SELF-REFERENCING AND SENSITIVITY OPTIMIZATION IN PHOTONIC CRYSTAL SLABS FOR BIOSENSING APPLICATIONS

by

Ryan Schilling
Supervisor: Dr. Ofer Levi

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Graduate Department of Edward S. Rogers Sr. Department of Electrical and Computer Engineering
Institute of Biomaterials and Biomedical Engineering
University of Toronto

© Copyright 2013 by Ryan Schilling
Supervisor: Dr. Ofer Levi
Abstract

Self-Referencing and Sensitivity Optimization in Photonic Crystal Slabs for Biosensing Applications

Ryan Schilling
Supervisor: Dr. Ofer Levi
Master of Applied Science
Graduate Department of Edward S. Rogers Sr. Department of Electrical and Computer Engineering
Institute of Biomaterials and Biomedical Engineering
University of Toronto
2013

Photonic crystal slabs (PCS) are explored in the context of optofluidic refractive index (RI) sensing for portable, label-free, biosensing applications. The accuracy of RI sensors is limited by noise signals that cause a change in RI that cannot be differentiated from the signal of interest. For this reason self-referencing schemes that provide rejection of common mode signals, and an inherent temperature stabilization approach, are explored. A novel referencing method that allows for frequency shifts to be read out in the transmission power spectrum is proposed and characterized. In terms of improving sensing metrics the relevant characteristics of various PCS architectures are explored numerically. In addition, a novel suspended air-substrate device that offers greatly improved sensitivity is proposed and characterized. An experimental measurement near the theoretical detection limit for a PCS is demonstrated. In understanding measurement errors the crossed-polarization effect and its practical limitations are explored numerically.
Acknowledgements

First, I would like to thank my family, and especially my parents, for your unwavering support and belief in me. For me this is the one thing I know I can always rely on. Much of life is uncertain, but I know my family is always there for me.

The second acknowledgment goes to my friends throughout the years, some of whom I’ve spoken with today and others that I have not seen for years. I rely on you for your honest opinions, for your perspectives that help me see things in a different way, for your humor, for your company, and of course for your ability to convince me to do things that I soon regret.

In the context of this thesis I thank my supervisor for your guidance, support, and breadth of knowledge. To my friends and colleagues in the group, I couldn’t have done this without you and I certainly would have enjoyed it a lot less.

This degree has been a journey, and I have grown throughout it. I hope that I have become not just a better scientist but a better person as well.
# Contents

## 1 Introduction

1.1 Methods of Biosensing ................................................. 2
1.2 Label-Free Sensing .................................................. 2
1.3 Photonic Crystal Sensors .......................................... 4
1.4 Thesis Content ...................................................... 4

## 2 Photonic Crystals

2.1 Photonic Crystal Slabs ........................................... 7
2.1.1 Physical Principles ............................................. 8
2.1.2 Resonance Characteristics .................................... 10

## 3 Simulation

3.1 Simulation Tools .................................................... 13
3.1.1 Finite-Difference Time-Domain Method ..................... 14
3.1.2 Scatter Matrix Method ........................................ 14
3.2 Resonance Fitting .................................................. 15
3.3 Simulation Analysis of General Device Types ................. 16
3.3.1 Substrate-Bound Architecture ............................... 18
3.3.2 Suspended Symmetric Architecture ......................... 24
3.3.3 Air-Substrate Architecture .................................. 25
3.4 Crossed-Polarization Effect ..................................... 28

## 4 Fabrication

4.1 Film Deposition ..................................................... 36
4.1.1 Silicon Dioxide ................................................ 37
4.1.2 Silicon Nitride ................................................ 37
8 Experimental Measurement of Detection Limit

8.1 Determination of Alcohol Dilution RI ........................................... 91
8.2 Intensity Measurement ................................................................. 92
8.3 Spectral Shift Measurement .......................................................... 94

9 Discussion

9.1 Device Performance ................................................................. 96
9.2 Sources of Error ........................................................................ 97
  9.2.1 Crossed-Polarization Power Stability .......................................... 97

10 Future Work

10.1 Multiplexed PCS arrays ............................................................. 100
10.2 Air-Substrate Sample ................................................................. 102
10.3 Power Differential Referencing in Air-Substrate Design .................. 104
10.4 Split-Flow Polarization Conversion .............................................. 105

11 Conclusions ................................................................................. 107

A Contributions

A.1 Chapter 5 ................................................................................. 110
A.2 Chapter 6 ................................................................................. 110
A.3 Chapter 7 ................................................................................. 110
A.4 Chapter 8 ................................................................................. 111
A.5 Chapter 10 ............................................................................... 111

B Cleanroom Recipes

B.1 Film Deposition Recipes ............................................................. 112
  B.1.1 LPCVD SiNx Film Recipe ......................................................... 112
  B.1.2 PECVD SiNx Film Recipe ....................................................... 112
B.2 Photoresist Recipes .................................................................. 113
  B.2.1 ZEP 520A EBL Resist Spin Recipe ........................................... 113
  B.2.2 ZEP 520A EBL Resist Development Recipe ............................ 113
  B.2.3 Shipley S1818 Resist Spin Recipe ............................................ 114
  B.2.4 Shipley S1818 Resist Development Recipe ............................... 114
B.3 Etch Recipes ............................................................................. 115
List of Figures

1.1 Generic optical RI biosensor, demonstrating immobilization of an analyte and subsequent interaction with the resonant mode (shown in red) [7] .................................................. 3

1.2 Monolithically integrated PCS biosensor, with microfluidic flow channel above and miniature laser and detector readout system below [12] .................................................. 4

2.1 Illustration of the varying dielectric structure of photonic crystals in one, two, and three dimensions ................................................................. 7

2.2 Illustration of photonic crystal slab unit cell with a square lattice and circular patterning 8

2.3 Band diagram in reduced-zone scheme for the (a) even and (b) odd modes of a uniform dielectric slab (n=3.46) in air. Band diagram in reduced-zone scheme for the (c) even and (d) odd modes of a dielectric slab (n=3.46) in air, with a periodic array of holes patterned to form a photonic crystal slab [17] .................................................. 9

2.4 Normalized transmission spectrum for a silicon (n = 3.46) PCS with r = 0.2a and t = 0.5a, excited at normal incidence. Red circles indicate the transmission response for a uniform slab with a frequency-dependent effective dielectric [17, 12] ......................... 11

2.5 Fourier transformation of time domain slowly decaying field amplitude of a normal incidence excited PCS revealing a Lorentzian line shape .................................................. 12

3.1 Unit cell of dielectric layers excited by a plane wave (vector $\mathbf{k}_{inc}$) [23] ....... 14

3.2 Least-squares curve fitting of simulation data to the Fano equation 2.5 ............. 16

3.3 (a) Fitted resonance and $\epsilon |E|^2$ in the cross-section of a unit cell for a TE-like GMR in a PCS with radius = 100nm and lattice constant = 980 nm. (b) Corresponding figure for a TM-like GMR in a PCS with radius = 240nm and lattice constant = 1010 nm. .... 18

3.4 (a) TE-like GMR quality factor and sensitivity as a function of radius and for unit cell with a = 980 nm. (b) TE-like GMR detection limit as a function of radius for unit cell with a = 980 nm .................................................. 20
3.5 TE-like GMR peak location as a function of radius for unit cell with \( a = 980 \text{ nm} \) and (b) as a function of lattice constant for unit cell with \( r = 180 \text{ nm} \) .......................................................... 21

3.6 TE-like GMR quality factor and sensitivity as a function of lattice constant for unit cell with \( r = 180 \text{ nm} \). (b) Detection limit as a function of lattice constant for unit cell with \( r = 180 \text{ nm} \) .......................................................... 22

3.7 TM-like GMR quality factor and sensitivity as a function of radius for unit cell with \( a = 1010 \text{ nm} \). (b) TM-like GMR detection limit as a function of radius for unit cell with \( a = 1010 \text{ nm} \) .......................................................... 23

3.8 TM-like GMR peak location as a function of radius for unit cell with \( a = 1010 \text{ nm} \) .......................................................... 24

3.9 (a) TM-like GMR lineshape and (b) percentage of light reflected on resonance as a function of \( \text{SiO}_2 \) thickness for unit cell with \( r = 150 \text{ nm} \) and \( a = 1010 \text{ nm} \) .......................................................... 24

3.10 (a) TE-like GMR quality factor and sensitivity as a function of radius for unit cell with \( a = 1020 \text{ nm} \). (b) TE-like GMR detection limit as a function of radius for unit cell with \( a = 1020 \text{ nm} \) .......................................................... 25

3.11 TM-like GMR quality factor and sensitivity as a function of radius for unit cell with \( a = 1080 \text{ nm} \). (b) TM-like GMR detection limit as a function of radius for unit cell with \( a = 1080 \text{ nm} \) .......................................................... 26

3.12 (a) TM-like GMR electric field in air-substrate device for unit cell with \( a = 1110 \text{ nm} \), \( r = 200 \text{ nm} \). (b) TE-like GMR electric field in air-substrate device for unit cell with \( a = 990 \text{ nm} \), \( r = 100 \text{ nm} \) .......................................................... 26

3.13 (a) TE-like GMR quality factor and sensitivity as a function of radius for unit cell with \( a = 990 \text{ nm} \). (b) TE-like GMR detection limit as a function of radius for unit cell with \( a = 990 \text{ nm} \) .......................................................... 27

3.14 (a) TM-like GMR quality factor and sensitivity as a function of radius for unit cell with \( a = 1110 \text{ nm} \). (b) TM-like GMR detection limit as a function of radius for unit cell with \( a = 1110 \text{ nm} \) .......................................................... 28

3.15 (a) SEM image of a PCS lattice with the axes of propagation for fundamental GMRs indicated by white arrows. (b) PCS unit cell with exaggerated elliptical hole with \( r_1 \) and \( r_2 \) being the radii corresponding to orthogonal propagation axes. The x and y axis shown is the lattice axis. The polarization of the incident field (\( |E_x|^2 \)) is shown in red and the polarization of the recorded field (\( |E_y|^2 \)) is shown in blue. (c) Unit cell rotated by 45° with respect to the polarization axis .......................................................... 29
3.16 Simulation of CP transmission as a function of rotation of the unit cell (3.15(b)) for TE-like GMR in structure with $r = 100$ nm and $a = 980$ nm.

3.17 (a) Experimental result achieved by Altug et al. [27, 28] showing variation in peak CP amplitude in PCS as a function of rotation angle. (b) Peak amplitude of the simulated CP effect as a function of rotation angle.

3.18 GMR propagation in a PCS with excitation polarization at $45^\circ$. The area of a focused excitation laser is shown in dark red, with GMR propagation along orthogonal axes shown in light red.

3.19 (a) Polarization dependence of Q using CP for TE-like GMR in structure with $r = 100$ nm and $a = 980$ nm. (b) Resonance splitting demonstrated by varying $r_2$ as a percentage of $r_1$ from 105% to 125%.

3.20 (a) TE-like resonance shift as a function of unit cell rotation in CP transmission and (b) direct transmission.

4.1 Dielectric layers of a substrate-bound PCS device - typically 260 nm of SiNx on a 2.36 µm thermally grown SiO$_2$ film [12].

4.2 Illustration of tensile and compressive stress in thin film materials [32].

4.3 Monolayer formation in ALD process [34].

4.4 (a) PCS sample before suspension, and (b) sample after cavity has been formed by BOE wet-etching process.

4.5 Dielectric layers of a air-like substrate PCS device with a 50 nm layer of SiNx grown on a silicon substrate, onto which a 5 nm layer of Al$_2$O$_3$ is deposited, and finally a 260 nm layer of SiNx is deposited onto which the PCS will be patterned.

4.6 Etch profile for KOH wet etch of $<100>$ silicon wafer [38].

4.7 Process steps for suspending air-like substrate samples following patterning of the PCS structure.

4.8 (a) Topside pattern on air-substrate sample with PCS mesas shown in green and two sets of alignment marks used for backside etching. The backside mask is shown in (b) with corresponding alignment marks and square windows for KOH etching (note the mask is flipped for presentation purposes).

4.9 (a) Topside of PCS on air-substrate sample and (b) backside of sample after KOH etch (viewed under optical microscope).
4.10 (a) Cross-section of non-ALD sample showing individual PCS holes and (b) close-up of single hole. (c) Cross-section of ALD sample showing individual PCS holes and (d) close-up of single hole.

4.11 (a) TM-like resonances of sample processed with old AR coating method and (b) with optimized AR coating method.

5.1 Optical apparatus used for crossed-polarized characterization of PCS devices.

5.2 (a) T-junction design dimensions with location of PCS structures indicated and (b) corresponding lithography mask.

5.3 (a) PDMS t-junction channel mounted on PCS sample and encased in epoxy (view through microscope of characterization setup) and (b) view showing threaded mount attached to rotation plate.

5.4 (a) and (b) show a liquid interface being moved across a PCS using the t-junction channel. (c) zoomed out view of t-junction during flow experiment.

5.5 Pixel intensity as a function distance across the interface between water and water with food coloring. Analysis of video was used to determine stability of the split-flow.

5.6 (a) Syringe pumps feeding into temperature maintaining flasks immersed in a temperature controlled thermal bath and (b) close-up image of temperature maintaining flask.

5.7 (a) Fluid exchange measurement during early development of the microfluidics system and (b) the same measurement made 6 months later.

5.8 Fano fitting to experimental measurement of TE-like GMR in a PCS structure with \( r = 110 \) nm and \( a = 980 \) nm.

6.1 Thermo-optic coefficients at 1550 nm and room temperature.

6.2 (a) Comparison between NIST formulation calculated at 1064 nm and atmospheric pressure (blue) and Richerzhagen measurement at 1064 nm (black). (b) Same comparison with NIST calculated at 1550 nm and Richerzhagen measurement offset to match.

6.3 Derivative of the NIST formulation calculated at 1550 nm, giving the linear TOC approximation as a function of temperature.

6.4 Thermal expansion coefficients at room temperature (20 °C) for materials comprising the PCS structure.

6.5 (a) Simulation of thermal behavior for \( r = 100 \) nm and (b) \( r = 110 \) nm.

6.6 Effects of thermal expansion on athermal point.
6.7 Comparison of $|E|^2$ for PCS with $a = 980 \text{ nm}$, $t = 260 \text{ nm}$, and (a) $r = 300 \text{ nm}$ or (b) $r = 100 \text{ nm}$. Note that with $r = 300 \text{ nm}$ field confinement within the PCS slab is greatly reduced, causing a significant enhancement of the effect that water and $\text{SiO}_2$ have on the athermal point.

6.8 (a) Side view of TEC mount and (b) top view of TEC mount with microfluidic channel and thermistor sandwiched between PCS device and plastic clamping layer.

6.9 Temperature dependent resonance shift for PCS with $r = 130 \text{ nm}$, $a = 980 \text{ nm}$, and $t = 263 \text{ nm}$ with air above the surface. The red dash-dot line shows the experimental result using a TEC for temperature control and the solid blue line shows the shift predicted by simulation.

6.10 Temperature dependent resonance shift for PCS with $r = 130 \text{ nm}$, $a = 980 \text{ nm}$, and $t = 263 \text{ nm}$ with water above the surface. The red and black dash-dot lines show the experimental results of two experiments using a TEC for temperature control and the solid blue line shows the shift predicted by simulation.

6.11 (a) Temperature dependence of the FP cause by the Si substrate and (b) resulting composite of PCS GMR and substrate FP at 32, 35, and 38 $^\circ\text{C}$.

7.1 Schematic representation of a single one-dimensional biosensor where capture proteins have been applied to part of the structure. Circles indicate the region that is seen by a single camera pixel. Those pixels within the protein region correspond to the active sensor and those outside are the reference.

7.2 (a) Design structure for a split-mesa device shown in top view and (b) cross-section of device indicating design dimensions, materials, and gap between mesas. Note that a variety of radii and lattice constant choices were explored for the devices in this chapter.

7.3 Experimental measurement of TE-like resonances in split-mesa design with 1 $\mu\text{m}$ Si$\text{N}_\text{x}$ gap. Solid lines indicate measurement data and dashed lines indicate Fano fitting. The red and blue plots are measured when the center of the focused laser beam (beam waist of 40 $\mu\text{m}$) is 50 $\mu\text{m}$ from the center of the gap between the reference and active sensors.

7.4 Experimental measurement of TM-like resonances in split-mesa design with 1 $\mu\text{m}$ Si$\text{N}_\text{x}$ gap. Solid lines indicate measurement data and dashed lines indicate Fano fitting. The red and blue plots are measured when the center of the focused laser beam (beam waist of 40 $\mu\text{m}$) is 50 $\mu\text{m}$ from the center of the gap between the reference and active sensors.
7.5 (a) FDTD simulation of GMR propagation across the gap between adjacent mesas for un-etched (top) and etched (bottom) gaps. (b) Optical image of final split-mesa design with 3.78 µm etched gap.

7.6 Split-flow of two different RI fluids over a split-mesa PCS.

7.7 Each sensor is excited individually (blue and red) and both sensors are excited together (black). Inset shows the position of the laser spot for each measurement.

7.8 Experimental measurement of wavelength differential device with water in the microfluidic channel at a temperature of 30 °C (black) and 40 °C (red).

7.9 Differential measurement comparing a split flow of 4% IPA on both sensors, and water on the shifted with blue-shifted resonance and 4% IPA on the other sensor.

7.10 Demonstration of power differential effect illustrating the summation of two resonances (dashed lines) and the resulting line shape with a local minimum between the resonant peaks that changes as a function of the differential shift of one peak relative to the other.

7.11 (a) Calculation of change in power at local minimum for various wavelength shifts and (b) change in power as function of wavelength shift (determined by quadratic fitting to the local minimum).

7.12 (a) Side view of the simulation object showing two photonic crystals, in a water sensing medium and on an SiO$_2$ substrate with etched gaps in between them. (b) Same object shown from the top view. The dimensions of the PCS are indicated as 20 unit cells long by 1 unit cell thick. Periodic boundary conditions are shown by green dashed lines. The yellow arrow indicates the axis of polarization.

7.13 Unit cell simulations of PCS 1 and PCS2 with $r = 110$ nm and $r = 106$ nm shown in blue and red respectively. The weighted sum of these simulation shown with black dots. The corresponding simulation of PCS 1 and PCS 2 using the split-mesa simulation object from figure 7.12 shown in purple (difficult to see as it coincides with the black dots).

7.14 Experimental measurement of power differential device with each resonator measured individually (blue and red) and together (black).

7.15 (a) Experimental observation of power differential measurement using a split-flow with water over the reference sensor and varying IPA concentrations in water over the active sensor. (b) The change in transmission power at the local minimum is determined by fitting a quadratic function to the local minimum area, and is plotted as a function of IPA concentration.
8.1 Static cross-polarized transmission measurement showing shift of the resonance due to the IPA presence in water. Inset shows spectral shift as a function of IPA concentration.

8.2 (a) Water and 0.02% IPA in water are periodically interchanged using microfluidics and a t-junction channel. (b) Real-time cross-polarized transmission measurement showing resolution of 0.02% IPA in water (red), which is contrasted to the baseline measurement of water being exchanged with water (blue).

8.3 (a) Temperature stabilized high resolution spectral shift measurement of the side of a resonance peak for when the PCS is immersed in water and 0.04% IPA dilution. (b) The calculated spectral shift of 2.9 pm +/- 1.0 pm found by fitting the data from (a). Note that fluids were exchanged between measurements 2 and 3 as well as 4 and 5.

9.1 (a) CP transmission power and (b) derivative of CP transmission power as a function of incident polarization angle with respect to the PCS axes, for unit cell with r = 100 nm and a = 980 nm.

9.2 (a) Change in CP transmission power and (b) change in quality factor as a function of tilt for unit cell with r = 100 nm and a = 980 nm.

9.3 Change in resonance line shape as a function of tilt for unit cell with r = 100 nm and a = 980 nm.

10.1 Optical images of (a) a novel triple-mesa showing honeycomb configuration and (b) closer view showing 4 μm decoupling gaps.

10.2 (a) Spectral measurement of TM-like GMRs (a) when single mesas are excited and when all are excited with a single beam. (b) Sum of individual measurements overlayed with all resonances excited with single beam demonstrating successful decoupling.

10.3 (a) CP transmission measurement and (b) direct transmission measurement of TE-like GMR for air-substrate PCS device with air above.

10.4 (a) CP transmission measurement and (b) direct transmission measurement of TE-like GMR for air-substrate PCS devices with Cargille immersion oil with RI of 1.30 above.

10.5 CP transmission measurement of TM-like GMR for air-substrate PCS device with Cargille immersion oils.

10.6 (a) Construction of power differential referencing line shape from the Fano resonances of a suspended PCS and (b) the change in line shape as a result of a shift to the resonance of the active sensor.
10.7 Subtracting the resonance peak from the notch height provides a linear relation to resonance shift over an 130 pm range when (a) subtracting peak 1 or (b) subtracting peak 2.

10.8 (a) Transmission spikes observed during fluid interchange and (b) diagram with the laser spot shown in red and the point in the fluid exchange process when the transmission spikes occur.
Chapter 1

Introduction

Explosion of research in the area of optical biosensing has been driven in large part by the need for diagnostic tools that require little training to operate, can perform analysis quickly, are low cost, and can be packaged into portable devices [1 2 3 4 5 6 7]. This need exists for a range of developing applications in modern medicine. One such application is emergency response to viral outbreaks, where the ability to immediately determine whether a patient is infected on the spot would serve to significantly improve containment. In addition, strain from rising health care costs has motivated a move towards home health care where infrastructure costs are greatly reduced and health care needs can be addressed with minimal medical expertise. Here the benefit of optical biosensors would be to provide affordable diagnostic monitoring within the home that could carried out by a caregiver or directly by the patient. However, arguably the most valuable application for such diagnostic tools will be to improve to the quality of life for people living in developing regions and remote territories. In these communities, infrastructure of the type found in modern developed cities is simply non-existent. Often people must make long journeys to receive medical attention and in the case that diagnostic tests are performed it may take several weeks to know the result. The outcome is that patients will often forgo medical treatment or leave without being diagnosed as the logistics become impracticable. A portable diagnostic system of the type described here would allow for rapid on the spot diagnosis and could be operated by someone with no medical background [8]. The efficacy in containment of diseases such as HIV by performing regular testing in a simple and cost-effective way would be truly monumental.
Chapter 1. Introduction

1.1 Methods of Biosensing

The biosensing of interest to this thesis, with the applications described above, operates by extraction of a fluid or biological material and subsequent analysis outside of the body. This type of biosensing, where the sample of interest is isolated from its natural environment (i.e., the body) and then analyzed, is known as \textit{in vitro} diagnostics. Currently, clinical diagnostics of this type first chemically amplify the analyte of interest, which can be a virus, DNA strand, molecule, or cell, and then labels this amplified analyte with a marker that provides a signal that can be detected. An example that illustrates the principle of chemical amplification is polymerase chain reaction (PCR). PCR is a process whereby a sample of DNA is replicated by a biochemical process to increase its concentration by several orders of magnitude. The biochemical mechanism relies on an enzyme to replicate DNA in the sample from small fragments of DNA that are added in solution. The result is exponential growth in DNA concentration. Once the concentration of DNA is increased sufficiently, a biochemical tag that attaches only to the DNA of interest is added. This tag includes a fluorescent label that allows the presence of the DNA of interest to be determined, by monitoring the fluorescent signal \cite{1}. Methods such as PCR are extremely powerful for detection of small analyte concentrations. However, fluorescent detection is inherently a lab-based biosensing method as it requires a complex process of chemical amplification and attachment of fluorescent labels. These processes must be carried out by highly trained personnel in a laboratory environment and thus do not meet the needs described here.

1.2 Label-Free Sensing

Label-free biosensing offers a significant advantage over fluorescent techniques, in terms of automation, as it does not require chemical amplification or labeling with fluorescent molecules. Moreover, it avoids the problems that arise from altering the surface characteristics of the analyte by attachment of fluorescent markers, which in turn alter binding behavior. Label-free methods rely on immobilized capture molecules that only bind to the analyte of interest and immobilize it on a surface. Once captured, the presence of an analyte can be determined by a variety of methods, including electrical, mechanical, chemical, and optical processes. The choice of methodology depends largely on the intended application. Of these available label-free processes, optical sensing has proven to be one the most sensitive methods and is also amenable to integration in low cost, automated, low power, portable systems \cite{2}.
Refractive Index Sensing

Label-free optical biosensors typically employ a resonator with a resonance that is sensitive to local changes in refractive index (RI). In such structures the resonant mode partially interacts with the sensing medium, and a change in RI of this sensing medium results in a frequency shift in the resonance. This change in frequency is treated as the sensing signal that allows for quantification of the change in RI. In the case of biosensing, capture molecules are immobilized on the resonator surface and when the analyte of interest binds to these molecules a local change in RI results, producing the resonance shift that allows for quantification of the analyte concentration within the sample [1]. The principle of operation for a generic optical RI biosensor is shown in figure 1.1.

In recent years the field of optofluidics, which combines optical detection and microfluidic systems, has developed to include optical bio-sensors integrated with microfluidics [4]. Optofluidics provide high sensitivity and real-time analyses of small sample volumes, beneficial for efficient point-of-care diagnostics. Currently realized chip-scale RI optical biosensors span a wide range of technologies [9]. One of the most important figures of merit is the detection limit (DL), which is defined as the smallest change in RI that can be differentiated from measurement noise. Many of the existing RI biosensors possess low DL but are usually limited in their sensing area, require complex fabrication procedures, challenging functionalization, and are sensitive to the incident angle or polarization of incoming light.

Some examples of RI sensors that are suited to optofluidic implementation are ring resonators, microtoroids, fiber gratings, Mach-Zehnder interferometers, photonic crystals, and surface plasmon resonance (SPR) platforms. Currently, SPR biosensors are generally considered the gold standard for label-free detection [10]. SPR provides excellent sensitivity, but requires a high power laser source for operation,
and elaborate detection system alignment, resulting in a complex, inefficient, and bulky device. This greatly reduces its feasibility as a portable diagnostic tool. In comparison, photonic crystal slab (PCS) biosensors potentially have equal or better sensitivity [11] while requiring very low power laser sources (< 1mW) for operation.

1.3 Photonic Crystal Sensors

Not only are PCS devices well suited to portable applications, but they also exhibit large sensing areas and simple free space coupling. Additionally, integration of microfluidics is straightforward as the PCS sensor can be located at the bottom of a flow channel, and in principle be read out by a miniature integrated laser and detector system [11, 13]. An envisioned monolithically integrated PCS biosensor is shown in figure 1.2. A miniaturized, low power, high sensitivity, flexible biosensor has the potential to substantially improve reliable health care access for people living in areas that lack sophisticated health care infrastructure. Such a device could also provide a very important tool for real-time monitoring of pathogenic threats, and reduce the burden placed on hospitals by providing home health care alternatives.

1.4 Thesis Content

Chapter 2 describes the physical principles of PCS structures. Chapter 3 describes the sensing characteristics of PCS devices and numerically investigates various structural architectures in terms of RI sensing. The fabrication processes used to produce the PCS devices characterized in this work are described in chapter 4. Chapter 5 discusses the experimental apparatus and procedures used to characterize the PCS systems under study. Temperature stabilization is investigated both numerically and experimentally in
chapter 6. Chapter 7 looks at the design and characterization of referencing schemes to reduce noise signals in RI measurements. In chapter 8, the experimental detection limit of current generation PCS devices integrated within a microfluidic system is determined. Current experimental limitations are discussed in chapter 9. Promising new directions in PCS research undertaken in this thesis are described in chapter 10. Finally, chapter 11 presents the major results of the work carried out in this thesis.
Chapter 2

Photonic Crystals

Photonic crystal structures are materials that transmit electromagnetic waves except in a specific range known as a photonic band gap. Photons in the wavelengths that fall within the photonic band gap are reflected rather than being transmitted. The concept of a photonic band gap in a photonic crystal is analogous to the concept of an electronic band gap in a semiconductor. In both cases the band gap phenomenon arises from the periodic structure of the material. In semiconductors the periodic units are atoms, and in photonic crystals the units are two alternating materials with different refractive indexes. These properties of photonic crystal structures were first described by John and Yablonovitch in 1987 [14][15].

The photonic crystals described by John and Yablonovitch are comprised of a periodic dielectric in three dimensions as shown in figure 2.1. This structure type results in a true photonic band gap in that electromagnetic waves at the resonant frequencies are confined in three dimensions. However as shown in the same figure the concept of photonic crystals can be extended to lower dimensions. The most simple version of a photonic crystal is a quarter-wave stack which consists of an alternating stack of two dielectric materials with different refractive indexes (RIs). At the interfaces between the two materials partial reflection occurs and reflected light that constructively interferes forms a resonance. Note that this is not a true photonic band gap. The correlate to three-dimensional photonic band gaps in lower dimensional structures are referred to as stop bands.

Photonic crystal can be described by Maxwell’s equations in the form suited to dielectric materials, where charge and current densities are zero. This description as given by Joannopoulos et al. assumes that the dielectric materials behave linearly, that the materials are non-dispersive, and they are lossless (have no absorption). Using these simplifications, and the periodicity of the photonic crystal, Maxwell’s
equations can be expressed as harmonic modes. By this method the Helmholtz equation for a photonic crystal can be derived, and can solved to find the supported electromagnetic modes given by $\mathbf{H}(\mathbf{r})$ [16].

$$\nabla \times \left( \frac{1}{\epsilon(\mathbf{r})} \nabla \times \mathbf{H}(\mathbf{r}) \right) = \left( \frac{\omega}{c} \right)^2 \mathbf{H}(\mathbf{r}) \quad (2.1)$$

2.1 Photonic Crystal Slabs

The devices under study in this work are the two dimensional realization of a photonic crystal, known as photonic crystal slabs (PCS). In this case a periodic variation in the dielectric materials RI exists in the plane of a slab while the direction normal to the slab is aperiodic. Typically such a structure is realized by etching a periodic pattern into a dielectric slab. In such a device the slab forms one of the periodic RI materials and the medium that fills the etched pattern forms the other. Typically this medium is either air or water. A PCS structure may be fully described according to its unit cell, as shown in figure 2.2. Here the etched pattern in a circle, however, it could be be a variety of other shapes such as a triangle, a square, a hexagon, and so on. In this work a circle is chosen as it more easily fabricated and also its symmetry reduces its sensitivity to polarization. A structure composed of a finite number of these unit cells, often referred to as a PCS mesa in this work is the physical realization of a PCS. The numerical realization of such a structure is composed of an infinite number of unit cells. However, when a sufficient number of unit cells are used, which for devices in this work is approximately 150 x 150 unit cells, physical devices show very close agreement with the infinitely periodic simulation case.

In 2002 Fan and Joannopoulos published a numerical analysis exploring the behavior of thin-film PCS produced in dielectric materials [17]. This findings of this work will be summarized in the following
2.1.1 Physical Principles

By forming an array of unit cells a two dimensional lattice of alternating indexes of refraction is created. Fan and Joannopoulos showed computationally that this periodic structure leads to frequency ranges in which leaky guided resonances will exist within the slab. At these frequencies incident free space radiation couples to propagating resonant modes within the slab.

We will consider the structures investigated in [17], which are composed of the unit cell previously mentioned. The slab material is silicon (n = 3.46) in air (n = 1). Units are given in terms of the lattice constant (a) of the cell, which allows for a more general description of behavior since the properties discussed are scale invariant. Therefore, frequency is given in units of $\frac{2\pi c}{a}$. The slabs considered have a thickness of 0.5a.

To understand how these leaky guided resonances form we can first consider the simple case of a uniform dielectric slab. The band diagram of the slab is shown in figure 2.3(a) and (b). Here the guided modes are plotted as a function of the in plane wavevector in reduced-zone scheme. Dark lines indicate doubly degenerate modes, while dashed lines show the singly degenerate modes. Modes are separated in figure 2.3(a) and (b) into even and odd modes, which are defined as such with respect to the plane of the slab. The lowest order even modes have their electric field in the plane of the slab. The lowest order odd modes have their electric field normal to the slab. These lowest order even and odd modes are commonly referred to as transverse electric (TE) and transverse magnetic (TM) modes. The light line, above which the radiation modes lie, is indicated by the light gray area. It is observed that some guided modes exist above the light line, but these modes cannot in fact couple to external radiation due
Figure 2.3: Band diagram in reduced-zone scheme for the (a) even and (b) odd modes of a uniform dielectric slab \((n=3.46)\) in air. Band diagram in reduced-zone scheme for the (c) even and (d) odd modes of a dielectric slab \((n=3.46)\) in air, with a periodic array of holes patterned to form a photonic crystal slab \([17]\).
to the structures continuous translational symmetry. Therefore these modes have an infinite lifetime. Note that the \( \Gamma \) point on the band diagrams indicates a normally incident wave with \( k \) vector parallel to the slab. At this point the guided modes are seen to converge (red circles in figure), forming a four-fold degeneracy.

Figure 2.3(c) and (d) shows how the band structure is altered with the introduction of a hole into the unit cell. Now the structures continuous translational symmetry becomes a discrete one, defined by the lattice constant. The result is a reduction in the degeneracy of the structures modes from doubly degenerate to singly degenerate. The modes above the light line are now able to couple to radiation, as the periodic hole array effectively acts as a phase matching structure for certain frequencies. Since these modes now couple to radiation their lifetime becomes finite and they can no longer be called guided modes. These *leaky* modes allow for radiation to be both scattered into and out of the slab structure. However, as these modes still confined much of their energy to the slab they are generally referred to as guided mode resonances (GMRs) to indicate their close relation to guided modes. Similarly the TE and TM modes are now referred to as TE-like and TM-like. It is observed that the previous four-fold degeneracy at the \( \Gamma \) point (red circles) is reduced to two doubly degenerate modes and two singly degenerate modes. These modes exhibit resonant behavior and it can be shown that the frequency of the modes is dependent on the radius of the circular unit cell hole, as well as the lattice constant, slab thickness, and material RIs.

It can be seen in figure 2.3(c) and (d) that in a PCS true guided modes with infinite lifetimes still exist. However, these modes exist below the light line and do not overlap with the GMRs. Therefore there is no interaction between the infinite lifetime guided modes existing below the light line and the GMRs created by introduction of holes into the slab.

### 2.1.2 Resonance Characteristics

Normal incident light is used to excite resonances in the PCS studied here. This light is scattered into the PCS by means of the periodic dielectric perturbation created by the patterning of holes. As discussed this light couples to leaky guided modes, which are referred to as GMRs, that resonant with in the slab. There are many GMRs at various frequencies that can be excited in a PCS, as shown in figure 2.4. Here the lowest frequency modes, and correspondingly the longest wavelength modes, are the fundamental TE-like and TM-like modes.

The complex transmission behavior of figure 2.4 can be understood as the combination of two different resonant processes. The slowly varying amplitude indicated with red circles is simply a Fabry-Pérot (FP)
effect that results from interference between reflected and transmitted light at the two interfaces of the PCS slab. The reflection caused by the change in RI at the slab interface can be described by

$$R = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2$$

(2.2)

and the phase difference between the two sides of the PCS slab is defined as

$$\delta = \left(\frac{\omega}{c}\right) 2nl \cos \theta$$

(2.3)

Using equations 2.2 and 2.3 the transmission through a dielectric slab can be calculated as

$$T_{total} = \frac{(1 - R)^2}{1 + R^2 - 2R \cos \delta}$$

(2.4)

We see that the values for $r$ and $\delta$ depend not only on $\omega$ but on the values of $n_1$ and $n_2$, which are the RIs of air and the PCS respectively. The RI of air is constant for all frequencies but it can be shown the RI of the PCS will vary according to frequency with lower frequencies experiencing an RI which is close to the average RI of the PCS for low frequencies but that becomes closer to the RI of silicon at higher frequencies [17]. Using this frequency-depend RI the FP effect shown in figure 2.4 can be calculated.

It should be noted that in the PCS structures under study in this thesis (4) the $SiO_2$ layer and
the substrate also create FP effects. In fact, as discussed later the FP effect from the substrate creates significant measurement issues that must be addressed.

As mentioned the transmission behavior of the PCS can be understood in terms of two resonant pathways. One pathway is the FP resonance as described above. This can be thought of as the direct pathway or the pathway that passes directly through the PCS. The second pathway is the one that scatters into the slab and excites GMRs as discussed in section 2.1.1. This pathway can be observed as the slowly decaying electric field in time domain analysis after the direct pathway transmission process has occurred. Looking at the time evolution of the electric field energy a Fourier transform can be performed on the slowly decaying field to reveal the typical Lorentzian resonance line shape as shown in figure 2.5. This is the indirect pathway. Therefore the line shape of a PCS results from interference between the direct pathway and indirect pathway. A very similar interference effect observed in atomic physics in commonly referred to as Fano resonance [18]. This Fano behavior has also been analyzed in plasmonic systems [19]. Drawing from these ideas the PCS resonance amplitude can also be described as a Fano resonance [17] by the following equation

\[ F(\omega) = A_0 + F_0 \left( q + \frac{2(\omega-\omega_0)}{\gamma} \right)^2 \left( 1 + \frac{2(\omega-\omega_0)}{\gamma} \right)^{-2} \]  \hspace{1cm} (2.5)

where \( A_0 \) is the direct transmission coefficient, \( F_0 \) is the amplitude of the resonance mode, \( q \) is the coupling parameter, and \( \omega_0 \) and \( \gamma \) are the center frequency and line width of indirect pathway resonance. The Fano equation 2.5 for PCS line shapes is used throughout this thesis for analysis of simulation and experimental data.
Chapter 3

Simulation

For the purposes of this thesis the behavior of the devices under study is predicted using numerical simulation methods. These methods combined with custom written analysis scripts allow for mapping of the relevant parameter space for PCS architectures. In this chapter numerical methods are used to predict guided mode resonance (GMR) spectral location, sensitivity, quality factor, and detection limit. In addition numerical simulation is used to understand the behavior of cross-polarization (CP) measurement and to determine the limitations of TM-like GMRs in substrate-bound devices. More advanced numerical methods are used in chapters 6, 7, and 10 to analyze more complex phenomenon such as temperature effects and GMRs in hybrid multi-resonator structures. Note that in the simulations that follow materials are treated as lossless at 1550 nm. This is of course not completely accurate but serves as a very good approximation for the materials considered. In addition, for all simulations a hole radius of 100 nm is treated as a lower bound for how small a hole can be. The reason is that below this limit fabrication errors become unacceptably large resulting in a poorly defined hole.

3.1 Simulation Tools

For the sake of brevity I will not describe in detail finite-difference time-domain (FDTD) or scatter matrix methods (SMM). Both methods are well established numerical approaches for electromagnetic simulation. For an excellent explanation of principles of FDTD the reader is referred to the textbook of Allen Taflage on the subject [20]. Likewise a good source for understanding the principles of SMM can be found in the original paper of Whittaker and Culshaw [21].
3.1.1 Finite-Difference Time-Domain Method

The FDTD method employs a discretized form of Maxwell’s equations to propagate electromagnetic fields through a discretized space composed of building blocks known as Yee cells \[22\]. The Yee cell exists as a square in two dimensional space and as a cube in three dimensional space. The boundaries of these cells are treated as the discrete electric field components while the magnetic fields components are normal to the faces. The method steps through discrete time and at each step the fields are updated according to fields of the neighboring cells at the previous time step. By this method fields are propagated through a discrete space in discrete time. FDTD is extremely versatile and puts little constraint on the type of geometry that can be simulated. At the same time computational requirements grow as a square function of the cell size in two dimensional space and a cubic function in three dimensional space. Therefore high resolution requirements come with a large computational penalty. FDTD was used to confirm the accuracy of SMM results for periodic structures such as those simulated in this chapter. However, FDTD is far too slow to simulate the large parameter spaces examined here and thus SMM was chosen as a more effective tool. In addition, FDTD was used to confirm the validity of the SMM split-mesa models used to simulate the structures examined in chapter \[7\].

3.1.2 Scatter Matrix Method

SMM is an electromagnetic propagation solver that is specifically adapted to solving layered three-dimensional structures that are periodic in the plane of layering. In this case the structure is modeled as a unit cell that is periodic in the x and y directions and aperiodic in the z-direction (see figure \[3.1\]). This is exactly the case for the PCS structures studied in this thesis, as described in chapter \[2\].
The SMM software used in this work was developed by Victor Liu at Stanford, and the program is known as the Stanford Stratified Structure Solver (S\textsuperscript{4}) \cite{23}. This method uses Fourier modal method (FMM) \cite{24} to expand the electromagnetic fields within each layer as eigenmodes. These eigenmodes are expressed by a Fourier basis in the plane of each layer, and are coupled to each other according to the refractive index pattern of the layers. In this way the layers are treated as infinitely periodic. Each layer can be thought of as a scattering matrix and these matrices are combined to form the complete structure by matching coefficients at the layer interfaces to satisfy field continuity conditions. Using this strategy an electromagnetic field can be propagated through such a structure.

For PCS structures this method offers a huge computational advantage over FDTD methods, while allowing for very high accuracy simulations. This simulation tool is used predominantly in this thesis due to its efficiency and accuracy. FDTD was used to confirm the results in certain cases where unusual structures needed to be simulated, such as the devices in chapter 7.

3.2 Resonance Fitting

The structures under design in this thesis require high precision analysis of simulation data. It is necessary to determine both the GMR linewidth and resonance location as accurately as possible in order to quantify parameters such as sensitivity and quality factor. For example in chapter 6 changes in RI on the order of $10^{-5}$ RIU are examined. In chapter 7 accurate quantification is also critically important to balancing the reference and active sensors in terms of sensitivity and Q. SMM does not provide a time domain representation of electromagnetic propagation and therefore resonance attributes must be quantified by fitting of a lineshape to simulation results. Therefore an accurate fitting method is an essential tool to probe the behavior of the PCS designs under study.

As mentioned in chapter 2.1.2 the resonance lineshapes observed in PCS structures are a result of interference between the direct (FP) and the indirect (transmission) pathways. The result is a Fano lineshape that is described by equation 2.5. For evaluation of numerical results this equation is applied by least-squares curve fitting. Many variations of this algorithm were written, including ones for fitting multiple Fanos which were used to evaluate devices such as the power differential self-referenced PCS structure (section 7.4). A single Fano fitting version of this algorithm is included in appendix C.2.1. Figure 3.2 shows a Fano fit to simulation of a PCS structure that is similar to many of those studied in this work.

The combination of SMM and Fano fitting has allowed for quantification of resonance shifts on the order of femtometers as well as subtle changes in resonance linewidth. This ability has provided
3.3 Simulation Analysis of General Device Types

This section presents computational analysis of three general types of PCS architecture. In all three cases the PCS slab design is effectively the same, and follows the geometry described in section 2.1.2.

The device type that is of primary focus to this thesis is the substrate-bound PCS. In this case the 260 nm SiN\textsubscript{x} PCS slab has a 2.35 \( \mu \)m layer of SiO\textsubscript{2} below it and the silicon substrate beneath that. Suspended symmetric architecture is a design type that has been previously numerically investigated by El. Beheiry and shows potential in terms of enhanced sensitivity \[11\]. In this case the SiN\textsubscript{x} PCS is completely suspended with the sensing medium surrounding it. Unfortunately, issues of mechanical robustness confound actual fabrication of such devices, and they have not been characterized within our group. A brief analysis is included here for completeness and also to allow for comparison to a potentially more promising device that is also more amenable to fabrication. This device type is the air-substrate architecture which consists of a 260 nm SiN\textsubscript{x} PCS that is sealed on one side by a very thin SiN\textsubscript{x} layer. The result is an air-like substrate rather than an SiO\textsubscript{2} substrate as with the substrate-bound architecture.
Sensing Metrics

In the following sections SMM along with the Fano fitting method described previously is used to determine the GMR peak location and the full-width at half-maximum (FWHM). The FWHM and GMR center wavelength ($\lambda_{peak}$) are used to compute quality factor (Q) by

$$Q = \frac{\lambda_{peak}}{\text{FWHM}} \quad (3.1)$$

Sensitivity (S) is computed by varying the refractive index of the sensing medium and quantifying how far the resonance shifts ($\delta\lambda$) for a given change in RI ($\delta n_{\text{liquid}}$),

$$S = \frac{\delta\lambda}{\delta n_{\text{liquid}}} \quad (3.2)$$

When evaluating the performance of an optical RI sensor it is not sufficient to look at Q or S alone. The most important metric is the detection limit (DL), which indicates the smallest change in RI that can be reliably measured. The DL is often described by the equation

$$DL = k \frac{R}{S} = k \frac{\Delta\lambda}{S} = k \frac{\lambda_{peak}}{QS} \approx \frac{1}{QS} \quad (3.3)$$

where $\Delta\lambda$ is the GMR FWHM and $\lambda_{peak}$ is the center wavelength. Equation 3.3 follows the DL analysis of optical RI sensors given by White et al. [6]. In this case $k$ is a dimensionless proportionality constant that describes the sensor resolution (R) as a function of $\Delta\lambda$. Therefore $k\lambda_{peak}$ describes the smallest shift in wavelength that can be accurately determined for a given sensor. Substituting the Q definition of equation 3.1 DL is given as $k \lambda_{peak} QS$. Taking into account, laser wavelength ambiguity, thermal noise, power fluctuations, and Q for the devices under study, $k\lambda_{peak}$ can be approximated as one [6]. Therefore the DL is given as approximately the inverse product of Q and S. Since this approximation assumes typical variance values for the noise parameters mentioned and ignores other noise sources such as mechanical stability of the sample, this metric cannot perfectly describe what is experimentally realizable. However, since it is applied universally in this work it gives a standard metric of comparison between the device types investigated. For devices investigated in the following pages Q, S, and DL are compared for various architectures.

Fundamental GMRs

When looking at the simulation results that follow it is instructive to keep in mind a picture of the profile of the electric field energy ($\epsilon |E|^2$) for the fundamental GMR types. Figure 3.3 shows $\epsilon |E|^2$ in
Figure 3.3: (a) Fitted resonance and $\epsilon|E|^2$ in the cross-section of a unit cell for a TE-like GMR in a PCS with radius = 100nm and lattice constant = 980 nm. (b) Corresponding figure for a TM-like GMR in a PCS with radius = 240nm and lattice constant = 1010 nm.

3.3.1 Substrate-Bound Architecture

Substrate-bound PCS devices are the primary focus of experimental work in this thesis. Therefore significant emphasis is given to the simulations of this architecture. This device type was chosen for
Chapter 3. Simulation

characterization of sensing metrics and development of referencing and athermal devices due its mechanical robustness, straightforward fabrication, and excellent agreement with simulation predictions in the case of TE-like modes. These samples consist of a 260 nm thick SiN$_x$ PCS on a 2.36 $\mu$m thermally grown SiO$_2$ film on an Si wafer. There is nothing special about these specific numbers. The SiN$_x$ value is in the acceptable range of values for a PCS device operating at wavelengths near 1550 nm, but the SiO$_2$ thickness is in fact not suitable to designs using TM-like modes, as will be discussed. These values are used for simulation as they are the values of the provided wafers used for experiments. Likewise the parameter space explored is limited to that which results in GMRs in the range of 1480 - 1590 nm, which corresponds to the wavelength range of commonly available tunable laser sources. The sensing medium used is water, which has a RI of 1.315 at 1550 nm (see chapter 6). The RI values used for SiN$_x$, SiO$_2$, and Si are 2.00, 1.46, and 3.48 respectively, which are the values for 1550 nm wavelengths at room temperature.

In this section the parameter space for hole radius, lattice constant, and slab thickness in terms of their effect on sensing metrics is explored. The fundamental TE-like and TM-like GMRs are explored separately. In the subsection on TM-like GMRs the rationale is given for the choice made in this thesis to focus on TE-like GMRs.

It should be noted that for all the graphs that follow where data points are represented by an open circle this circle indicates the result of a simulation that was performed for a given set of values. In the case where the data being shown is sensitivity two simulations were performed, with the sensing medium having either the RI value of 3.15 (water) or 3.18. The shift in the GMR location was then calculated as shown by equation 3.2. Note that the linearity assumption for sensitivity can be shown to hold true for over 0.2 RIU with both TE-like and TM-like GMRs.

**TE-like Modes**

Referring back to figure 3.3 we observe that the TE-like mode has a significant field presence in the holes of the dielectric slab. As a result significant scattering occurs in the hole region of the PCS, which limits the lifetime or Q of the resonance. It would be expected that as the hole radius is reduced the Q would increase due to reduced scattering. Conversely a reduction in hole radius, and thus reduction in interaction with the sensing medium, would lead to a reduction in sensitivity as changes in the sensing medium RI would have a lesser effect on the GMR. In figure 3.4(a) the effect of varying the hole radius in a substrate-bound PCS is shown for values from 100 and 300 nm. It can be seen that sensitivity exhibits a linear response to change in radius while Q shows an exponential response. This can be restated in the following way: S is roughly proportional to the hole perimeter while Q is inversely proportional to the
Figure 3.4: (a) TE-like GMR quality factor and sensitivity as a function of radius and for unit cell with \(a = 980\) nm. (b) TE-like GMR detection limit as a function of radius for unit cell with \(a = 980\) nm

hole area. The effect on \(Q\) can be thought of in terms of increasing the area occupied by scattering centers in the PCS (i.e., the holes). The change to \(S\) can be thought of as a change to the length of the interaction area with the sensing medium. This length of interaction area is the hole perimeter. It is observed that decreasing the hole radius from 300 to 100 nm increases the \(Q\) by a factor of 16 while decreasing \(S\) by a factor of 1.5. Since DL is given as the inverse product of \(S\) and \(Q\), the result is that DL is proportional to the hole radius as shown in 3.4(b). Therefore if a low DL is the end goal the smallest radius that can be reliably fabricated should be chosen. In the case of this work that radius is chosen to be 100 nm. As we can see this corresponds that a theoretical detection limit of \(2 \times 10^{-6}\).

Note that for the structures shown in figure 3.4, a lattice constant of 980 nm was chosen such that the TE-like GMRs for radii from 100 to 300 nm are within the wavelength range of a typical communication band tunable laser. The spectral locations of the resonances from the previous figure are shown in figure 3.5(a). Like with sensitivity the resonance wavelength shift is also linearly proportional to the radius. In fact figure 3.5(a) and figure 3.4(a) show two results of the same phenomenon, which is that as the radius increases the percentage of the electric field energy, \(\epsilon |E|^2\) that exists in the sensing medium increases proportionally. This lower effective RI experienced by \(|E|^2\) results in a blue shift (shift to shorter wavelengths) of the resonance, while at the same time the increase in \(|E|^2\) existing in the sensing medium results in greater sensitivity to changes in RI.

Once a desired hole radius has been chosen it is often useful to place the associated GMR of interest into the center of the available scanning range of the tunable laser. This can be achieved by changing the unit cell lattice constant. In figure 3.5(b) the GMR location of a PCS with a hole radius of 180 nm is given as a function of the lattice constant length. First of all we see that the behavior is linear, but
more significantly we can see that the GMR location is extremely sensitive to the lattice constant, with a wavelength shift of 1.5 nm for a change in lattice constant of 1 nm. On the other hand figure 3.5(a) shows that a change in radius of 1 nm only shifts the resonance center wavelength by 0.4 nm, meaning that the resonance location is approximately 4 times more sensitive to lattice than radius. This is important to keep in mind when considering fabrication errors, especially when precise spectral placement is critical such as for the structures in chapter 7.4.

If tuning of the resonance location is to be done by varying the lattice constant then it is important to consider how this will effect Q, S and ultimately DL. Figure 3.6 addresses this question. In figure 3.6(a) we see that changes in lattice constant have a roughly linear effect on both Q and S. To understand what is happening here we must consider how a GMR propagates within a PCS. The GMR does not spread out in all directions from an excitation point. In fact it can only propagate only the two axes defined by the lattice constant. Therefore when considering Q if we extend the concept of the hole being a scattering center it should be expected that as the lattice constant, or distance between scattering centers (holes), is increased the Q increases proportionally. This trend is expected to be linear as seen in figure 3.6(a), however the sign is the opposite of what is expected. It turns out that the Q decreasing, rather than increasing, with increasing lattice constant. To understand this we recall that the GMR wavelength redshifts (increases in length) by 1.5 nm for a change in lattice constant of 1 nm. Therefore although the physical distance between holes is increased, the distance experience by the electromagnetic wave is actually decreased since the wavelength has increased more than the lattice length. Similarly it is counterintuitive that S would increase in response to an increase in lattice constant since an increase in lattice constant means that less area is occupied by the holes. However, simulation shows an increase
Chapter 3. Simulation

Figure 3.6: TE-like GMR quality factor and sensitivity as a function of lattice constant for unit cell with \( r = 180 \text{ nm} \). (b) Detection limit as a function of lattice constant for unit cell with \( r = 180 \text{ nm} \)

in S. Here, as with Q, it is wavelength scaling that outperforms the change to geometry. Although the hole area is in fact reduced, the longer wavelength GMR is now less confined in the PCS, resulting in a small overall boost to S.

The lattice constant effect is interesting in its counterintuitive nature. However, for the purposes of this work it is used as a tuning parameter to bring the GMR within a desired spectral window. Therefore the main concern is how tuning with it effects the performance of a device. Since it has a roughly linear effect on Q, S, and DL it does not complicate design considerations. Moreover, as can be seen in figure 3.6(b) changes in the lattice constant result in a very small change to DL, even when tuning over a very large spectral region. Therefore in the analysis of the other devices in this chapter lattice constant effects are not considered.

It has been established in this section that for the TE-like GMR of substrate-bound structures the increase in Q that results from decreasing the hole radius far outweighs the loss in S. In fact we will see that this principle applies to all structures shown in this chapter. However, this does come with a few caveats. The most significant one is that Q cannot be increased arbitrarily in a real structure. In chapter 9 I seek to established a practical upper limit for Qs that can be achieved in devices made using current fabrication procedures and measurement techniques. As a guide to analyzing the structures in the following sections that number for Q is approximately 10 000.

TM-like Modes

Referring again to figure 3.6 we observe that the TM-like mode has very little field presence in the holes of the dielectric slab. As was discussed the TE-like mode undergoes significant scattering as a
result of its interaction with the slab holes. The TM-like mode on the other hand scatters very little in comparison. In the TM-like mode the electric field exists mostly normal to the slab. As can be seen in figure 3.7(a) the reduced interaction with the holes provides a huge boost to Q, over that of TE-like GMRs, of approximately 30x for a given radius. Again the same exponential relation to radius is observed for the TM-like Q as a result of scattering from the holes. However, the behavior of S is distinctly different for the TM-like mode. Overall the change in radius has little effect on S, with it changing by only 5% when the radius goes from 100 nm to 300 nm.

As a result of the high Q nature of the TM-like mode a very low DL of approximately 1x10^{-7} RIU (figure 3.7(b)) is predicted for a hole radius of 100 nm. This is over an order of magnitude improvement compared to the TE-like mode with the same radius. However, the TM-like Q is about 80 000 for an r of 100 nm, which is almost certainly not realizable due to fabrication limitations. A Q under 10 000 should be the aim for a practical device. With this consideration the TM-like mode does not significantly outperform the TE-like one in terms of DL.

For completeness the resonance wavelengths for the simulations in figure 3.7 are given in figure 3.8. It can be noted that hole radius has a much smaller effect on resonance location than in the TE-like case, which is not surprising given the transverse nature of the TM-like mode.

The simulations in figures 3.7 and 3.8 were carried out assuming an infinite SiO_2 thickness. In fact for the 2.35 μm SiO_2 layer used in this study the TM-like modes are not well supported. As we have seen the modes extend significantly into the sensing medium and the SiO_2 (figure 3.3). In fact, they extend preferentially into the SiO_2 due to its lower RI contrast. Therefore it is important to have a sufficient thickness of SiO_2 such that negligible energy reaches the Si substrate. If the mode interacts
Figure 3.8: TM-like GMR peak location as a function of radius for unit cell with $a = 1010$ nm

Figure 3.9: (a) TM-like GMR lineshape and (b) percentage of light reflected on resonance as a function of SiO$_2$ thickness for unit cell with $r = 150$ nm and $a = 1010$ nm

with the high RI substrate significant energy will be lost as shown in figure 3.9(a). Broadening of the resonance and loss of power is observed as the SiO$_2$ thickness is reduced below 4 $\mu$m. In figure 3.9(b) the percent of power reflected on resonance is plotted as a function of SiO$_2$ thickness. It shows that for a 2.35 $\mu$m SiO$_2$ layer approximately 90% of the power is lost to the substrate. Furthermore, this power loss is a function of Q with higher Q resonances losing more power. Therefore as this substrate interaction makes it very hard to predictably design TM-like substrate-bound PCS devices the focus of the experimental work presented on substrate-bound devices in this thesis employs TE-like modes.

3.3.2 Suspended Symmetric Architecture

In this chapter suspended symmetric PCS devices are analyzed. This device type is so named because the PCS is freely suspended within the sensing medium, meaning that no substrate is present and both
sides of the PCS are exposed to the sensing medium. In the case of substrate-bound devices the substrate severely limits sensitivity as the electric field energy is preferentially drawn into the material that presents the lower index contrast. In the case of the substrate-bound devices studied here that material is SiO$_2$. Therefore by removing the substrate and surrounding the PCS with the sensing medium S is increased over two fold. The result for TE-like modes is shown in figure 3.11. Here S increased by a factor of approximately 2.5 while Q remains roughly unchanged. The result is a reduction in DL over substrate-bound devices that is approximately proportional to the increase in S (figure 3.11(b)).

Likewise the TM-like mode can be supported in a suspended structure and in this case S is increased by a factor of nearly 4. Q on the other hand is reduced by approximately 2. However, referring back to the the limitation on Q of 10 000 we see that with a corresponding radius of 260 nm a DL of 12x10$^{-8}$ RIU can be achieved. For the same Q in the substrate-bound device with a TM-like mode a DL of 6x10$^{-7}$ RIU was possible. Therefore, in a practically realizable device the suspended symmetric architecture provides a 2.5x improvement in DL for TE-like modes and a 5x improvement for TM-like modes. However, a major caveat to keep in mind is that the sensing area is also doubled in this suspended design type over substrate-bound devices. In terms of biosensing the sensitivity per unit area may be a more relevant parameter than the overall sensitivity.

3.3.3 Air-Substrate Architecture

The suspended symmetric architecture shows potential to improve the sensitivity of current devices. However, it comes with a few substantial caveats. First the suspended membrane is inherently fragile
Figure 3.11: TM-like GMR quality factor and sensitivity as a function of radius for unit cell with $a = 1080$ nm. (b) TM-like GMR detection limit as a function of radius for unit cell with $a = 1080$ nm.

Figure 3.12: (a) TM-like GMR electric field in air-substrate device for unit cell with $a = 1110$ nm, $r = 200$ nm. (b) TE-like GMR electric field in air-substrate device for unit cell with $a = 990$ nm, $r = 100$ nm.
Figure 3.13: (a) TE-like GMR quality factor and sensitivity as a function of radius for unit cell with a = 990 nm. (b) TE-like GMR detection limit as a function of radius for unit cell with a = 990 nm

and in order to achieve a practical Q the hole radius should be at least 260 nm. This means over 20% of the PCS surface is filled by holes, further increasingly fragility. Making matter even more complicated a flow-through system is required so that the sensing liquid can be brought from one side of the PCS to the other. Finally, the boost in S is in a large part attributed to doubling the sensing area.

The air-substrate device presented in this section seeks to address the drawbacks of the suspended symmetric device while at the same time maintaining the benefits. This is achieved effectively by applying a thin (50 nm) SiN\textsubscript{x} slab to the back of a suspended symmetric sample (details: 4.4.1). The result is increased robustness due to the support of the SiN\textsubscript{x} slab. In addition the slab serves to seal the backside of the PCS so there is no leaking and a flow-through system is not required. The air-substrate architecture works by the principle that on the side of the PCS with the thin SiN\textsubscript{x} slab the electric field of the TM-like mode experiences an effective RI that is close to that of air. The result is that the field is pushed almost entirely into the sensing medium as it provides a substantially smaller index contrast. The TM-like GMR $\epsilon|E|^2$ of an air-substrate device is shown in figure 3.12(a). Here it can be seen that almost no electric field exists in the thin SiN\textsubscript{x} slab, and the electric field is pushed substantially into the sensing medium as compared to figure 3.3(b). However, the in-plane TE-like GMR for the air-substrate design does have substantial electrical field energy in the thin slab (figure 3.12(b)).

It can be seen from figure 3.13 that the air-substrate design doesn’t provide much benefit to TE-like modes over substrate-bound devices. Here Q is boosted by approximately 25% and S by 12%. Correspondingly DL sees a boost of about 18%. However, figure 3.14 tells a much different story. Here an improvement in S similar to that of the symmetric suspended device occurs. In fact an air-substrate structure with a TM-like Q of approximately 10 000 achieves a corresponding DL of $15\times10^{-8}$ RIU which
Figure 3.14: (a) TM-like GMR quality factor and sensitivity as a function of radius for unit cell with \( a = 1110 \text{ nm} \). (b) TM-like GMR detection limit as a function of radius for unit cell with \( a = 1110 \text{ nm} \) is very close to the \( 12 \times 10^{-8} \text{ RIU} \) achieved in the suspended symmetric design.

Therefore in TM-like modes the air-substrate design gives performance comparable to the suspended symmetric design, while providing mechanical robustness and straightforward flow-over microfluidics integration. In addition since the air-substrate sample only uses one side of the PCS as opposed to the symmetric sample it has nearly double the sensitivity per unit area. This factor is very important in terms of biosensing, where low quantities of an analyte must be detected.

### 3.4 Crossed-Polarization Effect

Crossed-polarization (CP) is an experimental measurement technique wherein the PCS is placed between two orthogonal linear polarizers. The polarizer that is in the path between the incident laser beam and the PCS is oriented such that linearly polarized light excites the sample. The second orthogonal polarizer will block the transmission of all light that does not undergo polarization conversion. This means FP oscillations caused by the substrate of substrate-bound devices will not be transmitted. However, it has been demonstrated that GMR of PCS undergoes polarization conversion, at least in certain cases, and this light that undergoes conversion will therefore be transmitted \[25, 26\]. This technique has proven to be extremely effective in removing FP noise from substrate-bound PCS devices, resulting in huge improvements in detection limit \[27, 28\]. Indeed, for all devices characterized in this work, other than those that were suspended, CP is not only an asset but is necessary to making a meaningful measurement. Therefore, since the CP method is needed and it also introduces further complexity to measurements it is fundamentally important to understand how it can be optimized and what pitfalls should be avoided.
Although this phenomenon has been studied experimentally, to the author’s knowledge the mechanism of operation has not been described.

Here it is proposed that the mechanism of polarization conversation is the ellipticity of the holes of the PCS. At first glance this seems to be a tenuous claim, as it would require that every PCS that has been measured using CP, in various labs all over the world, exhibits this ellipticity. However, as will be shown the requirement for ellipticity in this situation is sufficiently loose to apply to any fabricated PCS device.

It can be shown that the fundamental GMRs of a PCS may only propagate along the two orthogonal directions axes where the holes are spaced by the design lattice constant. In other words the GMRs may not propagate along an arbitrary vector. The allowed axes of propagation are shown on an scanning electron microscope (SEM) image of a fabricated PCS structure in figure 3.15 (a). For the purposes of this
Chapter 3. Simulation

description the ellipticity requirement is that the radius along one axis of propagation is not identical to
the radius along the orthogonal axis. It is sufficient to define these two radii by the average radius along
each axis. In a fabricated structure these two radii will never be identical due to errors associated with
fabrication. Such errors include discretization of the device pattern in creating the lithography mask
or for e-beam writing, the inherent resolution limit of the photoresist, imperfections in the material
comprising the PCS, and sample tilt during reactive ion etching (RIE) etching to name a few. Simply,
it can be stated that it is not possible to fabricate a perfect circle.

For the simulations shown in this section the simulation space is defined according to the unit cell
shown in figure 3.15(b). Here \( r_1 \) and \( r_2 \) are defined as the radii along the x and y axes respectively
which are the orthogonal axes of propagation. The PCS is excited by a linearly polarized electromagnetic
wave \( (|E_x|^2) \) that is polarized along the x axis in figure 3.15(b). The electrical field with orthogonal
polarization along the y axis is recorded \( (|E_y|^2) \) is recorded. In simulation the axes of the lattice are
rotated with respect to the polarization axis (figure 3.15(c) shows the hole rotated by 45\(^\circ\)). This exactly
simulates the experimental situation where the PCS is placed between two crossed polarizers and is free
to be rotated with respect to the polarization axis. However, the sample could be fixed and the incident
polarization and recorded polarization polarizations could be rotated. This is situation is physically
equivalent. Therefore, rotation in this context simply means rotation of the lattice axis with respect to
the axis of polarization.

For the first simulation the field component \( |E_y|^2 \) is recorded as the PCS is rotated. The polarization
of the incident field is shown in red in figure 3.15(b). A 0\(^\circ\) rotation corresponds to the incident field
polarization being aligned along the \( r_1 \) axis and along the \( r_2 \) axis for 90\(^\circ\). Note that for illustrative
purposes the ellipticity of the hole shown in figure 3.15(b) is greatly exaggerated with the simulation
values for \( r_1 \) and \( r_2 \) being 100 nm and 102 nm, respectively. This difference of 2 nm is chosen as a number
in the range where simulation resolution limits do not lead to numerical dispersion. However, it is also
chosen because 2 nm corresponds to the highest resolution currently available with e-beam fabrication,
and it is therefore considered as an ultimate upper limit on resolution when fabricating a PCS. The
device simulated is of the substrate-bound type (as are all devices simulated in this section), with a
lattice constant of 980 nm, a thickness of 260 nm, and the PCS material is \( SiNx \). This corresponds to
a typical experimental device in this work.

The simulated CP transmission that occurs when rotating the PCS sample as described is shown in
figure 3.16. Only the angles from 0\(^\circ\) to 45\(^\circ\) are shown as the transmission results from 45\(^\circ\) to 90\(^\circ\) are
identical. We note that when polarization is aligned with one lattice axis (0\(^\circ\) or 90\(^\circ\)) no transmission
occurs, and transmission is maximized when polarization is split between the two axes (45\(^\circ\)). Referring
Figure 3.16: Simulation of CP transmission as a function of rotation of the unit cell (3.15(b)) for TE-like GMR in structure with $r = 100$ nm and $a = 980$ nm.

To figure 3.17(a) we see that the rotation dependence of CP peak transmission amplitude has been observed experimentally by Altug et al.\[28\], with the amplitude varying sinusoidally as a function of rotation angle. By plotting the peak amplitude of the simulated CP effect as a function of rotation angle (figure 3.17(b)) we see the very same phenomenon as was observed by Altug et al.

It is important to note that when a perfect circle is simulated no CP transmission occurs, regardless of the sample rotation angle. Hole ellipticity and a rotation angle that couples incident radiation along both propagation axes are strict requirements to observe polarization conversion.

The elliptical hole rotation simulation demonstrates numerically the mechanism of CP transmission. However, an analytical description is beyond the scope of this thesis. A qualitative argument can be made by considering the GMR propagation in the PCS, which is shown in figure 3.18 for a rotation of 45°. Here the region of GMR propagation (light red) is indicated for a focused excitation source (dark red). I propose that polarization conversion results from strong coupling in the region where orthogonal GMRs overlap. Further analysis is certainly required to validate this postulation, but the requirement of having two slightly different radii, and correspondingly two slightly different GMRs, to observe CP transmission is highly suggestive that coupling results in polarization conversion. Furthermore, when two decoupled PCS structures with slightly different radii (as in chapter 7) are simulated no CP transmission
Figure 3.17: (a) Experimental result achieved by Altug et al.\cite{27, 28} showing variation in peak CP amplitude in PCS as a function of rotation angle. (b) Peak amplitude of the simulated CP effect as a function of rotation angle

is observed when the holes are circular. This indicates that polarization conversion occurs in the PCS slab and not in free space. Finally it is observed that CP transmission is maximized when power is equally split into orthogonal GMRs.

From an experimental point of view it is important to understand how phenomenon unique to the CP measurement process can effect experiments. For example, from the previous results it is not clear how CP effects the Q of the resonance as compared to direct transmission (with no polarizers) and it is also not clear whether Q has an angle dependence in CP measurements. In fact, both of these questions are answered by figure 3.19(a). Here we see that at $5^\circ$ and $85^\circ$ the Q is maximized. Referring back to figure 3.16 we see that this is the case when transmission power is minimized. In fact at these rotation angles transmission power is reduced by over an order of magnitude, while Q increases by approximately 13%. In some cases where signal to noise is not a concern this gain in Q may be worthwhile. However, one should also be aware that this is the regime where Q changes most rapidly as a function of rotation angle. Therefore, in terms of Q stability a $45^\circ$ rotation is the optimum operational point. Happily, this rotation is also the point were CP transmission power is maximized and is most robust to changes in rotation. Interestingly, if we compare the Q values between direct transmission and CP transmission for the same structure with a hole radius of 100 nm and lattice constant of 980 nm we see that CP provides a significant boost to Q. In this case the direct transmission Q value is approximately 3300 while the lowest CP value is 4600, providing a 40% boost in Q.

Turning our attention to figure 3.19(b) we see how the ellipticity of the PCS hole affects the resonance lineshape in CP. The same parameters are used as in figure 3.16 but now $r_2$ is varied between being 105%
Figure 3.18: GMR propagation in a PCS with excitation polarization at 45°. The area of a focused excitation laser is shown in dark red, with GMR propagation along orthogonal axes shown in light red.

Figure 3.19: (a) Polarization dependence of Q using CP for TE-like GMR in structure with $r = 100$ nm and $a = 980$ nm. (b) Resonance splitting demonstrated by varying $r_2$ as a percentage of $r_1$ from 105% to 125%.
to 125% the length of $r_1$. Clearly resonance broadening occurs as the ellipticity increases. Moreover, in this case at the point where $r_2$ is 115% of $r_1$ the resonances begin to split. This splitting effect is dependent on the Q of the device. For example in high Q TM modes such as those discussed in section 3.3.1 resonance splitting can be observed for differences between $r_1$ and $r_2$ on the order of 1%.

It is interesting to note that in CP transmission ellipticity has a smaller effect than in direct transmission. For example, comparing the cases for $r_1$ and $r_2$ differing by 5% and 10% in the structure in figure 3.19(b), the direction transmission Q is reduced by 67% while in CP transmission Q is only reduced by 37%. This result suggests that the CP method is more resilient to fabrication errors - at least in terms of Q.

In addition to looking at how CP affects Q, it is also of experimental concern to consider how the resonance may be shifted by changes in rotation of the sample. Once again we return to the same structure with a radius of 100 nm and lattice constant of 980 nm. This time as the unit cell is rotated wavelength shifts of the TE-like resonance are calculated. This is done for the case of CP transmission as well as direct transmission, shown in figure 3.20(a) and (b), respectively. In figure 3.20(a) the maximum resonance shift is 0.14 pm for a rotation of 45°. This shift is completely insignificant experimentally considering that the linewidth is on the order of 300 pm. However, looking at figure 3.20(b) it is observed that the same rotation results in a resonance shift over two orders of magnitude larger. This shift would still not be of real concern since rotations of concern in experiments would typically be less than 1°. Regardless, it is interesting to observe that CP measurement seems almost immune to resonance shifts caused by rotation.

The previous simulations have explored some effects associated with CP that are of particular interest experimentally. It is observed that Q is significantly boosted in CP measurement.

Analysis of the CP phenomena shown above is very instructive for purposes of experimental optimization. In addition, it has led to the discovery of an optofluidic method to further enhance polarization conversion. The method, which is outlined in chapter 10.4, is analogous to the CP mechanism demonstrated here and shows phenomenal potential in terms of reducing the DL of PCS devices.
Figure 3.20: (a) TE-like resonance shift as a function of unit cell rotation in CP transmission and (b) direct transmission
Chapter 4

Fabrication

The sections in this chapter detail the steps that were taken to realize the devices studied in the previous chapters. The fabrication process described herein is typical of a thin film nanofabrication process. First the films are deposited on a silicon substrate and then the PCS pattern is defined by electron beam lithography (EBL). Finally reactive ion etching (RIE) is used to transfer the pattern to the thin film.

The fabrication of two general device types is described in this chapter. First is the substrate-bound device where the PCS structure rests on a SiO$_2$ film which in turn sits upon a silicon substrate. This device type is of primary interest to this thesis. However, a second device type that promises significant sensing improvement, as described earlier, is the air-substrate device described in the final section of this chapter. In this device a unique dual SiN$_x$ slab film process is used to allow the PCS to be suspended after fabrication using a potassium hydroxide (KOH) backside wet-etch process. The fabrication processes discussed in this chapter can be found in appendix B.

4.1 Film Deposition

Film quality and fabrication ease are of critical importance to realizing the devices under study. Films must provide low absorption at the wavelength of interest, biocompatibility, and must be amenable to standard CMOS deposition and patterning processes. For this reason silicon based films are used to construct the photonic crystals in this work. The majority of devices studied in this work are substrate-bound, which is to say that the films that compose the PCS remain attached to the silicon substrate on which they are grown. In this case the PCS structure is etched into a SiN$_x$ film of approximately 250 nm, resting on 2.36 $\mu$m of SiO$_2$ which is thermally grown on the silicon wafer. These film layers are depicted in figure 4.1.
4.1.1 Silicon Dioxide

A 2.36 µm thermal SiO₂ film is grown on a 100 mm < 100 > silicon wafer in a wet oxidation furnace at 1050-1100 °C. This process results in SiO₂ film on both sides of the wafer. The refractive index of wet oxidation grown thermal SiO₂ is typically 1.46 at 1550 nm [29]. This value for the samples under study has been previously confirmed in our laboratory [12].

The purpose of this film is to provide a low-index cladding on the back of the PCS. This serves two primary purposes. First, the film layer is necessary to isolate the GMR from the silicon substrate that would result in significant absorption. Secondly, as described in chapter [3], the evanescent field of the GMR exists preferentially in the material with a refractive index closest to SiNₓ. Since the sensing side of the PCS is exposed to water, with a refractive index of approximately 1.315 at 1550 nm and room temperature (see chapter [6]), the dielectric underneath the PCS should have as low a refractive index as possible. In addition this material should also be transparent at 1550 nm. For these purposes SiO₂ is a natural choice.

It should be noted that the thickness value of 2.36 µm has no special significance. Since the wafers used were oxidized in a batch process and 2.36 µm was sufficient to insulate the TE-likes GMRs from the substrate, this particular value was used for the experiments performed in this thesis.

4.1.2 Silicon Nitride

The SiNₓ layer is deposited on top of the SiO₂, and it is on this film that the PCS structure is patterned. The film used in this fabrication process is produced by means of low-pressure chemical vapor deposition (LPCVD). The volatile precursors used in this process are silane and ammonia. Ideally the products of this reaction are \( Si_3N_4 \) and H₂ gas. However, in practice there is not perfect desorption of hydrogen from the surface and the resulting silicon nitride film typically contains 2-3 at.% hydrogen [30]. Therefore
the film is referred to as $\text{SiN}_x$ to indicate that it is not a stoichiometric material.

Two major considerations affect the choice of material for the PCS structure. The primary consideration is the optical properties of the film. It is necessary that the material have low absorption at 1550 nm in order to allow for reasonable quality factors. The film must also be amenable to high resolution features with low roughness in order to minimize scattering. In addition, since high index materials lead to stronger confinement of the GMR, for sensing purposes a low-index material is ideal such that the interaction between the sensing medium and the electric field is maximized. Secondly, for suspended devices it is important that the film must be mechanically robust and under tensile stress such that it does not break or warp when the substrate is removed. $\text{SiN}_x$ meets both the optical and mechanical requirements imposed and thus is a suitable material for the structures of interest.

**Deposition Methods and Related Properties**

Silicon nitride films can be deposited by either LPCVD or plasma-enhanced chemical deposition (PECVD) processes. The processes differ primarily in the temperatures and a pressures required. LPCVD is typically done between 700 and 800 °C while LPCVD occurs at much lower temperatures between 300 and 400 °C [30]. Furthermore, as the name suggests LPCVD operates at low pressures of 20-70 Pa, while PECVD operates at pressures of 60-700 Pa. PECVD is suitable for depositing a $\text{SiN}_x$ film on one side of a sample, as in the case of an anti-reflective coating, since the sample sits flat on the sample chuck. This differs from the case of an LPCVD furnace where the sample is held upright and the resulting film is deposited on both sides.

The films that result from LPCVD and PECVD methods differ fundamentally in two ways: film stress and hydrogen content. Since hydrogen content is largely determined by deposition temperature [31] PECVD contains a much higher percentage of hydrogen than LPCVD. The amount of hydrogen for PECVD and LPCVD are typically 20 at.% and 3 at.% respectively. Hydrogen content in turn has a strong effect on the resulting $\text{SiN}_x$ film stress, with lower hydrogen content resulting in higher film stress.

Film stress for deposited materials can be described by the sum of the intrinsic stress caused by growth phenomena and the thermal stress that results from a mismatch between the thermal expansion coefficients of the substrate and the film. In the case of $\text{SiN}_x$ the dominant factor is the intrinsic stress. This intrinsic tensile stress results from hydrogen desorption that occurs at a rate that is slower than the rate limiting step of the $\text{SiN}_x$ deposition [31]. This means that hydrogen desorption continues after the deposition of silicon and nitrogen, which causes the material to shrink. Higher temperatures associated with LPCVD increase desorption and thus increase intrinsic tensile stress. On the other hand, relatively
low temperature PECVD SiNx films exhibit compression stress as a result of the mismatch between the thermal expansion coefficients of silicon and SiNx. Figure 4.2 illustrates the difference between tensile and compressive stress in thin films.

Low hydrogen content has two benefits for the devices of interest. The associated tensile stress results in a film that remains taught and does not deform when suspended. Therefore in suspended devices it is critically important to use SiNx to avoid buckling upon substrate removal. The second benefit of low hydrogen content is chemical robustness, which means that the film is not damaged by cleaning processes such as piranha (H2SO4 and H2O2) or substrate etching with potassium hydroxide.

### 4.1.3 Aluminum Oxide Films

For the applications discussed in sections 4.4.1 and 4.5 it is desirable to have a thin film that can be applied beneath the SiNx PCS layer and used as an etch-stop material. In this case etch-stop refers to the material having a much lower etch rate than SiNx for the chemistry used to pattern the PCS - in this case NF3. It has been found that Al2O3 produced by atomic layer deposition (ALD) has an etch rate of approximately 0.35 nm/min when using NF3. In comparison the etch rate for LPCVD SiNx is approximately 35 nm/min. This means that Al2O3 etches at a rate 100 times slower than SiNx, or has a selectivity of 1:100.

ALD is a specialized chemical vapor deposition technique that allows a film to be deposited one monolayer at a time. This is made possible by using self-terminating gas-solid reactions in series. The process of ALD film growth is depicted in figure 4.3. The first step involves chemisorption of the first reactant onto the surface of the substrate placed in a reaction chamber. After the chemisorption is complete the chamber is evacuated. It is important to note that the adsorption of the first reactant species must be irreversible and must form a monolayer in order to satisfy the requirements of ALD. The reaction must be irreversible so that none of the monolayer is desorbed during evacuation. The reaction must form a monolayer as ALD by definition only forms one monolayer per cycle. Chemisorption involves
the breaking and sometimes making of bonds, which satisfies both of these criteria. After evacuation the second reactant species is introduced to the chamber, which reacts with the first reactant to form a product on the substrate surface. The chamber is then evacuated again to remove any by-products and unreacted species. This process is repeated until the required number of monolayers has been formed.

ALD forming Al$_2$O$_3$ has been well studied and can be described by equations 4.1 and 4.2. These equations describe the two self-terminating reaction steps. The molecules with the * are the surface molecules. In the case of ALD forming Al$_2$O$_3$ there is no Al-OH but instead there is the hydroxylated film surface. The first product formed is therefore Si-O-Al(CH$_3$). In the second reaction this forms the product Al-O-Al(OH)$_2$ [35]. This reaction forms an Al$_2$O$_3$ monolayer on the hydroxylated film surface.

$$\text{AlOH}^* + \text{Al(CH}_3\text{)}_3 \rightarrow \text{Al}_2\text{O(CH}_3\text{)}_2^* + \text{CH}_4 \quad (4.1)$$

$$\text{AlCH}_3^* + \text{H}_2\text{O} \rightarrow \text{AlOH}^* + \text{CH}_4 \quad (4.2)$$

4.2 Pattern Definition

PCS patterns are rendered using Tanner EDA L-Edit layout tool. The patterns are designed to fit onto 15 x 15 mm sample pieces that are diced from the sample wafer. An individual PCS mesa is typically rendered as a circular array of unit cells with a diameter of 300 $\mu$m or 500 $\mu$m. The circular mesa
pattern is chosen to spread the spread the $SiN_x$ stress evenly to avoid damage to the structure.

Transfer of the rendered pattern to the sample piece is accomplished by electron beam lithography (e-beam), which uses a focused beam of electrons to directly write the design pattern onto photoresist. The Vistec EBPG5000+ e-beam system used for fabrication of the devices in this thesis is capable of resolutions as high as 2.5 nm. Although e-beam provides a resolution far above that of optical lithography it is also a slow process as patterns are written serially as the e-beam scans across the surface of the sample. For the devices in this work the average processing time for a single 15 x 15 mm sample with 8 PCS mesas having a diameter of 300 $\mu$m was 45 minutes.

Before e-beam writing the samples were baked in an oven at 140 $^\circ$C for 30 minutes to remove any moisture from the surface. The samples were then spin coated with a 400 nm layer of ZEP 520A positive e-beam resist. The spin coated samples were then baked in an oven at 180 $^\circ$C for 23 minutes. The ZEP 520A was then pattern by the e-beam using a 100 kV excitation voltage and a 240 $[\mu C/cm^2]$ dose.

After exposure the samples were developed in ZED N50 developer for 30 seconds. A 9:1 mixture of methyl isobutyl ketone and isopropyl alcohol was used to stop development.

4.3 Pattern Transfer

After e-beam writing and development the samples were taken to Stanford by Ofer Levi for reactive ion etching (RIE). This process uses a combination of chemical etching by plasma activation and physical etching by ion bombardment. A $NF_3$ based etch recipe was used to transfer the PCS patterns from the ZEP 520A to the $SiN_x$ PCS slab. In order to ensure that the PCS hole sidewalls were straight the $SiN_x$ was over-etched by approximately 50 nm into the $SiO_2$ layer. After RIE patterning of the $SiN_x$ using $NF_3$ an $O_2$ plasma RIE process was used to strip the remaining e-beam resist from the samples.

4.4 Membrane Suspension

Suspension of a PCS has the potential to greatly enhance sensitivity, as described in 3 as well as previous work form our lab group [11, 12]. Previous work from El Beheiry et al. attempted to suspend a PCS using an isotropic wet-etch solution of hydrofluoric acid buffered with oxygen, commonly known as buffered oxide etchant (BOE) to penetrate the holes in the PCS structure and etch a cavity in the underlying $SiO_2$. This suspension process is depicted in figure 4.4. However, this process led to cracks and sometimes complete collapse of the suspended membrane. During my thesis work it was determined that the damage to the membrane occurred after the final water rinse step post BOE processing. We
speculate that during drying the high surface tension of water puts excessive stress on the membrane, leading to damage. Therefore new samples were suspended using ethanol rather than water in the final rinse step. The much lower surface tension of ethanol proved to be advantageous as no membrane damage was observed.

Although a reliable suspension method using BOE was established, further work in this direction was not pursued as it was determined that this design type is not suitable for diagnostics. The reason is that such a design involves having the sensing medium on both sides of the PCS, or in other words the etched cavity is filled with the sensing medium. In this case the exchange of fluid in the cavity is limited by the diffusion rate through the PCS holes. The result would be slow and inaccurate refractive index measurement which is naturally not suited to rapid and portable diagnostics. Furthermore, although this process suspends the sample it does not remove the substrate and so substrate FP noise remains. This means that it is still necessary to perform a CP measurement, adding significant bulk and complexity to the light coupling scheme. With these considerations in mind a new approach to sample suspension was pursued and is outlined below.

### 4.4.1 Air-like Substrate Devices

The previous section describes a suspension process that results in a ‘symmetric’ PCS, or in other words a PCS that has the sensing medium on both sides. This is the best case in terms of maximizing sensitivity as the electric field overlap is maximized. However, as noted above the practical realization of this scheme comes with some major caveats. Therefore an alternative scheme is suggested here that rather than having the sensing medium on both sides of the PCS, enhances sensitivity by using an air-like substrate underneath the PCS that pushes the electric field evanescence into the sensing medium above the PCS. The design and measurement details of this system are discussed in chapters 8 and 10.

Processing of the air-like substrate devices utilizes a unique dual-slab of SiNx with a 5 nm layer of ALD Al2O3 between the slabs. The thin film layers for this sample type are shown in figure 4.5. In this case the PCS structure is etched into the topmost SiNx film of approximately 260 nm, with
the Al₂O₃ layer acting as an etch stop. The 50 nm SiNx layer on top of the substrate serves to seal the backside of the PCS from having the sensing medium leak through and also provides mechanical re-enforcement. This mechanical re-enforcement is particularly relevant to fabrication of devices with large features, such as the suspended split-mesa devices discussed in chapter 10.3 which would collapse without the stabilizing SiNx slab.

Potassium Hydroxide Etching

In order to suspend the PCS it is necessary to etch out the silicon behind it, creating a window through the wafer. Potassium hydroxide (KOH) is a long known alkaline anisotropic wet etchant for crystalline silicon[36]. The etch rate for KOH is strongly dependent on the crystal plane being etched, with < 100 > planes etching 35 times faster than < 111 > planes [37]. The resulting etch profile when etching a silicon wafer cut along the < 100 > plane, such as those used in this work, is shown in figure 4.6.

Aqueous KOH solution is prepared by mixing solid KOH pellets with water. Maximum etch rates are achieved for KOH concentrations between 15 and 25 wt.% [37]. In this work a KOH mixture of 25 wt.% at 90 °C was used and a corresponding etch rate along the < 100 > plane was found to be 2 μm/min, which is in good agreement with literature values [39]. The etch rate for SiNx could not be determined.
It is often described as a perfect masking material for KOH etch \[40\], with cited values for selectivity between SiNx and silicon on the order 1:100 000 \[41\].

The fabrication process for constructing an air-like substrate PCS device in shown in figure 4.7. First the PCS is patterned on a double side polished wafer, of the type in figure 4.5, according to the processes described in sections 4.2 and 4.3. Afterwards a 1 µm layer of Shipley s1818 positive photoresist is spun onto the top (PCS) side of the wafer and baked in an oven at 90 °C for 30 minutes. This photoresist layer is used to protect the PCS during the subsequent RIE etching process. Next a 1 µm layer of s1818 photoresist is applied to the wafer back side in the same manner. Now the PCS structures on the top of the sample must be aligned to the windows that will be etched through the back of the wafer.

The step of aligning a pattern on the top of a wafer to one on the back is known as backside alignment. When the PCS structures are patterned on the top of the wafer a special alignment mark scheme illustrated in figure 4.8(a) is used to allow for alignment to the backside mask used to create the SiNx windows for KOH etching (figure 4.8(b)). The mask aligner used for backside alignment in this work is a Karl Suss MA6 mask aligner. The MA6 has a system for doing backside alignment with a single objective lens, which is necessary in this case as the sample is 15 x 15 mm in size. First the backside mask is loaded into the MA6, but the sample is not. The objective lens underneath the transparent sample chuck is used to capture and store an image of the mask through the chuck. Next, the sample is loaded with the topside facing down towards the objective lens. The real-time video capture through the objective lens is displayed overlaid with the stored image of the backside mask. The sample chuck is then positioned by moving micrometers until the alignment marks on the sample and the stored image of the mask are aligned. The sample is then exposed for 3 seconds and then removed from the sample chuck.

Figure 4.7: Process steps for suspending air-like substrate samples following patterning of the PCS structure.
After exposure the sample is developed in MF-319 developer for 1 minute. Next the backside mask pattern is transferred to the SiN$_x$ layer by means of a SF$_6$-based RIE etch recipe. The details of this recipe, which is different from the one used to pattern the PCS, can be found in appendix B.3.3. Following the SiN$_x$ etching the s1818 photoresist is stripped from the sample in a bath of acetone. The sample is then immersed in 25 wt.% KOH at 90 $^\circ$C for 3 hours to ensure complete etching through the silicon wafer which is approximately 350 $\mu$m thick. During the KOH etch the sample is held in place with a teflon sample holder inside a glass beaker with a magnetic stirring bead at the bottom that sits on a hotplate to maintain temperature. The square windows (figure 4.8(b)) etched into the SiN$_x$ act as a mask for the KOH. The width of the windows is 900 $\mu$m. Since the silicon etch proceeds at a 54.74$^\circ$ angle along the $<111>$ plane as shown in figure 4.6, we can calculate that the window will be approximately 400 $\mu$m in width beneath the PCS. Figure 4.9 shows an optical microscope view of a PCS mesa on an air-substrate sample after KOH etching. Note that the is not perfectly square as a result of using an acetate mask, but this does not affect the performance of the PCS so long as it is completely suspended. It should be noted that KOH etch is not a CMOS compatible process as it contains alkali metal ions \[39\]. However, since KOH is performed as a final step after the patterning of the PCS it does not create a contamination problem.
4.5 ALD Optimization

Currently PCS devices are fabricated by using RIE to drill holes in an SiNx film deposited on a layer of SiO₂ as described in section 4.3. In order to ensure that the holes have a uniform cross-section in the SiNx layer, the etch is extended approximately 50 nm into the underlying SiO₂. This technique has the effect of keeping the hole within the SiNx very uniform, but at the expense of having partial etching in SiO₂. This over-etching is expected to have a detrimental effect on the Q-factor as the roughened SiO₂ layer will cause scattering effects that may be quite significant [42]. In addition the varying hole profiles that result from this etching method disturb the periodicity of the structure, reducing the resonant behavior. A cross-section SEM image of etched holes in figure 4.10(a) demonstrates this aperiodicity. Note that the apparent difference in hole diameter is a result of a cleaving plane that cuts through the holes on an angle. Also note that the surface charging seen in figure 4.10(b) occurs at the interface between SiNx and SiO₂.

Ideally we would like to have an holes with vertical sidewalls that stop abruptly at the SiNx to SiO₂ interface. Unfortunately, due to the poor selectivity between SiNx and SiO₂ this cannot be achieved with the current fabrication technique. Therefore, an sample has been fabricated that uses a 5 nm ALD layer of Al₂O₃ between the SiNx and SiO₂ films as way to create very high selectivity at the interface. Figure 4.10(c) and (d) shows the result of using this ALD sample. Note that both the ALD and non-ALD samples shown in figure 4.10 were processed together, and so both experienced exactly the same processes and parameters. It is seen that when using ALD Al₂O₃ the PCS holes stop abruptly at the SiO₂ layer, which is very promising for future development of very high Q PCS structures.

It is worth noting that there is a very close match between the index of thermal SiO₂, which is 1.46 at 1550 nm [29] and standard temperature ALD of Al₂O₃, which is 1.65 at 1550 nm [43]. However, it has been shown that low temperature ALD deposition of Al₂O₃ results in a film with an index of
Figure 4.10: (a) Cross-section of non-ALD sample showing individual PCS holes and (b) close-up of single hole. (c) Cross-section of ALD sample showing individual PCS holes and (d) close-up of single hole.

1.51 almost identical to that of thermal oxide. In fact ALD Al₂O₃ is so well matched optically to SiO₂ that the two materials cannot be differentiated by ellipsometry [35]. This makes low temperature ALD deposition ideal for an etch stop layer in a SiNx on SiO₂ PCS. In addition, it has been found that ALD Al₂O₃ has a very smooth surface with a roughness under 0.5 nm [35]. This smoothness is not affected by using NF₃ RIE, as is used for etching the SiNx. The result is expected to be a significant reduction in scattering that is caused by etched SiO₂, which can have roughness as high as 25nm [44].

4.6 Anti-Reflective Coating

First generation devices were severely limited by FP oscillations caused by the substrate (chapter 2.1.2, as seen in figure 4.11a). The FP does not just introduce noise into the measurement, but has a much more parasitic effect. Since the PCS acts as one mirror of the silicon FP cavity, and its peak reflectivity corresponds to the GMR spectral location the FP effect is greatly enhanced on resonance. Furthermore, in the current samples the FP have Qs of approximately 5000 which mean that they share the same frequency components as the GMRs of interest. These two factors make post-processing ineffective in removing the FP effect since the frequency components cannot be removed and the amplitude depends on the GMR location. As discussed in detail in section 5.5 the FP effect creates significant ambiguity.
in precisely fitting the resonance. Ultimately the solution to the problem of substrate FP is removal of the substrate as in section 4.4.1. However, many of the devices under study in this thesis are of the substrate-bound type and thus it is necessary to have a good anti-reflective (AR) coating for high resolution measurements, such as those in section 8.

The AR coating used in this work a simple single layer interference coating, the parameters of which are described by the quarter wave stack equation:

\[ t_{coating} = \frac{\lambda_0}{4n_{coating}} \]  

(4.3)

where \( t_{coating} \) is the thickness of the AR coating and \( n_{coating} \) is defined as

\[ n_{coating} = \sqrt{n_0n_s} \]  

(4.4)

with \( n_0 \) and \( n_s \) being the RI of the materials on either side of the AR coating. In this case the materials are air and Si, with RIs at 1550 nm of 1 and 3.5 respectively. Therefore we find that \( n_{coating} \) should be approximately 1.9. For this purpose PECVD SiN\(_x\) fits well as it is readily available and has an RI of 2. Solving equation 4.3 we find that \( t_{coating} \) should be 195 nm for \( \lambda_0 = 1550\text{nm} \).

An AR coating of PECVD SiN\(_x\) is applied to the back side of the sample. As described in this chapter the devices are fabricated on a double-sided polished Si wafer with a 2.35 \( \mu \)m thermal SiO\(_2\) layer and 260 nm SiN\(_x\) layer on both sides. Before depositing the AR coating it is necessary to remove the SiO\(_2\) and SiN\(_x\) from the backside of the sample. The challenge here is to end up with a clean and polished Si surface after etching through 2.35 \( \mu \)m of SiO\(_2\). Previously an SF\(_6\) RIE recipe was used to etch through the SiO\(_2\) and SiN\(_x\) (measurement result shown in figure 4.11(a)). The recipe consistently produced an uneven and heat-damaged surface. Since a clean Si surface could not be achieved the SiN\(_x\) was not as effective as desired in reducing FP. In addition, because the etch process did not produce a clean Si surface the deposited SiN\(_x\) could not be measured by ellipsometry to determine its thickness.

In the efforts to produce an optimized AR coating it was determined that organic cleaning of the sample followed by etching with a CHF\(_3\) based RIE process produced a very clean and uniform Si surface that is ideal for deposition of the AR coating. During etching great care was paid to keep the sample as cool as possible, as early results suffered from overheating and burning of the surface. Cooling was performed by placing the samples on a polished Si carrier wafer with helium flowing underneath. In addition, the recipe was cycled on and off in 130 second intervals. Using a PECVD SiN\(_x\) deposition process it was then possible to deposit a 195±2 nm film. This very high accuracy resulted in an AR coating that is optimized spectrally within ±16 nm of the target location. As can be seen in figure 4.11(b)
Figure 4.11: (a) TM-like resonances of sample processed with old AR coating method and (b) with optimized AR coating method.

The result is vastly improved. This AR coating is fundamental to producing and characterizing the devices in chapters 7 and 8.
Chapter 5

Experimental Procedures

In the following chapters various photonic crystal slab (PCS) structures are characterized in terms of bulk sensitivity (S), quality factor (Q), temperature dependence, and detection limit (DL). In addition, multi-resonator structures are investigated for the purposes of self-referencing and multiplexing. For many of these experiments precise fluidic control was required to allow for exchange of fluids with varying refractive indexes (RI) while minimizing noise introduced to the system. In addition microfluidics were used to create a split flow of two fluids with different RIs for more sophisticated optofluidic experiments. Every experiment shown in this work utilizes the crossed-polarization (CP) method described in section 3.4 save for the suspended device measurement of section 10.2. For substrate-bound PCS devices CP was used out of necessity, because in direct transmission the GMRs were completely overwhelmed by substrate Fabry-Pérot.

The following sections provide an overview of the optical apparatus used, fluidic control system, general measurement procedure, and analysis of experimental data.

5.1 Optical Characterization Setup

The tunable laser source (TLS) used for all experiments in this work other than a those in section 8 was a Photonetics Tunics PRI. This TLS is capable of providing constant power of up to 3 mW and is tunable in wavelengths from 1490 nm to 1580 nm in steps of 1 pm. Detection of transmitted light was achieved using a Newport photodiode which was read out with a Newport 1835-C optical power meter. Control of the TLS and data acquisition from the optical power meter was done in MATLAB using a GPIB interface. Lenses were purchased from Thor labs and were AR coated for 1550 nm (c coating).

The characterization setup is shown in figure 5.1 allows for the PCS sample to sit with the slab in
Figure 5.1: Optical apparatus used for crossed-polarized characterization of PCS devices
the plane of the table. This z style setup directs the laser beam parallel to the table, then folds it at 90° for normal incident coupling to the PCS, then folds the beam again to travel parallel to the table and be collected by a photodiode. This configuration provides many benefits in characterization. Firstly, it allows for a (14) camera to directly visualize the sample surface through a (15) microscope and (4) beam splitter. This visual feedback is very important when measuring samples such as the spit-mesa type (7.1) where it is sometimes necessary to know precisely where the laser beam is on the sample in order to make adjustments. In addition the camera can be used to image split-flow of two fluids which is extremely useful in experiments such as those of chapter 7. Finally, having the (5) PCS sample platform oriented parallel to the table surface provides better stability for the rotation plate on which it is mounted and this is crucial in high-precision measurements such as in section 8.

Referring back to figure 5.1 we see that light enters the setup via a fiber connected to a (1) collimated lens (f = 11 mm). Next it passes through a (2) Thor Labs Glan-Laser calcite polarizer (extinction ratio 100 000:1) mounted on a rotation plate and tilt stage. The beam is then passing through a (3) focusing lens (f = 75 mm), followed by a (4) beam splitter that redirects the beam normal to the (5) PCS sample which is mounted on a rotation plate and tilt stage connected to a (17) 3 axis micrometer. The beam is then folded again by a (6) mirror to travel parallel to the table through a (7) second polarizer, (8) focusing lens (f = 150 mm), and is finally collected by a (9) photodiode. After the (4) beam splitter there is a second pathway that goes through a (4) collimated lens (f = 50 mm) and is collected by a (10) second photodiode. This second pathway provides a power reference that is used to remove laser power fluctuations from measurement data. A red (11) laser diode on a tilt stage is directed to the PCS sample by a (12) mirror and a secondary removable mirror (not shown) to visualize the TLS laser spot on the sample during alignment. The focal point (o the PCS) of the TLS has a beam waist of approximately 40 µm.

5.2 Microfluidics System

For the experiments in this thesis it was necessary to have a system that allowed for precise control of two fluids with different RIs while minimizing noise input to the measurement. The abilities to quickly exchange the fluid environment of the PCS as well as to create a split-flow of two fluids over the PCS were required. The system also needed to fit on a 15 x 15 mm sample. In addition it was important to be able to control the temperature of the fluid to minimize thermal noise in the measurement. The system described in this section was developed to meet these requirements.
5.2.1 Isopropyl Alcohol Dilutions

For the purposes of this work it was critically necessary to be able to modulate the RI of water. Typically the desired modulation was very small, on the order of $10^{-4}$ RIU or smaller. Some investigation into methods of modulating the RI of water revealed that isopropyl alcohol (IPA) was an excellent candidate for this task and was able to modulate RI linearly as a function of concentration [45, 46, 47]. However, literature values for the relationship between alcohol concentration in water and RI value showed some disagreement in exactly how the RI scaled with IPA concentration. Therefore we chose to determine this relationship experimentally as described in section 8.1. It was determined by these measurements that 1% IPA in water corresponds to a change in RI with respect to pure water of $3 \times 10^{-4}$.

5.2.2 T-junction Channel

Several microfluidic channel types were tested, but in the end the t-junction shown in figure 5.2 served well for all situations involving fluid exchange or creating a split flow. Therefore this channel was universally used for the microfluidic experiments in this work. The t-junction was designed to be mounted on a 15x15mm chip. This severe size restriction created a design challenge as the liquids in the two channels feeding into the center channel should be in laminar flow when they meet in order to create a split-flow. To meet the size constriction the two inlets were folded from the classic T shape with the corners being gently rounded. Careful attention was paid to making sure the channel cross-section was kept constant at the bends (figure 5.2(b)). Note that the dimensions shown in figure 5.2(b) are tightly constrained between the necessity of fitting the channel on a 15x15mm sample and the goal of having the highest performance possible within this limitation. In addition, the necessity of mount the channel by had needed to be considered when deciding on the channel width (1 mm). The PCS mesa locations indicated in yellow are designed to be spaced far enough apart to allow for backside etching through the substrate in order to suspend the mesas (see section 4.4.1). An L-Edit template was created that places the PCS mesas at the right locations to fit this t-junction design.

Microfluidic channels were made from poly(dimethyl) siloxane (PDMS) using the replica molding replica molding (REM) soft lithography technique [43]. PDMS was chosen due to optical transparency and its chemical inertness which make it well suited for optofluidic biosensing. The mask pattern in (figure 5.2(b)) was used to create an SU-8 mold with a feature height of 150 µm, which was used to transfer the pattern to PDMS. A 10:1 PDMS prepolymer and a curing agent (SYLGARD 184) mixture were poured into the mold and cured in an oven at 80 $^\circ$C for one hour. After curing a 15 x 15 mm square around the t-junction was cut from the bulk PDMS. An O$_2$ plasma bonding process [49] was
Figure 5.2: (a) T-junction design dimensions with location of PCS structures indicated and (b) corresponding lithography mask.

used to mount the PDMS channel to the PCS sample. Immediately prior to this the PCS sample underwent piranha cleaning, which involves submerging the sample in a 3:1 mixture of sulfuric acid and 30% hydrogen peroxide for 20 minutes. This process, which strips organic materials from the surface, was critical to achieving a good bond. After undergoing $O_2$ plasma treatment the PDMS and PCS sample were bonded by hand using a stereo-microscope and a bright white light source to excite higher order resonances in the PCS so that the location of the mesas could be seen while applying the channel. It was found that the $SiN_x$ material that comprises the sample surface presents some difficulty in $O_2$ plasma bonding, which relies on silanization of the materials. Best results were achieved when the sample and PDMS channel were treated with $O_2$ plasma for 5 minutes and the materials were bonded within 30 seconds of plasma treatment. It was also found that better bonding occurred when the samples were placed in an oven at 80 °C after plasma bonding.

After bonding of the t-junction to the sample tubing is inserted in the inlets and it is placed on a threaded mount that is used to attach it to the optical setup. Next the entire structure is encased in epoxy, permanently attaching it to the threaded mount while leaving a window for the t-junction channels. The final result is shown in figure 5.3 with the sample is mounted on the optical characterization setup. Encasement in epoxy was found to greatly improve mechanical robustness, particularly in strengthening the tubing junctions that had previously tended to break easily. In addition, gluing the sample to the mount appeared to reduce measurement noise by removing any potential for movement.
5.2.3 Control of Split-Flow

The t-junction channel described above was intended to be used to precisely control the interface between two liquids in a single channel. This is accomplished by having one syringe pump connect to each inlet of the t-junction channel and varying the flow rate of each pump independently. This control method can be used to flow two different liquids over each half of a PCS split-mesa as shown in figure 5.4. Figure 5.4(a) and (b) show the interface between water and water with food coloring as it is moved to align with the split between two half mesas. Figure 5.4(c) shows a zoomed-out image of the t-junction being used for this flow control. The split-flow shown here has great potential as a method to make differential measurements between two solutions and also for functionalization of self-referenced sensors (see chapter 7). It is possible to functionalize both the reference and active halves of a split-mesa and then by precise control of the fluid interface flow a blocking agent over the reference sensor while flowing a buffer solution over the active sensor. However, in order for this strategy to be effective it is necessary
Figure 5.5: Pixel intensity as a function distance across the interface between water and water with food coloring. Analysis of video was used to determine stability of the split-flow to have very high stability of the fluid interface. The gap in the split-mesa is approximately 4 $\mu$m and so oscillation of the split-flow so be no greater than this distance. To test the split-flow stability the interface between water and water with food coloring were imaged during split-flow and the pixel values were plotted as a function of distance, as shown in figure 5.5. Here a diffusion region of approximately 12 $\mu$m is shown. The size of the diffusion region is dependent on the fluid flow rate and the size of the diffusing molecules. Therefore for a given molecule this region can be made smaller or larger if needed by adjusting the flow rate. On the other hand, the stability of this interface is critical for the functionalization scheme described as well as for the differential measurements shown in chapter 7. The Harvard Apparatus Pico 11 Elite Plus syringe pump demonstrated stability within a 2 $\mu$m region over several minutes, and this was one of the primary reasons for choosing that model for the microfluidic system. Indeed, it bested the stability performance of other syringe pumps tested by over an order of magnitude.

5.2.4 Temperature Stabilization

Measurements made during this thesis were done an in an optics room without any temperature stabilization. In order to make precision measurements such as those in section 8 it was necessary to stabilize fluid temperatures as much as possible. To address this necessity the system shown in figure 5.6 was constructed.

In this system liquid is fed from the syringe pump to the inlet of the temperature-maintaining flask that sits in a temperature controlled water bath and acts as a reservoir of identical fluid that is maintained
at a set temperature as shown in figure 5.6. The inlet injects fluid to the base of the flask and the outlet tube siphons fluid near the top of the flask. This design places as much fluid as possible between the inlet and outlet. A maximum flow rate of 1.5 ml/min was needed and for this purpose a 150 ml flask was chosen, meaning that approximately 1% of the liquid in the flask is replaced every minute. These two design decisions insure that the fluid is kept at a precisely controlled temperature in the water bath in which it is submerged. In addition to providing a constant temperature fluid, the setup in figure 5.6 also serves to damp any fluctuations in flow rate from the syringe pumps due to the compressibility of the air that sits in the top of the flask. Furthermore, this temperature control system provided the opportunity to raise the fluid temperature to the athermal point for the PCS device (see chapter 6). This ability was used in the detection limit experiment described in section 8.

5.2.5 System Development

As mentioned earlier one important requirement for the microfluidics system was that it introduce very little noise into the measurement. The noise caused by the syringe pumps was quantified by setting the TLS to a fixed wavelength on the side of a resonance and monitoring the dynamics of the transmission power (which would ideally be static) when the microfluidic pump was running and when it was turned off. The difference in transmission power noise between these two cases was associated with pumping noise (pulsing of the fluid flow) being translated into vibration of the sample. Several models of Harvard Apparatus syringe pumps were tested according to this criteria as well as the split-flow stability criteria.
Figure 5.7: (a) Fluid exchange measurement during early development of the microfluidics system and (b) the same measurement made 6 months later discussed in section 5.2.3. The Pico 11 Elite Plus was chosen due to its extremely low pumping noise which resulted in negligible transmission power noise as well as phenomenal split-flow stability.

The evolution of the microfluidics system is best summarized by figure 5.7 with the plot in (a) showing a measurement during the early stage of development of the microfluidic system and (b) showing the same measurement 6 months later. Identical PCS samples were used for the experiments, with the same liquids being exchanged. In this experiment microfluidics are used to periodically exchange two fluids, which in this case are water and water with 0.02% IPA. Both measurements show a step response which results from a torque on the sample which is dependent on which inlet channel is being pumped. High frequency noise is associated with the microfluidic pump while low frequency drifts are a result of changes in the ambient room temperature. We observe that both the slow temperature drift and the pumping noise are vastly improved in figure 5.7(b). It should be mentioned that the spikes seen in this data are not noise, but in fact a bone-fide signal that was observed as a result of the improvement in fluidic control. Further explanation of this data can be found in section 10.4.

### 5.3 Fitting Measurement Data

The Fano fitting method described in section 3.2 was also used for fitting of experimental data. An example Fano fit to an experimentally measured TE-like resonance with considerable Fabry-Pérot (FP) noise is shown in figure 5.8. Since this fitting method seeks to find the Fano lineshape of the GMR it is
Figure 5.8: Fano fitting to experimental measurement of TE-like GMR in a PCS structure with $r = 110$ nm and $a = 980$ nm

quite robust to FP noise. However, certain situations exist where the FP creates ambiguity in the fit. These cases occur when a FP maximum on minimum coincides closely with the peak of the GMR. In this case the fitting reliability is significantly increased. However, even in the worst case situations fitting errors are found to be about 100 pm or or approximately 10% of the resonance linewidth (section 6.4). The effect of FP on fitting accuracy is discussed in detail in section 6.5.
Chapter 6

Athermal Designs

In recent years photonic RI biosensors have shown great promise for rapid diagnostics in label-free lab-on-a-chip configurations, due to their excellent sensitivity, real-time detection, and amenability to CMOS fabrication techniques. However, an inherent issue with RI sensing in such devices is that the device materials themselves often have significant temperature-based RI dependence or thermo-optic coefficients (TOCs) [50]. There are many ways this problem can be addressed either in device design or data processing. The most direct way to deal with this problem is integration of temperature control system, such as a Peltier element [51]. However, in addition to adding bulk to a structure, thermal elements often have high power requirements as well making them non-ideal for monolithic portable devices. The literature also shows many designs methods that can be used to greatly reduce temperature effects which generally employ some type of common-mode rejection method such as MZI structures [52, 53], FP interferometry [54], or use of a "reference" structure [55]. While these methods have typically shown very good performance it may be desirable to complement such common-mode rejection with an inherent temperature insensitivity. In this case researchers have focused on methods to cancel the positive TOCs of dielectrics with a negative TOC material - often a polymer [56, 57, 58]. It has been shown that by creating the right overlap between the evanescent field and the negative TOC polymer it is possible to cancel TOCs over a small temperature range.

Following the idea of TOC cancellation the simulations and measurements in this chapter explore the effect of using the non-linear negative TOC of water to create a desired athermal point. This is particularly relevant in the context of biosensing when we consider plasma, which is commonly used in assays, is over 90% water and even whole blood is approximately 85% water [59]. With this in mind it is clear why using the inherent optical properties of water for temperature stabilization is a compelling
6.1 Thermal Behavior of Materials

As mentioned above, in refractive index sensors it is often necessary to account for the effect of thermal fluctuations that will alter the behavior of the resonator as a function of the TOCs of the materials comprising the device. The sensors developed and characterized in this work consist of a SiN x PCS slab on an SiO 2 insulator on a Si substrate. A water based solution flows above the PCS slab and changes in this solution are detected. Any change in RI, resulting in a resonance shift, that is caused by temperature fluctuations is considered noise and should be reduced as much as possible. Figure 6.1 shows the thermo-optic coefficients at 1550 nm and room temperature for the materials comprising the sensors being investigated.

The linearity of the RI temperature dependence for these dielectric materials between 10 and 50 degrees Celsius has been demonstrated in numerous recent works [60, 56, 61, 62]. However, the temperature dependence for water is strongly non-linearity over this range and thus cannot be treated in such a simple manner [63]. The NIST has accepted a quantitative equation originally developed developed by Harvey et al. in 1998, that was based on the compilation of many sets of data measuring RIU of water for varying wavelength, pressure, and temperature [64]. This work was later expanded upon by Wagner et al. and the resulting formula and its constants are now used by the NIST as the standard by which the index of water is described [65]. However, due to water’s high absorption above 1 µm there is little experimental data available for the temperature dependence of water in the IR range. Therefore the NIST considers that this formulation is not fully reliable at these longer wavelengths. However, there is an example of direct experimental measurement of RI temperature dependence at 1064 nm produced using a Michelson interferometer [66]. In this paper the RI of water was measured between 20 and 60 degrees Celsius. The resulting data, which the authors determined to have a displacement limited precision of 5x10^{-5} RIU was fitted with a fourth-order polynomial. By comparing this polynomial to the NIST Wagner formulation it is possible to evaluate the reliability of the Wagner formulation at 1064 nm as shown in figure 6.2(a). Here we see close agreement between formulations in the temperature range.

<table>
<thead>
<tr>
<th>Material</th>
<th>Si @ 1550nm</th>
<th>SiO 2</th>
<th>SiN x</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>3.48</td>
<td>1.46</td>
<td>2.05</td>
<td>1.315</td>
</tr>
<tr>
<td>dn/dT (x10^4 RIU-K^-1)</td>
<td>2.3</td>
<td>0.1</td>
<td>0.4</td>
<td>non-linear</td>
</tr>
</tbody>
</table>
Chapter 6. Athermal Designs

Figure 6.2: (a) Comparison between NIST formulation calculated at 1064 nm and atmospheric pressure (blue) and Richerzhagen measurement at 1064 nm (black). (b) Same comparison with NIST calculated at 1550 nm and Richerzhagen measurement offset to match of 20 to 50 degrees Celsius.

Unfortunately, literature review reveals no experimental data available for thermal behavior in the 1550 nm range. Therefore for the purposes of the simulations in this chapter the NIST formulation is used to predict the thermo-optic behavior of water at 1550 nm and an offset version of the Wagner polynomial is used as a qualitative check. These calculations are compared in figure 6.2(b). Again we see a close agreement between the NIST formulation and the offset version of the interferometric measurement made at 1064 nm between 20 and 50 °C. Although this comparison suggests that the NIST formulation is valid in the temperature and pressure (atmospheric) range of interest it should be noted that we are not able to confirm this behavior without experimental validation. Despite this limitation in accuracy it is clear from both the Richerzhagen experiment and the NIST formulation that the refractive index of water has a non-linear dependence on temperature near room temperature. This becomes more apparent when we take the derivative of the NIST formulation shown in figure 6.2(b). The result shown in figure 6.3 is the TOC of water as a function of temperature. Strikingly it can be observed that the TOC changes by an order of magnitude between 10 and 43 °C. Certainly this makes a compelling case that it is possible to engineer an athermal temperature point, as will be demonstrated in the following section. In this section the NIST formulation is used to predict the thermal behavior of water at 1550 nm.

In addition to accounting for the TOCs of the materials used in the PCS devices studied, it is also necessary to consider how thermal expansion will alter the geometry of the structures, which will also lead to resonance shift and thus measurement noise. Figure 6.4 shows the thermal expansion coefficients near room temperature for the dielectric materials that compose the PCS structures [67, 68]. In this case the thermal expansion of water is not of interest since the channel is not pressurized and therefore
Simulation of Thermal Behavior

Simulation of thermal effects was written in lua scripting language (appendix C.1.1) and computation was done using S4 [69]. The lua script steps through a range of temperatures and updates the RI of the dielectric materials according to their thermo-optic coefficients (figure 6.1). At the same time the RI of water is updated according to the NIST formulation. Finally, for each temperature step the geometry of the PCS structure is updated according to the thermal expansion coefficients in table 6.4.

The data generated is processed using a custom MATLAB code that fits the resonances according to the Fano lineshape equation (appendix C.1.1). This process provides highly accurate determination of the resonance peak location and lineshape. The program then plots resonance shift as a function of temperature as well as Q as a function of temperature. The change in Q between 10 and 60 °C was found to be less than 0.1% and therefore only resonance shift is considered in this chapter.

The results of these athermal simulations for resonance shift are shown in figure 6.5 for hole radii of 110 nm and 100 nm with both structures having a lattice constant of 980 nm. The derivative of these curves gives the thermal dependence of the resonance as a function of temperature, which are indicated on the plots in units of $\frac{\text{pm}}{\text{°C}}$ for 21 °C (the average temperature of the room in which the devices are...
Chapter 6. Athermal Designs

Figure 6.5: (a) Simulation of thermal behavior for $r = 100$ nm and (b) $r = 110$ nm characterized) as well as at the athermal point. Note that the athermal point corresponds to the point where the derivative is zero. For the purposes of this work the (discrete) derivative is taken over a 1 °C temperature step.

It can be observed from figure 6.5 that a smaller hole radii leads to a higher athermal point. This behavior can be understood in terms of the fill factor for the evanescent field. As discussed in chapter 3, decreasing the hole radius leads to higher QF, which means that $|E|^2$ is more strongly confined within the slab. Stronger confinement means that there is less interaction with the fluid medium (in this case pure water) and therefore the water's negative TOC has less influence at lower temperatures. Referring back to figure 6.3 it can be seen that the TOC increases with increasing temperature and therefore when the temperature is sufficiently high the TOC of water is able to cancel that of the dielectrics despite the reduced field interaction.

The above figures do not account for the thermal expansion. However, as mentioned in section 6.1, an accurate simulation must account for the thermal expansion of the PCS materials. This matter must be carefully considered because the PCS device is composed of three dielectric materials with differing coefficients. To illustrate the complication that arises figure (fig: 6.6) shows the thermal dependence of the device in figure 6.5(a) when expansion is determined by the expansion coefficient of SiN$_x$ (red), SiO$_2$ (blue), Si (green), or when there is no expansion (black). Since each dielectric has its own expansion coefficient and the materials are bonded together the effective expansion rate of SiN$_x$ - which is the
material on which the PCS is patterned - is not the same as bulk SiNₓ on its own. In order to be completely rigorous in determining how the SiNₓ expands a study involving both finite element modeling as well as experimental validation would be necessary. However, since the Si substrate is more than 3 orders of magnitude thicker than the SiNₓ and two orders of magnitude thicker than the SiO₂ it is reasonable to expect that the SiO₂ and SiNₓ conform to the expansion of the Si. In fact, this is a common rule of thumb when growing thin films on an Si substrate \[70\]. Therefore the remaining simulations shown in this chapter assume that the thermal expansion of the SiNₓ is the same as that of Si, or \(2.6 \times 10^{-6}\).

### 6.3 Tuning of the Athermal Point

It is often desired to create an specific operational athermal point. This might be room temperature (20 °C) for chemical sensors or in the range of 40 °C) for biosensors \[71\ \[72\]. As noted for figure 6.5 a reduction in the PCS hole size results in a higher athermal point. This trend can be observed in the comparison of two extreme cases shown in figure 6.7 which compares the \(|E|^2\) profile in cross-section for \(r = 100\) nm and \(r = 300\) nm. When the field is more strongly confined in the PCS there is less interaction with the water and thus higher temperatures are required for the change in water RI to cancel the change in RI of the dielectrics. Likewise quality factor and thus the athermal point can also be tuned by changing the lattice constant of the PCS. As mentioned, these tuning techniques come at the cost of requiring a change in the quality factor. Although it is not studied in this work it is possible to tune...
the athermal point by changing the refractive index of the material lying underneath the PCS - which is SiO$_2$ in the case of the sensors studied here. The principle in this case is similar to that of changing the hole radius. As demonstrated in chapter 3, the evanescent field of the PCS will preferentially exist in the surrounding material whose RI is closest to that of SiNx, as this material presents less impedance to the $|E|^2$. Therefore, if the material underneath the PCS is modified to present a higher RI contrast this will cause more of the evanescent field to exist in the sensing medium - in this case water. A higher field concentration in the water lowers the athermal point just as is the case with increasing the hole radius. Likewise, the athermal point can be increased by decreasing the RI contrast between the PCS and the underlying material, as a result of reducing the $|E|^2$ fill in the sensing medium.

### 6.4 Experimental Measurement of Thermal Behavior

In order to test the validity of the athermal model discussed in the previous sections experimentally a method of precisely controlling the temperature of the PCS device materials as well as the water in the microfluidic channel was required. For this purpose a 3W OEM proportional-integral-derivative (PID) controller was used to control the temperature of a 6W thermoelectric cooler element onto which the PCS device was mounted as shown in figure 6.8. Both of these devices were purchased from Thor Labs. A 10 kΩ thermistor, sandwiched between the PCS device and plastic clamping layer with thermal compound to maintain good thermal contact, was used to provide feedback to the PID controller. A high resolution Agilent 8164B TLS with built-in wavemeter, set to tune in steps of 1 pm, was used for the experiments performed in this section.

The goal of the work in this chapter is demonstrate the ability to create an athermal temperature
point by utilizing the negative TOC of water. However, in order to verify the validity of the model the most simple case that could be experimentally verified was tested first. This case involves modulating the temperature of the PCS device without water above it. Instead the top side of the PCS was exposed to air. In this case it is not necessary to rely on the validity of the NIST formulation for the RI of water at 1550 nm. The complexity of the model is thus greatly reduced since air can be treated as a vacuum with no thermo-optic behavior. The PCS device studied in this section has a hole radius of 130 nm, a lattice constant of 980 nm, and a SiN\textsubscript{x} slab thickness of 260 nm.

The simulation for this section only needed to rely the well studied and quantified TOCs of SiN\textsubscript{x}, SiO\textsubscript{2}, and Si. For the corresponding experiment the set point of the TEC was moved in 3 °C steps beginning at 23 °C (1 °C above the ambient room temperature) and once the set point was reached for each temperature a high resolution scan of the TE-like resonance was performed using the Agilent TLS. The Fano line shape equation was used to fit the experimental data for each scan as shown in chapter 5. As discussed, the Fano equation can be used to precisely locate the resonance wavelength. The resonance wavelength was located for each temperature step. To simplify analysis 23 °C was treated as the zero-shift point and thus was subtracted from the resonance location of each subsequent temperature step. In this way the resonance shift that corresponds to each temperature step (for example from 23 °C to 26 °C) could be plotted. The resulting experimental data arrived at using this process is shown in figure 6.9 in the red dash-dot line. First it should be noted that there is no athermal point for this data, as should be expected since all materials involved have a positive TOC and there is no negative TOC material to counteract them. Second, it is observed that the temperature dependent shift observed is linear over the temperature range measured. This is also to be expected as the materials have linear
Simulation was performed according to the method described in section 6.2 to mimic the experimental conditions. Therefore, simulation of the temperature dependent behavior was carried out between 23 °C and 38 °C. The resulting calculated resonance shifts are shown in figure 6.9 with a solid blue line. Excellent agreement between experiment and simulation is observed with the exception of the data point at 35 °C. This data point differs from the predicted value by 90 pm. The cause of this discrepancy is discussed in section 6.4.

In addition to allowing for comparison between the simplified thermal simulation model and experiment data, the data shown in figure 6.9 allows us to quantify the fitting error associated with the thermal experiments. As mentioned, the resonance center wavelength is determined by fitting a Fano line shape to the experimental data. Measurement noise, and in particular FP oscillations, create an ambiguity in fitting the line shape. Since we know that the resonance shift as a function of temperature should be linear, a linear regression fit to the experimental data points is used to determine the standard deviation. In this case a standard deviation of 35 pm is found and this is shown in the error bars of figure 6.9. It is important to realize that this error is not attributable to temperature fluctuation. It was found that the peltier element kept the PCS sample stable within ±0.1 °C, which corresponds to a shift in the resonance center wavelength of ±2.2 pm. Therefore, the standard deviation arises from ambiguity in fitting the resonance rather than ambiguity in knowing the PCS temperature. It should also be mentioned that this error is not random, but is highly repeatable over successive measurements as shown in figure 6.10. The fitting ambiguity determined in this simple experiment, where the resonance is known to shift linearly with temperature, can be applied equally to the measurements done in water (figure 6.10) where the temperature dependence is not well defined. Thus the same 35 pm standard deviation is applied to the experiments shown in figure 6.10. The cause of the resonance fitting ambiguity is discussed in section 6.4.

In order to validate the athermal design model in the case of a water-based medium existing above the PCS surface the experimental process outlined above was repeated but with water in the microfluidic channel. Once again the the set point of the TEC was moved in 3 °C steps beginning at 23 °C and the resonance was recorded with a high resolution scan. The same analysis as done with the air medium was performed and the resulting experimental data is shown in figure 6.10 in the red and black dash-dot lines. As in the air case the initial experiments used the λ-zeroing feature of the Agilent TLS between temperature steps. This feature uses the internal wave meter to recalibrate laser between each measurement to account for changes in ambient conditions such as temperature and humidity. However, the resulting data (red) had an anomalous trend at 32 °C and 35 °C. To determine if this
Figure 6.9: Temperature dependent resonance shift for PCS with \( r = 130\text{nm}, a = 980\text{nm}, \) and \( t = 263\text{nm} \) with air above the surface. The red dash-dot line shows the experimental result using a TEC for temperature control and the solid blue line shows the shift predicted by simulation.
behavior was resulting from the measurement equipment the experiment was repeated without \( \lambda \)-zeroing (black). However, it was observed that the same trend repeated for subsequent measurements regardless of whether \( \lambda \)-zeroing was used. The predicted behavior from the simulation model shown in the solid blue line of figure 6.10 exhibits a similar trend to that observed in experiment with a 18 pm and 32 pm deviation at the 32 °C and 35 °C, respectively. This issue is explored in the following section, however putting it aside for the moment it is observed that when water is introduced the trend in temperature dependence appears to become quadratic in nature - as predicted. In addition, the presence of an athermal point in the mid 30 °C seems to be indicated. Also, importantly, the resonance shift between 23 and 38 °C is only 75 \( \pm \) 35 pm when water is present as opposed to 310 \( \pm \) 35 pm when it is not.

Certainly the large fitting error puts a limit on how confident we can be in our conclusions, but a more careful consideration of this error in the following section shows that the error is in fact temperature dependent. As we see in both figures 6.9 and 6.10 the data points at 35 °C have by far the largest deviation from the model, with the adjacent points at 32 and 38 °C affected to a smaller extent.

### 6.5 Experimental Limitations

In order to understand the major source of error in section 6.4 we must consider a secondary source of resonance in the PCS structure. This secondary source is the Si substrate based Fabry-Pérot (FP) cavity (section 4.6). Despite having an AR coating on the backside of the Si there is still a field component that will be reflected back towards the PCS. Although the PCS allows for nearly perfect transmission outside the resonance, around the resonance it acts as a very effective mirror. Therefore in the spectral region close to a resonance peak FP effects are no longer negligible and are in fact clearly presented in the data as shown in figure 6.11(a). The result is a line shape that is a composite of the intrinsic Fano resonance of the PCS as well as the FP from the substrate.

When observing small wavelength shifts (less than 100 pm), as would be the case when biosensing, this FP does not present a significant problem. As can be seen in figure 6.11(a) the free spectral range is approximately 1.3 nm and when the PCS resonance is shifted a small fraction of that the line shape does not change significantly. The Fano fitting code used in this thesis does not account for this FP but small changes in line shape do not have a detrimental effect on accurate location of the PCS resonance wavelength. However, certain problematic cases exist, such as a shift that causes the PCS resonance to go from existing near a FP minimum to a maximum. In the former case the resonance will narrow and appear to be either red or blue shifted depending on whether the minimum exists on the blue or red side respectively. In the later case the opposite behavior occurs: if the FP falls on the blue side the
Figure 6.10: Temperature dependent resonance shift for PCS with $r = 130$ nm, $a = 980$ nm, and $t = 263$ nm with water above the surface. The red and black dash-dot lines show the experimental results of two experiments using a TEC for temperature control and the solid blue line shows the shift predicted by simulation.
resonance appears blue shifted and vice versa.

In the case of the data analyzed in figure 6.10 the FP maximum falls close to the blue side of the resonance peak at 35 °C and to a lesser extent at 32 °C (figure 6.11(b). As a result of this superposition the peak appears to blue shift. This leads to the disagreement with simulation at those two data points. Typically, the problem does not present itself as the optics room is stable with ±1 °C. However, as is shown in figure 6.11(a), the FP location has a strong temperature dependence as a result of the large thermo-optic and thermal expansion coefficients of Si. It is seen that the FP shifts approximately 220 pm for every 3 °C step. Therefore, although the athermal design provides very good stabilization of the peak at the athermal point, the FP behavior adds a sizable ambiguity when attempting to fit the experimental resonance data.

6.6 Future Work on Athermal Designs

Unfortunately, since the FP and the PCS resonance share the same frequency components it is not possible to simply remove the FP components. In order to address this problem the device design must be modified in some way. One option is to either significantly thicken or thin the substrate such that FP does not occupy the same frequency range as the PCS resonance. In this case a fast Fourier transform can be used to remove the FP, although this may not even be necessary. Another option is to use a more sophisticated multilayer AR coating that provides very low reflection around the resonance. Finally, perhaps the best option is to remove the substrate altogether, thus removing the FP source. Although significant steps have been made in suspended device design (section 3.3.3), fabrication (section 4.4.1), and characterization (section 10.2) the development of an athermal suspended device is outside the scope of this thesis.
Figure 6.11: (a) Temperature dependence of the FP caused by the Si substrate and (b) resulting composite of PCS GMR and substrate FP at 32, 35, and 38 °C.
Chapter 7

Self-Referenced Designs

A common problem among RI optical biosensors are signals caused by an input to the system other than the analyte of interest. This issue must be addressed when measuring small molecules or low molecular concentrations of large molecules. Optical biosensors have proven to have extremely low detection limits ranging from $10^{-5}$ to $10^{-9}$ RIU, in many cases having the ability to detect binding of a single molecule \[73\]. In these cases measurement noise can be on the order of or greater than the signal of interest. Moreover, in order to accurately quantify the concentration of an analyte of interest measurement noise must be removed from the measurement signal. Sources of noise relevant to optofluidic RI sensors include fluctuations in bulk fluid RI, non-specific adsorption, temperature fluctuation, and TLS wavelength tuning inaccuracies. Typically, the solution to this problem is to develop a system that employs both a reference and active sensor so that common-mode noise can be removed from the measurement. In the case of optofluidic biosensors only the ”active” sensor is exposed to receptor ligands, so that the analyte of interest will only bind to the active sensor and not the reference sensor. In this case by monitoring both sensors common-mode signals can be removed so that only the signal of interest remains.

The principle of self-referencing has been demonstrated by Chan et al. in the case of one-dimensional photonic crystals \[55, 74\]. In this case the authors make use of the fact that the resonance only propagates along one axis in one-dimensional structures to create a very simple self-referencing scheme. Referencing is achieved by applying receptor ligands to only the center part of the photonic crystal as shown in figure \[7.1\]. The part with ligands is treated as the active sensor as this is where the analyte of interest will bind and the part without ligands is the reference. Detection is accomplished by illuminating the sensor with a white light source and using an imaging spectrometer to determine the peak wavelength value of individual pixels \[75\]. Since the one-dimensional structure is inherently decoupled in the direction
orthogonal to the resonance propagation the reference region and active region can be used to perform self-referencing, by subtraction of the reference value from the active value.

Although one-dimensional photonic crystals are amenable to a referencing scheme as illustrated that is simplistic in terms of device design (figure 7.1), a high power broadband light source is required for excitation and a complex and costly imaging system is required to read out the spatial dependence of reflected wavelengths. In this work the goal is to produce a self-referenced device that can be interrogated using short wavelength sweeps (less than 10 nm) for interrogation and a photodiode for readout. As described in chapter 1 such a system in principle fits the requirements for on-chip integration and portability.

Another drawback to the one-dimensional referencing scheme is that it requires that the excitation source be specifically polarized. PCS structures do not have this polarization requirement (caveat for CP measurement 3.4), but this also means the assumption of lateral decoupling does not hold. This ability to couple an arbitrary polarization is an advantage in moving toward on-chip integration as the system complexity is reduced. However, since the GMRs may propagate along either axis in the two-dimensional plane of the PCS in order to create a self-referenced structure as described here a mechanism for decoupling two adjacent crystals must be found. These two adjacent crystals are then used as the reference and active sensors.
Figure 7.2: (a) Design structure for a split-mesa device shown in top view and (b) cross-section of device indicating design dimensions, materials, and gap between mesas. Note that a variety of radii and lattice constant choices were explored for the devices in this chapter.

7.1 Split-Mesa Design

This section describes the split-mesa structure that is used in both of the self-referencing systems analyzed in section 7.2. Self-referencing, as discussed in this chapter, requires that the sensor and reference be placed as close together as possible so that they experience the same environment in terms of temperature, bulk fluid RI, analyte concentration, and fluid dynamics (in the case of a microfluidic channel). Furthermore, proximity ensures that they experience the same environment during fabrication, which is important for high precision structures such as those in section 7.4. In addition, they must be close enough such that they can be excited by the same laser source. The second requirement can always be met for an arbitrary separation by increasing the laser power. However, as portability is an end goal a low power source such as a VCSEL is desired. In this case the beam waist at the focal point is on the order of 50 µm (diameter 100 µm). Since photonic crystals couple radiation to GMRs that propagate in two dimensions having two crystals very close together on the same dielectric layer presents a problem in that if no decoupling strategy is used the GMRs will couple and therefore the reference and active PCS will not be able to function independently.

Initial self-referenced designs consisted of two semi-circular PCS mesas separated by a 1 µm gap according to the strategy shown in figure 7.2(a). This diagram shows the principle of split-mesa design from a top view of the structure. Here two semi-circular PCS lattices with the same lattice constant of 984 nm and differing radii (120 nm and 150 nm) are placed adjacently with a 1 µm gap between them. The 1 µm gap was intended to stop the GMRs of the two lattices from interacting, and thus coupling, while keeping the mesas as close together as possible. The differing radii were chosen to create a small wavelength separation between the TE-like resonances that was large enough to completely separate the line shapes and allow for a shift of several nanometers without the resonances beginning to overlap.
At the same time the separation should not be any larger then necessary to allow for rapid scanning of the resonances using a TLS, or eventually in a integrated structure using a VCSEL. Naturally the larger the spectral separation the more time it takes to perform each sweep. In addition, scanning errors accumulate as a function of the wavelength being scanned, which means that accuracy in quantifying the wavelength separation becomes larger for larger separations. Further discussion of design considerations for this self-referencing strategy is provided in section 7.4.

Initial simulations indicated that a 1 $\mu$m gap would be sufficient to decouple the two mesas. However, in experiment the appearance of additional spectral features seemed to indicate coupling. Considerable effort was spent on characterization of this sample, to determine whether coupling was occurring. Fano line shapes were fitted to resonances observed (section 5.3) when both mesas or only single mesas were excited using a focused laser with a beam waist of 40 $\mu$m. As shown in figure 7.3 when the laser spot was placed on a single mesa at a distance of $\pm 50$ $\mu$m from the center of the gap between mesas a single TE-like resonance was excited and no additional features appeared, as expected. When the laser spot was placed at the center of the gap, exciting both mesas, two TE-like modes were observed, as expected. However, significant reduction in Q as compared to excitation of a single mesa was observed. Furthermore, unexpected spectral features were observed between the resonances. These affects indicate that coupling was occurring between the two crystals. Measurement and analysis of TM-like resonances in the same structure also indicated that coupling was occurring. As can be seen in figure 7.4 reduction in Q and additional spectral features are also seen when the laser spot is placed at the center of the gap exciting both mesas, as compared to when only a single mesa is excited. In addition, the high-Q TM-like resonance is seen to undergo a significant spectral shift when both mesas are excited which is also an indication of coupling.

Returning to simulation to explore the cause of the coupling seen in experiment, FDTD simulation was used replicate the geometry of the actual split mesa structure. It was observed that with an un-etched gap, or in other words a gap where the Si$_{Nx}$ is not removed the GMR will easily propagate across between the mesas as shown in the top image of figure 7.5(a). The simulation at the top of the figure shows the PCS mesa on the left being excited and the mode propagating across an (un-etched) Si$_{Nx}$ gap to the adjacent PCS where it can couple with the GMR of that PCS.

For the next iteration of split-mesa designs the gap between the two semi-circular mesas was etched through theSi$_{Nx}$ layer so that the GMR from one mesa could not be guided through the bulk Si$_{Nx}$ to the other mesa. This principle is demonstrated in the FDTD simulations shown in figure 7.5(a). This demonstrates that an Si$_{Nx}$ gap is not sufficient to decouple the two crystals. However, as shown in the simulation at the bottom of figure 7.5(a) if the gap is etched through the Si$_{Nx}$ the mode can no
Figure 7.3: Experimental measurement of TE-like resonances in split-mesa design with 1 µm SiNx gap. Solid lines indicate measurement data and dashed lines indicate Fano fitting. The red and blue plots are measured when the center of the focused laser beam (beam waist of 40 µm) is 50 µm from the center of the gap between the reference and active sensors.

Figure 7.4: Experimental measurement of TM-like resonances in split-mesa design with 1 µm SiNx gap. Solid lines indicate measurement data and dashed lines indicate Fano fitting. The red and blue plots are measured when the center of the focused laser beam (beam waist of 40 µm) is 50 µm from the center of the gap between the reference and active sensors.
propagate across the gap the adjacent PCS mesas are now decoupled. Note that when the gap is etched out it is then filled with the bulk sensing medium, just as the PCS holes are, which is in this case water. Figure 7.5(b) shows an optical image of the final split-mesa design with a 3.78 µm etched gap used in the referencing structures demonstrated in this chapter. This gap length was chosen to be sufficiently large so that the evanescent field does not extend to the adjacent crystal. In addition, it was necessary to consider that the gap may act as a FP cavity with the two mesas on either side acting as mirrors. Therefore the exact length of the gap was chosen so that any resulting FP was far outside the spectrum of the PCS resonances.

It should be noted that the direction of GMR propagation is dependent on the polarization of the excitation source (see section 3.4). In the FDTD simulations shown in figure 7.5(a) the worst-case scenario when the GMR propagates normal to the gap was chosen to ensure that the mesas are decoupled for all possible polarizations.

7.2 Self-Referencing Systems

The following sections describe two types of self-referencing schemes that were implemented in PCS devices utilizing the split-mesa design shown in figure 7.5. Both referencing schemes employ the same split-mesa topology with two adjacent sensing surfaces (PCS mesas) that are interrogated simultaneously in making a differential measurement. The structures are excited by a single focused laser beam with a 40 µm beam waist. The two halves of the split-mesa act as the reference and active components producing the two TE-like GMRs from one light source. Both design types investigated herein employ
the same basic referencing strategy of subtracting the spectral shift of the reference sensor resonance from that of the active sensor. The result is a measurement where common mode signals are removed and only the differential signal remains.

In the optofluidic context demonstrated here, this method allows for determination of the difference in bulk RI that each sensor experiences. To make this optofluidic measurement a system capable for flowing two different liquids over each sensor is required. The system used for this purpose is the t-junction microfluidics described in section 5.2.3. As mentioned there it is possible to control the split between two fluids with a stability of ±2µm. Therefore is the following experiments where a differential measurement is made the split between the two fluids is placed at the etched gap between the reference and active sensors, as shown in figure 7.6. Although measurements this section are made used optofluidic control of two alcohol dilutions, similar experiments can be imagined in the context of biosensing. In this context only the active sensor would be functionalized (see section 5.2.3) and therefore it would be possible to determine the shift that is caused by binding of the analyte of interest while removing shifts caused by noise sources such as temperature fluctuation, non-specific binding, and changes in bulk RI.

Each of the two schemes has associated advantages and disadvantages which are discussed within the relevant sections. However, it is the author’s opinion that the power differential design of section 7.4 possesses significant unique advantages over other types of referencing schemes and therefore significant attention is paid to this device type.
7.3 Wavelength Differential Design

This structure type is referred to as the wavelength differential design as measurement is based on observing the change in a spectral gap between two resonances. The spectral gap is created by making a 4nm change in the PCS lattice constant. For accurate referencing it is necessary that the sensor and reference have nearly identical sensitivity and quality factors (Q). Having nearly identical sensitivities (S) means that for a given change in RI each resonance will shift by the same amount. Having nearly identical Q results in having the same fitting ambiguity for the reference and active sensors. To achieve this result it was necessary to change the lattice constant rather than the hole radius. As shown in the numerical investigations of chapter 3 the change in hole radius required to shift resonances apart by several 5 nm would result a nearly 10% change in S and would result in Q decreasing by close to a factor of 2. On the other hand a 4 nm change in the lattice constant results in change to S of approximately 2% and a change to Q of approximately 3%. The numerically expected spectral gap is approximately 6 nm.

In the fabricated wavelength differential structure both sensors had the same hole radius of 110 nm, while one sensor had a lattice constant of 980 nm and the other 984 nm. Measurement results demonstrating the decoupling of the two resonators are shown in figure 7.7. It is noted that when both resonators are excited at the same time no additional spectral features appears and the Q of the resonances is not reduced. An aberration can be observed on the red shifted resonator when it is excited.
Figure 7.8: Experimental measurement of wavelength differential device with water in the microfluidic channel at a temperature of 30 °C (black) and 40 °C (red)

individually. This a result of a defect near the edge of the PCS mesa. Unfortunately in order to excite only that mesa it was necessary to move the laser near the edge of the PCS where the defect was. The Q values for the two resonators were found to be 3140 and 2990, which corresponds to a difference in Q of 5%, which is very close to the predicted 3%. Sensitivity was characterized using Cargille RI liquids, and was found to differ by 1.8% with the blue shifted resonator having an S of 163 nm/RIU.

An identical sample to the one in figure 7.7 was mounted with microfluidics in order to characterize its referencing ability. Before conducting the split flow experiment, an experiment was performed to test the temperature stability of the spectral gap. The microfluidics temperature control system described in the chapter was used to modulate the temperature of the liquid in the channel and the measurement shown in figure 7.8 was performed. The resonances are shown with the water at a temperature of 30 °C (in black) and 40 °C (in red). This temperature results in a 372pm resonance shift for each resonance as shown in the inset. However, the change in the spectral gap between the resonances is with the margin of error (2pm). This is a powerful demonstration of the temperature stabilizing effect of self-referencing. However, the device must also be able to make a differential measurement between the reference and active sensors. The experiment demonstrating this ability is shown in figure 7.9. In this experiment the resonator corresponding to the red-shifted resonance is treated as the reference sensor and the resonator with the blue-shifted resonance is treated as the active sensor. The initial measurement shown in red
Chapter 7. Self-Referenced Designs

Figure 7.9: Differential measurement comparing a split flow of 4% IPA on both sensors, and water on the shifted with blue-shifted resonance and 4% IPA on the other sensor flows a 4% IPA dilution in water over both sensors. The differential measurement is shown in black using a split-flow of water over the reference sensor and 4% IPA in water over the active sensor. The peak corresponding to the active sensor is seen to shift $297 \pm 10$ pm, where the resonance of the reference sensor remains stable. Therefore the change in the spectral gap is the same as the shift of the active resonator. This clearly demonstrates a self-referenced differential measurement where the spectral gap can used to determine the shift in the resonance of the active sensor.

7.4 Power Differential Design

The power differential design sensor follows the same principles as the wavelength differential sensor, however a subtle but powerful difference is made in how the measurement is read out. The wavelength differential sensor relies on the use of a very accurate tunable laser in order to determine the spectral gap between the resonances. The means that the accuracy of the referencing scheme is inherently limited by the accuracy of the laser used. Lasers capable of making pm resolution measurements rely on the use of wavemeters, require a stable environment, are very expensive, and are typically the size and weight of a small table. This poses a significant barrier to using a device that relies on such a system in the context of portable sensing. Therefore in the following design the goal was to design a system that had a built-in
Figure 7.10: Demonstration of power differential effect illustrating the summation of two resonances (dashed lines) and the resulting line shape with a local minimum between the resonant peaks that changes as a function of the differential shift of one peak relative to the other.

The power differential design proposes to separate two TE-like resonances by a spectral gap that is approximately equal to their full-width at half maximum (FWHM). If these resonances can be decoupled then the resulting line shape will simply be the sum of the individual resonances. The principle of this summation effect is shown in figure 7.10. The two individual TE-like resonances are shown in dashed lines. The line shape that results from the summation of the individual peaks is shown in solid lines. It is shown that a local minimum occurs between the peaks of the individual resonances and that when one resonance shifts relative to the other the transmission power at the local minimum is changed. In this system the resonance of the reference sensor, shown by the black dashed line, acts as an internal reference for the active sensor. When a resonance shift occurs due to a common mode signal, such as temperature fluctuations, changes in bulk fluid RI, or non-specific binding then both peaks shift together and equally. The result is that the summation line shape also shifts but the shape is unchanged. On the other hand if a signal of interest, such as a binding event on the active sensor occurs then the active sensor resonance
Chapter 7. Self-Referenced Designs

Figure 7.11: (a) Calculation of change in power at local minimum for various wavelength shifts and (b) change in power as function of wavelength shift (determined by quadratic fitting to the local minimum will shift while the resonance of the reference sensor remains fixed. The resulting summation line shape changes accordingly and a decrease in power at the local minimum between the peaks is observed. The power of such a technique is that wavelength accuracy is no longer important. In fact in figure 7.10 the labels on the x-axis could be removed entirely and the shift of the active sensor could be determine purely from transmission power information. Therefore in such a situation having a laser that provides accurate wavelength information is no longer important. The laser requirement is greatly reduced to having a laser that can sweet the wavelength range of the line shape and read out the power spectrum. Then the local minimum can be found and used to determine how far the resonance has shifted.

The assumption made in the description of power differential referencing above is that the change in transmission power at the local minimum changes linearly with wavelength shift. Referring to the Lorentzian line shapes of the individual resonances shown in 7.10 this seems to hold true within a range. Nevertheless, it is instructive to plot the change in power at the local minimum to confirm this intuition. This change in power is quantified by quadratic fitting to the minimum as shown in figure 7.11. From the result in figure 7.11(b) we see that the change in power is a linear function of resonance shift. The property holds true for a range that is approximately one quarter of the FWHM, or in this case about 250 pm. A metric is extracted from the plot in figure 7.11(b) and that is the shift in shift in wavelength per change in power. The number found for this design is 0.127%/pm. When we consider that 1 pm resolution is near the upper limit of the most advanced tunable lasers available the significance of this finding becomes clear. In such a system if more resolution is desired then simply more input power is
Figure 7.12: (a) Side view of the simulation object showing two photonic crystals, in a water sensing medium and on an SiO₂ substrate with etched gaps in between them. (b) Same object shown from the top view. The dimensions of the PCS are indicated as 20 unit cells long by 1 unit cell thick. Periodic boundary conditions are shown by green dashed lines. The yellow arrow indicates the axis of polarization required. Moreover, stabilizing a power measurement is can be done in a very trivial way by using a second detector to pick laser power fluctuations and using this to normalize measurement data.

### 7.4.1 Simulation of Overlapping Resonances

The power differential design appeared very promising, but its performance rested on the assumption that resonances that are spectrally overlapping would remain decoupled. In order to test this assumption simulation was done in SMM and FDTD to see whether the simulation of a split-mesa crystal with overlapping resonances gave the same result as the simulation of the two resonators separately and then summed together. The simulation object used to test answer this question is shown in figure 7.12. Here each PCS is made to be 20 unit cells in length and one unit cell wide. The dimension of 20 unit cells determined as the minimum number that would support the GMR. Below this number the GMR was not properly supported and thus the Q was reduced. Recall that in an ideal PCS the number of unit cells is infinite. Such a small number of unit cells was achieved by orienting the source polarization along the axis of aperiodicity as shown by the yellow arrow. Since the GMR propagates orthogonally to the polarization of the source a small number of unit cells along the axis of polarization were sufficient. The decoupling gap of the split-mesa is shown between the two PCS and in addition a half length of the gap is placed at the boundaries of the simulation space. Since this simulation object is treated as periodic these half gaps match up to form complete gaps separating the simulation objects along an infinite array.
Figure 7.13: Unit cell simulations of PCS 1 and PCS 2 with \( r = 110 \) nm and \( r = 106 \) nm shown in blue and red respectively. The weighted sum of these simulation shown with black dots. The corresponding simulation of PCS 1 and PCS 2 using the split-mesa simulation object from figure 7.12 shown in purple (difficult to see as it coincides with the black dots).

Figure 7.13 shows the simulation results for the object described above. In this case the transmission (not CP) spectrum was analyzed. The reason for this choice is that CP relies on ellipticity of the PCS holes to couple two resonances resulting in polarization conversion. As discussed in chapter 3, this effect requires that GMRs propagate along both axes of the structure. CP simulation was not suitable for a simulation space that would be computationally reasonable. Regardless, the transmission spectrum is equally suitable for analysis in this case. What we see in figure 7.13 is the result of simulating two resonators with \( r = 110 \) nm and \( r = 106 \) individually using a single unit cell with periodic boundary conditions (blue and red respectively). The weighted sum of these two simulation results is shown by the black data points and the simulation results of the split-mesa object shown above is given by the purple line. Note that it is difficult to see the purple line as it exactly coincides with the sum of the individual resonances. This confirms the assumption that the power differential design does indeed produced two decoupled resonances that sum together. Note that this simulation was performed in SMM and FDTD, yielding the same result.

7.4.2 Experimental Results

Transmission measurement of the realized power differential structure is show in figure 7.14. As done with other split-mesa structures the reference and active sensors were measured individually, shown in blue and red. The line shape observed when both resonators were excited together is shown in black. The design parameters for this device were lattice constant of 980 nm for both resonators and radii of
Figure 7.14: Experimental measurement of power differential device with each resonator measured individually (blue and red) and together (black)

106 nm and 110 nm. The numerically predicted different in $S$ was 3% and the difference in $Q$ was 10%. Note that having identical $Q$s is not a requirement for power differential sensors. The main consideration for $Q$ is that the higher the $Q$ the more dramatically the power will change for a given wavelength shift.

Experimental measurement of a power differential device using a split-flow of water and IPA dilution is shown in figure 7.15(a). Note that as opposed to the calculation shown in figure 7.10 where the longer wavelength resonance is shifted away from the shorter one, in this version of the device the shorter wavelength resonance is shifted toward the longer wavelength one. There is no significant difference between these two methods, except that in figure 7.10 the longer wavelength resonance corresponds to the active sensor and in figure 7.15(a) it is the shorter wavelength resonance. In this experiment, as with wavelength differential experiment, a split-flow of water and an IPA dilution is used to differentially shift the active sensor. For this experiment three different dilutions of IPA were used in addition to a split-flow of water and water. Note that in this experiment the peaks shift close together and thus the amplitude of the local minimum increases as the active sensor shifts differentially. The area of the local minimum for each measurement was fitted with a quadratic function to determine the minimum. The result is shown in figure 7.15(b), normalized to the amplitude of the minimum with a split flow of water and water (ie the baseline measurement). The result shows a linear change in power as a function of a linear change in RI (the change in IPA concentration). We note that according to the calibration done in chapter 8 a 2% IPA dilution corresponds to a change in RI of $1 \times 10^{-3}$ as compared to pure water. We know the numerically determined value for sensitivity of a device with $r = 110$ nm and $a = 980$ nm
Figure 7.15: (a) Experimental observation of power differential measurement using a split-flow with water over the reference sensor and varying IPA concentrations in water over the active sensor. (b) The change in transmission power at the local minimum is determined by fitting a quadratic function to the local minimum area, and is plotted as a function of IPA concentration.

is 165 nm/RIU (see 3.3.1). Therefore with a change in RI of $1 \times 10^{-3}$ a shift of 165 pm is expected. Looking at the calculation in figure 7.11(b) we see that a shift in the resonance of 165 pm should result in a change in power of approximately 20%. The result of this experiment shows a change in power of 23%. To account for this difference between the calculation of figure 7.11(b) and measurement we need to keep in mind that although the device used in this measurement has the same design parameters that fabrication errors result in small differences in hole radii between devices, and that for this device type with this radius a difference of 2 nm will result in a change in Q of about 5%. This change in Q will then change the rate that the power changes per pm shift. Therefore for accurate measurement calibration to a known RI liquid is necessary. In this experiment the measurement allows us to calculate the relation between power change and resonance shift, which is given by

$$\frac{23\%}{1 \times 10^{-3} RIU \times 165000 \left(\frac{\text{pm}}{\text{RIU}}\right)} = 0.140 \frac{\% \text{Power}}{\text{pm}}$$  \hspace{1cm} (7.1)$$

Note that here we use the $S$ that was determined numerically. This does not significantly affect the accuracy of the calculation since $S$ changes very slowly as a function of radius, as seen in section 3.3.1. Therefore even if the hole radius is different then expected by 5 nm (a fairly significant error) the $S$ is only different by about 1.3%. In addition if it is only desired to know the relationship between power change and RIU change, as in a typical biosensing experiment, then no assumptions need to be made.
the calculation is simply

\[
\frac{23\%}{1 \times 10^{-3} \text{RIU}} = 23000 \frac{\% \text{Power}}{\text{RIU}}
\] (7.2)
Chapter 8

Experimental Measurement of Detection Limit

The objective of the experiments described in this chapter was to quantify an experimental detection limit (DL) for the TE-like GMR of a substrate-bound PCS sensor. To this end the microfluidics system described in chapter 5 was employed in order to exchange two liquids with slightly different RIs in a way that introduced minimal noise into the measurement. The temperature stabilization system shown in section 5.2.4 was used to minimize noise caused by fluctuation in the ambient temperature of the optics room. The laser power was stabilized by using a beam splitter to send half of the incident light to a second detector that was used to normalize the measurement data to the laser power fluctuations. The sample under study in this chapter has a hole radius of 105 nm, lattice constant of 980 nm, and a slab thickness of 260 nm. Referring to figure 3.4 in this device a DL of $2.5 \times 10^{-6}$ can be resolved in principle.

8.1 Determination of Alcohol Dilution RI

Before attempting to make a very precise measurement changes in refractive index (RI), we needed to characterize the RI of the solutions to be used in experiment. For these experiments the alcohol dilution method described in section 5.2.1 was used to prepare solutions of varying RI. Although literature provides an approximate value for the RI to be expected for a given dilution, we chose to characterize the RI in our lab to ensure the precise of our measurements. In order to do this we first needed a sensor with a known sensitivity (S). The sensor chosen for this task was the same one that would later be
used for the DL limit experiment. The S value for this sensor was quantified using Cargille RI liquids, which are precisely calibrated to have a specific RI. Calibration was done by making measurements of the GMR spectral location for varying RI liquids. These results where then fitted to determine an experimental S value of 163 nm/RIU. We can note that this value is nearly identical to the value of 160 nm/RIU predicted by numerical simulation in section 3.3.1. Using this sensor with its known S value measurements of GMR shift were made for varying dilutions of IPA in water as shown in figure 8.1. By fitting the shift in resonance as a function of IPA concentration in water it was found that 1% IPA in water corresponds to a shift in resonance of 50 pm. Therefore the relationship between IPA concentration in water and RI was determined by

\[
\frac{50 \text{ pm}}{163000 \text{ pm/RIU}} = 3.07 \times 10^{-4} \frac{\text{RIU}}{\% \text{IPA}}
\]  

(8.1)

8.2 Intensity Measurement

The measurement made in this section was done by setting the wavelength of the tunable laser to a value that coincided with the side of the resonance as shown by the green arrow in figure 8.1. Since the laser wavelength sits on the linear area of the Lorentzian line shape a change in transmission power caused by the resonance shifting can be directly translated into a value for the spectral shift of the resonance. The specific wavelength used in this measurement was 1551.76 nm. Using this single wavelength measurement method and the t-junction channel described in section 5.2.2 two fluids, one being water and the other water with a small concentration of IPA, were exchange periodically and the transmission power was
Figure 8.2: (a) Water and 0.02% IPA in water are periodically interchanged using microfluidics and a t-junction channel. (b) Real-time cross-polarized transmission measurement showing resolution of 0.02% IPA in water (red), which is contrasted to the baseline measurement of water being exchanged with water (blue).

recorded over time. The method of liquid exchange is shown in figure 8.2(a). We see that the process begins with the IPA dilution mixture flowing at 300 µm/min and after 30 seconds the IPA mixture flow rate is ramped down while the flow rate of pure water is ramped up. After another 30 seconds the flow rate of water is ramped down while the flow of the IPA dilution is ramped back up. By this method the sequence begins with the channel filled with the IPA mixture and then switches to being filled with pure water, then back to the IPA mixture and so on. This sequence repeats periodically as the transmission power is recorded. Ramping is used to minimize noise caused by the changing of flow rates. However, as can been in figure 8.2(b) the exchange of liquids still has a significant effect on the measurement. To account for the transmission response caused by exchange of the liquids a baseline measurement is made where water and water are exchange (see blue line in figure 8.2(b)). In this case there is no change in RI and therefore any change in transmission power is a result of mechanical noise. This noise is seen as a step response each time the liquids are exchanged. However, in data shown in red water is exchange with a 0.02% IPA dilution and the step response is seen to increase. This increase in step response as compared to the baseline measurement was shown to be repeatable and therefore established the ability to detect a 0.02% dilution, which corresponds to a DL of 6.0 × 10⁻⁶ [RIU]. It should be noted that simulation showed that a change in RI of 6.0 × 10⁻⁶ resulting in a change in transmission power of 0.6% when monitoring the side of the resonance peak. This value matches well to the change in power observed in figure 8.2(b).
8.3 Spectral Shift Measurement

The measurement shown in the previous section allowed observation of a change in transmission power from a change in RI of $6.0 \times 10^{-6}$ which is just over a factor of 2 away from the theoretical DL. However, although this method is sensitive due to noise in the measurement it is not easy to quantify the change in RI of two fluids based solely on the transmission power. Therefore for the measurement in this section the resonance line shape was repeatedly scanned using an Agilent 8164B tunable, which has a specified wavelength accuracy of 0.5 pm. The liquid exchange system shown above was also used in this measurement. However, initial measurements showed the lineshape shifting unpredictably. It was determined that this unpredictable shifting resulted from temperature fluctuations in the room. To address this issue the temperature stabilization system shown in section 5.2.4 was developed. Measurements were made with the liquid temperature at 35 °C, which corresponds to the athermal point for the device, as discussed in section 5.4. The results of this measurement are shown in figure 8.3. Each time the liquid in the microfluidic channel was exchanged two scans of the resonance were performed. The result of this experiment for an IPA dilution of 0.04% is shown in the figure 8.3. In figure 8.3(a) a close view of the side of the resonance is shown and a spectral gap between the measurements made for water and 0.04% IPA is seen. Fitting this data to determine the resonance peak location gives the plot shown in figure 8.3(b) indicating a resolved spectral shift of $2.9 \pm 1.0$ pm. In measurements made for 0.02% IPA dilutions the resonance shift fell with the range of uncertainty and so a observation of resonance could not be claimed. Therefore in the spectral shift measurement a DL of $1.2 \times 10^{-5}$ was resolved, which is a factor of 2 larger than that achieved by intensity measurement.
Figure 8.3: (a) Temperature stabilized high resolution spectral shift measurement of the side of a resonance peak for when the PCS is immersed in water and 0.04% IPA dilution. (b) The calculated spectral shift of 2.9 pm +/- 1.0 pm found by fitting the data from (a). Note that fluids were exchanged between measurements 2 and 3 as well as 4 and 5.
Chapter 9

Discussion

9.1 Device Performance

The work of this thesis has focused on substrate-bound PCS device that were characterized using the crossed-polarization (CP) method. Many interesting phenomenon have been investigated both experimentally and numerically, including the thermal dependence of TE-like resonances in a PCS, self-referencing schemes using a split-mesa structure, and precision microfluidic measurements used to determine the detection limit of a substrate-bound PCS. This discussions on these investigations can be found within their respective chapters. To summarize briefly: PCS devices were found to have a non-linear response to changes in temperature as a result of the non-linear thermo-optic coefficient of water. Self-referenced devices were found to have exhibit very high resolution metrics, with the power differential design capable of translating a 1 pm shift in resonance into a 0.140% change in transmission power. The detection limit experiments resolved a change in RI that differed from the theoretical limit by a factor of approximately two.

Although some very nice experimental results were achieved, the experiments performed also suffered from a high degree of instability and a very high sensitivity to mechanical noise. During experiments the mechanism of CP was not understood, but now in reflection it is possible to parse where some of the major measurement instabilities come from. For this reason the following section focuses on the measurement errors that arise from use of the crossed-polarization technique in TE-like modes of PCS similar to those studied in this work.
9.2 Sources of Error

Some typical sources of error that can be cited for measurements such as those made in this thesis are laser power fluctuations, temperature fluctuations, and mechanical stability. In this work the laser power fluctuations were accounted for by splitting the incident beam and sending half of it to a second photo detector. The measured power fluctuations from this reference beam were then used to normalize the measurement data. Temperature fluctuations certainly did add to measurement noise in this work, however these effects and methods to mitigate them have been explored in great detail in chapter 6 and chapter 7 as well as section 5.2.4. These leaves mechanical stability as a mostly unexamined noise source. Typically it has been assumed that PCS are quite robust to mechanical issues that result in changes to the incident polarization or small changes to the incident angle. Although this may be the case in direct transmission measurement, when CP is used these assumptions no longer hold up.

9.2.1 Crossed-Polarization Power Stability

Although much has been made of the polarization insensitivity of two-dimensional photonic crystals as compared to the one-dimensional variety, it can be demonstrated that much of this advantage is lost when measurements are done using the crossed-polarization technique explored in chapter 3.4.

Polarization Sensitivity

The plot produced for the CP transmission power as a function of the incident polarization with respect to the axes of the PCS shown in figure 9.1(a) was discussed previously. Here it is observed that when polarization is aligned with one the axes of the PCS no CP transmission occurs. On the other hand when the polarization is at 45° to the PCS axes transmission power is maximized. If this change in power as a function of polarization angle is plotted as done in chapter 3.4 it seen to vary sinusoidally with angle. This indicates that a rotation of the sample will cause a significant effect in measurement. To see how significant this effect is the discrete derivative of the change in CP power as a function of polarization (determined from figure 9.1(a)) is taken and is plotted in figure 9.1(b). What is shown in this figure is the rate at which the CP power will change due to a rotation for a given polarization angle. It is observed that in the worst case a change in power of 3.5% per degree rotation will be experienced. This plot also indicates that in CP the best polarization angle to use is 45°, which is where the rate of power change is lowest. This also coincides with where the CP power is maximized.
Figure 9.1: (a) CP transmission power and (b) derivative of CP transmission power as a function of incident polarization angle with respect to the PCS axes, for unit cell with \( r = 100 \) nm and \( a = 980 \) nm

**Effect of Sample Tilt**

In this section it is demonstrated that CP transmission measurements are extremely sensitive to sample tilt. Figure 9.2(a) shows how the CP power changes as the sample is tilted over a range of \( 0.15^\circ \). The plot shows that at a tilt of \( 0.15^\circ \) the transmission power is reduced to 30% of its original value. Moreover, in the range of \( 0.10^\circ \) to \( 0.15^\circ \) the power drops at a rate of \( \frac{500\%}{\text{degree}} \). This means that if a measurement is made on a sample that is slightly tilted that measurement will be extremely sensitive to mechanical noise. The trend can also be shown by the relationship of \( Q \) to sample tilt in figure 9.2(b). It is observed that \( Q \) also drops significantly with small changes in tilt. Therefore as the sample is tilted the resonance broadens and thus the incident power is spread over a larger spectral range leading to a decrease in transmission power. As the tilt angle is increased past \( 0.15^\circ \) the resonance begins to split and at a tilt of \( 0.30^\circ \) the resonance effectively disappears.

With the tilt and rotation sensitivity of CP measurements in mind it is not hard to understand the step response of the CP transmission power shown in figure 8.2 that occurred when inlets on the microfluidic t-junction were being cycled between. Likely the change to where force was being applied to the sample as a result of switching channels was leading to very small changes in tilt that resulted in changes in transmission power of approximately 1.5%. It should be noted that this effect occurred despite attempts to anchor the sample as well as possible using epoxy glue (see figure 5.3).
Figure 9.2: (a) Change in CP transmission power and (b) change in quality factor as a function of tilt for unit cell with $r = 100$ nm and $a = 980$ nm.

Figure 9.3: Change in resonance line shape as a function of tilt for unit cell with $r = 100$ nm and $a = 980$ nm.
Chapter 10

Future Work

10.1 Multiplexed PCS arrays

Figure 10.1 shows a novel triple-mesa structure which is designed and fabricated in a packed 'honey comb' configuration (Figure 3 inset) for interrogation with a single optical beam. A thin 5.0 nm atomic layer deposition (ALD) film of $\text{Al}_2\text{O}_3$ was deposited between the $\text{SiO}_2$ substrate and the $\text{SiN}_x$ slab layer, as an etch-stop layer. The ALD layer ensures a similar etch depth for the three different hole radii ($r = 150$ nm, 180 nm, 210 nm) of the mesas located on this triple-mesa device. Circular etched gaps surrounding each mesa were used to decouple the resonators. This decoupling mechanism follows the same principal as those used in chapter 7 for the split-mesa structures. Decoupling of the resonators is demonstrated in figure 10.2. Here each mesa is excited by a focused laser beam, and then all three mesas are excited together using a larger spot size beam. Measurement demonstrates that the line shape resulting from all three resonators being interrogated is equivalent to the sum of each mesa being interrogated individually. This demonstrates the ability to pack many resonators close together without creating interference.

This design can be extended to an arbitrary size and thus shows good potential for realization of a massively parallel, compact biosensor on a single chip using 2D PCS structures. With a single light beam illumination, several resonances can be used to sense different analytes in a single measurement [4]. Furthermore, a triple-mesa architecture composed of three lattices with significantly different sensitivities can be used for error correction of measured spectral sensitivities or analyte concentration [77]. Moreover, use of resonances with different sensitivities can potentially be used to parse bulk fluid effects from analyte binding. In addition, a dense $108 \ \mu m$ center to center PCS grating spacing as shown here, is well suited for expansion to a multiplexed sensing array using antibody inkjet printing techniques [78, 79].
Figure 10.1: Optical images of (a) a novel triple-mesa showing honeycomb configuration and (b) closer view showing 4 µm decoupling gaps.

Figure 10.2: (a) Spectral measurement of TM-like GMRs (a) when single mesas are excited and when all are excited with a single beam. (b) Sum of individual measurements overlayed with all resonances excited with single beam demonstrating successful decoupling.
Chapter 10. Future Work

10.2 Air-Substrate Sample

The air-substrate architecture proposed in section 3.3.3 shows potential to increase $S$ by a factor of nearly 4 as compared to current devices. In addition characterization of a sample without a substrate greatly reduces measurement complexity as crossed-polarization (CP), along with all of its problematic effects (section 9.2) is not required since substrate Fabry-Pérot (FP) is no longer a concern. Even more significantly the removal of the substrate will greatly enhance measurement resolution by removing the substrate FP oscillations that plague current measurements and make it extremely difficult to accurate fit Fano line shapes to the observed resonances even in the case where CP is used and an AR coating is applied to back of the sample.

The fabrication process to realize an air-substrate structure has been discussed in this thesis and the successfully suspended air-substrate device with $r = 105$ nm and $a = 1000$ nm has been measured experimentally. The initial measurement made in air is shown in figure 10.3. Here one can easily move between direct transmission measurement (a) and CP measurement (b), with the GMR being clearly resolved in both. It should be noted that the $Q$ enhancement in CP predicted by numerical simulation is observed in this measurement.

In order to quantify the $S$ of this device Cargille RI oil with $n = 1.30$ was applied to the sample and the resonance was measured again (figure 10.5). The measured resonance shift corresponds to an $S$ of 185 nm/RIU. This agrees closely with the numerical result of section 3.3.3. However, the $Q$ measured in (figure 10.5) is significantly different from the simulation value of approximately 3000.

Although it is exciting to have realized and measured an air-substrate sample, the TE-mode is not
Figure 10.4: (a) CP transmission measurement and (b) direct transmission measurement of TE-like GMR for air-substrate PCS devices with Cargille immersion oil with RI of 1.30 above.

Figure 10.5: CP transmission measurement of TM-like GMR for air-substrate PCS device with Cargille immersion oils.
Figure 10.6: (a) Construction of power differential referencing line shape from the Fano resonances of
a suspended PCS and (b) the change in line shape as a result of a shift to the resonance of the active
sensor

of significant interest to this design, since Q and S are only marginally enhanced over the values for a
substrate-bound PCS. The true potential of the air-substrate design is revealed in the TM-like modes
of this device, shown in figure 10.5. The resonance location for the TM-like GMR is shown for 3 RI
values. The shift in center frequency as a function of RI gives an experimental S of 707 \( \text{nm RIU} \). This
is an improvement of nearly 4.5x over the substrate-bound devices studied in this thesis. Moreover, a
relatively high Q value of 1900 is maintained, resulting in a DL of 7.4x10\(^{-7}\) RIU. It should be noted that
the experimental results show some disagreement with the simulation predictions of section 3.3.3. The
experimental S of 707 \( \text{nm RIU} \) is larger than the numerically determined S of approximately of 640 \( \text{nm RIU} \).
On the other hand the experimental Q value is more than an order of magnitude lower than predicted.
This is likely a result of SiN\(_x\) etching during the KOH process. This would result in thinning of the PCS
slab, thinning of the underlying SiN\(_x\) slab, and enlargement of the PCS holes. These effects would be
consistent with the experimentally observed discrepancies. Further efforts should focus on optimization
of the underlying SiN\(_x\) slab thickness in order to find the optimum value in terms of maximizing DL.

10.3 Power Differential Referencing in Air-Substrate Design

The power differential referencing scheme investigated in section 7.4 offers significant benefits in terms
of producing high accuracy differential measurements using low accuracy lasers, such as VCSELs. However,
the devices discussed in this thesis were fabricated on a substrate-bound sample and utilized CP for
measurement, which produced Lorentzian line shapes. These line shapes showed a linear behavior in
terms of the change in the amplitude at the local minimum between peaks for a given shift in the
resonance of the active sensor. For future devices the goal should be to make direct transmission measurements using substrate-free PCS. In this case the resonance line shape will be the characteristic Fano shape as seen in figure 10.5(b). Therefore it is instructive to consider whether a power differential device can be made using such a line shape. The answer to this question is provided by figures 10.6 and 10.7. In figure 10.6(a) the construction of a power differential device using the Fano resonances observed in a direct transmission measurement is shown. In 10.6(b) the change in the line shape as the red-shifted peak shifts to longer wavelengths is shown. The calculations of the 10.7 show two ways that the shift in resonance can determined from a linear metric that holds over a range of 130 nm. In this case the amplitude of the dip between the resonances is not the only parameter that should be watched. The peak height of one of the two resonances should also be monitored and this value should be subtracted from amplitude of the the dip. Using this strategy it is demonstrated that the power differential referencing method can be easily translated to suspended devices.

10.4 Split-Flow Polarization Conversion

Analysis of the CP phenomena shown in sections 3.4 and 9.2 is very instructive for purposes of experimental optimization. In addition, consideration of this phenomenon in terms of an unexpected measurement behavior may have led to the discovery of an optofluidic method to further enhance polarization conversion. This process was first observed in the measurements of section 8.2. It was noticed that when the fluids in the microfluidic channel were exchanged sharp spikes appeared in the transmission spectrum, as indicated by the green circles in figure 10.8. It was determined that the the spike occurs at the point where the fluid interface passes through the excitation laser focal spot. This circumstance is very
suggestive of a polarization conversion process. We can consider that CP occurs as a result of interaction between two slightly shifted resonances that arise as a result of two slightly different radii in the PCS structure. A fluid interface where the fluids have different RIs will also give rise to two slightly shifted resonances. It is proposed by this author that this effect is analogous to the CP one and that the same polarization conversion process occurs resulting in an increase in transmission power as indicated by the spikes shown in figure 10.8.

After initially observing these spikes the author adjusted the split flow such that it remain fixed in the area of the excitation focal point. Fluids with varying RIs were introduced to attempt to establish how small an RI could still give rise to this effect. At the time the weakest dilution prepared was a concentration of 0.0001% IPA, which corresponds to a change in RI with respect to water of $3 \times 10^{-8}$. A change in transmission power was easily observed for this dilution. If this phenomenon can be confirmed then this method of RI sensing shows phenomenal potential in terms of reducing the DL of PCS devices. Unfortunately, attempts to simulate this behavior have so far been unsuccessful as the difference between RI required is well below the limit of numerical dispersion for the software presently available to the author.
Chapter 11

Conclusions

This thesis has introduced the photonic crystal slab (PCS) as a candidate for label-free optofluidic biosensing applications. In particular it is postulated that PCS structures are well suited to portable sensing applications where low power requirements and the potential for on-chip integration provide significant advantages. Strong motivation for such devices is given in chapter 1. The physics of PCS have been explored in chapter 2 which describes how the resonant features observed arise from a periodic dielectric slab and also a way to understand the resonant line shapes in terms of a direct and indirect pathway as originally put forward by Fan et al. Chapter 3 uses numerical methods to explore the three PCS architectures in detail and to compare them in terms of sensing potential. In chapter 4 the fabrication methods employed for the work shown in this thesis are described.

In this work several of the major problems that limit the implementation of PCS devices for RI sensing applications are investigated. One of the issues that can reduce the accuracy of PCS sensors is the thermal behavior exhibited by the dielectric materials from which they are composed. A change in temperature of the device results in a change in the RI of the materials comprising it. This change in RI leads to a shift of the resonance, which cannot be distinguished from a shift that is caused by binding of an analyte or a change in the sensing mediums composition. The effects of temperature on the PCS devices under study is discussed in detail in section 6. It is demonstrated that the non-linear negative thermo-optic coefficient of water not only counteracts the positive coefficients of the dielectric materials, but creates an athermal point temperature point where the shift in resonance caused by temperature fluctuations is locally zero. It is demonstrated that the location of this athermal point point can be engineered by tuning the device sensitivity. Experimental results from this study show a resolution limit as a result of the substrate Fabry-Pérot (FP) noise. However, good agreement is seen between the
behavior predicted by numerical simulation and the behavior observed in experiment.

Engineering an athermal point is a powerful tool to making a system inherently temperature stable passively and without introducing any complexity into the measurement. However, this type of system does not account for other noise sources that cause a shift in resonance location and can result in the false detection of an analyte in the case of a biosensor. For these noise sources, which include non-specific binding and changes in bulk RI, or for environments where larger temperature fluctuations need to be accounted for a more robust stabilization method is required. For this purpose the self-referenced sensors of chapter 7 are introduced. Here a novel split-mesa structure that allows for two decoupled PCS structures to be placed a few micrometers apart is used to create a system where the two PCS structures form a reference and active sensor that can be interrogated by single focused laser beam. In the context of biosensing a method to selectively functionalize only the reference sensor is outlined. Two types of self-referenced sensors are proposed, analyzed, fabricated and characterized using optofluidic techniques. One sensor type, referred to as the wavelength differential design uses the two PCS to create two TE-like resonances with a Q of approximately 3000 that are spaced about 5 nm apart spectrally. Measurement is made by sweeping a tunable laser across the spectrum occupied by these two resonances and determining the spectral gap in between them. When a common mode signal is present the resonances shift together, but when the differential signal of interest is present only the resonance of the active sensor undergoes a shift. Therefore it is demonstrated that by making a differential measurement between the resonances noise signals, such as temperature fluctuations, are removed from the measurement. The other self-referenced sensor type proposed is the power differential design. In this structure the TE-like resonances of the reference and active PCS are brought so close together spectrally that the resonances overlap. It is shown that the resulting line shape is a pure sum of the individual resonances, which results in a local minimum between the resonance peaks. This device follows the same principles are the wavelength differential design, but in this case when the active sensor shifts differentially with respect to the reference sensor the amplitude of the local minimum between the resonances change. The change in this amplitude is a linear function of the shift in the active sensor resonance. Therefore as opposed to the wavelength differential device that requires the gap between resonances to be determined using a tunable laser, the resonance shift is read out in the power spectrum thus removing the requirement for an accurate laser. This subtle but very significant difference means that the power differential design is amenable to on-chip integrate with compact low power tunable lasers that do not have high wavelength accuracy, such recently developed mechanically tunable VCSELs [80]. In addition, the inherently wavelength-referenced design shows promise in table top optics where the power read out method may be able to out perform even the highest accuracy tunable lasers available in terms of detecting small resonance shifts. A metric
for this device that converts a change in power at the local minimum to a spectral shift in resonance is determined experimentally as 0.140 \% \frac{\text{power}}{\text{pm}}.

Having proposed several methods to improve sensing accuracy in PCS devices the final experimental chapter of this thesis focuses on making a measurement of RI change at the detection limit (DL) in a un-referenced photonic crystal. The principles of chapter 6 are used to reduce temperature effects by making the measurement at the *athermal point* of the device under study. By measuring the change in transmission power as two fluids with slightly different RIs are exchanged a DL of 6 \times 10^{-6} \text{RIU} is achieved experimentally, which compares favorably with the theoretical DL of 2.5 \times 10^{-6} \text{RIU}. In addition a second measurement is made to determine the DL when a measurement is made of spectral shift rather than change in transmission power. In this case a spectral shift of 2.9 \pm 0.9 \text{pm} is resolved, corresponding to a DL of 1.2 \times 10^{-5} \text{RIU}.

In the future work section fabrication and characterization of a novel triple-mesa structure is presented. This structure demonstrates decoupling between small (108 \, \mu\text{m} diameter) PCS mesas in a honeycomb configuration. This device type can in principle be extended arbitrarily to produce massively multiplexed sensors. In addition the diameter and circular shape of the individual mesas make such a structure suitable for functionalization using antibody inkjet printing.

The future work also demonstrates the realization of the suspended air-substrate architecture discussed in section 3.3.3. Here the TE-like mode is measured by direct transmission and CP transmission. The sensitivity is also determined experimentally. However, as discussed in section 3.3.3 the TE-like mode is not of much interest in air-substrate devices as it does not experience a significant boost in S or Q. The potential of this device type is revealed in the experimental measurement of the TM-like mode, with an S of 707 \, \text{nm} RIU and Q of 1900. This represents a nearly 4.5x improvement in S over the substrate-bound devices studied in this work while maintaining a relatively high Q. The resulting DL is 7.4 \times 10^{-7} \text{RIU}.

Finally the last concept discussed in the future work chapter is referred to as the *split-flow polarization conversion* measurement. This technique comes from an experimentally observed phenomenon where creating a split-flow of two different liquids over a uniform PCS appears to allow for polarization conversion to occur, similar to the CP effect analyzed in section 3.4. Initial measurements appeared to resolve a change in RI of 8 \times 10^{-9} \text{RIU}. If this is in fact correct, then the *split-flow polarization conversion* measurement has the potential to resolve RI differences below that of any optofluidic sensor known to this author.
Appendix A

Contributions

First it must be stated that my work builds upon the fundamental steps taken by Mohammad El Beheiry and Dr. Hooman Akhavan in setting up the photonic crystal lab and fabricating the first photonic crystal slabs in our lab group.

The e-beam processing of samples (ie. spin coating, mounting, developing, fracturing of designs) was always done as a group effort with Dr. Hooman Akhavan, Deniz Aydin, and myself. We would each create our own sample designs, but these cleanroom steps were done as a team. Professor Ofer Levi performed the RIE etching step at Stanford.

The specific acknowledgments for work presented in this thesis are as follows:

A.1 Chapter 5

The microfluidics t-junction channel in section 5.2.2 was developed in collaboration with Deniz Aydin.

A.2 Chapter 6

The mounting system used to attach the peltier element, as shown in figure 6.8 was developed by Deniz Aydin.

A.3 Chapter 7

The initial split-mesa measurements shown in figures 7.3 and 7.4 were done in collaboration with Dr. Hooman Akhavan.
The experimental measurement of the power differential referencing device shown in figure 7.15 was done in collaboration with Dr. Hooman Akhavan.

**A.4 Chapter 8**

The detection limit measurements made in this chapter were done in collaboration with Dr. Hooman Akhavan. This experiment took place over the span of more than one year, with each of us contributing roughly equally to the work. My focus was weighted a little more towards optimization of the microfluidics and measurement algorithms, while Dr. Akhavan’s was more weighted to conducting the measurements.

**A.5 Chapter 10**

The measurements of figure 10.5 were made by Costa Nicholaou.
Appendix B

Cleanroom Recipes

B.1 Film Deposition Recipes

B.1.1 LPCVD SiN$_x$ Film Recipe

Deposition performed with Tylan LPCVD Furnace in the Stanford Nanofabrication Facility

- **Deposition Rate:** 30 Å/minute
- **Temperature:** 800 °C
- **Pressure:** 250 mT
- **Gases:**
  - 5% SiCl$_2$H$_2$
  - NH$_3$

B.1.2 PECVD SiN$_x$ Film Recipe

Deposition performed with Oxford Instruments Plasmalab System 100 PECVD

- **Deposition Rate:** 25 nm/minute
- **Temperature:** 300 °C
- **Pressure:** 800 mT
- **RF Power:** 70 W (13.56 MHz)
• **LF Power:** 50 W (100 KHz)

• **Gases:**
  - 5\% \text{SiH}_4/\text{N}_2 (400 sccm)
  - \text{NH}_3 (20 sccm)
  - \text{N}_2 (400 sccm)

• **Pulse Time:** 13 seconds RF, 7 seconds LF

### B.2 Photoresist Recipes

#### B.2.1 ZEP 520A EBL Resist Spin Recipe

• **Resist Thickness:** 400 nm

• **Cleaning:**
  - 10 minutes ultrasonic bath with acetone
  - 10 minutes ultrasonic bath with isopropyl alcohol
  - 20 minutes piranha organic etch

• **Pre-Bake:** 150°C for 30 minutes

• **Spin Rate:**
  - 3 seconds at 300 RPM
  - 40 seconds at 3000 RPM
  - 20 seconds at 150 RPM
  - **Acceleration:** 584 RPM/second

• **Post Bake:** 180°C for 23 minutes

#### B.2.2 ZEP 520A EBL Resist Development Recipe

• 1. ZED N50 developer for 60 seconds

• 2. 9:1 methyl isobutyl ketone / isopropyl alcohol 30 seconds

• 3. Dry with \text{N}_2
B.2.3 Shipley S1818 Resist Spin Recipe

This recipe is used to coat both sides of the PCS sample with S1818 photoresist before RIE etching square patterns in the $SiN_x$, which are used as a hard mask for KOH substrate etching. The front side of the PCS is coated with S1818 to protect the PCS pattern during RIE etching. In this process the front side is coated first, and a soft bake is performed on a hot plate for 1 minute at 100 $^\circ$C before coating the backside side.

- **Resist Thickness:** 400 nm

- **Cleaning:**
  - 10 minutes ultrasonic bath with acetone
  - 10 minutes ultrasonic bath with isopropyl alcohol
  - 20 minutes piranha organic etch

- **Pre-Bake:** 100$^\circ$C for 30 minutes

- **Primer:** P-20 Primer

- **Spin Rate:**
  - 10 seconds at 500 RPM
  - 30 seconds at 4000 RPM
  - 20 seconds at 500 RPM
  - **Acceleration:** 600 RPM/second

- **Post Bake:** 100$^\circ$C for 20 minutes

B.2.4 Shipley S1818 Resist Development Recipe

- 1. MF-321 developer for 60 seconds

- 2. Distilled $H_2O$ rinse for 60 seconds

- 3. Dry with $N_2$
B.3 Etch Recipes

B.3.1 RIE SiN\textsubscript{x} Etch Recipe (PCS patterning)

This etch recipe is performed using the AMT RIE at Stanford. This process is used to pattern the PCS holes in the SiN\textsubscript{x} slab.

- **SiN\textsubscript{x} Etch Rate:** 32 nm/minute
- **SiO\textsubscript{2} Etch Rate:** XX nm/minute
- **Pressure:** 40 mT
- **Bias Voltage:** -370 V
- **Gases:**
  - NF\textsubscript{3} (15 sccm)

B.3.2 O\textsubscript{2} Ashing Recipe

This recipe is performed using the Drytek 4 plasma oxide chamber at Stanford. This process is used to remove residual ZEP 520A resist after patterning of the PCS holes.

- **Pressure:** 100 mT
- **Plasma Power:** 150 W
- **Gases:**
  - O\textsubscript{2} (20 sccm)

B.3.3 RIE SiN\textsubscript{x} Etch Recipe (Backside etch)

This etch recipe is performed using the Trion Phantom RIE at the University of Toronto. This process is used to pattern squares in the backside SiN\textsubscript{x} for KOH substrate etching, as well as to remove the backside SiN\textsubscript{x} prior to deposition of anti-reflective coating. Backside helium gas is used to cool the sample.

- **SiN\textsubscript{x} Etch Rate:** 30 nm/minute
- **Pressure:** 40 mT
• **RF Power:** 25 W (13.56 MHz)

• **ICP Power:** 200 W

• **Gases:**
  - $SF_6$ (45 sccm)
  - $O_2$ (5 sccm)
  - Backside Helium (10 sccm)

### B.3.4 RIE SiO$_2$ Etch Recipe

This etch recipe is performed using the Trion Phantom RIE at the University of Toronto. This process is used to remove the backside SiO$_2$ prior to deposition of anti-reflective coating. Backside helium gas is used to cool the sample.

• **SiO$_2$ Etch Rate:** 215 nm/minute

• **Pressure:** 15 mT

• **RF Power:** 70 W (13.56 MHz)

• **ICP Power:** 400 W

• **Gases:**
  - $CHF_3$ (50 sccm)
  - Backside Helium (10 sccm)

### B.3.5 KOH Wet Etch Recipe

This wet etch recipe is used to etch windows through the silicon substrate for to create the *air-substrate* samples. Temperature is maintained using a hotplate and a magnetic stirring bead is used to continuously stir the solution during etching.

• **Si Etch Rate:** 120 µm/hour

• **Temperature:** 90° $^\circ$C

• **KOH Concentration:** 25 wt.% in $H_2O$
Appendix C

Simulation Code

C.1 Scatter Matrix Simulation Code (LUA language)

C.1.1 Temperature Dynamics Simulation

Ann thesis IR, r110 auto.lua This script simulates thermal expansion and thermo-optic dispersion in dielectric PCS structures over a range of temperatures with user defined steps. Each simulation is output in a tab delimited text file with the normalized frequency and transmission data. Each text file has the temperature of the simulation appended to the name. The particular script shown simulations a PCS with a = 980 nm, r = 110 nm, SiN thickness = 260 nm, SiO2 thickness = 2.35 μm, and an infinite thickness silicon substrate.

```
1
2 ——Author: Ryan Schilling, 2012
3 ——Simulates thermal expansion and thermo-optic
4 ——dispersion in dielectric PCS structures over
5 ——a range of temperatures with user defined steps
6
7
8 start_temp = 0          —— set this
9 end_temp = 40           —— set this
10 temp_step = 2          —— set this
11 start_wavelength = 1.555 —— set this
12 stop_wavelength = 1.580 —— set this
13 exp_coeff = 2.6e-6     —— thermal expansion term for Si at
```

— ...
room temperature

real_a = .980  — vary this

r = 0.110  — vary this

r_norm = r/real_a

Th = 0.260  — vary this

Th_norm = Th/real_a

ThOxide = 2.35  — vary this

ThOxide_norm = ThOxide/real_a

thin_SiN_slab = 0.050  — vary this

thin_SiN_slab_norm = thin_SiN_slab/real_a

num_points= 1000  — number of sample points

num_threads = 16  — number of processors

num_blocks = math.ceil(num_points/num_threads)

for Δ_temp = start_temp, end_temp, temp_step do

T = Δ_temp + start_temp

start_lambda=real_a*exp_coeff*Δ_temp/start_wavelength

end_lambda=real_a*exp_coeff*Δ_temp/stop_wavelength

—create text file

xprecision = 10;

yprecision = 10;

fstr = "%."..tostring(xprecision).."f "%."..tostring(yprecision).."f\n"

fp=io.open("r110_a980_temp_" .. T .. ".txt","w+")

—

—calculate water index

n0 = 1.32439
54 \( a_1 = 1.80493 \times 10^{-6} \)
55 \( a_2 = -3.51125 \times 10^{-7} \)
56 \( a_3 = -3.43087 \times 10^{-8} \)
57 \( a_4 = 1.92607 \times 10^{-10} \)
58 \( n_{\text{water}} = n_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \)
59
60 — setup simulation
61
62 \( a = 1 \)
63 \( S = S4.\text{NewSimulation}() \)
64 \( S:\text{SetLattice}\{\{a,0\}, \{0,a\}\} \)
65 \( S:\text{SetNumG}(49) \)
66
67
68 — define material values for a given temperature
69
70 \( S:\text{AddMaterial}\{\text{"air"}, \{1,0\}\} — \text{real and imag parts} \)
71 \( S:\text{AddMaterial}\{\text{"water"}, \{\left(n_{\text{water}}\right)^2,0\}\} \)
72 \( S:\text{AddMaterial}\{\text{"silicon\_nitride"}, \{(2+a_{\text{temp}} \times (40+10^{-6}))^2,0\}\} \)
73 \( S:\text{AddMaterial}\{\text{"dlc"}, \{2.56,0\}\} \)
74 \( S:\text{AddMaterial}\{\text{"silicon\_oxide"}, \{(1.46+a_{\text{temp}} \times (10+10^{-6}))^2,0\}\} \)
75 \( S:\text{AddMaterial}\{\text{"silicon"}, \{(3.48+a_{\text{temp}} \times (230+10^{-6}))^2,0\}\} \)
76
77 — define structure geometry
78
79 \( S:\text{AddLayer}\{\text{"waterabove"}, 0, \text{"water"}\} \)
80
81 \( S:\text{AddLayer}\{\text{"pc\_slab1"}, \text{Th\_norm}, \text{"silicon\_nitride"}\} \)
82
83 \( S:\text{SetLayerPatternCircle}\{\text{"pc\_slab1"}, \text{"water"}, \{0,0\}, \text{r\_norm}\} \)
84
85 —
86 — Use the following 2 lines for substrate-bound structures
87
88 \( S:\text{AddLayer}\{\text{"bottom"}, \text{ThOxide\_norm}, \text{"silicon\_oxide"}\} \)
89
90 \( S:\text{AddLayer}\{\text{"Substrate"}, 0, \text{"silicon"}\} \)
Use the following 2 lines for suspended structures

S:AddLayer('bottom', thin_SiN_slab_norm, 'silicon nitride')
S:AddLayer('Substrate', 0, 'air')

—

Use the following 1 line for symmetric structures

S:AddLayer('Substrate', 0, 'water')

—

S:SetExcitationPlanewave({0,0}, — incidence angles
{1,0}, — s-polarization amplitude and phase (in degrees)
{0,0}) — p-polarization amplitude and phase

— Turn on smoothing for better convergence behavior w.r.t. NumG ...
S:EnableLanczosSmoothing()

S_sweep = {}
freq = {}
forward = {}

for j = 1, num_blocks do

— Populate array for frequency sweep
for i = 1, num_threads do
    S_sweep[i] = S:Clone()
freq[i] = start_lambda - (start_lambda - end_lambda) * (i + ...
    j*num_threads)/num_points
    S_sweep[i]:SetFrequency(freq[i])
end

— Solve in Parallel
C.2 MATLAB Scripts

C.2.1 Simulation Data Fitting with Fano Equation

required m-files: extrema.m, fit_fano_eqn.m, fwhm.m

```matlab
%%Author: Ryan Schilling, 2012
%%Convert S4 output file to wavelength domain and find resonance locations
%%and Q
%%give (txt) file name and lattice constant (in nm) as inputs
%%This function REQUIRES the following m-files: extrema.m, fit_fano_eqn.m,
%%and fwhm.m

function [peak_loc, QF] = s4fcn(file,a)

res_width = 1; %change value between 0.005 - 2 (small for high Q, large
%for low Q (represents the FWHM of resonance in [nm])

%load data%
arg=strcat(file,'.txt');
data=load(arg);

% x=fliplr((data(:,1))');
% y=fliplr((data(:,2))');
x=(data(:,1))';
y=(data(:,2))';

%convert normalize frequency (f = a/lambda) to wavelength
```
x=(a./x)';
y=y';

%% automatically find approx. resonance width
res_width = abs(fwhm(x,y))

%% find extrema using extrema.m function
[ymax,imax,ymin,imin] = extrema(y)
% imin

if length(imin) ≥1
tep = x(imin(1))
end

if length(imin) ≥2
tmp = x(imin(2));
end

%% check if extrema represent TE/TM peaks, and flag if peak doesn’t exist
te_exists = 1;
tm_exists = 0;

if length(imin) ≥1
if y(imin(1)) ≥ 0.5  %% default .5
    te_exists = 0;
end
end

if length(imin) ≥2
if y(imin(2)) < 0.3  %% default .3
    tm_exists = 1;
end
end

% if length(imin) ≥1
% if 0.5 > y(imin(1)) && y(imin(1)) > 0.1
% % tm_exists = 1;
% tmp = tep;
% end
% end
% end

if length(imin) < 1
    te_exists = 0
end

% tm_exists = 0
% te_exists = 1

%% Split data into two parts to fit peaks
if tm_exists == 1
    tm_x = x;
    tm_y = y;
end

if te_exists == 1
    te_x = x;
    te_y = y;
end

if te_exists == 1 && tm_exists == 1
    split_dist = imin(1) - imin(2);
    tm_A = round(split_dist/3);
    te_A = round(split_dist*.8);
    tm_i0 = imin(2) - tm_A;
    if tm_i0 < 1
        tm_i0 = 1;
    end
    tm_x = x(tm_i0:imin(2)+tm_A);
    tm_y = y(tm_i0:imin(2)+tm_A);
    te_ix = imin(1)+te_A;
    if te_ix > length(x)
        te_ix = length(x);
    end
    te_x = x(imin(1)-te_A:te_ix);
    te_y = y(imin(1)-te_A:te_ix);
end
if tm_exists ==1
  \%\ guess fitting parameters for TM resonance
  a0=[0,-1e-6,.1,tmp,.1];
  \%\ fit to data using Fano Lineshape\%
  options = optimset('Display','off','iter','TolFun',1e-23,'TolX',1e-23,...
  'MaxFunEvals',2400,'MaxIter',3000);
  [tm_result,tm_resnorm] = lsqcurvefit(@fano_fit_eqn,a0,tm_x,tm_y,...
  [],[],options);
  tm_xDelta = ((tm_x(2)-tm_x(1)))/10;
  tm_x = tm_x(1):tm_xDelta:tm_x(end);
  tm_F = tm_result(1) + tm_result(2)*(((tm_result(3)+2*...
  (tm_x-tm_result(4))/tm_result(5)).^2)./(1+(2*(tm_x-tm_result(4))...
  /tm_result(5)).^2));
end

if te_exists ==1
  \%\ guess fitting parameters for TE resonance
  a0=[1,1e-6,.1,1517,2];
  \%\ fit to data using Fano Lineshape\%
  options = optimset('Display','off','iter','TolFun',1e-23,'TolX',1e-23,...
  'MaxFunEvals',2400,'MaxIter',3000);
  [te_result,te_resnorm] = lsqcurvefit(@fano_fit_eqn,a0,te_x,te_y,...
  [],[],options);
  te_xDelta = ((te_x(2)-te_x(1)))/10;
  te_x = te_x(1):te_xDelta:te_x(end);
  te_F = te_result(1) + te_result(2)*(((te_result(3)+2*...
  (te_x-te_result(4))/te_result(5)).^2)./(1+(2*(te_x-te_result(4))...
  /te_result(5)).^2));
end

\%\ use q to decide whether peaks are TE or TM
if te_exists ==1 && tm_exists ==1 && abs(tm_result(3)) \geq 0.25
temp_F = tm_F;
temp_tm_x = tm_x;
temp_tm_result = tm_result;

tm_F = te_F;
tm_x = te_x;
tm_result = te_result;

te_F = temp_F;
te_x = temp_tm_x;
te_result = temp_tm_result;
end

if te_exists ==1 && abs(te_result(3)) < 0.25
    tm_F = te_F;
tm_x = te_x;
tm_result = te_result;
te_exists = 0;
tm_exists = 1;
end

%% calculate quality factors
if tm_exists ==1
    tm_width = fwhm(tm_x,tm_F);
tm_qf = tm_result(4)/tm_width;
tm_Q_Fano = tm_result(4)/tm_result(5);
QF = tm_Q_Fano;
peak_loc = tm_result(4);
end

if te_exists ==1
    te_width = fwhm(te_x,te_F);
te_qf = te_result(4)/te_width;
te_Q_Fano = te_result(4)/te_result(5);
QF = te_Q_Fano;
peak_loc = te_result(4);
end

if te_exists ==1 && tm_exists ==0
    plot(te_x,te_F,'-b',x,y,'xk','Linewidth',3);
% add legend
hleg1 = legend('TE Fano Fit', 'Measurement Data', 'FontSize', 14);
end

% if te_exists == 0 && tm_exists == 1
plot(tm_x, tm_F, '-r', x, y, 'xk', 'Linewidth', 3);
% add legend
hleg1 = legend('TM Fano Fit', 'Measurement Data', 'FontSize', 14);
% also adjust imin for proper resonance text labels
imin(2) = imin(1);
Bibliography


[2] Daniela Threm, Yousef Nazirizadeh, and Martina Gerken. Photonic crystal biosensors towards on-chip integration. *Journal of Biophotonics*, 5(8-9):601 – 616, 2012. 1-D photonic crystal; Biomolecular; Compact devices; Detection limits; Environmental applications; Low cost fabrication; Mass scale; Microfluidic channel; On-chip; On-chip integration; Pathogen detection; Photonic crystal microcavities; Photonic crystal sensors; Photonic crystal slab; Photonic crystal waveguide; Sensitive sensors.


