Design, Fabrication, and Testing of an Integrated Optical Hydrogen and Temperature Sensor

by

Nicholas Osawa Carriere

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

© Copyright by Nicholas Osawa Carriere 2013
Design, Fabrication, and Testing of an Integrated Optical Hydrogen Sensor

Nicholas Osawa Carriere
Masters of Applied Science
Graduate Department of the Edward S. Rogers Sr. Department of Electrical and Computer Engineering
University of Toronto
2013

Abstract

In this thesis, the details of the design, fabrication, and characterization of an optical, integrated hydrogen gas and temperature sensor are explored. The hydrogen sensor is implemented by coating a ridge waveguide with a thin layer of palladium and shows very good response time and detection response for hydrogen concentrations ranging from 0.5-4%, both of which compare very favourably to similar existing technologies. Multiple film thicknesses were tested and it was found that thinner films give a faster response time at the expense of a reduced detection response. The temperature sensor is implemented with a multi-mode interferometer coupled ring resonator and has a sensing range of 100 K with good sensitivity. Both sensors are fabricated on a silicon-on-insulator platform and could easily be integrated together onto a single chip as part of an optical nose technology that would have the ability to sense multiple environmental factors simultaneously.
Acknowledgments

First and foremost, I would like to thank my supervisor, Professor Stewart Aitchison. His helpful guidance and support throughout my studies have been invaluable. Someone I would also like to thank, who had a role which was almost equally as important, is Muhammad Alam. This work would not have been possible without him and I owe him a great deal of gratitude for his patience and help.

There are many other colleagues and professors who I have to thank for their help throughout my studies: Farshid Bahrami for his help in the cleanroom and for his support in the early part of the project, Sean Wagner for his instruction and patience in the lab, Arash Joushaghani for his insights and help with testing and fabrication, Pisek Kultavewuti for his support throughout the project, Xiao Sun for her help with fabrication, Niklas Caspars and Ksenia Dolgaleva for their support in the characterization lab, Mariya Yagnyukova and Sutha Sathananthan for the helpful discussions concerning fabrication, Professors Mo Mojahedi and Glenn Hibbard for the discussions and support, and last but not least, Alex Tsukernik, Henry Lee, and Yimin Zhou for ensuring that my cleanroom visits were efficient and productive.

Finally, I would like to thank my family and my girlfriend, Emily. Their continuing love and support is very much appreciated.
Table of Contents

Acknowledgments .................................................................................................................... iii

Table of Contents ................................................................................................................ iv

List of Tables ....................................................................................................................... vii

List of Figures .................................................................................................................... viii

Chapter 1 Introduction ........................................................................................................ 1

1 Introduction ....................................................................................................................... 1

1.1 Motivation for Optical Hydrogen Sensors ................................................................. 1

1.2 Summary of Thesis ....................................................................................................... 1

Chapter 2 Literature Review: Hydrogen Sensors .............................................................. 3

2 Literature Review: Hydrogen Sensors ........................................................................... 3

2.1 Existing Hydrogen Sensor Technologies ..................................................................... 3

2.2 The Palladium Hydrogen System ............................................................................... 5

2.3 Palladium-Based Hydrogen Sensors ........................................................................... 6

2.3.1 Interferometric-Based Sensors ................................................................................ 6

2.3.2 Grating-Based Sensors .......................................................................................... 13

2.3.3 Intensity-Based Sensors ......................................................................................... 17

2.4 Table of Comparison .................................................................................................. 24

Chapter 3 Literature Review: Temperature Sensors ........................................................ 26

3 Literature Review: Temperature Sensors ...................................................................... 26

3.1 Integrated Sensors ....................................................................................................... 26

3.2 Fibre Sensors ............................................................................................................... 35

Chapter 4 Hydrogen Sensor Design ................................................................................... 44
4 Hydrogen Sensor Design ........................................................................................................ 44
  4.1 Waveguide Width and Pedestal Height ........................................................................ 45
  4.2 Palladium Layer Dimensions ..................................................................................... 49
Chapter 5 Hydrogen Sensor Fabrication ............................................................................. 50
  5 Hydrogen Sensor Fabrication .......................................................................................... 50
    5.1 Waveguide Fabrication .................................................................................................... 50
      5.1.1 Pattern Exposure and Development ........................................................................ 52
      5.1.2 Pattern Etching ......................................................................................................... 53
    5.2 Lift-Off Preparation ...................................................................................................... 54
    5.3 Metal Deposition and Lift-Off ..................................................................................... 56
    5.4 Hydrogen Sensor Fabrication Results ......................................................................... 57
Chapter 6 Sensor Characterization .......................................................................................... 60
  6 Hydrogen Sensor Characterization ................................................................................... 60
    6.1 Experimental Setup ........................................................................................................ 60
    6.2 Losses ........................................................................................................................... 61
    6.3 Temporal Response ......................................................................................................... 62
      6.3.1 Results for Palladium Depositions Ranging from 2-5 nm ........................................ 63
      6.3.2 Results for Palladium Deposition of 1 nm ............................................................... 66
    6.4 Hysteresis ...................................................................................................................... 68
      6.4.1 Results for 2-5 nm Palladium Deposition ................................................................. 69
      6.4.2 Results for 1 nm Palladium Deposition .................................................................... 70
    6.5 Response Time ............................................................................................................... 71
      6.5.1 Results for 2-5 nm Palladium Deposition ................................................................. 71
      6.5.2 Results for 1 nm Palladium Deposition .................................................................... 73
Chapter 7 The Optical Nose: Design and Implementation of a Temperature Sensor .......... 75
  7 The Optical Nose: Design and Implementation of a Temperature Sensor ....................... 75
7.1 The Optical Nose ........................................................................................................... 75
7.2 Temperature Sensor Design ............................................................................................. 75
7.3 Temperature Sensor Fabrication ....................................................................................... 78
7.4 Temperature Sensor Characterization ............................................................................... 80
   7.4.1 Experimental Setup .................................................................................................... 80
   7.4.2 Results ....................................................................................................................... 81
Chapter 8 Conclusions and Future Work ............................................................................. 85
8 Conclusions and Future Work ............................................................................................ 85
   8.1 Summary of Contributions ............................................................................................. 85
   8.2 Future Work .................................................................................................................. 85
      8.2.1 Palladium Alloys to Reduce Hysteresis Effects ......................................................... 86
      8.2.2 Extensive Characterization of Thin Palladium Films ................................................. 86
References .............................................................................................................................. 87
List of Tables

2.1 Summary of existing hydrogen sensor technologies.

5.1 Parameters used for the RIE etching recipe.

5.2 Details of the lift-off recipe used for hydrogen sensor fabrication.
List of Figures

2.1 Phase diagram of the palladium-hydrogen system showing $\alpha$ and $\alpha'$ ($\beta$) phases.

2.2 The absorption process of hydrogen into palladium. a) Palladium atoms before hydrogen absorption. b) Palladium lattice is in the $\alpha$-phase as hydrogen atoms are absorbed. c) Lattice expands as more hydrogen is absorbed and lattice enters the $\beta$-phase. d) After the palladium is flushed with nitrogen, the lattice mostly recovers, but retains some deformation.

2.3 MZI-based hydrogen sensor by Butler.

2.4 Schematic of the LPG-based hydrogen sensor by Kim.

2.5 Schematic of the fs-laser processed micro-cavity hydrogen sensor by Wang.

2.6 Schematic (a) and cross-section (b) of the integrated MZI sensor by Bearzotti.

2.7 Schematic of the intrinsic cavity sensor by Maciak.

2.8 Schematic of the extrinsic FP cavity sensor by Yang.

2.9 Schematic of a typical fibre Bragg grating and refractive index profile.

2.10 Reflection spectrum of a typical Bragg grating.

2.11 Schematic of the Bragg grating hydrogen sensor by Sutapun.

2.12 Schematic of the Bragg grating sensor by Schroeder.

2.13 a) Sensor response as a function of hydrogen concentration for $T = 30^\circ$C. b) Sensor response as a function of hydrogen concentration for $T = 100^\circ$C, $T = 150^\circ$C, $T = 200^\circ$C.

2.14 Structure of a typical micromirror sensor.

2.15 Detection response (a) and response time (b) of Pd micromirror sensor as a function of gas temperature at when exposed to a constant 4% atmospheric hydrogen concentration.
2.16 Detection response of the micromirror sensor as a function of optical power for a variety of hydrogen gas temperatures.

2.17 Detection response of stripped MMF sensor to 0.6% hydrogen.

2.18 Structure of tapered SMF hydrogen gas sensor.

2.19 Detection response of tapered SMF sensor to hydrogen concentrations ranging from 1.8-10%.

2.20 Schematic of SMF embedded into quartz fibre-holding circular groove.

2.21 Detection response of sensor coated in (a) 20 nm Pd and (b) 100 nm Pd, also showing response and recovery times. c) Simulated transmission losses of the sensor when coated in Pd layers ranging from 5-40 nm.

3.1 Schematic of the Fabry-Perot sensor.

3.2 Transmitted intensity of the device for cavity lengths of 1700 µm and 100 µm.

3.3 Schematic and SEM (inlaid) of the silicon ring resonator device making use of grating couplers for input and output coupling.

3.4 Measured transmission spectrum of the ring resonator temperature sensor.

3.5 a) Transmission spectrum, showing a single resonance peak, for a range of temperatures from 16-45°C

b) Sensitivity of the device for a range of waveguide widths.

3.6 a) Transmitted spectrum of the device, showing a single resonance peak, for temperatures ranging from 21-22°C b) Location of the measured resonance peak over a range of temperatures, showing a sensitivity of 77 pm/K.

3.7 Schematic of the bi-modal Y branch temperature sensor.

3.8 Spatial interference profile and output intensities for temperatures of 25°C (a) and for 300°C (b).
3.9  Output power at outputs A and B for temperatures ranging from 25-300°C.

3.10  Schematic of the multimode interferometer sensor.

3.11  Results of the multimode interferometer sensor compared to the bi-modal Y branch sensor.

3.12  Asymmetric transmitted intensity as a function of temperature.

3.13  Simulated results showing how the sensitivity of the device can be tuned by the length of the fibre ring.

3.14  Diagram of the fluorescent epoxy micromirror sensor.

3.15  Detected spectrum showing both the fluorescence signal as well as some of the input light that has been reflected off the micromirror and coupled into the detection fibre.

3.16  a) Fluorescence intensity of the sensor with respect to temperature (ranging from 20-100°C)
   b) Time response of the fluorescent sensor compared to the time response of a commercially available thermocouple.

3.17  Schematic of the Fabry-Perot cavity sensor.

3.18  a) Simulated reflectivity of the Fabry-Perot cavity as a function of refractive index of the cavity material  b) Reflected signal intensity detected by the OTDR for temperatures ranging from -30-80°C.

3.19  OTDR trace for three temperature sensors on the same fibre, showing the detected response for -30°C (indicated by line a, in black) and for 30°C (indicated by line b, in red).

3.20  Diagram of the tapered fibre MMI sensor.

3.21  a) Spectrum of the device output for temperatures ranging from -21.6-78.8°C
   b) Output power of the device for temperatures ranging from -20-80°C.
4.1 Schematic of the Pd-coated hydrogen sensor waveguide.

4.2 Structure of hydrogen sensor waveguide used in Lumerical MODE Solutions (Pd thickness exaggerated for easy viewing).

4.3 Simulation results showing the simulated metal losses for different waveguide configurations.

4.4 Simulated TE mode profiles for waveguides with a) no pedestal and b) 90 nm pedestal.

4.5 Simulation results showing the simulated metal losses for different waveguide configurations assuming full sidewall deposition of the metal.

4.6 Simulated TE mode profile with no pedestal and full sidewall metal deposition.

5.1 CAD layout showing a section of the hydrogen sensor. Each cell (separated by crosses) contains waveguides of different widths. Crosses are used for alignment during lift-off stage.

5.2 CAD layout of the designed taper. Red indicates the non-exposed area where the waveguide is defined. Blue indicates an area of low resolution exposure and green indicates an area of high resolution exposure.

5.3 CAD layout of a section of waveguide.

5.4 Diagram showing the process of resist application and pattern etching. a) Un-etched SOI wafer. b) Un-etched SOI wafer with positive resist that has been applied, exposed, and developed into the desired pattern. c) SOI wafer after etching. d) SOI wafer after etching and resist removal showing the waveguide ridge.

5.5 CAD layout of the lift-off mask. Red areas are chrome (opaque).

5.6 CAD layout of the waveguide and lift-off masks to illustrate how the lift-off procedure works. a) CAD layout of a section of the waveguide mask. b) CAD layout of a section of the lift-off mask. c) The lift-off mask superimposed on top of the waveguide mask. The thin strips align perfectly with the waveguides, creating a window for metal deposition. The square block is used as a marker and for thickness testing purposes.
5.7 Diagram showing the metal deposition process. a) Etched SOI wafer. b) SOI wafer after resist is applied, exposed, and developed. Resist creates a window for metal deposition. c) Wafer after metal deposition. Metal is deposited only within the windows created by the resist. d) Wafer after metal deposition and final resist removal. The end result is a ridge waveguide with a strip of metal coating a section of it.

5.8 SEM image of the two adjacent troughs that were etched in order to create a single waveguide.

5.9 Zoomed-in SEM image of a single etched waveguide.

5.10 SEM image of a 2 nm thick deposition of palladium (of lengths 8 µm and 12 µm) onto two separate waveguides.

5.11 Zoomed-in SEM image of a 2 nm thick palladium deposition onto a single waveguide.

6.1 Schematic of the experimental setup for hydrogen sensor characterization.

6.2 Metal losses of the various Pd-coated waveguides.

6.3 Temporal response of a Pd-coated waveguide when exposed to hydrogen gas.

6.4 a) Detection response values for different lengths of palladium films (2 nm thickness) and waveguides with different pedestal heights b) Average detection response of waveguides for varying pedestal heights (2 nm palladium thickness).

6.5 Detection response for varying hydrogen concentrations for a waveguide with pedestal height of 90 nm, palladium thickness of 3 nm and length of 20 µm.

6.6 Temporal response of a waveguide coated in 1 nm of Pd.

6.7 Plot showing the hysteresis effect present in a typical Pd-coated waveguide when exposed to hydrogen.

6.8 Hysteresis loops for palladium thicknesses of 2,3, and 5 nm Pd depositions.

6.9 Hysteresis loop for palladium thickness of 1 nm.
6.10 Response time data for palladium thicknesses of 2, 3, and 5 nm.

6.11 Theorized phase diagrams for thick and thin palladium films.  a) Phase diagram for thick palladium film (approaching bulk)  b) Theorized phase diagram for very thin palladium film.

6.12 Response time data for palladium thickness of 1 nm.

7.1 Diagram showing the relevant dimensions when designing an MMI coupler.  i) Height of the coupler (equal to the silicon top layer height minus the etch depth)  ii) Center-to-center input/output waveguide separation  iii) MMI width  iv) MMI length.

7.2 SEM image of a 4.5 µm long MMI coupler.

7.3 Zoomed-in SEM image of the input waveguide gap on an MMI coupler.

7.4 SEM image of MMI coupled ring resonator.

7.5 Schematic showing the experimental setup for temperature sensor characterization.

7.6 Transmission spectrum for one of the ring resonator temperature sensors (50/50 coupler, 4.5 µm wide coupling section, 5 µm ring radius).

7.7 A single resonance peak of the sensor for temperatures varying from 20-50°C.

7.8 Free spectral range (a), sensitivity (b), and Effective sensing range (c) of the device for varying ring radii.

7.9 Intensity-based sensing scheme for the ring resonator temperature sensor.  a) Experimental data for a single resonance peak showing the transmitted intensity at a specified wavelength for each temperature  
b) Normalized transmission of the sensor as a function of temperature.
Chapter 1
Introduction

1 Introduction

1.1 Motivation for Optical Hydrogen Sensors

The high price and volatile supply source of oil as well as the desire to move towards greener sources of energy has created an interest in the use of alternative fuels, such as hydrogen. According to the Canadian Hydrogen and Fuel Cell Association, the global hydrogen and fuel cell market is poised to be worth $8.5 billion by 2016 [1]. As hydrogen gas is odourless, colourless, tasteless, and can be explosive in volumetric quantities as low as 4% [2], it is vital to have an inexpensive device that can quickly, reliably and safely monitor hydrogen concentrations in case there is a leak.

Currently, many different technologies for hydrogen detection are being used or are under development including: semiconductor sensors, thermoelectric sensors, electrochemical sensors, and mass spectroscopy [3]. Unfortunately, these sensing methods have a number of disadvantages, such as large size, high cost, dependence on the presence of oxygen, or potential to create electrical sparks that would be dangerous in explosive environments.

Optical hydrogen sensing offers a number of advantages over competing technologies including compact size, increased safety and immunity from electromagnetic interference. Silicon-on-insulator (SOI) is an excellent platform for implementation of optical sensors as it is easy to mass fabricate using CMOS fabrication technology, it is very compact, and it has the potential to integrate electronics and photonics on the same platform. Moreover, by using an integrated SOI platform, the number of sensing elements on a single chip could be increased in order to create an optical nose. As there would be no need to have any electrical components on the sensor package, there would be no risk of electrical spark, which makes the sensor very safe for use in potentially explosive environments.

1.2 Summary of Thesis

This thesis will begin with a literature review of relevant hydrogen and temperature sensors, in chapters 2 and 3 respectively. The details of the palladium-hydrogen system as well as existing
palladium-based hydrogen sensors will be the subject of chapter 2, while chapter 3 will focus on a review of integrated and fibre-based temperature sensors.

Chapters 4, 5, and 6 will focus on the design, fabrication, and characterization of the hydrogen sensor. Chapter 4 will include the design details and decisions that are relevant to the hydrogen sensor. Chapter 5 will include all of the fabrication steps and processes that were used in order to create working samples of the hydrogen sensor. Chapter 6 will discuss the experimental results that were obtained from testing the hydrogen sensor samples.

The topic of chapter 7 will be the idea of an optical nose as well as a theoretical and experimental demonstration of a temperature sensor that could be integrated onto the same platform as the hydrogen sensor. The design, fabrication and characterization of the temperature sensor will all be thoroughly detailed.

Finally, chapter 8 culminates with a summary of the contributions of this thesis as well as some possible area that future work could be done in order to improve and better understand the work that this thesis is focused on.
Chapter 2
Literature Review: Hydrogen Sensors

2 Literature Review: Hydrogen Sensors

2.1 Existing Hydrogen Sensor Technologies

Before we go into more details about the theory and operation of optical hydrogen sensors, it would be good to first get an idea of the other technologies that are available and their respective strengths and weaknesses. There are a number of different technologies and configurations that exist both in academia and commercially. For a more detailed description and review of existing hydrogen sensor technologies, an excellent paper by Hubert [3] was recently published which goes into far more details than presented here.

Before discussing optical hydrogen sensing in more detail, I will first summarize the advantages and disadvantages of other existing technologies in order to better understand where optical sensing can fit in the current landscape. These advantages and disadvantages are summarized in table 2.1.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic</td>
<td>• Robust</td>
<td>• Not completely selective to hydrogen gas</td>
</tr>
<tr>
<td></td>
<td>• Wide operating temperature</td>
<td>• Requires oxygen (5-10%) in the atmosphere for operation</td>
</tr>
<tr>
<td>Thermal</td>
<td>• Simple configuration</td>
<td>• Doesn’t have a very low detection limit</td>
</tr>
<tr>
<td>Conductivity</td>
<td>• Resistant to poisoning</td>
<td>• Cross sensitive to helium gas</td>
</tr>
<tr>
<td></td>
<td>• Low cost</td>
<td></td>
</tr>
<tr>
<td>Electrochemical</td>
<td>• Fast response time</td>
<td>• High cost</td>
</tr>
<tr>
<td></td>
<td>• Low power consumption</td>
<td>• Cross sensitive to CO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Limited lifetime</td>
</tr>
<tr>
<td>Resistance</td>
<td>• Low cost</td>
<td>• Humidity and temperature</td>
</tr>
<tr>
<td>Type</td>
<td>Advantages</td>
<td>Disadvantages</td>
</tr>
<tr>
<td>--------------------</td>
<td>----------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Work Function</td>
<td>• Fast response time</td>
<td>• Interference</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Poor selectivity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Requires oxygen for operation</td>
</tr>
<tr>
<td></td>
<td>• Low cost</td>
<td>• Sensor response drift</td>
</tr>
<tr>
<td></td>
<td>• Small size</td>
<td>• Hysteresis</td>
</tr>
<tr>
<td></td>
<td>• Possible to mass produce with existing infrastructure</td>
<td>• Saturates at low concentrations</td>
</tr>
<tr>
<td>Mechanical</td>
<td>• Small size</td>
<td>• Slow response time</td>
</tr>
<tr>
<td></td>
<td>• No source of ignition (usable in potentially explosive environments without risk)</td>
<td>• Susceptible to poisoning from other gases</td>
</tr>
</tbody>
</table>

Table 2.1.: Table comparing the advantages and disadvantages of the different types of hydrogen sensors
2.2 The Palladium Hydrogen System

The palladium hydrogen system is one of the most studied metal hydrogen systems. As palladium is exposed to hydrogen gas, it will absorb hydrogen atoms. Below the critical point \( (T_c = 293^\circ C) \) [4], PdH is a two-phase system. The phase diagram of this system can be seen in figure 2.1.

![Phase diagram of the palladium-hydrogen system showing α and α' (β) phases.](image)

At room temperatures (~300K), at H/Pd ratios lower than approximately 0.015 [5], the medium exists solely in the α-phase. At H/Pd ratios higher than approximately 0.6, the medium fully undergoes a phase transformation into the β-phase, which has a larger lattice constant than the α-phase. As a result of this, as the material undergoes full phase transformation from the α-phase to the β-phase, there is a volume expansion of approximately 10% due to the amount of hydrogen that has been absorbed [6]. For intermediate H/Pd ratios, a mixture of the α and β-phases is observed. The α-phase is a solid solution phase where the hydrogen atoms mix into the palladium lattice without forming chemical bonds. The β-phase is a hydride phase, where the hydrogen atoms bond with the palladium lattice to form Pd-H bonds. The phase diagram is an
interesting one as it displays an upper critical solution temperature (labeled $T_c$), above which the components of the system (Pd and H) are miscible in all proportions. This means that at temperatures above the upper critical solution temperature, there is only a solid solution phase, and the solution will behave like the $\alpha$-phase. The absorption process of hydrogen into palladium is illustrated in figure 2.2.

![Fig. 2.2: The absorption process of hydrogen into palladium. a) Palladium atoms before hydrogen absorption. b) Palladium lattice is in the $\alpha$-phase as hydrogen atoms are absorbed. c) Lattice expands as more hydrogen is absorbed and lattice enters the $\beta$-phase. d) After the palladium is flushed with nitrogen, the lattice mostly recovers, but retains some deformation. Reprinted from [7], © (2010) with permission from the International Association of Hydrogen Energy.](image)

Another notable property of palladium that changes as it absorbs hydrogen is the electron density [6]. As palladium absorbs hydrogen, the reduced density of the metal leads to a reduced density of free electrons. This change in electron density leads to a change in the complex refractive index of the material, which is a very useful transducer for hydrogen gas detection.

### 2.3 Palladium-Based Hydrogen Sensors

Palladium is an excellent transducer for hydrogen sensors as it offers good sensitivity, fast response times, and minimal cross-sensitivity. The majority of palladium-based hydrogen sensors can be divided into three different categories, based on the optical scheme used for sensing. The three categories are: interferometric-based, grating-based, and intensity-based. Each of these configurations offers their own advantages and disadvantages, which will be explored below.

#### 2.3.1 Interferometric-Based Sensors

Fundamentally, interferometric-based sensors rely on the fact that when palladium is exposed to hydrogen, it sees a volume expansion as well as a change in its complex refractive index. These
two changes can change the properties of an interferometric device by changing the optical path length. This change in optical path length can be detected at the output of the interferometer and correlated to the hydrogen concentration.

Interferometric sensors were the first palladium-based hydrogen sensors to be demonstrated in the literature by Butler, in 1984, who was able to demonstrate a fibre-based Mach-Zehnder interferometer, with one of the fibre arms having a 3 cm long section coated in a 10 µm thick Pd layer [8]. Along with the Fabry-Perot cavity, the Mach-Zehnder is one of the two most commonly used devices for interferometric-based hydrogen sensing. These two sensing modalities will be explored shortly.

**Mach-Zehnder Interferometer**

A typical Mach-Zehnder interferometer sensor works by splitting a single input light source into two separate arms: a reference arm and a sensing arm. The reference arm is isolated from the external variation that is to be detected and the sensing arm is exposed to this variation. In order to make the sensing arm respond to hydrogen, the sensing arm requires some sort of transducer (i.e. Palladium) that is sensitive to hydrogen and is able to induce a change in optical path length in the sensing arm. In this case, the change in optical path length is induced by the volume expansion and change in refractive index of the palladium transducer upon exposure to hydrogen. By not having a similar transducer on the reference arm, we are effectively preventing it from having any significant change in optical path length due to hydrogen exposure.

In this scheme, we are able to detect a change in the output intensity of the device:

\[ I_{output} = \frac{1}{2} (1 + \cos \Delta \phi) I_{input}. \]  

(2.1)

The \( \Delta \phi \) term is the relative phase shift of the light in the reference and sensing arms, which is induced by the change in optical path length in the sensing arm during hydrogen exposure.

As previously mentioned, the first demonstrated MZI hydrogen detector was by Butler in 1984 [8]. The device consisted of two single mode fibres which served as the reference and sensing arms. A 3 cm section of the sensing arm was coated in a 10 µm thick layer of Pd which was
sputtered over a 10 nm thick titanium layer for improved adhesion. The device is illustrated in figure 2.3.

![MZI-based hydrogen sensor by Butler](image)

Fig. 2.3: MZI-based hydrogen sensor by Butler. Reprinted from [8], © (1984) with permission from Applied Physics Letters.

To detect changes in hydrogen concentration, the number of shifted fringes created by the change in optical path length of the sensing arm was counted at the output of the device. The sensor was able to detect 0.6% (v/v) hydrogen with a response time of less than 3 minutes. Subsequent improvements to this configuration involved extending the sensing arm to a length of 28 cm and reducing the Pd layer thickness to 1 µm [9]. With the thinner palladium layer, the sensor was able to detect hydrogen concentrations as low as 2 ppb with a response time of less than 30 seconds.

While traditional MZIs use two separate arms for sensing and reference, this scheme has been steadily abandoned in favour of inline MZIs, which use only a single arm instead of two. The shift to the inline MZI was precipitated by the advent of the long period fibre grating (LPG). LPGs are a type of fibre Bragg grating (FBG) with periods typically between 100 µm – 1 mm [10]. The function of an LPG is to transfer a portion of the power from the fundamental modes in the core of the fibre to the cladding modes. In order to accomplish this, the grating period must be set such that the difference between the propagation constant of the fundamental mode and the phase matching vector of the grating is equal to the propagation constant of one of the outer cladding modes. The principle of operation of LPGs can be seen in more detail in [11].
A popular technique in sensing involves using a LPG to couple a portion the light from the fibre core to the fibre cladding. In this case, the fibre cladding effectively serves as the sensing arm and the core serves as the reference arm. This method is much more practical than using two separate arms as it is easy to fabricate and is much easier to characterize as only a single fibre is required.

In terms of hydrogen sensors, Kim demonstrated an LPG sensor that used a 50 mm long grating (with 500 μm grating period) coated in a 50 nm layer of palladium, as seen in figure 2.4 [12]. The method of operation for this sensor relies on the properties of the LPG. In the 50 mm section containing the grating, a portion of the power in the fundamental mode is pushed out into a cladding mode. The cladding mode is close enough to the outer surface of the cladding that its effective index is affected by the refractive index of the palladium layer. As the palladium layer absorbs hydrogen, the effective index of the cladding mode is increased, which causes a 2.3 nm blue shift in the output spectrum of the device when exposed to 4% hydrogen. The response time for this device was rather slow as it exhibited only -0.29 nm/min resonant wavelength shift, with the sensitivity saturating at approximately 8 minutes.

![Fig. 2.4: Schematic of the LPG-based hydrogen sensor by Kim. Reprinted from [12], © (2008) with permission from SPIE.](image)

Pd-based MZI hydrogen sensors have also been demonstrated using fs-laser processing. Wang demonstrated a MZI hydrogen sensor using a micro-cavity MZI that was fs-laser ablated into a bulk silica substrate, as seen in figure 2.5 [13]. In this case, the micro-cavity functions as an inline MZI. The path through the cavity acts as the sensing arm while the path through the lower portion of the fibre core acts as the reference arm.
A Spectral Physics fs-laser was used to create the micro-cavity (laser parameters: central wavelength of 800 nm, pulse width of 120 fs, repetition rate of 1 kHz, average on-target laser power of 12 mW) and a magnetron sputtering system is used to deposit the palladium film. Micro-cavity lengths of 40 µm and 100 µm are tested and the Pd film thickness used is approximately 110 nm thick. The core and cladding diameters of the single-mode fibre are 8.2 and 125 µm, respectively. When plotting the resonance shift versus chance in volumetric hydrogen concentration, the sensor was able to exhibit a resonance shift as great as 0.155 nm/% for the 40 µm cavity and 0.042 nm/% for the 100 µm cavity.

Even though the bulk of MZI-based sensors have been demonstrated in optical fibres, there has been some work done in integrated platforms. Bearzotti demonstrated an integrated MZI hydrogen sensor on a LiNbO₃ platform [14]. The device consists of an integrated, two-arm MZI on a LiNbO₃ platform, with a portion of the sensing arm coated in a 120 nm thick palladium layer, as seen in figure 2.6. The sensor was able to detect 1% hydrogen with a response time of 30 seconds. The fall time was also very fast, at only 10 seconds.
**Fabry-Perot Cavity**

A Fabry-Perot cavity is formed by creating two partially reflecting surfaces separated by a distance, \( d \) (cavity length). By changing the cavity length, the beam can be made to interference either constructively or destructively at certain wavelengths, due to the resonant nature of the cavity. A hydrogen gas sensor can be created by coating the cavity with palladium or by using palladium as one of the reflective surfaces.

The transmission through the cavity can be expressed as:

\[
T = \frac{1}{1 + F \sin^2 \left( \frac{2\pi nd}{\lambda} \right)}
\]  

(2.2)

\( F \) is the finesse of the cavity and is related directly to the mirror reflectivity, \( d \) is the cavity length, and \( n \) is the refractive index of the cavity. If the cavity is coated in palladium, as the palladium metal absorbs hydrogen gas, the cavity length will increase and the effective index of the cavity will change. Both of these changes will shift the resonant wavelength of the cavity, which can be detected at the output and correlated to ambient hydrogen gas concentration.

The most commonly used configuration is to use a Fabry-Perot cavity contained within an optical fibre (known as an intrinsic cavity). Maciak was able to demonstrate such a device in a standard multimode fibre with 62.5 \( \mu \text{m} \) core diameter [15]. The device is made up of a 10 nm Pd layer which is deposited on top of a 155 nm NiO\(_x\) layer which is deposited on the tip of the fibre, as seen in figure 2.7.

---

Fig. 2.7: Schematic of the intrinsic cavity sensor by Maciak. Reprinted from [15], © (2007) with permission from Elsevier.
The NiO$_x$ layer serves as the cavity of the device. The first reflective surface is located at the interface of the silica fibre and the NiO$_x$ layer and the second reflective surface is located at the interface of the NiO$_x$ layer and the Pd layer. In this case, there is a change in transmission due to the changing second mirror reflectivity as the palladium layer is exposed to hydrogen. The sensor was tested in hydrogen concentrations ranging from 0.5-3% in air. When exposed to 3% hydrogen, the sensor showed a change in transmission of approximately 40% with a response time of 30 seconds.

Another way to create a Fabry-Perot cavity is by using an air gap between two fibres. This is known as an extrinsic cavity. Extrinsic sensors are advantageous in the way that they are able to use higher reflectivity mirrors (higher index difference between air and silica) and are generally less expensive to fabricate. Some notable disadvantages are the fact that they must be precisely aligned and present notable packaging challenges [16]. One example of an extrinsic Fabry-Perot cavity sensor has been demonstrated by Yang, in 2010 [17]. The outer cladding of the sensor is made up of a hollow silica tube, which has 100 nm of Pd-Ag deposited on it. A 130 µm fibre is then inserted into the tube from both ends, leaving an air gap in the middle. A diagram of the sensor can be seen in figure 2.8.

![Diagram of extrinsic FP cavity sensor by Yang](image)

Fig. 2.8: Schematic of the extrinsic FP cavity sensor by Yang. Reprinted from [17], © (2010) with permission from Optics InfoBase.

The method of operation for the sensor is as follows: when the sensor is exposed to hydrogen, the Pd-Ag layer on the silica tube absorbs hydrogen and expands in volume. The expansion of the outer tube directly increases the length of the air gap between the two fibres that are inserted into the tube. This increase in gap length changes the output spectrum of the cavity. The sensor was tested in hydrogen concentrations varying from 0.2-4%. At 4% hydrogen, a change in gap length of up to approximately 9 nm was observed, but the response time was rather slow (approximately 20-30 minutes).
2.3.2 Grating-Based Sensors

The majority of grating-based hydrogen sensors rely on the fact that there is a change in refractive index when palladium is exposed to hydrogen. This changed in refractive index changes the spectral response of the grating and is the sensing mechanism of the device.

When it comes to palladium-based hydrogen sensors, there are chiefly two types of grating sensors in use: Bragg gratings and long-period gratings. The methods of operation are different, but the key similarity is that both devices make use of a shifting spectral response as the sensing mechanism.

Bragg Gratings

A Bragg grating is created by alternating the refractive index in a periodic fashion within a structure such as an optical fibre or an integrated waveguide. See figure 2.9 for a schematic of a typical device.

![Fig. 2.9: Schematic of a typical fibre Bragg grating and refractive index profile.](image)

By alternating refractive indices, the device creates a series of successive backwards reflections. By controlling the grating period and the refractive indices, these reflections can be made to interfere constructively at a desired wavelength, which effectively creates a stop band filter. See figure 2.10 for a typical reflection spectrum of a Bragg grating.
The center wavelength of the stop band is referred to as the Bragg wavelength, and is calculated as:

\[ \lambda_B = 2n_{eff} \Lambda. \]  

(2.3)

Where \( n_{eff} \) is the effective index of the grating and \( \Lambda \) is the grating period. More details on the theory and operation of Bragg gratings can be seen in [18].

![Graph showing the reflected power vs wavelength for Bragg gratings](image)

Fig. 2.10: Reflection spectrum of a typical Bragg grating.

The first palladium-based hydrogen sensor using a Bragg grating was demonstrated in 1999 by Sutapun [19]. The device consisted of a 2-3 cm long Bragg grating, with 829.73 nm Bragg wavelength, etched into a 125 µm single mode fibre with 5-10 µm diameter core. To increase the interaction between the core fibre mode and the palladium coating, the 2-3 cm long grating section was etched with chloroform to decrease the fibre diameter from 125 µm diameter to 35 µm diameter. From here, a 560 nm Pd layer was deposited onto the grating section. A diagram of the sensor can be seen in figure 2.11.
When exposed to 1.8% hydrogen gas, the sensor exhibited a 5 pm red-shift in Bragg wavelength. Due to the fact that a relatively thick palladium layer was used, the film tended to peel off when exposed to hydrogen concentrations higher than 1.8%. To combat this issue, the layer thickness could be reduced or an adhesion layer could be employed. Typical materials for an adhesion layer are chromium or titanium [20].

Schroeder was able to demonstrate a similar sensor with a different type of construction [21]. This sensor is made up of a 1.5 mm long Bragg grating etched into a single-mode fibre. To create a large evanescent field component, the fibre is slightly bent with a bend radius of 2 m. The bent section of the fibre is then cemented into a glass block. The surface of the glass block is then polished and a 50 nm palladium layer is deposited onto the surface of the block. See figure 2.12 for a schematic of the sensor.

When exposed to 4% hydrogen, the sensor exhibited a 4 pm red-shift with a relatively fast response time of 30 s. At lower concentrations (1%), the sensor response red-shifted by
approximately 1 pm and had a response time of approximately 2 minutes. Thinner layers of palladium were also tested, but they showed a much lower sensitivity (2 pm red-shift for 4% hydrogen).

**Long-Period Gratings**

Long-period gratings are versatile as they can be used in both interferometric-based [12] (see section 2.2.1) and grating-based configurations. Wei was able to demonstrate an example of a grating-based LPG sensor in 2008 [22]. The 500 µm period LPG was etched into a single mode fibre with a CO₂ laser. Following LPG fabrication, a 70 nm palladium layer was deposited on top of the grating section by DC magnetron sputtering.

When exposed to 4% hydrogen gas, the sensor exhibited a blue shift of approximately 4.3 nm with a relatively fast response time of 70 s at a temperature of 30°C. The sensor was also tested at higher temperatures. At 100°C, the response time was similar, but the sensitivity was greatly reduced. The sensor only showed a 0.41 nm blue-shift at the higher temperature. This is to be expected, as the hydrogen absorption capacity of palladium is greatly reduced at higher temperatures [5]. The sensor response for temperatures varying from 30-200°C can be seen in figure 2.13.

![Graph](image)

**Fig. 2.13.:** a) Sensor response as a function of hydrogen concentration for T = 30°C. b) Sensor response as a function of hydrogen concentration for T = 100°C, T = 150°C, T = 200°C. Reprinted from [22], © (2008) with permission from Elsevier.
2.3.3 Intensity-Based Sensors

Unlike interferometric and grating-based sensors, the hydrogen response of intensity-based sensors generally relies only on the changing refractive index of the metal, rather than its volume expansion. Fundamentally, intensity-based sensors rely on a direct change in the intensity of the light signal upon exposure to hydrogen, whether it is in reflection or transmission. There are three major types of intensity-based sensors, each having a slightly different sensing mechanism. The three types are micromirror sensors, evanescent field sensors, and surface plasmon sensors, which will all be discussed in more detail.

**Micromirror Sensors**

Micromirror sensors rely on the changing reflectivity of a metal as its refractive index changes upon exposure to hydrogen gas. The first such device was presented by Butler in 1991 [23]. The structure of the device was quite simple and was composed of a cleaved multimode fibre (core diameter of 50 µm and cladding diameter of 125 µm) with its cleaved end coated in a thin 10 nm Pd film. The device, which is very similar in structure to nearly all micromirror sensors, is illustrated in figure 2.14.

![Fig. 2.14.: Structure of a typical micromirror sensor. Reprinted from [24], © (2003) with permission from IEEE.](image)

When exposed to hydrogen gas, the reflectivity of the micromirror was reduced by a noticeable 22%, but no reliable response time information was presented.

Interested by the inherent simplicity of the sensor, in 2000 Benevot followed up on the initial work by Butler by creating a sensor consisting of a 13 nm thick Pd layer on a 400 µm core diameter MMF coated in a hard polymer layer [25]. The unique and most informative part of Benevot’s paper is a thorough analysis of the sensor response time and detection response as a function of gas temperature. As discussed in section 2.1, as temperature decreases, the ability of
palladium to absorb hydrogen gas increases. This causes a direct increase in the response of the sensor. This effect is illustrated in figure 2.15a, where the gas temperature was varied from -50-70 °C, while keeping the hydrogen concentration constant at 4%. Starting at a temperature of 70 °C, the sensor response is relatively low, as the Pd layer is unable to enter the β-phase at 4% hydrogen concentration. As the temperature is decreased, the ability of the Pd film to absorb hydrogen is increased, and the detection response increases. Eventually, a point is reached at 36 °C where the Pd film is able to enter the β-phase at 4% hydrogen concentration and a dramatic increase in the detection response is seen around this temperature. As the temperature continues to decrease, the response continues to increase until beginning to hit a plateau (signifying the Pd film reaching its limit as to the amount of hydrogen it can absorb) in detection response.

![Fig. 2.15. Detection response (a) and response time (b) of Pd micromirror sensor as a function of gas temperature when exposed to a constant 4% atmospheric hydrogen concentration. Reprinted from [25], © (2000) with permission from Elsevier.](image_url)

A similar effect is seen for the response time of the sensor, shown in figure 2.15b. At high temperatures (in the α-phase), the response time is quite fast, but as the temperature is decreased, the amount of hydrogen able to be absorbed is increased the response time increases.

The authors also had one more degree of freedom in controlling the point of the phase transition in the metal. By increasing the laser source power, they were able to create a heating effect on the micromirror, which suppresses the phase transition in an otherwise low temperature
environment (see figure 2.16). This is a very useful way to control the response time and detection response of the device in a low temperature environment.

![Graph showing detection response of the micromirror sensor as a function of optical power for a variety of hydrogen gas temperatures. Reprinted from [25], © (2000) with permission from Elsevier.]

**Evanescent Field Sensors**

Hydrogen sensors based on evanescent field sensing rely on the interaction of the evanescent tail of the waveguide mode with the palladium transducer. This type of sensor generally relies solely on the change in absorption of palladium upon exposure to hydrogen. Upon exposure to hydrogen gas, due to the decreased free electron density of palladium, there will be an increase in transmitted power.

Sensors of this type have been demonstrated almost exclusively on a fibre optic platform. The first such device was presented by Tabib-Azar in 1999 and consisted of a MMF (50 µm core diameter and 125 µm cladding diameter) with a 1.5 cm length that has had the fibre cladding manually stripped with hydrofluoric acid and the core then cleaned with acetone [26]. Thin films of palladium (varying in thickness from 10-100 nm) were then deposited on the exposed core region. The sensor was only tested in concentrations varying from 0.2-0.6% hydrogen (diluted in nitrogen) and showed a modest increase in transmission of approximately 1%. Response
times for 0.2% and 0.6% hydrogen concentrations were 30s and 20s, respectively. The transmission response of the sensor to 0.6% hydrogen can be seen in figure 2.17.

![Time-response graph](image)

**Fig. 2.17:** Detection response of stripped MMF sensor to 0.6% hydrogen. Reprinted from [26], © (1999) with permission from Elsevier.

The major downside of the approach by Tabib-Azar is the extreme delicacy of a stripped, 50 µm diameter fibre core, which is very brittle and prone to cracking. Villatoro attempted to counter this issue by using a more resilient fibre structure which did not require the cladding to be stripped [27]. A single mode fibre was adiabatically tapered down to a waist diameter of 25 µm using the travelling-burning technique [28] and then coated in a 12 nm thick layer of palladium. The device relies on the fact that the mode size will greatly increase in the tapered region and begin to actually expand beyond the cladding air interface in order to interact with the palladium coating. The device structure can be seen in figure 2.18.

![Device structure](image)

**Fig. 2.18:** Structure of tapered SMF hydrogen gas sensor. Reprinted from [27], © (2001) with permission from IEEE.
In order to make the device as polarization insensitive as possible, a two-stage deposition process was used, where the fibre was rotated 120° between consecutive depositions. This was done to obtain a quasi-circular deposition of palladium onto the fibre and ensure that the TE and TM modes will see the same thickness of palladium. The sensor was exposed to hydrogen concentrations as high as 10%, and showed a transmission increased of up to 60%, which is quite high for Pd-based evanescent field sensors.

The detection response results can be seen in figure 2.19, and notice that there is a significant increase in response around the 2% hydrogen point, which is consistent with the large increase in response expected around the α to β-phase transition point. Response time data was not reported, but appears to be relatively slow (~100s for 1.8% hydrogen).

![Fig. 2.19: Detection response of tapered SMF sensor to hydrogen concentrations ranging from 1.8-10%. Reprinted from [27], © (2001) with permission from IEEE.](image)

In an attempt to even further increase the durability of a fibre-based evanescent field sensor, Kim embedded a side-polished, single mode fibre into a quartz fibre-holding circular groove, as shown in figure 2.20 [29]. Palladium was then deposited onto the surface of the quartz holder in thicknesses varying from 20-100 nm.
In this configuration, the TM mode is able to penetrate into the metal sufficiently deep in order to be able to detect an increase in the transmission at the output when the sensor is exposed to hydrogen gas. The sensor detection response varied from approximately 0.55 dB (13.5% increase in transmission) for the 20 nm Pd layer to 1.4 dB (38% increase in transmission) for the 100 nm Pd layer. Response times ranged from 90-200s. As expected though, the thicker the Pd layer, the higher the insertion loss and response time of the device. These results can be seen in figure 2.21.
Fig. 2.21.: Detection response of sensor coated in (a) 20 nm Pd and (b) 100 nm Pd, also showing response and recovery times. c) Simulated transmission losses of the sensor when coated in Pd layers ranging from 5-40 nm.

Reprinted from [29], © (2007) with permission from IEEE.
## 2.4 Table of Comparison

This section offers a summary of the technologies that were covered, shown in table 2.1.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Detection Response</th>
<th>Response Time</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre MZI, 10 µm thick Pd [8]</td>
<td>- 0.6% detection limit</td>
<td>- &lt; 3 mins</td>
<td>- fringe shift at the output is the method of detection</td>
</tr>
<tr>
<td>50 mm long LPG (500 µm grating period), 50 nm thick Pd [12]</td>
<td>- 2.3 nm blue shift (4% hydrogen)</td>
<td>- 8 minutes</td>
<td></td>
</tr>
<tr>
<td>fs-laser etched micro-cavity MZI, 110 nm thick Pd [13]</td>
<td>- 0.155 nm% hydrogen (resonance shift)</td>
<td>- Not reported</td>
<td>- 40 µm and 80 µm cavity lengths were used (40 µm cavity exhibited greater sensitivity)</td>
</tr>
<tr>
<td>LiNbO₃ integrated MZI, 120 nm thick Pd [14]</td>
<td>- Detected 1% hydrogen</td>
<td>- 30 seconds</td>
<td></td>
</tr>
<tr>
<td>Fibre FP cavity, 10 nm Pd micromirror [15]</td>
<td>- 40% change in transmission for 3% hydrogen</td>
<td>- 30 seconds</td>
<td>- tested in concentrations ranging from 0.5-3%</td>
</tr>
<tr>
<td>Extrinsic fibre FP cavity, 100 nm thick Pd-Ag film [17]</td>
<td>- 9 nm air gap length change (4% hydrogen)</td>
<td>- 20-30 minutes</td>
<td>- tested in concentrations ranging from 0.2-4%</td>
</tr>
<tr>
<td>2-3 cm long Bragg grating, 560 nm thick Pd layer [19]</td>
<td>- 5 pm red-shift (1.8% hydrogen)</td>
<td>- Not reported</td>
<td>- 560 nm thick Pd film tended to peel off after repeated exposures</td>
</tr>
<tr>
<td>1.5mm long Bragg grating embedded in glass block, 50 nm thick Pd layer [21]</td>
<td>- 4 pm red-shift (4% hydrogen)</td>
<td>- 30 seconds (4% hydrogen)</td>
<td></td>
</tr>
<tr>
<td>500 µm period fibre LPG, 70 nm thick Pd layer [22]</td>
<td>- 4.3 nm blue-shift (4% hydrogen)</td>
<td>- 70 seconds</td>
<td>- sensor was tested in temperatures ranging from 30-200°C</td>
</tr>
<tr>
<td>Fibre micromirror, 10 nm</td>
<td>- 22% change in hydrogen</td>
<td>- Not reported</td>
<td></td>
</tr>
<tr>
<td>Thick Pd Tip [23]</td>
<td>Transmission</td>
<td>Response Time</td>
<td>Notes</td>
</tr>
<tr>
<td>---------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>MMF Fibre micromirror, 13 nm thick Pd tip [25]</td>
<td>- ~13% change in transmission (4% hydrogen at room temperature)</td>
<td>- ~100 seconds (4% hydrogen at room temperature)</td>
<td>- Sensor was tested using gas temperatures ranging from -50-70°C</td>
</tr>
<tr>
<td>Stripped MMF fibre, 10-100 nm thick Pd layer [26]</td>
<td>- 1% increase in transmission (0.2-0.6% hydrogen)</td>
<td>- 30 s (0.2% hydrogen)</td>
<td>- Tapered and stripped fibre section was very delicate and prone to cracking</td>
</tr>
<tr>
<td>Tapered fibre (non-stripped), 12 nm thick Pd layer [27]</td>
<td>- 60% increase in transmission (10% hydrogen)</td>
<td>- ~100 seconds for 1.8% hydrogen</td>
<td>- Accurate and thorough response time data not reported</td>
</tr>
<tr>
<td>Fibre embedded into quartz block, 20-100 nm thick Pd layer [29]</td>
<td>- 13.5% increase in transmission for 20 nm Pd, 38% increase in transmission for 100 nm Pd (4% hydrogen)</td>
<td>- 90 seconds for 20 nm Pd - 200 seconds for 100 nm Pd</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1.: Summary of existing hydrogen sensor technologies.
Chapter 3
Literature Review: Temperature Sensors

3 Literature Review: Temperature Sensors

3.1 Integrated Sensors

The majority of silicon-based integrated temperature sensors rely on the fact that the refractive index and size of silicon are both temperature dependent. These changes are governed by the thermo-optic coefficient \( \frac{dn}{dT} = 1.8 \times 10^{-4} \text{ K}^{-1} \) at 300 K for a wavelength of 1550 nm) [30], which is relatively high, and the thermal expansion coefficient \( \alpha = 2.5 \times 10^{-6} \text{ K}^{-1} \) at 300 K for a wavelength of 1500 nm) [31]. The thermo-optic coefficient of the insulating layer (SiO₂) is an order of magnitude smaller \( \frac{dn}{dT} = 1.0 \times 10^{-5} \text{ K}^{-1} \) at 300 K for a wavelength of 1550 nm) and can be ignored in most simulations. Photonic devices mainly rely on the change in one or both of these properties of silicon and different device configurations will be discussed further.

**Fabry-Perot**

The transmitted light intensity through a silicon waveguide Fabry-Perot cavity is given by:

\[
I_T = I_o \left\{ \frac{[1 - R e^{-\alpha L}]^2}{(1 - R)^2 e^{-\alpha L} + \frac{4F_R^2}{\pi^2} \sin^2 \varphi} \right\}^{-1} \tag{3.1}
\]

where \( I_o \) is the input intensity, \( L \) is the cavity length, \( \alpha \) is the absorption coefficient representing the intracavity losses of the device, \( R \) is the mirror (end-facet) reflectivity, \( F_R \) is the finesse of the device (dependent on mirror reflectivity), and \( \varphi \) is a phase factor.

The mirror reflectivity, \( R \), is given by:

\[
R = \frac{(n_{si} - n_{air})^2}{(n_{si} + n_{air})^2} \tag{3.2}
\]

The phase factor, \( \varphi \), is given by:

\[
\varphi = \frac{(2\pi n_{si} \cos \theta)}{\lambda} \tag{3.3}
\]
The reason that a Fabry-Perot cavity is sensitive to temperature changes is because the cavity length changes length in different temperatures due to thermal expansion and the mirror reflectivity and phase factor are both sensitive to changes in the refractive index of silicon.

Cocorullo demonstrated a Fabry-Perot based temperature sensor in 1997, in what was one of the earliest demonstrations of a silicon-based integrated optical temperature sensor [32]. The substrate is silicon-on-silicon, with an n- doped guiding layer and an n+ doped substrate. The waveguiding n- doped structure has dimensions of 15 μm wide and 4 μm high and the cavities tested range in length from 25 μm to several millimetres. The structure of the device can be seen in figure 3.1.

![Fig. 3.1.: Schematic of the Fabry-Perot sensor. Reprinted from [32], © (1997) with permission from Elsevier.](image)

Infrared light at a wavelength of 1.55 μm was coupled into the cavities with an optical fibre and collected at the output with a photodetector. The sensor was tested in temperatures ranging from 24-36°C and showed a noticeable, periodic change in output power with changing temperature. These results can be seen in figure 3.2.
One advantage of the device is that the sensitivity and range can be tailored for a specific application by changing the cavity length. Longer cavity lengths will give a greater sensitivity because of the steeper slope of the resonance peaks, but that comes at the cost of reduced range because of the lower free spectral range when compared to a shorter cavity length.

**Ring Resonators**

A ring resonator is a resonant device that is formed by coupling light from a straight bus waveguide into an adjacent ring or racetrack shaped waveguide section. The coupling can be accomplished either by directional coupler or multimode interferometer. Once the light is coupled into the ring section of the waveguide, if the total effective length of the ring is an integer multiple of the wavelength, then the ring is in resonance. The resonant wavelengths of the resonator are given by:

\[ \lambda_{res} = \frac{n_{eff} L}{m} \]  

(3.4)

where \( n_{eff} \) is the effective index of the mode, \( L \) is the length of the ring, and \( m \) is a positive integer. It is evident that this relationship is highly dependent on the effective index of the mode. Combine this with the fact that silicon has a relatively high thermo-optic coefficient, and it is clear why the ring resonator is a viable solution for temperature sensing.

The change in resonant wavelength (\( \Delta \lambda \)) of the device can be expressed as a function of the change in resonant wavelength due to the thermo-optic effect (\( \Delta \lambda_{th} \)) and change in resonant
wavelength due to the thermal expansion effect \((\Delta \lambda_T)\) \cite{33} \cite{34}:

\[
\Delta \lambda = \Delta \lambda_L + \Delta \lambda_T = \frac{n_{\text{eff}}}{n_g} \lambda \Delta T + \frac{d n_{\text{eff}}}{dT} \lambda \Delta T
\]  

(3.5)

where \(n_{\text{eff}}\) is the effective index of the mode, \(n_g\) is the group index, and \(\alpha\) is the thermal expansion coefficient.

Kim was able to demonstrate such a device in 2010, which is illustrated in figure 3.3 \cite{35}. The device dimensions were: height = 250 nm, widths = 300-500 nm, slab thickness = 50 nm, ring radius = 4 \(\mu\)m, ring-to-bus gap = 200 nm.

Fig. 3.3.: Schematic and SEM (inlaid) of the silicon ring resonator device making use of grating couplers for input and output coupling. Reprinted from \cite{35}, © (2010) with permission from Optics InfoBase.

Because the effective index of the waveguide is modified by changing temperatures, the sensitivity of the device can be somewhat controlled by waveguide width. Using the film mode matching method and FIMMWA E simulation software, the theoretical sensitivities of the device for waveguide widths of 500, 400, and 300 nm were 80, 79, and 72 pm/\(^{\circ}\)C, respectively. The theoretical free spectral range of the device was approximately 24.6 nm, giving the device an effective range of near 300\(^{\circ}\)C.

An SEM of the fabricated sensor can be seen in figure 3.3 (inlaid). The measured parameters of the device were an FSR of 23.4 nm, extinction ratio of 10 dB, resonance bandwidth of 0.076 nm, and \(q\)-factor of about 20000 (see figure 3.4).
The sensor was tested in temperatures ranging from 15-45°C using a thermo-electric cooler and showed a red-shift in resonant wavelength with increasing temperature. As expected, the sensitivity of the device varied with waveguide width and the results can be seen in figure 3.5.

The response time of the sensor was tested by attaching a heating electrode directly to the resonator and applying a voltage pulse which changed the temperature of the resonator. The optical output of the sensor was then measured and the response time was measured at approximately 6 µs.
More recently, in 2013, Xu demonstrated a similar device with dimensions of: waveguide height = 220 nm, waveguide width = 610 nm, ring radius = 11 µm, and ring-to-bus gap = 130 nm [36]. The device demonstrated a linear response in terms of resonant wavelength shift due to temperature change and exhibited a sensitivity of about 77 pm/K. The device was tested over a temperature range of 21-22°C, and the results can be seen in figure 3.6.

![Figure 3.6](image.png)

Fig. 3.6.: a) Transmitted spectrum of the device, showing a single resonance peak, for temperatures ranging from 21-22°C  b) Location of the measured resonance peak over a range of temperatures, showing a sensitivity of 77 pm/K. Reprinted from [36], © (2013) with permission from Optics InfoBase.

The focus of this device was not in achieving a large sensing range, but rather in achieving a high sensitivity. The sensitivity of the device was measured to be 40 µK, which is very high, and was limited by technical noise.

**Multi-Mode Interferometers**

The theory of multi-mode interferometer splitters relies on the principle of self-imaging. When light is allowed to propagate through a multi-mode waveguide, the input profile is reproduced in single or multiple images at periodic intervals along the direction of propagation of the waveguide (see figure 3.7) [37]. The guided modes in the multi-mode waveguide are strongly dependent on their effective indices, which are governed by the refractive index of the guiding layer material, which susceptible to changes because of the thermo-optic effect. Because of this fact, by using appropriate geometries, one can design an MMI that functions as a temperature sensor. More details on the theory and operation of MMIs are detailed by Soldano [37].
Breglio was the first to demonstrate an integrated, MMI-based optical temperature sensor in 2001 [38]. The design of the device is a bi-modal Y branch on a silicon-on-insulator substrate, which can be seen in figure 3.7.

The dimensions of the input and output waveguides are 2 µm x 2 µm with a 0.8 µm lateral etch. The bi-modal region is double the width, at 4 µm and supports the TE\(_{00}\) and TE\(_{01}\) modes. To create two waveguides separated by 10 µm at the output, s-bends with 8 µm radii of curvature were employed. The length of the bi-modal region was 7.6 mm.

The detection method of the sensor relies on the transfer of output power from output A to output B as temperature increases. At the designed start temperature, the power at output A should be at a maximum and the power at output B should be at a minimum. The opposite is true for the designed end temperature. The spatial interference of each of these cases as well as the output power profiles can be seen in figure 3.8.
The device was designed to detect a temperature range of 25-300°C. As the temperature increases, the effective index of the modes within the bi-modal region change, and this shifts the output power from output A to output B, as seen in figure 3.9.
Fig. 3.9.: Output power at outputs A and B for temperatures ranging from 25-300°C. Reprinted from [38], © (2001) with permission from SPIE.

Notable advantages of this device include true intensity detection as well as the fact that the device can be tuned for desired range by adjusting the length of the bi-modal region. The main disadvantage is the dimensions of the device, which must be very large in order to ensure adequate sensitivity, which is true for all silicon-based MMI temperature sensors.

An MMI device intended for temperature sensing was fabricated by Breglio in 2003 [39]. The substrate used was silicon-on-silicon, where the guiding layer is a low doped silicon epilayer and the bottom substrate is a highly doped silicon substrate. The bottom substrate acts as a cladding due to the lower refractive index. The device is a 1x2 MMI and a top view schematic of the device can be seen in figure 3.10.

Fig. 3.10.: Schematic of the multimode interferometer sensor. Reprinted from [39], © (2003) with permission from Optics InfoBase.
Sensitivity was optimized using in-house software (optimizing waveguide width, position of input waveguide, position of output waveguides, and device length) and is defined as $\Delta I/\Delta T$, where $\Delta I$ is the difference in light intensity out of the two output waveguides. In this case, a changing temperature will cause an imbalance in the light intensity out of the two output waveguides. The transfer function of the sensor (compared to the results of a previous bi-modal MMI sensor [40]) is seen in figure 3.11.

![Graph](image)

Fig. 3.11.: Results of the multimode interferometer sensor compared to the bi-modal Y branch sensor. Reprinted from [39], © (2003) with permission from Optics InfoBase.

### 3.2 Fibre Sensors

While the thermal expansion coefficient of fused silica is quite low and the thermo-optic coefficient of silica is an order of magnitude lower than that of silicon, which causes it to be much less sensitive to temperature variations for a device of similar dimensions, it does offer a number of other advantages. Sensors integrated into a silica fibre offer excellent deployability, as there is no need to couple into and out of a silicon chip. Another notable advantage is because of their flexible and durable nature, they can also easily double as external strain or vibration sensors [41]. Compared to integrated sensors, where all sensors are generally made up of only a small handful of photonic devices, there is a much wider variety of sensing schemes with fibre optics sensors. This section will attempt to capture and describe the most relevant and useful of these schemes below.
Fibre Optical Ring Resonator

Fibre optical ring resonators function on the same principles of integrated ring resonators, as discussed in the previous chapter. The coupling is often achieved by fusion splicing, where the cladding of the adjacent fibres are stripped and then fused together with a heat source.

Yao demonstrated a fibre optical ring resonator temperature sensor in 2005 [42]. In order to make it easier to distinguish if the spectrum is red shifting or blue shifting, two input frequencies were used in order to create an asymmetric resonance peak, seen in figure 3.12. This was attained by using a single wavelength source followed by a y-splitter with a frequency shifter on one of the arms before the two separate wavelengths were then recombined and served as the input for the device.

![Graph](image)

Fig. 3.12.: Asymmetric transmitted intensity as a function of temperature. Reprinted from [42], © (2004) with permission from SPIE.

By changing the length of the fibre ring, it is easy to tune the sensitivity and range of the device. Sensitivities ranging from 1-0.0001°C can be achieved by varying the fibre ring length from 0.1-100 m, respectively (see figure 3.13). One problem that is evident is that a relatively long fibre ring is needed (on the order of metres) in order to achieve high sensitivities, which makes this configuration not very suitable for deployability into small spaces or areas with limited accessibility.
Fig. 3.13.: Simulated results showing how the sensitivity of the device can be tuned by the length of the fibre ring.
Reprinted from [42]. © (2004) with permission from SPIE.

**Micromirror with Sensitivity Enhancing Membrane**

Because the thermal expansion and thermo-optic coefficients of fused silica are rather low, other materials are often used to enhance the sensitivity of a fibre temperature sensing device. One way to do this is to not rely on the thermal expansion and thermo-optic coefficients, but by using a fluorescing material as the sensor transducer. In a fluorescing material, excited fluorophore molecules can drop back down to the ground state by either absorbing incoming radiation or through collision with another molecule. This transition from the excited state to the ground state will produce a certain amount of energy, which is seen as a photon of emitted light. These processes are at equilibrium for a certain temperature, so by changing the temperature and thereby disturbing the equilibrium, the amount of emitted fluorescence will change.

Using low-cost epoxy glue as a fluorescent material, Tao demonstrated a fibre-based fluorescent transducer temperature sensor in 2006 [43]. The epoxy contains a number of polycyclic aromatic compounds, which fluoresce in the near-UV and visible wavelengths when excited with a UV source. The structure of the device consists of two matching, 300 µm silica optical fibres which are inserted into a 700 µm inner diameter quartz capillary. The two fibres are glued together with the fluorescing epoxy glue at the end of the capillary and a gold-coated aluminum film is attached afterwards to increase reflectivity and enhance fluorescence by increasing the amount of interaction the input light has with the fluorescing glue.
Fig. 3.14.: Diagram of the fluorescent epoxy micromirror sensor. Reprinted from [43], © (2006) with permission from Elsevier.

Fluorescent light is redirected to the input through one of the optical fibres where its intensity is detected with a UV spectrometer. A portion of the input light also ends up being reflected back to the input as well, so that is why there is a need for either a sharp filter or spectrometer for detection. The optical source consists of a 410 nm LED. The device and the spectrum of the detection signal can be seen in figure 3.15.

Fig. 3.15.: Detected spectrum showing both the fluorescence signal as well as some of the input light that has been reflected off the micromirror and coupled into the detection fibre. Reprinted from [43], © (2006) with permission from Elsevier.

The sensor was tested in temperatures ranging from 20-100°C and the results were compared to those of a commercially available thermocouple in order to test accuracy. As can be seen in figure 3.16a, the fluorescence intensity shows a noticeable decrease with increasing temperature. Figure 3.16b also shows the reversibility of the epoxy based sensor as it is cycled through a number of increasing and decreasing temperature cycles. The response time compared favorably
to that of the thermocouple, which was listed at less than 10 seconds on the manufacturer’s data sheets.

Fig. 3.16.: a) Fluorescence intensity of the sensor with respect to temperature (ranging from 20-100°C) b) Time response of the fluorescent sensor compared to the time response of a commercially available thermocouple. Reprinted from [43], © (2006) with permission from Elsevier.

**Fabry-Perot Cavity**

Fabry-Perot cavities are a good choice for a temperature sensor in either an integrated silicon or fibre-based platform due to their sensitivity to changes in refractive index of the cavity. Xu was able to fabricate such a device by inserting two single mode fibres into a hollow tube and inserting a temperature sensitive material in between them to serve as a cavity [44]. The temperature sensitive material that is used was measured to have a refractive index of 1.407. A diagram of the sensor configuration can be seen in figure 3.17.

Fig. 3.17.: Schematic of the Fabry-Perot cavity sensor. Reprinted from [44], © (2008) with permission from IEEE.
One major advantage of this sensor is that it is intensity based and works by detecting the reflected light, rather than the transmitted spectrum. Since the refractive index of the cavity is very close to the index of the fibre, the reflectivity of the interfaces are very low, and the overall reflectivity can be approximated by the two-beam interference equation given by [45]:

$$ R = r + r(1 - r)^2 + 2r(1 - r) \cos \phi $$

(3.6)

where \( r \) is the cavity reflectivity at each interface and is given by:

$$ r = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2} $$

(3.7)

and \( \phi \) is the round-trip phase shift given by:

$$ \phi = \frac{4\pi n_2}{\lambda} L $$

(3.8)

The cavity length, \( L \), was assumed to be constant. The reflectivity has a periodic nature to it and was simulated (see figure 3.18a). The cavity length was chosen to be approximately 15 µm in order to ensure the sensor operates in the near-linear regime over the desired temperature range of -30-100°C and with a cavity refractive index of 1.407. A commercially available optical time domain reflectometer was used as the source and detection device. This device works by sending out a 5 ns optical pulses at 1550 nm and measuring the reflected power as well as the corresponding delay. As the temperature around the cavity increases, the refractive index of the cavity also increases, which causes an increase in the reflected power, which can be measured by the OTDR. The temperature response of the device can be seen in figure 3.18b.
The main advantages of this device are in the commercially available and industry standard source and measurement device (the OTDR) and in the ability to attach multiple cavities together on the same fibre to create a series of distributed sensors on a single cable. If you have a series of sensors on the same cable, separated by delay lines, the OTDR is able to detect the reflected spectrum of each of the devices, since it also measures the reflected pulse delay. The OTDR trace for a network consisting of three separate cavity sensors separated by over 50m on a single fibre optic cable can be seen in figure 3.19.

Fig. 3.18.: a) Simulated reflectivity of the Fabry-Perot cavity as a function of refractive index of the cavity material b) Reflected signal intensity detected by the OTDR for temperatures ranging from -30-80°C. Reprinted from [44], © (2008) with permission from IEEE.

Fig. 3.19.: OTDR trace for three temperature sensors on the same fibre, showing the detected response for -30°C (indicated by line a, in black) and for 30°C (indicated by line b, in red). Reprinted from [44], © (2008) with permission from IEEE.
Multimode Interferometer

MMIs fabricated within a fibre function upon the same principles as an MMI waveguide structure on an SOI platform, but the structure of the device is generally much different due to the fact that it has to be contained within an optical fibre. Zhu demonstrated an MMI temperature sensor in an optical fibre by using a tapered section coated in thermally sensitive material [46]. By tapering the fibre down to a very small waist diameter, eventually the core cannot contain the mode, and the mode expands to the cladding. Now, the cladding becomes the new core and the temperature sensitive coating becomes the new cladding. Due to this sudden increase in effective core diameter, the tapered region is able to support multiple modes. A more thorough analysis of the mathematics of this are detailed by Lacroix [47].

![Diagram of the tapered fibre MMI sensor](image)

Fig. 3.20.: Diagram of the tapered fibre MMI sensor. Reprinted from [46], © (2011) with permission from SPIE.

The sensor was tested in temperatures ranging from -20-80°C. The detection mechanism is the same as that of the integrated SOI MMI sensor. Changes in temperature will change the refractive index of the temperature sensitive coating and the fibre itself, and these changes will modify the output power of the MMI. The authors also demonstrated that the sensitivity of the device can be tuned by the waist diameter of the fibre. The sensor results can be seen in figure 3.21.
Fig. 3.21.: a) Spectrum of the device output for temperatures ranging from -21.6-78.8°C
b) Output power of the device for temperatures ranging from -20-80°C. Reprinted from [46], © (2011) with permission from SPIE.
Chapter 4
Hydrogen Sensor Design

4 Hydrogen Sensor Design

It was decided that the hydrogen sensor would be fabricated on an integrated silicon-on-insulator substrate. While this platform is not as investigated or as mature as fibre technology, it offers a number of advantages. The use of silicon waveguides allows for the potential integrated with the massive silicon electronics industry. This is a long-term goal of the silicon photonics industry, and such a move would open up a wide array of uses and offer increased functionality to such a sensor. Another advantage is that it is easier to be able to integrate multiple sensors capable of detecting different analytes or environmental variables together on an SOI chip than it is to accomplish the same functionality on a fibre, especially with intensity based detection.

It was also decided that the detection method would be intensity based. This decision was made because is it generally much more inexpensive to detect a change in intensity than it is to detect an interferometric or spectral change. This would also be the first demonstrate of an integrated optical, Pd-based hydrogen sensor that uses intensity changes as a detection method.

The sensors were fabricated on silicon-on-insulator substrates with a 220 nm top layer (T+d) of silicon, 3 µm buried SiO₂ layer (H), and silicon substrate. Ridge waveguides were used to guide light through the sensor, and a thin film of palladium was used as the sensing element. A schematic of one of the sensing elements in question can be seen in figure 4.1.

![Schematic of the Pd-coated hydrogen sensor waveguide.](image-url)
As mentioned in section 1.2, as palladium absorbs hydrogen, it changes the electron density of the metal. In this case, as hydrogen atoms are absorbed into the palladium, there is a volume expansion of the metal. This volume expansion results in a reduced electron density, which causes decreased attenuation due to decreased scattering from free electrons [6]. Therefore, as hydrogen is absorbed into the palladium thin film, the transmission is going to change, which can be detected at the output. The design details of the different parameters of this sensor are detailed below.

### 4.1 Waveguide Width and Pedestal Height

The two parameters to consider in the design of the waveguide itself are the waveguide width and the waveguide pedestal height. The goal is to maximize the detection response of the sensor. In order to do that, the dimensions of the waveguide must be selected in order to maximize the mode interaction with the palladium film. The simulated structure was a ridge waveguide with the following configuration, as shown in figure 4.2.

![Waveguide Structure](image)

**Fig. 4.2:** Structure of hydrogen sensor waveguide used in Lumerical MODE Solutions (Pd thickness exaggerated for easy viewing).

In choosing the waveguide width and pedestal height, there are certain restrictions which must be taken into account. The first restriction is single mode operation. In order to ensure this, the waveguide width was restricted from 600-700 nm. Since reactive ion etching is an isotropic process, the actual etched waveguide widths will be lower than the designed widths. This is the
reason that the 600-700 nm range may seem a bit high, theoretically. The second limitation is that the light must be confined within the waveguide and not leak into the adjacent slab. For this reason, the pedestal height has been practically limited to around 120 nm.

In order to maximize the mode interaction with the palladium layer, simulations were conducted using Lumerical MODE Solutions, which includes both an eigenmode solver and a 2.5D FDTD propagation method. A sweep was conducted over the waveguide widths of 600, 650, and 700 nm. The pedestal height was varied between 0-120 nm, in 20 nm increments. Since the bare waveguide (without metal film) is theoretically lossless since it has perfectly smooth sidewalls, the calculated metal loss is a good measurement for the mode interaction with the metal film. The results of the simulation can be seen in figure 4.3.

![Simulation results showing the simulated metal losses for different waveguide configurations.](image)

As can be seen from the simulation results, the mode interaction with the metal layer reaches a peak with a pedestal height of approximately 80-100 nm. This can be explained from the following simulated mode profiles, seen in figure 4.4.
In looking at the mode profiles for a Pd-coated waveguide with no pedestal compared to the same waveguide with a 90 nm pedestal, it is clear that there is increased interaction between the mode and the deposited palladium on the pedestal. From these mode profiles, the maximum mode interaction can be seen to coincide with the geometry where the pedestal is at a height that is approximately equal to the center of the mode (the portion of the mode with the largest horizontal dimension).

Note that the previous simulations were done assuming zero metal deposition on the waveguide sidewalls. This is a fairly safe assumption, as it would be difficult to get a noticeable deposition on the waveguide sidewalls using electron-beam evaporation and sub 10 nm thickness palladium layers. Nonetheless, a simulation was conducted assuming full sidewall thickness deposition, shown in figure 4.5.
It is clear that if the metal completely coats the sidewalls, the pedestal height has a completely different effect. If there is a complete sidewall coating, the interaction of the mode with the metal layer actually decreases with pedestal height. This is expected, as it is clear that there will be the greatest interaction when there is no pedestal, since there will be 220 nm palladium coated sidewalls on both sides of the mode, seen in figure 4.6.

Fig. 4.5.: Simulation results showing the simulated metal losses for different waveguide configurations assuming full sidewall deposition of the metal.

Fig. 4.6.: Simulated TE mode profile with no pedestal and full sidewall metal deposition.
Since the effect of pedestal height is completely different for coated and uncoated sidewalls, the actual geometry of the palladium deposition can later be verified experimentally. To further confirm results, a scanning electron microscope can be used.

4.2 Palladium Layer Dimensions

Since it is clear that a larger detection response will coincide with a larger mode interaction with the palladium layer, in order to increase the detection response, it is clear that the palladium layer must be made thicker and longer. The downside with this approach is the increased metal losses. When the metal losses combined with the intrinsic waveguide losses are great enough that the signal at the output becomes very difficult to detect, then the increased detection response is probably not worth the very poor signal-to-noise ratio. Another factor to take into consideration is the increased response time that comes with a palladium layer of increased thickness.

Because of these reasons, there are no optimal dimensions for the palladium layer, and any dimensions that are chosen will be the result of a trade-off between different factors (output SNR, detection response, and response time). For a hydrogen safety sensor, speed would be the most important metric to measure. Because of this, the thinnest palladium layer possible would likely be chosen (that displays a detection response large enough to be detected). In order to further explore the effect that different palladium dimensions have on the response time and detection response however, the palladium layers were deposited in a series of lengths (8 µm, 12 µm, 16 µm, and 20 µm). A range of different palladium thicknesses were also used. From here, the corresponding detection response and response times were determined experimentally, as will be discussed in Chapter 6.
Chapter 5
Hydrogen Sensor Fabrication

5 Hydrogen Sensor Fabrication

The fabrication process for the palladium waveguides is a three step process: waveguide fabrication, lift-off preparation, metal deposition/lift-off. In order to create waveguides capable of single mode operation, electron beam lithography was chosen for the pattern definition. After the pattern was defined and developed, reactive ion etching was used to etch the waveguides into the SOI substrate. For lift-off preparation, a metallized mask and UV photolithography were used to expose the areas of the waveguides where the palladium metal was to be deposited. Finally, electron beam evaporation was used to deposit the palladium metal layer onto the substrate.

All the fabrication steps were completed at facilities available at the University of Toronto. The waveguide fabrication step was completed in a Class 100 cleanroom which contains a state-of-the-art Vistec EBPG5000+ Electron Beam Lithography System. The lift-off preparation and metal deposition steps were completed in a Class 1000 photolithography/wet chemistry cleanroom and an adjacent Class 10000 etching/deposition cleanroom.

5.1 Waveguide Fabrication

Waveguide fabrication is largely a two-step process consisting of pattern definition and development followed by pattern etching. To begin, a pattern for the waveguides was designed using commercial CAD software called L-Edit. A high level view of the design can be seen below in figure 5.1.
The design is arranged into three separate cells of waveguides, arranged horizontally. Each cell is identical to one another except for the waveguide width. Three designed widths of 600, 700, and 800 nm were used. The red crosses are used for alignment purposes during lift-off preparation and will be explained in section 5.2. The blue vertical bars are simply markers to identify the 600 nm section of the chip.

In order to reduce the insertion loss of the device, the overall length of the nano-waveguide sections must be kept to a minimum. To accomplish this, the outer ends of the waveguides have a designed width of 2 μm. This larger waveguide section will have much lower scattering losses due to sidewall roughness when compared to the nano-waveguide sections. Roughly at the middle of the designed device, the 2 μm waveguides will taper down to their designed widths.
(600, 700, or 800 nm) over a length of 50 μm, which ensures a taper angle of less than 1° to minimize losses. This designed taper can be seen in figure 5.2.

![Fig. 5.2.: CAD layout of the designed taper. Red indicates the non-exposed area where the waveguide is defined. Blue indicates an area of low resolution exposure and green indicates an area of high resolution exposure.](image)

### 5.1.1 Pattern Exposure and Development

This defined pattern was then exposed onto an SOI substrate which has been spin-coated with ZEP-520A positive resist. A fracture resolution of 10 nm (5 nA beam current) was used for the taper and nano-waveguide sections and a resolution of 25 nm (35 nA beam current) was used for the 2 μm waveguide sections. A dose of 250 μC/cm² was used in both cases and was obtained based on work done in etching similar waveguides [48].

Since a positive resist must be used for SOI substrates (HSQ, a negative resist, must be removed using hydrofluoric acid, which attacks the oxide layer in SOI), the area that must be exposed on the substrate is actually the negative of the pattern that we wish to define. In order to considerably reduce the e-beam write time, it was decided that thin trenches would be exposed adjacent to the desired waveguide sections. The trench width was chosen to be 1.15 μm, which both ensures that the e-beam write time is low and that the optical waveguide mode will not leak across the trench. The trench design can be seen in figure 5.3 (shown in green).

![Fig. 5.3.: CAD layout of a section of waveguide.](image)

Following exposure, the samples were developed in a ZED-N50 solution for 60s with constant agitation followed by a stationary 30s in an MIBK/IPA solution. Finally, the samples were dried
with a nitrogen gun for 40s. An exposure of 60s was found to be the optimal amount of time before overexposure was witnessed.

### 5.1.2 Pattern Etching

Following exposure and development, the samples were etching using a Trion Phantom II reactive ion etching system. RIE uses chemically reactive plasma, where highly energetic ions bombard the substrate to slowly remove desired areas of silicon as defined by the lithography process. The etcher is capable of supplying SF$_6$, CHF$_3$, CF$_4$, O$_2$, and other inert gasses for the purposes of etching and cooling. The RIE power and chamber pressure can also be controlled. An etching recipe was obtained from [48] and consists of the parameters shown in table 5.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>RIE RF Power</td>
<td>80 Watt</td>
</tr>
<tr>
<td>Chamber Pressure</td>
<td>80 mTorr</td>
</tr>
<tr>
<td>Etching Gas Flow Rates</td>
<td>25 sccm SF$_6$, 12 sccm O$_2$</td>
</tr>
<tr>
<td>Backside Cooling Gas Flow Rate</td>
<td>10 sccm He</td>
</tr>
</tbody>
</table>

Table 5.1.: Parameters used for the RIE etching recipe.

In order to fabricate waveguides with different pedestal heights, the time in the etch chamber has to be adjusted. The recipe shown in table 5.1 was used to fabricate samples with etch depths ranging from 100-220 nm.

A schematic drawing of the etching process is shown in figure 5.4.

![Diagram showing the process of resist application and pattern etching](image_url)

Fig. 5.4.: Diagram showing the process of resist application and pattern etching. a) Un-etched SOI wafer. b) Un-
etched SOI wafer with positive resist that has been applied, exposed, and developed into the desired pattern. c) SOI wafer after etching. d) SOI wafer after etching and resist removal showing the waveguide ridge.

5.2 Lift-Off Preparation

In order to be able to deposit thin palladium layers onto the desired locations of the waveguides, a lift-off process must be performed. A lift-off process is one where an etched sample is coated with a thin layer of photoresist and then the areas where the metal deposition is desired are exposed and developed, creating windows to the underlying silicon substrate where the metal can be deposited.

The challenging part of this process is the alignment, and that is where the aforementioned crosses defined in the pattern come into play. The lift-off layer was defined using a metallized photomask and UV photolithography. The layout of the lift-off mask can be seen in figure 5.5.

![Fig. 5.5.: CAD layout of the lift-off mask. Red areas are chrome (opaque).](image)

In the photomask diagram, the red area represents a layer of chrome, which blocks UV radiation. The white areas are pure quartz and allow transmission of UV light in order to expose those areas. In this case, notice that the crosses on the mask layer align perfectly with the crosses on the waveguide layer. This allows the mask to be precisely aligned with the sample in order to deposit the palladium metal strips exactly where they need to be, which is across the waveguides within the 100 μm long nano-waveguide section. A diagram showing how the lift-off mask will be aligned with the etched sample is shown in figure 5.6.
Fig. 5.6.: CAD layout of the waveguide and lift-off masks to illustrate how the lift-off procedure works. a) CAD layout of a section of the waveguide mask. b) CAD layout of a section of the lift-off mask. c) The lift-off mask superimposed on top of the waveguide mask. The thin strips align perfectly with the waveguides, creating a window for metal deposition. The square block is used as a marker and for thickness testing purposes.

The lift-off recipe uses S1811 resist, and is detailed in table 5.2.

<table>
<thead>
<tr>
<th>Step</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Spin Coat P20, 5000 rpm, 90s</td>
<td>- P20 serves as an adhesion layer between the silicon substrate and S1811 resist</td>
</tr>
<tr>
<td>2. Spin Coat S1811, 5000 rpm, 90s</td>
<td>- S1811 is the active resist layer to be exposed to define the windows for metal deposition</td>
</tr>
<tr>
<td>3. Soft-Bake, 100°C, 90s</td>
<td></td>
</tr>
<tr>
<td>4. Expose, soft exposure, 5s, 100 µm mask to sample distance</td>
<td></td>
</tr>
</tbody>
</table>
5. Develop, MF321, 90s with agitation - Develop time can be tuned within 60-90s for desired results
6. Rinse, DI water, 60s
7. Hard Bake, 60°C, 30 mins

| Table 5.2.: Details of the lift-off recipe used for hydrogen sensor fabrication. |

Once this process is completed, the sample is ready for metal deposition.

### 5.3 Metal Deposition and Lift-Off

A BOC Edwards Auto 306 Electron Beam Evaporator is used for metal deposition. Electron beam evaporation works by heating a target material with an electron beam contained in a vacuum chamber. As the target materials heats, it converts to the gaseous phase and then precipitates in the chamber, coating everything within line of sight of the target with a thin layer of solid target material.

The target material in this case was a small amount of palladium pellets contained within a 4 cc Al₂O₃ crucible. After inserting the samples into the chamber and pumping it down to near-vacuum, the electron beam gun power is increased to 11 mA to allow the target to pre-bake. Note that the shutter over the target is kept closed during pre-bake so that the samples aren’t exposed to any errant target material. After a pre-bake of 4 minutes, the beam current is increased to 22 mA and then the shutter is opened. This current gives a very slow deposition rate of approximately 0.5-1 Å/s.

After the metal deposition is complete, the only step remaining is to remove the remaining lift-off resist. In order to do this, the sample is allowed to soak in ZDMAC stripper for 15 minutes at a temperature of approximately 60°C and then placed in an ultrasonic bath for 1 minute. If the resist has hardened and isn’t completely removed at this point, the sample can be allowed to soak in ZDMAC overnight.

A schematic showing the metal deposition and resist removal can be seen in figure 5.7.
Fig. 5.7.: Diagram showing the metal deposition process. a) Etched SOI wafer. b) SOI wafer after resist is applied, exposed, and developed. Resist creates a window for metal deposition. c) Wafer after metal deposition. Metal is deposited only within the windows created by the resist. d) Wafer after metal deposition and final resist removal. The end result is a ridge waveguide with a strip of metal coating a section of it.

5.4 Hydrogen Sensor Fabrication Results

After fabrication was completed on the hydrogen sensor samples, SEM images were acquired to determine the etch quality as well as the take a look at the metal layers.

As expected, there is a decent amount of surface and sidewall roughness due to the etching process, as can be seen in figure 5.8. Both of these contribute to the overall insertion losses in the device. Even though the surface and sidewalls appear to be quite rough, the optical losses of the device are still within an acceptable range, as will be discussed in chapter 6. The roughness of the etch can be further improved by more fine tuning of the etch recipe.

Fig. 5.8.: SEM image of the two adjacent troughs that were etched in order to create a single waveguide.
Another unwanted effect that RIE produces is slanted sidewalls. See figure 5.9 for a zoomed in SEM image of the waveguide etch profile. The angle of the sidewalls was verified to be approximately 10° by atomic force microscopy. Unfortunately, since RIE is an isotropic process, slanted sidewalls cannot be prevented. One way to have more vertical sidewalls is to etch the sample with deep reactive ion etching (DRIE).

![Zoomed-in SEM image of a single etched waveguide](image)

**Fig. 5.9:** Zoomed-in SEM image of a single etched waveguide

As for the palladium metal, it deposited very cleanly and quite evenly for lengths between 8 µm and 20 µm. See figures 5.10 and 5.11 for SEM images of palladium metal layers that were deposited on top of waveguides.
Fig. 5.10.: SEM image of a 2 nm thick deposition of palladium (of lengths 8 µm and 12 µm) onto two separate waveguides.

Fig. 5.11.: Zoomed-in SEM image of a 2 nm thick palladium deposition onto a single waveguide.
Chapter 6
Sensor Characterization

6 Hydrogen Sensor Characterization

6.1 Experimental Setup

All samples were tested in an optical characterization lab. A diagram of the optical setup can be seen in figure 6.1. Light from a Thorlabs S5FC superluminescent diode with 1531.6 nm center wavelength, 60 nm bandwidth, and output power of approximately 21 mW was coupled in and out of the sensor using Newport 60X objectives lenses (a Thorlabs tunable laser was used for loss measurements). A JDS Erbium-doped fibre amplifier was used to amplify the input power. Polarization paddles and a half-wave plate were used to maximize the amount of power through the polarization beam cube, which was used to control the input polarization. The end fire coupling rig supporting the sample and objective lenses were covered by a polycarbonate box of dimensions 38.5 cm × 18.5 cm × 12.5 cm. To minimize the effects of noise, two Stanford Research Systems SR830 lock-in amplifiers were used for both input and output signal detection. An optical chopper was placed in the setup after the alignment mirrors to modulate the input light at a frequency of 364 Hz.

![Diagram of the experimental setup for hydrogen sensor characterization.](image)

To control the gas composition inside the box containing the sample, the control of gas flow from the two cylinders containing compressed nitrogen and 4% hydrogen (balanced by 96%
nitrogen) are controlled by two Brooks 5850S digital mass flow controllers (MFC) using a Brooks 0154 control unit. The individual flow rates are computer controlled and the outputs lead to a T-junction to mix the gasses to the desired hydrogen concentration. The output of the T-junction then leads to a union connection on the box where it is connected to a stainless steel tube which directs the gas flow directly onto the sample. The tube to sample separation was about 5 mm. A commercial hydrogen sensor from Nova Analytical Systems was used to verify the hydrogen gas concentration in the gas mixture.

6.2 Losses

In order to measure the linear losses of the waveguides, the Fabry-Perot method was used [49]. Since each waveguide behaves as a cavity, they will exhibit a resonant effect that will be different based on the losses within the cavity.

The losses for uncoated waveguides with a 90 nm pedestal ranged from 0.9 – 2.1 dB with an average value of 1.48 dB (for waveguides that are not visibly damaged).

Metal-coated waveguides were also measured in order to determine the metal losses per micron length of palladium. Losses were directly measured for Pd thicknesses of 1, 2, and 3 nm. Results are shown in figure 6.2.
The samples with 5 nm of deposited Pd were too lossy to obtain accurate measurements. From the above plot though, if a linear fit is assumed, the losses can be estimated around 2.96 dB / μm.

### 6.3 Temporal Response

The detection mechanism of the hydrogen sensors that have been tested is the change in transmission with respect to exposed hydrogen gas concentration. An interesting and notable feature of palladium thin films, in contrast to bulk palladium, is that the films exhibit different properties with respect to their thickness.

In 1985, Ming-Way was one of the first to investigate the pressure concentration isotherms of the palladium-hydrogen system with respect to thickness [50]. What he found was that the pressure concentration isotherms of the palladium-hydrogen system actually change with thickness. Specifically, it was noticed that the thin films behaved much like bulk palladium until the thickness approaches a certain threshold value of around 50 nm. Below this specific thickness, which is dependent on the substrate material, the palladium-hydrogen system begins to show a drastic change in certain properties when compared to bulk palladium. When speaking about temporal response, the most notable of these properties is the effect that grain boundaries and
defects have on the ability of the metal to absorb hydrogen. As the palladium layer gets thinner, the effect that grain boundaries have on the film’s surface area to volume ratio become more pronounced, and for a thinner film, this will reduce the amount of available hydrogen sites per palladium atom [51]. What this implies is that as the film thickness is reduced, the localized size of and locations of grain boundaries can have a profound effect on the amount of hydrogen that is locally absorbed. This idea will be discussed in further detail as the different palladium thicknesses and detection response results are discussed.

6.3.1 Results for Palladium Depositions Ranging from 2-5 nm

The temporal detection response experiments were carried out by first exposing a sample to a constant flow of pure nitrogen gas to establish a baseline response. Next, the gas flow was suddenly changed from pure nitrogen to 4% hydrogen (with a balance of nitrogen). Once the sensor response reached a maximum, it was allowed to settle for a brief amount of time, and then the sensor was flushed with pure nitrogen gas to reestablish the baseline response. This procedure was repeated a number of times and the results were averaged. This test was repeatable over hundreds of cycles with similar results. A typical response is shown below, in figure 6.3, and is the temporal response of a waveguide with 700 nm width, 90 nm pedestal height, 3 nm Pd thickness, and 8 µm Pd length. In order to ensure that the response arises from the presence of hydrogen rather than some other factor, an uncoated waveguide was also tested. The uncoated waveguide showed no response to hydrogen other than a momentary (~1 second) and very limited (< 1% change in transmission) change in transmission when the hydrogen was activated (due to a sudden change in gas flow rate onto the sample). For this reason, we can be assured that the demonstrated responses are the result of the introduction of hydrogen gas into the system.
As can be seen, when hydrogen gas is introduced, the transmission increases. This increase is a result of the reduced electron density of the metal after hydrogen is absorbed and expands the lattice.

For a given palladium thickness and waveguide dimensions (width and pedestal height), the one variable remaining was palladium film length. It would seem logical that the longer the palladium film, the greater the sensor response, since the waveguide mode would be exposed to a greater amount of palladium. This means that a change in the absorptive properties of the metal should cause a greater change in transmission for a long strip than it should for a short strip. For these extremely thin films, however, that is not always the case. Revisiting the early idea of the increased effect that defects and grain boundaries play on very thin palladium films, it is theorized that the somewhat varying detection response values (seen in figure 6.4) arise from this issue. While some of the individual waveguide responses can vary, if we look at the average detection response values for different pedestal heights, it is clear that there is a trend between the two variables. Another fact that supports this theory is that sensors with a 13 nm film almost always demonstrated an increased detection response as the palladium length increased, which
would be consistent with the theory that grain boundaries and defects on the surface have a much smaller effect since the 13 nm film has a much larger volume than the thin 2-5 nm films.

Fig. 6.4.: a) Detection response values for different lengths of palladium films (2 nm thickness) and waveguides with different pedestal heights  b) Average detection response of waveguides for varying pedestal heights (2 nm palladium thickness).

The temporal detection response for one of the waveguides is shown in figure 6.5. As can be seen, the magnitude of the detection response decreases as the hydrogen gas concentration decreases. This is consistent with theory, as a lower hydrogen gas concentration will create a smaller concentration gradient between the ambient atmosphere and the palladium metal layer, which will cause a smaller amount of hydrogen to be absorbed into the metal. The lowest concentration of hydrogen that the sensors were tested in was 0.5%, but the signal to noise ratio is quite high at this point and that the sensor was not able to clearly detect any concentration lower than this, effectively making the detection limit of the sensor somewhere near 0.5%, depending on the detection equipment available.
Fig. 6.5.: Detection response for varying hydrogen concentrations for a waveguide with pedestal height of 90 nm, palladium thickness of 3 nm and length of 20 µm.

6.3.2 Results for Palladium Deposition of 1 nm

When the palladium film thickness is reduced to 1 nm, a decrease in transmission is seen when the sensor is exposed to hydrogen (as opposed to an increase in transmission for thicker palladium films). This sensor response can be seen in figure 6.6.
The theorized reason for this change in response is due to the fact that a 1 nm deposition is so thin that effectively turns the sensor into a nanogap sensor. A nanogap sensor is created when the film is not able to deposit evenly. As a result, instead of a continuous film, we have a series of discrete palladium islands forming. As investigated by Lee, when these nanogap sensors are exposed to hydrogen, the discrete palladium islands expand in volume and connect together to form a continuous film [52]. This actually results in a decrease in resistance of the palladium film, which opposes and has a greater effect than the increase in resistance that normally occurs. This change in resistance represents a change in material property which should manifest itself optically as well. Although island formation was not able to be verified by conventional SEM, it is possible that the gap geometry is too small to see (possible as a relatively low electron beam voltage rating is required to obtain good contrast for Pd on SOI, which results in lower resolution) or that the surface is continuous while there are volume gaps within the metal. In order to verify island formation, it would be necessary to image the sample with a higher resolution SEM or to cut into the metal with a focused ion beam and image the cross section under SEM. While island formation was not visually verified, the results presented by this sensor correspond very well to conventional nanogap sensor presented in literature, and this is theorized to be the reason for the negative sensor response.

Fig. 6.6.: Temporal response of a waveguide coated in 1 nm of Pd.
6.4 Hysteresis

Due to the fact that a pure Pd film was used, a significant hysteresis effect was expected and observed, as seen in figure 6.7. To explain this phenomenon, we look back to section 2.1 and note that palladium can exist in two different phases. As the palladium lattice enters the β-phase, H-H bonds are broken and Pd-H bonds are formed. Since it takes a greater amount of energy to break a Pd-H bond than it does to break a H-H bond, the absolute value of the hydrogen concentration gradient required to break a Pd-H bond is greater than that required to break a H-H bond [7]. This explains why there is a hysteresis effect in the transmission when we look at the transmission during absorption and desorption. For example, if we look at figure 6.7, we can see that a certain change in transmission can be achieved from increasing the hydrogen concentration from 3% to 3.5%. Once at 3.5% concentration though, in order to return the metal layer to the same state it was in when originally exposed to 3% hydrogen concentration, the concentration must be reduced to approximately 2%.

Fig. 6.7.: Plot showing the hysteresis effect present in a typical Pd-coated waveguide when exposed to hydrogen.

To examine the hysteresis effect of the palladium-hydrogen system on the SOI waveguides, three waveguides were chosen that are designed to be identical in all respects except for the deposited palladium thickness. The waveguide dimensions are: waveguide width of 800 nm, pedestal height of 85-90 nm, and palladium length of 8 μm. To obtain these plots, the hydrogen concentration is gradually increased, first from 0-4% in 0.5% increments and then decreased from 4-0% in 0.5% decrements. At each increment, the transmission is allowed to stabilize
before the concentration is changed to the next increment. From this plot, the average response at each concentration level is extracted.

6.4.1 Results for 2-5 nm Palladium Deposition

The resultant hysteresis loops for palladium thicknesses of 2, 3, and 5 nm are shown in figure 6.8.

![Hysteresis loops for palladium thicknesses](image)

Fig. 6.8.: Hysteresis loops for palladium thicknesses of 2,3, and 5 nm Pd depositions.

Note that the results are adjusted, assuming a linear power draft (fairly consistent with experiments) in order to ensure that the starting and ending values are the same (increasing clarity). It has been determined from experiments that the different starting and ending transmission values is largely a result of power drift due to relaxing stage micrometers and the difficulty of precisely aligning nano-waveguides. The presence of this drift was verified on uncoated waveguides in order to ensure that it wasn’t due to an effect arising from the palladium metal deposition.

The most noteworthy feature to note here is the increasing size of the hysteresis loops as the palladium thickness is increased. This can be explained by the clamping effect, which is an effect that relates the tensile stiffness of a film to its thickness. Specifically, it states that the
thinner the film, the higher the tensile stiffness [53]. For very thin films, this high tensile stiffness limits the amount of volume expansion the film can undergo, which in turn limits the amount of hydrogen that the film can absorb. These effects were demonstrated in much greater detail by Lee [7], who determined that thinner films always demonstrated smaller hysteresis loops, but generally also showed a lower response. Note that the measurements conducted by Lee were resistance measurements on very large films (in dimensions orthogonal to thickness).

For the results presented here, note that the hysteresis effect was never completely eliminated (unlike Lee, who was able to demonstrate a 5 nm film that exhibited no hysteresis). The discrepancy is likely due to the fact that the palladium strips on the waveguides had dimensions on the order of microns, while the palladium layers tested by Lee were deposited onto a 12.5 mm x 12.5 mm piece of silicon, which likely had a much greater adhesion to the substrate.

6.4.2 Results for 1 nm Palladium Deposition

As can be seen in figure 6.9, a 1 nm deposition of palladium on the sensor still exhibits a noticeable hysteresis effect. The reason for this effect is the same as was explained in the previous section, as the palladium is still demonstrating a phase transition during hydrogen exposure.
Due to the presence of hysteresis, the sensor would be better served as an on-off type hydrogen gas safety sensor rather than a sensor that is able to continuously monitor ambient hydrogen gas concentration in real-time. In section 8.2.1, some strategies that can be used to eliminate this hysteresis effect will be discussed.

6.5 Response Time

The response time of a sensor is one of the most important metrics to consider in any practical implementation. The United States Department of Energy target for hydrogen safety sensor response time is <1s for measurement ranges from 0.1-10% [54]. So far, very few palladium-based hydrogen sensors have been able to demonstrate response times even approached that speed, and even fewer over the measurement range of interest. Creating a palladium-based, optical hydrogen sensor that meets those goals and is also robust is quite a challenge.

6.5.1 Results for 2-5 nm Palladium Deposition

The main problem with most palladium-based hydrogen sensors is that the response time increases as the hydrogen concentration decreases. Because of this, a hydrogen sensor that achieves a response time of 5 seconds for 4% hydrogen may demonstrate a response time that is
ten times as long for 0.5% hydrogen. An interesting property of very thin palladium films is that they don’t completely show this trend. From experimental data, seen in figure 6.10, it is shown that the response time values for palladium films measuring 5 nm or thinner actually demonstrate an intermediate peak, with the lowest response times near the highest and lowest hydrogen concentrations measured (0.5% and 4%, respectively).

![Graph showing response time data for palladium thicknesses of 2, 3, and 5 nm.](image)

Fig. 6.10.: Response time data for palladium thicknesses of 2, 3, and 5 nm.

Another interesting property that the results show is that the response time peak actually demonstrates a rightward shift. It is theorized that the intermediate peaks and the apparent shift in peak location is due to the changing pressure-composition isotherms of the palladium-hydrogen system as palladium films get thinner [50]. As the thickness of the palladium film is reduced, there is a reduction in the overall width of the mixed α and β phase (with respect to hydrogen concentration at a fixed temperature. Combine this with the fact that the hysteresis effect of palladium has been shown to be eliminated for extremely thin films (as a result of completely suppressing the phase transition by reducing the critical temperature of the material) [7], and it appears as if reducing the film thickness shifts the overall phase diagram curve downward, as shown in figure 6.11.
As can be seen in figure 6.11a, for thick films at 50°C, the α-phase is very thin and the phase transition phase is extended. Compare this to the theorized phase diagram in figure 6.11b, and we notice that the α-phase is now extended to encompass a wider range of hydrogen concentrations, and the phase transition phase is shortened. It is theorized that the shifting peak in the response time curves is due to these changes in the phase diagram. Specifically, the peak in the curve likely corresponds to the phase transition.

So far, no work has been done to extensively study the properties of the hydrogen-palladium system for thicknesses 5 nm and under, so more work would need to be done on the materials science front in order to fully explain these effects.

### 6.5.2 Results for 1 nm Palladium Deposition

While the magnitude of the detection response for 1 nm palladium sensors is rather low (less than a 1% change in transmission), they do exhibit the fastest overall response time when compared to the thicker palladium film depositions. The sensor has a maximum response of approximately 15 seconds when exposed to 2% hydrogen and has a response time of lower than 10 seconds for much of the hydrogen exposure spectrum between 0.5-4%, shown in figure 6.12.
Fig. 6.12: Response time data for palladium thickness of 1 nm.

Even with the hysteresis limitation, the sensor shows great potential as a hydrogen safety sensor due to its large response to hydrogen gas concentrations below the lower explosive limit and relatively fast response time.
Chapter 7
The Optical Nose: Design and Implementation of a Temperature Sensor

7 The Optical Nose: Design and Implementation of a Temperature Sensor

7.1 The Optical Nose

One of the main advantages of using an SOI platform for a hydrogen gas sensor is ease at which multiple sensors can be integrated onto the same device. Using a simple 1 x N MMI power splitter at the input, it is easy to have a single input source feed into multiple channels, each of which would be able to detect a different environmental parameter. For each channel, using a different coating or device structure would make it possible to integrate a multitude of sensors onto a single device.

Some coatings that would be of interest would be either N\textsubscript{2}O\textsubscript{3} [55] or SnO\textsubscript{2} [56] for carbon monoxide detection or Al\textsubscript{2}O\textsubscript{3} for humidity [57]. A possible device that could be used would be a type of resonant structure such as a ring resonator, grating, or cavity for temperature sensing, as was explored in chapter 3.

Of the possible additional sensing elements that could be added to an optical nose sensor, a temperature sensor was chosen for demonstrational purposes. An MMI-coupled ring resonator was chosen as the sensing structure as it offers excellent flexibility in terms of sensing range and sensitivity and it is relatively easy to fabricate and integrate onto the same SOI platform as the hydrogen sensor. The following sections will explore the design, fabrication, and characterization of this temperature sensor.

7.2 Temperature Sensor Design

The first design decision to be made is the coupling method. The two choices are either using a directional coupler or a multimode-interference (MMI) coupler. Each coupling method has its advantages or disadvantages.
A directional coupler has more versatility in terms of controlling the coupling. The amount of light coupled into the ring can be controlled quite precisely with the ring-to-bus gap. Because there is no need for an extended coupling section (as there would be with an MMI coupler), much higher quality factors and free spectral ranges can be obtained for very small ring radii. There are a couple of major disadvantages with directional couplers. The first is the difficulty of fabrication. Because of the typically very small ring-to-bus radius (around 100-200 nm), it is very difficult to be able to etch a high quality gap of those dimensions, especially with RIE. This plays directly into the second disadvantage, which is the sensitivity of the device to dimensional variations. The smaller the ring radius gets, the device will become more sensitive to variations in the group index of the waveguide, which change as the dimensions of the waveguide change. Since is it very difficult to create multiple devices with identical dimensions, this makes a sensor utilizing directional couplers challenging to reproduce in large quantities.

MMI couplers are almost the opposite in terms of advantages and disadvantages when compared to directional couplers. They are constrained in terms of the possible power splitting ratios that can be used (50/50 and 85/15 are commonly used). The additional length that they introduce into the resonant area (equal to the length of the coupler multiplied by two) makes it very difficult to achieve high quality factors or free spectral ranges [58]. On the other hand, they are very easy to fabricate, and the additional length added into the resonant area makes the devices much less sensitive to dimensional variations. The coupling itself it also much less sensitive to dimensional variations when compared to a directional coupler, where a small difference in ring-to-bus distance can make a big difference in coupling ratio.

For these reasons discussed above, an MMI coupler was chosen for the design. This will allow for relatively easy on-site fabrication and is a more repeatable and easily testable configuration.

To achieve critical coupling, the losses in the resonant area of the device must be balanced out with the coupling into the ring [58]. Since the exact propagation losses are not easily simulated, in order to ensure that one of the fabricated devices will come close to achieving critical coupling, a series of different couplers were designed and fabricated. 50/50 couplers were designed with widths of 3.3 and 4.5 µm and 85/15 couplers were designed with widths of 2.2 and 3.0 µm. A schematic showing the relevant dimensions involved in the design of an MMI coupler is shown in figure 7.1. For an 85/15 coupler, the center-to-center separation of the input and
output waveguides must be exactly half of the total coupler width and for a 50/50 couplers, the separation must be equal to one third of the coupler width.

![Diagram](image)

Fig. 7.1.: Diagram showing the relevant dimensions when designing an MMI coupler. i) Height of the coupler (equal to the silicon top layer height minus the etch depth) ii) Center-to-center input/output waveguide separation iii) MMI width iv) MMI length.

When designing an MMI coupler, a desired width is typically chosen first and then the appropriate length is directly related to the width. In order to choose the optimal dimensions of the MMI coupler, a series of simulations were conducted in Lumerical MODE Solutions, where the correct coupler lengths were calculated for a series of widths.

One design detail to keep in mind is as the coupler width decreases, the separation between the two input waveguides also decreases. Once edge to edge separation of the adjacent waveguides reaches a distance of 300 nm, there will be some coupling between the two waveguides for a pedestal height of 90 nm. Since this is an undesired effect, the coupler width is therefore limited to a value of approximately 2.2 μm for 85/15 couplers and 3.3 μm for 50/50 couplers.

For each coupler length, a series of different ring radii will also be fabricated in order to be able to tune the desired FSR and extinction. Ring radii of 5, 10, and 15 μm were chosen for each designed coupler.

Finally, in order to determine an approximate sensitivity of the device, refractive index data was obtained from [59] for silicon for a series of wavelengths ranging from 1.2 to 3 μm for temperatures of 250 K and 300 K. This data was used in a Lumerical MODE simulation and the simulated sensitivity of the device was determined to be approximately 64 pm/K.
7.3 Temperature Sensor Fabrication

The temperature sensor was patterned using electron beam lithography using the same parameters as the hydrogen sensor waveguides except for the fact that the ring section was exposed using 5 nm resolution and a 1 nA beam current as opposed to a 10 nm resolution and 5 nA beam current for the taper and active section of the hydrogen sensor waveguides. All other parameters for lithography exposure and development were the same. The devices were then RIE etched using the same recipe and parameters described in section 5.1. Some SEM images of the MMI coupler and overall device can be seen in figures 7.2, 7.3, and 7.4.

Fig. 7.2.: SEM image of a 4.5 µm long MMI coupler.
Fig. 7.3.: Zoomed-in SEM image of the input waveguide gap on an MMI coupler.

Fig. 7.4.: SEM image of MMI coupled ring resonator.
7.4 Temperature Sensor Characterization

7.4.1 Experimental Setup

The experimental setup for the temperature sensor characterization consists of a source, polarizers, detectors, coupling rig, optical spectrum analyzer, and camera and can be seen in its entirety in figure 7.5.

![Experimental Setup Diagram]

Fig. 7.5: Schematic showing the experimental setup for temperature sensor characterization.

The source is a Thorlabs S5FC superluminescent diode with 1531.6 nm center wavelength, 60 nm bandwidth, and output power of approximately 21 mW. Light from the source is fed through a single mode fibre into a fibre-to-free-space collimator. The beam is then aligned with two silver-coated mirrors and passed through a half-wave plate and a polarizing beam cube (which are used for polarization control along with polarization paddles on the input fibre). A beam sampler is then used in order to determine the input power. Light is then coupled into the sample using a Newport Ultralign end-fire coupling stage with a pair of Newport 60x objective lenses. At the output, light is coupled back into a fibre using a translating stage and 20x objective lens and is fed into an Ando AQ6317B optical spectrum analyzer. Data from the spectrum analyzer is collected by a computer through a GPIB connection using a Matlab script.

For temperature control, the sample is mounted on top of a copper block, which is located on top of a thermo-electric cooling unit with dimensions 6 mm x 10 mm x 1 mm. There is a groove located in the copper block where a 10 kΩ thermistor is placed. Excess space within the groove
is filled with thermal paste. The TEC unit and thermistor are then connected to an ILX Lightwave LDC-3916 laser diode controller, which is used for its TEC controller capabilities. Using feedback from the thermistor, this device is able to control the temperature of the sample using the TEC unit mounted underneath the copper block.

7.4.2 Results

In testing the fabricated samples, it was found that the devices with 50/50 couplers, 4.5 µm wide coupling sections, and 5 µm ring radii demonstrated the best performance in terms of extinction and free spectral range. The transmission result of one of these devices is shown in figure 7.6.

![Transmission Spectrum](image)

Fig. 7.6.: Transmission spectrum for one of the ring resonator temperature sensors (50/50 coupler, 4.5 µm wide coupling section, 5 µm ring radius).

The sensor demonstrates extinction ratios of approximately 7-9 dB with a free spectral range of around 7.7 nm. The low measured Q-factor (~1000) indicates that the waveguide and coupling losses are quite high. This isn’t a major problem though as a high Q is not really relevant to this sensor’s performance. In fact, having a low Q actually enables the possibility of intensity-based
sensing for this device, which will be explained in a moment after the sensitivity of the sensor is discussed.

The sensor was tested in temperatures ranging from 20°C to 50°C. In order to illustrate the shifting resonance peaks, only one of the resonance peaks was focused on (the peak located near 1532 nm). The results can be seen in figure 7.7.

![Fig. 7.7: A single resonance peak of the sensor for temperatures varying from 20-50°C.](image)

With increasing temperatures, the resonance peak experiences a red shift of approximately 0.748 nm per 10°C increase in temperature, giving the sensor a sensitivity value of 74.8 pm/K, matching up closely with simulated results. The increased sensitivity of the actual device compared to the simulated results can likely be attributed to the shift in resonance due to thermal expansion as well as fabrication imperfections.

Another property of the sensors that was examined was the effect of the ring radius on the sensitivity and the free spectral range of the device. These two properties determine the effective sensing range of the device if a wavelength based sensing scheme is used. The sensing range of
the device will be limited by the total temperature change that causes a specific resonance to shift an amount equal to the free spectral range of the device and can be expressed as:

\[
Sensing\ Range = \frac{FSR}{Sensitivity}
\]  

(7.1)

The experimental results for the free spectral range, sensitivity, and effective sensing range for ring radii of 5, 10, and 15 µm are shown in figure 7.8.

![Graphs showing free spectral range, sensitivity, and effective sensing range](image)

**Fig. 7.8:** Free spectral range (a), sensitivity (b), and Effective sensing range (c) of the device for varying ring radii.

As can be seen from the results, there is a clear tradeoff between sensitivity and sensing range. An increased sensitivity can be achieved by having a longer resonant length, but this will be at the expense of a reduced FSR, which gives a reduced sensing range. The optimal design will depend on the specific application of the device, but in general a larger range is more desirable than an increased sensitivity, as the properties of the hydrogen palladium system do not change drastically on a scale of single degrees. This specific device has a sensing range approaching 100 K, which is suitable for most indoor or outdoor applications.
One final interesting thing worth mentioning is that the low Q of the device (high full-width half-max) allows the detection mechanism of the sensor to be intensity based as opposed to wavelength based. This would make the sensor more compatible with the hydrogen sensor that has been developed and would reduce the cost and complexity of the overall detection system. In order to have an intensity based detection mechanism, the sensor would have to operate within half of one of the resonance peaks, as shown in figure 7.9.

![Fig. 7.9.: Intensity-based sensing scheme for the ring resonator temperature sensor. a) Experimental data for a single resonance peak showing the transmitted intensity at a specified wavelength for each temperature b) Normalized transmission of the sensor as a function of temperature.](image)

In this case, the wavelength of the source would be chosen such that the sensor would operate half way between the resonance peak and the start of the resonance dip for the desired baseline temperature. If the environmental temperature is increased, the resonance peak would red-shift and the transmission would increase. If the temperature is decreased, the peak would blue-shift and the transmission would decrease. The effective sensing range in this detection mechanism is equal to the spectral distance between the resonance peak and the beginning of the resonance dip, which becomes larger for smaller Q devices. For the specific resonance peak illustrated in figure 7.9, this distance would be about 2.5 nm. With a device sensitivity of 74.8 pm/K, this would make the effective sensing range 33.6 K. This could be tuned to even higher values by decreasing the Q-factor of the resonator. The downside of this approach is that intensity-based sensing would require more precise and frequent calibration than wavelength-based sensing and would be inherently less accurate.
Chapter 8
Conclusions and Future Work

8 Conclusions and Future Work

8.1 Summary of Contributions

An integrated, optical, intensity-based hydrogen sensor has been demonstrated on an SOI platform. The magnitude of the detection response is large (> 20%) and the response time is relatively fast (< 30s for a 2 nm thick palladium film) over the range of hydrogen concentrations below the explosive limit of 4%. A noticeable hysteresis effect is present due to there being a phase change present as hydrogen concentration increases. This effect would limit the practical use of the sensor to more of an on-off type device unless modifications are made to eliminate it, as will be discussed in section 8.2.1.

The configuration of hydrogen sensor presented would be very easy to integrate into an optical nose type device, which would be able to sense multiple environmental factors (different gases, temperature, humidity, etc.) in a single device. To demonstrate a device that could be integrated together with the hydrogen sensor on the same chip, an optical ring resonator temperature sensor was designed and implemented using a ring resonator structure. The sensor demonstrated good sensitivity and range, which can both be adjusted depending on the desired application. The demonstration of this device lays the groundwork for the future integration of multiple sensing elements on the same chip.

8.2 Future Work

In order to further improve this technology, there are two major things that should be done. The first is to further investigate and experiment with palladium alloys in order to remove the hysteresis effect from the sensor response. The other thing that needs to be done is a more completely and thorough study of the structure and properties of very thin palladium films. Both of these ideas will be discussed in the following sections.
8.2.1 Palladium Alloys to Reduce Hysteresis Effects

An excellent way to remove the hysteresis effect that palladium experiences upon exposure to hydrogen is to alloy the palladium with a metal such as nickel. By alloying palladium with nickel, the \( \alpha \) to \( \beta \) phase transition is suppressed, which for a sufficient amount of nickel content allows the sensor to operate solely in the \( \alpha \)-phase for a desired range of hydrogen concentrations [60].

Operating exclusively in the \( \alpha \)-phase and avoiding the phase transition to the \( \beta \)-phase has the result of preventing the hydrogen atoms from chemically bonding with the palladium atoms. As the forming and breaking of bonds is the reason for the hysteresis effect, preventing these bonds from forming completely eliminates the effect, allowing the sensor to operate in a fully linear regime. The tradeoff involved in this is that the sensor will have a greatly reduced detection response magnitude. As the bulk of the refractive index and absorption change is due to the phase transition into the \( \beta \)-phase, by operating completely in the \( \alpha \)-phase, the detection response will be reduced substantially. An approximate reduction (from experiments) is on the order of a \(~5\) times decrease in detection response.

8.2.2 Extensive Characterization of Thin Palladium Films

In order to completely understand the effects that these thin films exhibit when exposed to hydrogen gas, it is necessary to fully understand the palladium-hydrogen system for very thin (< 10 nm) film thicknesses. While some work has been done to characterize thin films of palladium, there has really been no extensive work done in characterizing films with thicknesses below 10 nm. In order to accomplish this, a first step would be to cut into one of the films with a focused ion beam in order to etch away a thin line of the film so that the full cross section can be studied with a scanning electron or transmission electron microscope.
References

   http://www.chfca.ca/files/10%2520Reasons%2520Brochure.pdf


    in Pd thin films during the process of absorption and desorption of hydrogen gas,"


2012.


   http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/safety.pdf


1, pp. 47-73, 2012.


