, cm</th>
</tr>
</thead>
<tbody>
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5.4.3 Additional Patterning of Porous Si

A second mask was obtained to further test patterning of porous Si through microcontact printing. A PDMS stamp consisting of 22 µm diameter circular holes spaced 42 µm between hole edges (Figure 5.7) was placed in contact with a roughed Si surface and heated at 150 °C for 3 hours as detailed in Figure 5.1. Etching of the PDMS masked surface followed by porous layer removal results in successfully patterned Si as photographed in Figure 5.7 through an optical microscope and imaged by SEM in Figure 5.8.
Figure 5.7 Images taken through an optical microscope of (A) a patterned PDMS stamp, (B) a PDMS imprinted Si sample, and (C) resulting patterned bulk Si when a PDMS imprinted Si sample is etched and the porous layer is removed.
Figure 5.8 Cross sectional SEM micrographs imaged at a 45° angle of the circular patterned Si etched with a rugate structure.


5.4.4 Sensing Application for Porous Silicon Diffraction Gratings

Volatile organic compound (VOC) sensing has been achieved with porous silicon diffraction gratings by monitoring their reflectivity spectrum with a CCD spectrometer.\textsuperscript{144} With a diffraction grating sensor the sensitivity can be enhanced through resonance effects.\textsuperscript{150,151} Previous work from the Hupp group\textsuperscript{150} utilized a micropatterned diffraction grating consisting of a vapochromic charge-transfer salt and a monochromatic light source. When the laser illuminating the sample matched the vapochromic charge-transfer transition of the grating, the sensor response was increased by 3.5 orders of magnitude. The motivation for producing porous silicon diffraction gratings was to etch a rugate filter grating where the reflectivity peak maximum coincided with a probing laser, thereby achieving resonance enhancement. For best resonance enhancement results, the rugate filter reflectivity spectrum would require a sharp, narrow reflectivity peak maximum with an intensity that is enhanced relative to Fabry Perot thin film interference fringes. One method to produce a porous silicon diffraction grating is through dry-removal soft-lithography.\textsuperscript{143,144} This method removes portions of the porous layer from bulk silicon, resulting in a sensor consisting of lines of porous silicon separated by empty space. A disadvantage of this technique is that it requires the porous silicon film to be thin, with a thickness of 1 \( \mu \)m. In order to obtain a rugate reflectivity peak with an intensity far greater than Fabry-Perot thin film interference fringes, a thick (several \( \mu \)ms) porous film must be etched. Thick films cannot be successfully patterned through dry-removal soft-lithography.
Therefore the PDMS microcontact printing method to etch diffraction gratings outlined above is a better method to produce a resonant porous Si grating sensor. Preliminary porous Si diffraction grating VOC exposure experiments have shown a response from the grating. The intensity of diffracted light changed when in the presence of isopropanol vapor at a concentration of 100 mg m\(^3\). Inconsistencies existed in the preliminary data, and further development of the VOC exposure experiments is needed.

5.5 Conclusions

Porous Si photonic crystals containing a diffraction grating in the x-y plane and a rugate filter structure in the z-direction were obtained by microcontact printing a line pattern mask onto a roughened silicon surface using a patterned stamp of PDMS prior to an electrochemical etch. A subsequent electrochemical etch successfully transfers the pattern into the bulk Si. The patterned bulk Si was etched 6 consecutive times to produce free standing patterned porous film that was illuminated with a laser. Up to 9 orders of diffracted light were produced. A second pattern consisting of an array of circles was successfully microcontact printed and etched in a Si wafer. The microcontact printing followed by etching method is a simple means to pattern Si and does not require the use of photolithography.
This chapter, in part, is a reprint (with co-author permission) of the material as it appears in the following manuscript: Ruminski, A.M., Barillaro, G., Secret, E., Sailor, M.J., Microcontact Printing for the Generation of Diffraction Gratings in Porous Silicon. (Manuscript in preparation). The author of this dissertation is one of the primary authors of this manuscript.
APPENDIX A:

SURFACE CHEMISTRY GRADIENT THROUGH A LIGHT-MEDIATED CHEMICAL REACTION
A.1 Introduction

In the late 1980s it was discovered that porous Si can exhibit room temperature photoluminescence.\(^2,3\) Modification of the etching procedure produced a porous layer that contained nanoscale quantum wires which displayed quantum confinement effects. The resulting bright red-orange fluorescence corresponded to an energy that is larger than the bandgap energy for bulk Si. It is now believed that the photoluminescence is due to a combination of quantum confinement and surface effects.\(^152\)

Chemical modification of photoluminescent porous silicon through exciton-mediated hydrosilylation of alkenes and alkynes has been reported by Buriak using an ordinary tungsten ELH light source.\(^82,153\) The reaction may be initiated by photogenerated holes on the surface that are attacked by alkene nucleophiles or photogenerated Si radicals resulting from the cleavage of weak surface Si-H bonds. Successful light-mediated hydrosilylation has only been found to occur on photoluminescent porous Si. Substrates that quench the photoluminescence have been found to have poor modification coverage.\(^154\)

An advantage of light-mediated hydrosilylation is the ability to easily photopattern the surface. Photopatterned porous Si was prepared by Buriak, and soaked in a basic solution which destroys as etched porous Si (Si-H) but has no effect on functionalized porous Si (Si-C). A well defined picture composed of porous silicon remained, indicating the chemical modification was successful.\(^82\)
The success of light-mediated chemical modification is linked to the intensity of the incident light. This factor can be utilized for chemical gradients on porous silicon where light is modulated from high to low intensity across the porous sample producing high to low chemical surface coverage. The resulting chemical gradient porous silicon sample can be further functionalized with another chemical modification (via thermal hydrosilylation, electrochemical alkylation, thermal oxidation, etc.) producing a surface with varying chemical properties, especially for example, if one modification produces a hydrophobic surface and the second is with a hydrophilic functional group. A potential application for chemical surface gradients is as a sensor array, where the response of individual positions on the sample is dependent on the extent of chemical modification at that position. By probing the reflectivity spectrum of the sample with a monochrome camera, each pixel in an image could be defined as a separate sensor.

A.2 Porous Silicon Fabrication and Light Mediated Chemical Modification

Photoluminescent porous silicon was prepared from p-type silicon (0.1–1 Ω-cm, Siltronix) through an electrochemical corrosion reaction in a 1:1 v:v solution of aqueous hydrofluoric acid:ethanol using a two-electrode configuration
with a platinum ring counterelectrode. A current density of 35.4 mA cm$^{-2}$ was applied while under white light illumination. The resulting porous layer was photoluminescent and contained an optical reflectivity spectrum consisting of Fabry-Perot interference fringes. Porous layer thickness was measured by SEM, the average value with one standard deviation was 2.1 +/- 0.3 µm.

Porous samples were placed in a glass airtight holder and connected to a Schlenk vacuum line. The sample chamber was placed under vacuum and back filled with nitrogen three times. A small volume of alumina filtered, degassed 1-decene was syringed into the chamber to just cover the sample. Lastly, samples were illuminated with white light from a tungsten ELH light source for 1 to 8 hours.

A.3 FTIR and Elemental Analysis SEM Characterization of Chemically Modified Porous Silicon

Surface modification was analyzed through attenuated total reflectance (ATR) and transmission mode Fourier transform infrared spectroscopy (FTIR). ATR-FTIR spectra (Germanium plate) of samples exposed to 1-decene under illumination for 8 hours displayed more intense C-H stretches at 2900 cm$^{-1}$ than Si-H stretches at 2100 cm$^{-1}$, indicating good coverage in surface modification (Figure A.1). However, spectra obtained with transmission mode FTIR displayed
smaller intensity C-H stretches in comparison to the larger Si-H stretches. The samples were examined again with ATR-FTIR, but using a Diamond plate. A larger Si-H stretch intensity than in Ge plate spectrum was observed. Transmission FTIR probes the entire thickness of the porous samples, while ATR-FTIR probes a thin portion of the porous samples. ATR penetration depth at 1000 cm$^{-1}$ for a sample with an index of refraction of 1.5 is 0.66 µm for a Ge plate, and 2.0 µm for a Di plate. Therefore the difference in C-H/Si-H peak (Figure A.1) intensity ratios in the 3 spectra indicates that the surface functionalization may not be uniform in depth.

Surface coverage was evaluated with scanning electron microscopy-electron dispersive x-ray spectroscopy (SEM-EDX) which evaluates elemental composition. Samples with three types of surface chemistries were prepared using 3,3,4,4,5,5,6,6,6-nonfluoro hexane, 5-bromo-1-pentene and 1-decene. Samples were prepared using the same method described above. Elemental analysis by SEM-EDX was measured at 3 sections in the porous layer: the top 1/3 of the sample at the air/porous Si interface, the middle 1/3 of the porous layer, and the bottom 1/3 at the porous Si/bulk Si interface. The elements measured were Si, which acted as the reference element, and the elements in the compounds used to modify the surface (C, F, and Br). A ratio of the measured elemental atomic %/Si atomic % was calculated and the results for 3,3,4,4,5,5,6,6,6-nonfluoro hexane are displayed in Table A.1, 5-bromo-1-pentene in Table A.2, and 1-decene in Table A.3. The results for all 3 samples clearly indicate that chemical
modification was greatest at the air/porous Si interface, and decreased with porous Si depth.

The uneven surface modification with increased porous layer thickness is a major limitation of the light-mediated hydrosilylation method. The extent of modification is dependent upon the penetration of white light into the porous layer. Buriak analyzed the elemental composition with porous layer depth using secondary ionization mass spectrometry. Modification was relatively constant up to 1 µm in thickness, which after that depth chemical coverage decreased through 3 µm.

### A.4 Surface Chemical Gradient Functionalization

A chemical functionalization gradient across the x-direction of the porous Si surface was achieved through a modification to the procedure above. Incident light intensity was modulated through a filter that consisted of a black gradient pattern (Figure A.2) that was printed onto a clear transparency. Three printed gradients were overlapped, formed into a slide, inserted into a projector and the light intensity gradient pattern was focused onto a silicon wafer. Samples were illuminated while covered with 1-decene and undecylenic acid for 3 hours. Transmission mode FTIR spectra were acquired at locations across the surface.
gradient displaying successful gradient modification with 1-decene (Figure A.3) and undecylenic acid (Figure A.4).
Figure A.1 FTIR spectra of a light-mediated 1-decene hydrosilylated porous Si sample. The material contains features at 2970, 2930, 2853 cm\(^{-1}\) (\(\nu \text{ CH}_x\)), 2114 cm\(^{-1}\) (\(\nu \text{ SiH}_x\)), 908 and 626 cm\(^{-1}\) (\(\delta \text{ SiH}_x\)). Oxidation of the material also occurs, producing a feature at 1074 cm\(^{-1}\) (Si-O). Spectra are obtained using 3 methods: (top) Ge-crystal ATR-FTIR, (middle) Di-crystal ATR-FTIR, and (bottom) transmission mode FTIR.
Table A.1  Ratio of Element Atomic % / Si Atomic % measured by SEM-EDX for porous silicon modified with 3,3,4,5,6,6,6-nonafluoro hexane. During analysis, the detector was focused on small portions of the porous layer: the top 1/3 at the air/porous Si interface, the middle 1/3 of the porous layer, and the bottom 1/3 at the porous Si/bulk Si interface.

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Table A.2  Ratio of Element Atomic % / Si Atomic % measured by SEM-EDX for porous silicon modified with 5-bromo-1-pentene. During analysis, the detector was focused on small portions of the porous layer: the top 1/3 at the air/porous Si interface, the middle 1/3 of the porous layer, and the bottom 1/3 at the porous Si/bulk Si interface.

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Table A.3  Ratio of Element Atomic % / Si Atomic % measured by SEM-EDX for porous silicon modified with 1-decene. During analysis, the detector was focused on small portions of the porous layer: the top 1/3 at the air/porous Si interface, the middle 1/3 of the porous layer, and the bottom 1/3 at the porous Si/bulk Si interface.

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Figure A.2 Black and white gradient pattern that was printed onto a transparency and used to filter incident light intensity for light-mediated chemical modifications.
Figure A.3  Transmission mode FTIR spectra of a light-mediated 1-decene hydrosilylated sample using a light intensity gradient across the sample. The material contains features at 2970, 2930, 2853 cm\(^{-1}\) (\(\nu\) CH\(_\alpha\)), 2114 cm\(^{-1}\) (\(\nu\) SiH\(_\alpha\)), 908 and 636 cm\(^{-1}\) (\(\delta\) SiH\(_\alpha\)). Oxidation of the sample occurs during the reaction, producing a feature at 1054 cm\(^{-1}\) (Si-O).
Figure A.4 Transmission mode FTIR spectra of a light-mediated undecylenic acid hydrosilylated sample using a light intensity gradient across the sample. The material contains features at 2930, 2853 cm$^{-1}$ ($\nu$ CH$_x$), 2114 cm$^{-1}$ ($\nu$ SiH$_x$), 1715 cm$^{-1}$ (C=O), 908 and 636 cm$^{-1}$ ($\delta$ SiH$_x$). Oxidation of the sample occurs during the reaction, producing a feature at 1080 cm$^{-1}$ (Si-O).
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