Hollow Core Bragg Waveguide Design and Fabrication
for Enhanced Raman Spectroscopy

by

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for the degree of Master of Applied Science

Graduate Department of Electrical and Computer Engineering

University of Toronto

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Abstract

Raman spectroscopy is a widely used technique to unambiguously ascertain the chemical composition of a sample. The caveat with this technique is its extremely weak optical cross-section, making it difficult to measure Raman signal with standard optical setups. In this thesis, a novel hollow core Bragg Reflection Waveguide was designed to simultaneously increase the generation and collection of Raman scattered photons. A robust fabrication process of this waveguide was developed employing flip-chip bonding methods to securely seal the hollow core channel. The waveguide air-core propagation loss was experimentally measured to be 0.17 dB/cm, and the Raman sensitivity limit was measured to be 3 mmol/L for glycerol solution. The waveguide was also shown to enhance Raman modes of standard household aerosols that could not be seen with other devices.
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List of Acronyms

CCD — Charge-Coupled Device

CW — Continuous Wave

BRW — Bragg Reflection Waveguide

BGRW — Bragg Groove Reflection Waveguide

DLS — Dynamic Light Scattering

EL — Electroluminescence

EM — Electromagnetic

FDE — Finite Difference Eigenmode

FTIR — Fourier-Transform Infrared Spectroscopy

FWHM — Full-Width at Half Maximum

HC–PCF — Hollow-Core Photonic Crystal Fiber

HRTEM — High Resolution Transmission Electron Microscope
MOF — Micro-Structured Optical Fiber
MSF — Micro-Structured Fiber
NA — Numerical Aperture
OD — Optical Density
PCF — Photonic Crystal Fiber
PEG — Polyethyleneglycol
PL — Photoluminescence/Photoluminescent
QD — Quantum Dot
SC–PCF — Solid-Core Photonic Crystal Fiber
SEM — Scanning Electron Microscope
SERS — Surface-Enhanced Raman Spectroscopy
SGW — Silicon Groove Waveguide
SO — Surface Optical
SPP — Surface Plasmon Polariton
TCT — Teflon Capillary Tube
TE — Transverse Electric
TEM — Transmission Electron Microscope
TIR — Total Internal Reflection
UV — Ultraviolet
Introduction

1.1 Motivation

In-situ sensing has been gaining traction as the golden standard of sensing platforms for over two decades. It is a method employed for detection and measurement of analytes and processes in their original state, with minimal interference from external sources. In-situ sensing platforms have been widely developed for real-time monitoring applications where target analytes or processes are continuously changing with time[1-4]. One example of this is the recent study tracking the reaction dynamics of ligand-particle binding speculated of thiolcapped CdTe quantum dots[5]. Hollow core photonic crystal fibers have been instrumental in studying the binding characteristics in different gold nanoparticle systems throughout the entire synthesis process. As a result of these recent advances, optical sensing devices have received much attention for next generation in-situ applications. There are many other types of platforms relying strictly on chemical processes for sensing and detection[6-8]. These generally take more time for analysis, often because samples must be cultured in controlled environments in order to achieve
reasonable detection accuracy[9-10]. On the other hand, optical techniques have demonstrated a high degree of reliability and sensitivity to many real world applications in real-time, while requiring only a few key components. These optical sensing techniques will be the focus of this chapter.

1.2 Sensing Applications

A variety of real world applications serves as motivation into research and development of optical in-situ sensing devices. Devices used for point-of-care solutions have the potential to provide cheap and accessible diagnostic data in a matter of minutes for personalized healthcare tracking. Research conducted by Enejder et al. [11] have shown optical Raman spectroscopy can be used to determine blood characteristics such as cell count, glucose levels, and hemoglobin concentration from nano-liter samples of blood. Research into early warning detectors for bio-hazardous aerosols have been conducted achieving micro-molar sensitivities [12-13]. Another application which is becoming increasingly important is water quality analysis. Access to clean, uncontaminated water has driven research towards optical detection systems that can pin-point harmful contaminants to be filtered from available water sources [14-15]. All these applications require a robust, low cost, and portable sensing device that can be used for detection in-the-field of target analytes having milli-Molar concentrations or less.

1.3 Current State-of-the-Art Optical Techniques

Portable form factor optical systems that detect specific analytes under controlled conditions have been largely studied, and show promising results in lab environments. Bahiery et al. demonstrated a highly sensitive glucose concentration monitoring system using a Photonic Crystal Slab (PCS) refractive index sensor[16]. Sapsford et al. showed promising performance of
label based bio-aerosol detection using fluorescence detection[13].

Although, these papers report nano-Molar threshold sensitivities in some cases, the experiments were kept under strictly controlled lab environments and have a very narrow range of applications. It is not clear whether these results can be replicated in field conditions.

1.3.1 Refractive Index Sensing

As an example, the PCS sensor reported by Beheiry et al. acts as a glucose sensor by fitting measured refractive index (RI) to glucose concentration. This study assumes only one independent variable, glucose concentration, during the course of the experiment. Hence, any change in RI is attributed to a singular change in glucose levels. A similar experiment conducted in field conditions could yield vastly different results. Slight changes in ambient temperature, added solvents, or unknown contaminants in the sample could all potentially change the measured RI[18-19]. The shear uncertainty in RI factors makes this platform ineffective for field applications.

1.3.2 Fluorescence Detection

Fluorescence marker sensing devices rely on carefully chosen light emitting antibodies. One such antibody is Horseradish Peroxide (HRP), which fluoresces after binding with select target molecules[20-22]. Based on the intensity of light detected at the emitted wavelength, the concentration of the target molecule can be inferred. Detecting multiple target analytes can often lead to very complicated engineering challenges in synthesizing antibodies that favor binding with select target molecules over others. The second disadvantage involving fluorescence markers is the change imposed on the molecule after binding. Many properties of the target molecule including its shape, conformation, affinity, and reactivity to other molecules can
significantly change[23-25]. Essentially, fluorescence markers can completely interfere with the chemical dynamics of a system.

### 1.3.3 Vibrational Spectroscopy

It is necessary to develop a more agnostic method which can probe fundamental chemical structures of complex compounds and identify its constituents, without the need for binding markers. The technique must also be able to produce data regarding the analyte which can be used for identification, and analyzing its chemical composition.

Vibrational spectroscopy techniques include Fourier Transform Infrared (FTIR) and Raman spectroscopy are optical techniques that can simultaneously excite and identify various vibrational modes of a molecule[26-27]. The vibrational modes are inherently linked to the molecular bonds of the system, and thus allow for real-time identification and chemical composition analysis. For example Figure 1.1 compares the Raman spectra of ethylene glycol and glycerol.

![Figure 1.1: Raman spectra of (a) ethylene glycol and (b) glycerol.](image-url)
The vibrational modes are represented by spectral peaks which are excited in each analyte, and serve as a unique fingerprint used for inference and identification. This thesis investigates the utility and enhancement of Raman spectroscopy specifically for detection and identification of liquid and aerosol based analytes.

1.4 Challenges with Raman Sensing

Although Raman spectroscopy has significant advantages in identifying molecules at the fundamental level, it suffers from poor sensitivity due to inherently low number of Raman scattering occurrences. In comparison to other forms of optical coupling such as fluorescence, the number of Raman scattering events upon light-matter interaction can be ten orders of magnitude less[28]. To compound this problem, Raman scattering is omni-directional and typical detectors only capture a small fraction of the total signal. Additionally, pump light used in stimulating Raman scattering is only focused on a small voxel of the analyte determined by the focusing optics of the system. Within the volume of this small voxel only a few target molecules (approximately $2.2 \times 10^{10}$) may exist in a solid sample, and far fewer for liquid and gaseous compounds. This makes the detection of liquids and gases significantly more challenging than solids.

1.5 Surface Enhanced Raman Spectroscopy

There exist many varieties of Raman spectroscopy used to enhance the Raman cross-section of the analyte. Surface enhanced Raman spectroscopy (SERS) has been used as a popular signal enhancement technique to amplify the collected Raman signal [29-31]. One method of SERS enhancement is to introduce metallic nano-particles into the solution. The optical coupling between the pump and the nano-particles induces surface plasmons, amplifying the intensity of
the electric field at the vicinity of the surface. The challenge is to aggregate the molecular specimen around the nano-particles, allowing for increase in Raman signal generation. Quite often the measured intensity of particular modes can be enhanced by orders of magnitude, while others can be suppressed, or even shifted from its native spectral position[32-34]. The reason for this vast skew between mode excitations has a large part to do with the fact that the analyte is directly binding with a nano-particle. This effectively changes the shape, conformity and the native vibrational modes of the target. The unpredictability of the technique does not make it well suited as an identification system, where the specific enhancement effect may not be known a priori for target molecules. This can lead to misclassification of analytes.

1.6 Total Internal Reflection Based Raman Enhancement

Recently, there has been another approach whereby hollow core photonic crystal fibers (HC-PCF) are used to enhance the collection efficiency of Raman measurements [5]. The PCF platform allows for increased confinement of Raman scattered photons, and increased interaction length between the exciting light source and the target analyte. By selectively filling the hollow core of the fiber with a relatively high index analyte ($n_{\text{analyte}}>1.05$), the pump source, and scattered Raman signal are guided within the core region by total internal reflection (TIR). HC-PCF experiments conducted by Mak et al. have shown Raman intensity enhancements of $3\times10^5$ times that of conventional Raman techniques. The use of the PCF has also demonstrated that Raman signal can be appropriately enhanced, using a hollow core waveguide structure, without significantly skewing the native modes of the analyte.

The main disadvantage of the current PCF device is that it is limited to sensing analytes with refractive index greater than the fiber cladding. This method of enhancement cannot be extended to sensing gases and aerosols with refractive index less than 1.05. Commercial HC-PCF guide
light at specific frequency ranges in the IR spectra. However, the Raman cross section has a $\lambda^{-4}$ dependency and is the reason why near-IR sources are preferred for spectroscopy. This makes commercially available HC-PCF unsuited for Raman applications. In addition, the cost of PCF fabrication, and the overall complexity of integrating the device with supporting optics such as a pump source, and detector, make it difficult for lab-on-chip applications.

As mentioned before, an ideal sensing device should be cheap, portable, and have a disposable component to avoid cross experimental contamination. Due to the many advancements in CMOS processing techniques, silicon photonics devices have become extremely popular. Designing and fabricating a hollow core waveguide using standard CMOS processes not only allows for a robust, and economical platform, but also allows for possible integration with semiconductor lasers and standard silicon charged-couple device (CCD) detectors to make a fully integrated sensing device.

1.7 Thesis Objective

The goal of this thesis is two-fold. The first goal is to determine whether on-chip hollow core waveguides are suited for Raman enhancement. The next step involves designing a waveguide tuned for near IR pump wavelengths, that can theoretically provide similar enhancements as HC-PCF for liquid analytes while extending its utility to aerosol and gas sensing. The second goal is to fabricate the waveguide and characterize the device performance.

Current research conducted by Barber et al. [35-37] has demonstrated a similar structure following an anti-resonant reflecting optical waveguide (AROW) design. The chip was fabricated using standard CMOS processes and could confine incident laser light within a hollow
core. By confining light over long distances it can provide *some* of the enhancements characteristic of the PCF device from Section 1.5. The research was mainly aimed at providing low loss single mode propagation along the waveguide, and to exploit the advantages of light propagation within air medium. There are two main limitations that do not make this waveguide ideal for Raman enhancement:

1. The waveguide has a limited collection angle, and as such, any scattered signal propagating outside this range will not be confined to the core.

2. Fabrication of the hollow core structure includes depositing a sacrificial core layer along the length of the waveguide which will have to be etched afterwards. The etching process limits the waveguide length to less than 1 cm. This imposes an upper bound on total interaction length that can be achieved between the light source and the analyte, and severely limits the generation of Raman scattered photons.

For these reasons, Bragg reflection waveguides are being primarily investigated in this thesis for their enhancement properties. In general, a Bragg stack is often used for broadband reflection applications, and could thus prove to have substantially broader angle of confinement, and lower propagation losses than its ARROW counterpart.

The thesis also aims at creating a robust fabrication process for Bragg reflection waveguides, which does not impose severe limitations on its length. The key is to apply flip-chip bonding methods to create a sealed air core rather than relying on sacrificial techniques.
The fabricated HC-BRW will then be characterized and compared with the PCF device with respect to Raman enhancement of various liquids and aerosols.

1.8 Thesis Organization

The thesis is structured into six chapters. Chapter 2 describes the basics of the Raman scattering processes, covering the three types of scattering processes that occur and their quantum mechanical representation. This chapter includes Raman cross section analysis and how it compares between analytes of various states. The angular dispersion of photon scattering is discussed and how it relates to signal leakage. Finally the Raman measurement setup used in the experiments is explored.

Chapter 3 first includes the optimization of the Bragg stack to guide scattered light in a broad range of angles. The chapter also looks at triangular waveguide structures and designs to allow for simple fabrication. Waveguide losses will also be analyzed using Finite Eigenvalue Mode (FEM) numerical solver, and compared to reported ARROW waveguide losses.

Chapter 4 covers aerosol detection and identification using current PCF methods. Household aerosols that have some association to known chemical warfare agents are analyzed.

Chapter 5 documents the fabrication of the triangular hollow core Bragg waveguide. The chapter explores the etching process of triangular grooves in silicon substrate using KOH, PECVD deposition of Bragg cladding layers, and adhesive bonding process to seal the groove to create final hollow core structure. This process uses standard silicon microfabrication procedures and
materials, making it highly advantageous over other device fabrication methods.

Chapter 6 includes characterization of the HC-BRW and Raman enhancement comparisons to the PCF device. Spectrum enhancement is measured for stock solvents and aerosols against the PCF. Waveguide loss of pump laser is also measured using the cut-back method and compared to ARROW waveguide and HC-PCF devices.

Chapter 7 discusses further applications of the HC-BRW. Future iterations to the HC-BRW are suggested for improving overall sensitivity and consistency to the sensing platform.
2 Raman Spectroscopy

2.1 Fundamentals of Raman Spectroscopy

Raman spectroscopy is an optical technique typically used to probe the vibrational modes of a system of molecules, rapidly and non-destructively. Vibrational (phonon) modes of a system are excited by inelastic scattering of incident photons. Depending on the initial state of the molecule, the scattered photon will have a slightly offset frequency from the source. By detecting the shifts in frequency and intensity of photons, a unique representation or fingerprint can be obtained from a sample. Raman spectroscopy typically measures these shifts from 0 to 4000 cm\(^{-1}\) wavenumbers. For a system utilizing a 633 nm red laser source, the corresponding frequency range starts at 633nm, and sweeps to 850nm. This spectra holds a wealth of information directly corresponding to the physical and chemical structure of the analyte, and is the primary reason why similar samples, at a molecular level, can be unambiguously identified. For example, we would expect ring molecules such as benzene to have different vibrational eigen-modes from molecular chains such as peptides.
Coupling of incident photons to vibrational modes results in three types of scattering processes: Rayleigh scattering, Stokes scattering, and anti-Stokes scattering [38,39]. Figure 2.1 shows a quantum representation of the three types of Raman processes.

Figure 2.1: Quantum representation of the various types of scattering processes involved in Raman Spectroscopy

Raleigh scattering constitutes the most dominant process of the three types of scattering, but provides little relevant information as the scattered and incident photons are of the same frequency. Stokes scattering refers to molecules that are excited to a higher vibrational state, and lower energy scattered photon, while anti-Stokes scattering refers to a molecule relaxing to a lower vibrational state and higher energy scattered photon. The energy of the scattered photon can be expressed as:

\[ E_{\text{scattered}} = E_{\text{incident}} - (E_{v,2} - E_{v,1}) \]  

(2.1)

Where \( E_{v,1} \) and \( E_{v,2} \) are the energies of the original and final vibrational states, respectively. The frequency can be derived using Planck’s constant:

\[ \nu_{\text{scattered}} = \frac{E_{\text{scattered}}}{h} \]  

(2.2)
The number of scattering occurrences taking place for each type of process is determined by the thermodynamic equilibrium of the system. As a general rule, for room temperature and standard ambient conditions, molecular systems have higher probability to be found in the ground vibrational state. Photon scattering can therefore only excite these molecules to a higher vibrational mode. Therefore, Stokes scattering is more likely to occur in practice, and is what is commonly measured during Raman spectroscopy.

2.2 Directionality of Scattered Photons

One key characteristic of Raman spectroscopy is the omni-directional nature of photon scattering. Due to conservation of momentum, the direction of the scattered photon is tied directly to the momentum of the coupled vibrational mode, and can be expressed as:

\[ \vec{k}_{\text{scattered}} + \vec{q}_{\text{phonon},2} = \vec{k}_{\text{incident}} + \vec{q}_{\text{phonon},1} \] (2.3)

where the vector \( q_{\text{phonon},i} \) represents the phonon momentum for the \( i^{\text{th}} \) vibrational mode, \( k_{\text{scattered}} \) and \( k_{\text{incident}} \) are the scattered and incident photon momentum vectors. This can be visually depicted with the following momentum diagram in Figure 2.2.
Figure 2.2 depicts how the scattered photon can propagate in any direction, depending on the coupled phonon. Generally, since the analyte is amorphous, meaning the molecules are not aligned to one orientation, incident photons coupling to the same vibrational mode will not correspond to the same scattering direction. Hence, if the analyte is assumed to have a collection of molecules in random orientations, it is difficult to use measured directionality of a scattered photon to infer more about the vibrational states that exist in a liquid or gas analyte. This is the reason why Raman spectroscopy relies solely on the specific light intensity of frequency shifted photons to detect and identify various compounds.

That being said, the directionality of scattered photons does play a significant role in the signal-to-noise ratio of the measurement. Since the collection optics of the system only collects photons radiating within a limited collection angle, much of the Raman signal propagating at angles beyond this range are lost. In Sections 2.4 and 2.5 we go into detail as to how magnifying optics and waveguide confinement can be used to increase signal collection.
2.3 Raman Cross Section

Generated power from Raman signals depends on a few key factors namely, the incident power, pump wavelength, and Raman cross section [38]:

\[ \sigma_{RS} = C \omega_s^4 |\alpha'_m| \]  \hspace{1cm} (2.4)

where \( C \) is a numerical constant, \( \omega_s \) is the scattering frequency and \( \alpha' \) is the polarizability derivative of the molecule. Raman cross section is specific to the sample being analyzed and to the individual vibrational modes and relates to its scattering efficiency. Of course, this is the Raman cross section for full 4\( \pi \) steradian, and sometimes the differential cross section \( \frac{d\sigma}{d\Omega} \) is used to represent scattering in a particular direction. The cross section can also be expressed as:

\[ \sigma_{RS} = \frac{I_{RS}}{I_0} \]  \hspace{1cm} (2.5)

where \( I_{RS} \) is the amount of scattered light in all directions [photons/s] and \( I_0 \) the incident photon flux [photons/s/m^2] giving the cross section units of [m^2].

Table 2.1 below compares the typical cross sections of various optical processes that can occur.

<table>
<thead>
<tr>
<th>Process</th>
<th>Cross-section of</th>
<th>( \sigma ) (cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>Ultraviolet</td>
<td>( 10^{-18} )</td>
</tr>
<tr>
<td>Absorption</td>
<td>Infrared</td>
<td>( 10^{-21} )</td>
</tr>
<tr>
<td>Emission</td>
<td>Fluorescence</td>
<td>( 10^{-19} )</td>
</tr>
<tr>
<td>Scattering</td>
<td>Rayleigh Scattering</td>
<td>( 10^{-26} )</td>
</tr>
<tr>
<td>Scattering</td>
<td>Raman Scattering</td>
<td>( 10^{-29} )</td>
</tr>
<tr>
<td>Scattering</td>
<td>Resonance Raman</td>
<td>( 10^{-24} )</td>
</tr>
<tr>
<td>Scattering</td>
<td>Surface Enhanced Raman Scattering</td>
<td>( 10^{-16} )</td>
</tr>
</tbody>
</table>

**Table 2.1:** Cross section of various optical processes that occur when excited by light source [28].
Raman scattering accounts for the least probable optical process, and is the primary concern limiting the utility of Raman spectroscopy for many applications.

### 2.4 Measured Raman Signal

The total scattered power generated from an analyte using a laser source is given by [40]:

$$P_s = K \cdot L \cdot 4 \pi \cdot P_0$$  \hspace{1cm} (2.6)

where $K$ is the product of the sample density and its Raman cross-section for a particular vibrational mode. $P_0$ is the incident laser power, and $L$ is the interaction length between the focused laser source and the analyte. Equation 2.6 describes the total scattered power in all directions. However, in practice, what is captured lies only within a small collection angle of the systems objective lens, and the measured scattered power is better described as:

$$P_s = KL \Omega P_0$$  \hspace{1cm} (2.7)

where $\Omega$ is the solid angle that can be collected by the Raman system. Several important conclusions can be drawn from this expression. First, one can observe that any enhancement comparison between different Raman systems is just a comparison of the product $L*\Omega$ also known as etendue. Secondly, optics aficionados will often come to the conclusion that by simply employing a system of imaging lenses the collection angle of the system can be increased. By increasing the lens magnification $M$ to be greater than one, the collection angle increases by a factor $M^2$, and the interaction length decreases by a factor $M^{-1}$, thereby giving total etendue enhancement by factor of $M$. However, limits to magnifying objectives, CCD size, and spectroscopic slit width, which place an upper bound on the collection angle of the system.
2.5 Raman Collection in a Waveguide

Optical waveguides offer unique advantages for Raman enhancement. Waveguides utilizing either total internal reflection (TIR) or bandgap confinement are low loss propagation devices, and can be used to increase the effective interaction length between incident laser light and the sample analyte. The idea is to increase the mode overlap of the guided laser mode with the analyte to maximize Raman scattering occurrences. For this reason hollow core waveguides where light and the sample analyte is confined to the main core have become increasingly popular for many Raman applications. Additionally, waveguides which are able to effectively confine light scattered at oblique angles within the channel, for a range of Stokes frequencies, serves to increase mode intensity.

Here the work presented by Eftekhar et al.\cite{78} is used to model the scattered signal power that can be measured using a waveguide system, the waveguide loss $\alpha$ [db/m] plays an important factor. If the power of the incident laser light at the beginning of the waveguide is $P_0$ then the pump power at any point $x$ along the length $L$ of the waveguide is given as:

$$P(x) = P_0 e^{-\alpha_p x} \quad (2.8)$$

where $\alpha_p$ is the loss of the pump mode in the waveguide. The Raman signal for a particular frequency $R$, generated at point $x$ is:

$$P_R(x) = \sigma_R 4\pi P_0 e^{-\alpha_p x} \quad (2.9)$$
We assume that the waveguide has a finite collection angle $\Omega$. In the forward scattering case the signal will propagate all the way to the end of the waveguide of length $L$. The total power of the Raman signal after propagation to the end facet of the waveguide is:

$$P_{RF,A}(x) = \sigma_R \Omega_R \cdot P_0 e^{-\alpha_R x} e^{-\alpha_p (L-x)}$$  \hspace{1cm} (2.10)

Variables $\alpha_R$ and $\Omega_R$ are the waveguide loss and collection angle for the scattered Raman signal of frequency $R$. The total scattered signal measured at the end of the facet can be obtained by integrating equation 2.10 along the direction of the waveguide. The resulting expressions is:

$$P_{RF} = \int_0^L \sigma_R \cdot \Omega_R \cdot P_0 e^{-\alpha_R x} e^{-\alpha_p (L-x)} \, dx$$  \hspace{1cm} (2.11)

Simplifying and integrating equation 2.11 yields:

$$P_{RF} = \sigma_R \Omega_R \cdot P_0 \cdot \frac{1}{\alpha_R - \alpha_p} \cdot e^{-(\alpha_R - \alpha_p) L}$$  \hspace{1cm} (2.12)

A similar derivation can be applied to the back scattering case, by multiplying $\alpha_R$ by $x$ instead of $(L-x)$, giving the expression:

$$P_{RB} = \sigma_R \Omega_R \cdot P_0 \cdot \frac{1}{\alpha_R + \alpha_p} \cdot e^{-(\alpha_R + \alpha_p) L}$$  \hspace{1cm} (2.13)

If we assume that losses $\alpha_R$ and $\alpha_p$ are equal, equations 2.12 and 2.13 simplify to:

$$P_{RF} = \sigma_R \Omega_R \cdot P_0 L e^{-\alpha L}$$  \hspace{1cm} (2.14)

$$P_{RB} = \sigma_R \Omega_R \cdot P_0 \frac{[1-e^{-2\alpha L}]}{2\alpha}$$  \hspace{1cm} (2.15)
This analysis assumes that the waveguide loss for scattered light within the collection angle $\Omega_R$ is constant. From equations 2.14 and 2.15 one can conclude that the Raman signal power measured through back-scattering is more efficient than that of forward scattering. This can be easily understood by noting that most of the Raman signal will be generated at the start of the waveguide where the pump power is highest. In the forward scattering case, the scattered light in this section must propagate the full length of the waveguide $x=L$, in which most of its power is radiated or absorbed by the system. In the back scattering case, the scattered light travels a fraction of that distance back to the point $x=0$ of the waveguide, therefore increasing the measurement efficiency. The main advantage of the waveguide is that for low loss propagation, the effective length of the light-analyte interaction can be effectively increased by many orders of magnitude over traditional optics. In the case of HC-PCF having typical losses of 1.7dB/km, the effective length $L$ in Equation 2.7 is replaced by the factor $\frac{1}{2\alpha_R} \frac{1 - e^{-2\alpha_R L}}{2\alpha_R}$ from Equation 2.15. Figure 2.3 compares the effective interaction length for both the back scattering and forward scattering configurations as a function of waveguide length $L$.

**Figure 2.3:** Interaction length term dependence on waveguide length for back scattering and forward scattering configurations. Waveguide loss taken to be 0.0017 dB/m
Using HC-PCF of 1 km in the back-scattering configuration, the effective interaction length is increased to nearly 300 m. In the forward scattering configuration, there exists an optimal waveguide length, after which point the Raman collection enhancement is overcome by mode propagation losses through the waveguide. Using traditional lens systems the effective length of the focusing beam is bounded by interaction lengths on the order of ten's of microns, making the overall enhancement for a kilometer long HC-PCF on the order of $1 \times 10^8$ counts.

### 2.6 Raman System Overview

The Raman system used in this thesis is a LabRam HR 800 high resolution spectrometer manufactured by Horiba Jobin Yvon. This Raman system collects back scattered Raman spectra through a confocal hole. The main components of the system are as follows:

The **laser** used in the system is a Helium Neon laser, emitting a collimated beam with max power of 17mW at 632.8nm.

Adjustable **density filter wheel** which comprises of optical density filters ranging from 0.3 to 4. The power of the laser source passing through the OD (optical density) is given by:

$$P_{\text{out}} = \frac{P_{\text{in}}}{10^{OD}}$$

(2.16)

**Objective lenses** used to focus the laser on to the analyte, or waveguide facet, and collect the back scattered light. The type of objective determines the collection angle from the facet of the
waveguide and plays a vital role in Raman enhancement. Available objective lenses are listed in Table 2.2.

<table>
<thead>
<tr>
<th>Magnification</th>
<th>NA</th>
<th>Working Distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10x</td>
<td>0.25</td>
<td>10.6</td>
</tr>
<tr>
<td>50x</td>
<td>0.7</td>
<td>0.38</td>
</tr>
<tr>
<td>100x</td>
<td>0.9</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 2.2: List of objectives with their respective magnification, numerical aperture, and working distance

A holographic **edge filter** is used to limit the frequencies of light measured to those above 120 cm$^{-1}$ in the Stokes region.

The **confocal hole** can be adjusted from 0-1000μm in size. It determines the amount of Raman signal collected by the spectrometer, and the field-of-depth of the measurement.

The Horiba system is equipped with a Czerny Turner **spectrograph**, with two grating patterns 1800 lines/mm and 600 lines/mm. The gratings separate incoming light into the various frequencies used to differentiate scattered photons.

Finally, the **detector** is an air-cooled silicon charged-coupled device (CCD) having a resolution of 1024x256 pixels.
The system schematic is shown in Figure 2.4.

**Figure 2.4:** Schematic of Horiba Raman detection system, following the light path from source to detector [41].
3 Optical Waveguiding in Low Index Materials

3.1 Introduction

This chapter examines methods of low index guiding, of which Bragg reflection optical waveguides is investigated in more detail. In the first section, index guiding, and its utility to Raman spectroscopy will be discussed. The second segment of this chapter covers photonic crystal guidance, which has garnered much interest for low index guiding configurations. Applications of photonic crystals to Raman Spectroscopy are also investigated.

3.2 Index Guiding

Conventional waveguides operate by confining the optical power within a high index core, surrounded by low index media [42-44], such as air. A typical slab waveguide following this structure is shown in Figure 3.1.
The structure in Figure 3.1 can be observed in many types of optical fibers, and the underlying guiding mechanism can be explained by the total internal reflection (TIR) phenomenon.

Applying Snell’s law at the interface between the core-cladding media, the relationship between $\theta_i$ and $\theta_t$ can be expressed as:

$$n_1 \sin(\theta_i) = n_2 \sin(\theta_t) \quad (3.1)$$

where $n_1$ and $n_2$ are the refractive index of the core and cladding respectively, and $\theta_i$ and $\theta_t$ are the incident and transmission angles of the light ray.

For the case of $n_1 > n_2$, there exists a critical incident angle $\theta_c$ in which the transmission angle is $90^\circ$ and light propagates parallel to the interface.

$$\theta_c = \sin^{-1} \left( \frac{n_2}{n_1} \right) \quad (3.2)$$

For incident angles greater than $\theta_c$, the value of $\theta_t$ becomes imaginary, and this corresponds to total internal reflection. The transverse wave vector in medium two is $k_{2x} = k_2 \cos \theta_t$.

Using Equations 3.1 and 3.2, the transverse wave vector in medium two can be expressed as,

$$k_{2x} = -i \frac{\omega n_2}{c} \left( \frac{\sin^2 \theta_i}{\sin^2 \theta_c - 1} \right)^{1/2} \quad (3.3)$$
where $\omega$ is the angular frequency of the propagating plane wave. The electric field inside medium two can be written as:

$$E = E_0 e^{i\omega t} e^{-ik_{2x}x - ik_{2z}z}$$  \hspace{1cm} (3.4)

While $k_{2x}$ is imaginary, the field still propagates along the $z$ direction, but decays exponentially in the $x$ direction.

Using the slab waveguide from Figure 3.1 as an example, it is expected that scattered light propagating at angles greater than $\theta_c$, the light is confined to the core, and propagates down the waveguide for its entire length. Mak et al. has demonstrated that TIR guidance in a HC-PCF showed a $3 \times 10^5$ Raman intensity enhancement [3] over corresponding glass slide measurements. Hollow core fibers made out of silica or Teflon tubing provide a simple platform to enhance signals by filling the core with high index liquids. The caveat to this method is that if the analyte is not of greater index than the cladding, light will leak into the cladding and substrate materials. In this configuration, Raman scattered light cannot be collected efficiently for any scattering angle. This limits the applications of these platforms to high index liquid sensing such as toluene (1.6) or benzene (1.57). For all other analytes involving gases with refractive index near one, other guiding techniques must be employed.
3.3 Photonic crystals

Photonic crystals are essentially periodic arrangements of optical media and have representations in 1D, 2D, and 3D schemes. These structures demonstrate very unique properties such as, slow light, tunable dispersion, and high reflectivity [45-47].

Figure 3.2: 1D, 2D, and 3D representations of periodic media [53]

3.3.1 1-D Photonic crystals

The reflection properties of a 1-D photonic crystal[48,49] is of direct interest for the design of the hollow core waveguide, and an example is shown in Figure 3.3. The periodic structure comprises of alternating optical media, $n_1$ and $n_2$ with associated layer thicknesses $d_1$ and $d_2$, with periodicity $\Lambda$.

Figure 3.3: 1D photonic crystal, showing two periods of infinite structure. Arrows represent directions of propagation for various coefficients.
In Figure 3.3 the coefficients $A$, $C$ and $B$, $D$ represent the amplitude of right and left propagating plane waves. Using the transfer matrix method[50-52], the relation between the field amplitudes from block $i$ to block $i+1$ can be derived, starting from the left hand side of Figure 3.3. The matrix transform relating the electric fields $[A_i, B_i]$ to $[C_i, D_i]$ are:

$$\begin{bmatrix}
A'_i \\
B'_i
\end{bmatrix} = \begin{bmatrix}
e^{-k_{i}d_i} & 0 \\
0 & e^{k_{i}d_i}
\end{bmatrix}\begin{bmatrix}
A_i \\
B_i
\end{bmatrix} \equiv M_1\begin{bmatrix}
A_i \\
B_i
\end{bmatrix}$$

(3.7)

$$\begin{bmatrix}
C_i \\
D_i
\end{bmatrix} = \begin{bmatrix}
1 & r_{2i} \\
t_{2i} & t_{21}
\end{bmatrix}\begin{bmatrix}
A'_i \\
B'_i
\end{bmatrix} \equiv M_2\begin{bmatrix}
A'_i \\
B'_i
\end{bmatrix}$$

(3.8)

$$\begin{bmatrix}
C_i \\
D_i
\end{bmatrix} = M_2M_1\begin{bmatrix}
A_i \\
B_i
\end{bmatrix}$$

(3.9)

The matrix $M_1$ represents the phase accumulation during propagation of the left-hand and right-hand plane waves across medium one with refractive index $n_1$. $M_2$ is the matrix representation of the field transition at the interface between medium one and two. The terms $r_{21}$ and $t_{21}$ are the Fresnel reflection and transmission coefficients and can be expressed for the TE case as:

$$r_{21} = \frac{k_{2x} - k_{1x}}{k_{2x} + k_{1x}}$$

(3.10)

$$t_{21} = \frac{2k_{2x}}{k_{2x} + k_{1x}}$$

(3.11)

The matrix relating the terms $[C_i, D_i]$ to $[A_{i+1}, B_{i+1}]$ can similarly be expressed as:

$$\begin{bmatrix}
C'_i \\
D'_i
\end{bmatrix} = \begin{bmatrix}e^{-ik_{2x}} & 0 \\
0 & e^{ik_{2x}} \end{bmatrix}\begin{bmatrix}
C_i \\
D_i
\end{bmatrix} \equiv M_3\begin{bmatrix}
C_i \\
D_i
\end{bmatrix}$$

(3.12)
Finally, the entire matrix relating the field in one period to the field in the next is the product of $M_4$ through $M_1$.

$$\begin{bmatrix} A_{i+1} \\ B_{i+1} \end{bmatrix} = \begin{bmatrix} I & r_{12} \\ t_{12} & 1 \\ r_{12} & t_{12} \end{bmatrix} \begin{bmatrix} C_i' \\ D_i' \end{bmatrix} \equiv M_4 \begin{bmatrix} C_i' \\ D_i' \end{bmatrix}$$  \hspace{1cm} (3.13)

The Bloch theorem can also be used to relate fields in adjacent periods of crystal structure by a constant phase factor [53,54]. The Bloch theorem definition of the electric field in a periodic structure yields the expression:

$$E(x) = E_K(x)e^{-ikx}e^{-i\omega t}$$  \hspace{1cm} (3.15)

$$E_K(x) = E_K(x+\Lambda)$$  \hspace{1cm} (3.16)

$E_k(x)$ is called the Bloch mode having the same periodicity $\Lambda$ as the structure, and $K$ is the Bloch wave number (i.e. the mode eigenvalue). Applying the Bloch equation the fields of adjacent periods can be expressed:

$$\begin{bmatrix} A_{i+1} \\ B_{i+1} \end{bmatrix} = M \begin{bmatrix} A_i \\ B_i \end{bmatrix} = e^{-iK\Lambda} \begin{bmatrix} A_i \\ B_i \end{bmatrix}$$  \hspace{1cm} (3.17)
Equating both the transfer matrix and Bloch representations for \([A_{i+1}, B_{i+1}]\) we approach the eigenvalue, eigenvector relation for the periodic structure. Solving the characteristic equation, 
\[\det(M - e^{-iKA}) = 0\]
leads to the following dispersion relation:

\[\cos(K\Lambda) = \frac{1}{2}(a+d)\]  \hspace{1cm} (3.18)

where the variables \(a\) and \(d\) are the transfer matrix parameters described in Equation 3.14.

For the TE case, considering normal incidence the right hand side simplifies to:

\[\cos(K\Lambda) = \cos(k_1d_1)\cos(k_2d_2) - \frac{1}{2} \left(\frac{n_2}{n_1} + \frac{n_1}{n_2}\right)\sin(k_1d_1)\sin(k_2d_2)\]  \hspace{1cm} (3.19)

The right hand side of equation 3.19 is wavelength dependent by relation to \(k_i\), and with closer inspection it can be found that the right hand side can exceed magnitude of one for certain wavelengths for which \(KA\) will take on imaginary values. A dispersion relation is plotted in Figure 3.4.

\[\text{Figure 3.4: 1D photonic crystal dispersion relation: } n_1=2, n_2=1.45, d_1=79.12\text{nm}, d_2=109\text{nm}\]

Figure 3.4 shows an example dispersion equation of \(KA\) for a 1D structure made up of alternating silicon nitride (\(n=2\)) and silica (\(n=1.45\)) layers, with \(d_1\) and \(d_2\) chosen as 79.12nm and
109nm respectively. Regions where the imaginary component of $K\Lambda$ are non-zero correspond to bandgap frequencies that cannot propagate inside the structure. From Equation 3.15, the factor $e^{iK\Lambda}$ evaluates to a real number less than one, which corresponds to a decaying field. Incident waves oscillating at these frequencies will simply attenuate within the periodic structure and no power will be transmitted.

Bandgap regions having larger imaginary $K\Lambda$ values will have light attenuated far more aggressively for each period. For the structure examined in Figure 3.4, the imaginary component is a maximum at 633nm. At this frequency the structure is referred to as a quarter wave stack or Bragg stack since the layer thicknesses satisfy the conditions: $k_1x_1d_1$ and $k_2x_2d_2$ are equal to $\frac{\pi}{2}$.

For a finite number of 1D alternating layers, some of the power for propagating waves within the bandgap regime can tunnel through the structure, and the incident light will not be completely reflected. Hence, in the finite case the stack reflectivity $R$ is of great interest, and serves as a direct measure towards the collection efficiency of a Bragg waveguide. The transfer matrix for an $N$ layer Bragg stack is simply $M^N$.

Reflectivity is derived to be $\left| \frac{c}{d} \right|^2$, for $M$, $c$, and $d$ defined in equation 3.14. The value can be computed for varying angles and wavelengths. The reflectivity contour plot of the Bragg stack for ten alternating layers is shown in Figure 3.5 (a).
The orange regions of the contour plots show the high reflectivity region of the stack between 0.9 and 1, and can be tuned by changing the layer thicknesses of the crystal, as seen in Figure 3.5 (b) having the high normal incidence reflection region tuned towards 725nm.

**3.4 Bragg Reflection Waveguides**

Bragg reflection waveguides[55-56] utilize the high reflectivity of Bragg stacks, discussed above, to confine light within a low index waveguide core. In this section, the characteristics of a 1D Bragg waveguide, as seen in Figure 3.6, are be explored.
3.4.1 TE Mode Analysis

Figure 3.6 depicts a low index core Bragg waveguide with propagation along the z axis, and crystal direction along the x axis. The electric field is expressed by:

\[
E(x,y,z,t) = E(x)e^{i(\omega t-\beta z)}
\]  

(3.20)

with \( \beta = \frac{2\pi n_{\text{eff}}}{\lambda} \), where \( n_{\text{eff}} \) is the effective index for the corresponding waveguide mode. The transverse electric field also satisfies the wave equation:

\[
\frac{\partial^2 E(x)}{\partial x^2} + k_i^2 E(x) = 0
\]  

(3.21)

where \( k_i \) is the transverse wave vector and is dependent on the properties of the medium at position \( x \) and is defined as:

\[
k_i = k_0 \sqrt{n_i^2 - n_{\text{eff}}^2}
\]  

(3.22)

As per the name of the waveguide, the cladding layer thicknesses \( a \), and \( b \) are chosen to satisfy the quarter wave condition \( k_i d_i = \frac{\pi}{2} \), thereby acting as a bandgap material, having the reflection region centered for the specific mode frequency and wave-vector.
For TE modes, the field components $H_x$ and $H_z$ can be derived from the $E_y$ component using Maxwell's equations, and hence the following analysis will focus on deriving $E_y$. The electric field of the fundamental mode inside the core and cladding region can be expressed as:

$$E_y(x) = \begin{cases} 
C_1^{TE} \cos(k_c x), & |x| \leq \frac{t_c}{2} \text{ (core)} \\
C_2^{TE} E_{K,TE} \left( |x| - \frac{t_c}{2} \right) \exp \left[ iK_{TE} \left( |x| - \frac{t_c}{2} \right) \right] & |x| > \frac{t_c}{2} \text{ (cladding)}
\end{cases} \quad (3.23)$$

where $k_c$ is the transverse wave vector inside the core, and $E_{K,TE}$ is the Bloch mode from Equation 3.15. Imposing continuity on $E_y(x)$ and $\frac{dE_y(x)}{dx}$ at the core-cladding interface results in the following dispersion relation [4]:

$$\frac{1}{k_c} \cot \left( \frac{k_c t_c}{2} \right) = \frac{-ie^{ik_{TE} x} - a_{TE} + b_{TE}}{k_j e^{ik_{TE} x} - a_{TE} - b_{TE}} \quad (3.24)$$

Where $a_{TE}$ and $b_{TE}$ are matrix elements of the alternating layer stack from equation 3.15. For the particular case of the quarter wave stack, the right hand side can be shown to equal zero[4]. This leads to the following constraint between the product of the core thickness and transverse momentum vector:

$$\frac{k_c t_c}{2} = \frac{(p + 1)\pi}{2}, \quad p = 0, 2, 4, \ldots \quad (3.25)$$

Concerning ourselves with the fundamental mode of the waveguide, for which $p=0$, the effective index simplifies to Equation 3.27:

$$k_c = \frac{2\pi}{\lambda} \sqrt{n_c^2 - n_{\text{eff}}^2} = \frac{\pi}{t_c} \quad (3.26)$$

$$n_{\text{eff}} = \left[ n_c^2 - \left( \frac{\lambda}{2t_c} \right)^2 \right]^{1/2} \quad (3.27)$$
For a Bragg waveguide with $t_c=0.5\mu m$ and alternating silicon nitride ($n_1=2$) and silicon oxide ($n_2=1.46$) cladding layers, the fundamental mode for pump wavelength of 633nm is given in Figure 3.7(a).

![Figure 3.7: TE fundamental mode profile, plotting $E_y$ for BRW with core widths (a) 0.5um, (b) 5um, (c) 50um.](image)

From the mode profiles shown in Figure 3.7, the mode power leaking into the cladding region is easily observed. With each new layer of the Bragg stack, the mode amplitude decays
exponentially. Another pattern that is worth noting is that the number of layers needed for the amplitude to settle to zero decreases as the core width increases. This can be understood by looking at the derivative of the mode profile $\frac{dE}{dx}$ at the core cladding interface. For smaller core widths, the derivative is larger in magnitude, and hence the time needed to settle ($\frac{dE}{dx} = 0$) takes more cladding periods.

Another interesting parameter to be studied is the ratio of $\beta$ to $k_c$ and its relation to core width. In essence, $\frac{\beta}{k_c}$ equals the tangent of the glancing angle of the mode, with respect to the core-cladding interface.

![Figure 3.8](image)

**Figure 3.8:** Waveguide glancing angle $\theta_g$ depicted with respect to propagation and transverse wave vectors.

Using equation 3.27 in combination with 3.22 the $\theta_g$ dependence on $t_c$ is plotted in Figure 3.9.
As would be expected, the high reflectivity region of the cladding structure encompasses the glancing angle. For core width of 0.5μm, the glancing angle is 50.72°, and the cladding reflectivity is shown in Figure 3.10(a).

**Figure 3.9:** Glancing angle plotted for BRW of varying widths

**Figure 3.10:** Reflection profile for BRW mode glancing angle. (a) Profile for 5μm core width BRW, (b) 100μm core width BRW. Cladding consists of 10 alternating layers of oxide and nitride
Similarly, Figure 3.10 (b) plots the reflectivity of the cladding structure for 100um core width, with glancing angle of 89.81°. Not only does the cladding structure exhibit high reflectivity at the glancing angle, but also maintains high reflectivity for a significant range of $\theta_i$ values near $\theta_g$. This property is particularly useful for Raman Spectroscopy, as Raman scattered light will strike the core-cladding interface at all angles between 0 and 90°. We are also interested in knowing the reflection properties of the cladding structure for the range of wavelengths between 633nm and 847nm to understand how well shifted Stokes frequencies are confined to the core.

Figure 3.11 shows the contour of the reflectivity spectra for the 0.5μm core width waveguide and the 100μm core waveguide respectively.

![Figure 3.11: Reflection profile for BRW Stokes scattering. (a) Profile for 5um core width BRW, (b) Profile for 100um core width BRW. Cladding contains 10 alternating layers oxide and nitride. Regions in white represent Reflectivity coefficient below 0.999.](image)

In Figure 3.11, the high reflectivity region is plotted for threshold reflectivity greater than 0.999, while values below this are depicted in white. This exact value of reflectivity is very important as it corresponds to a small amount of power lost with each reflection at the cladding interface.
After many such reflections along the propagation direction, the signal could attenuate to negligible values within the length scale of the waveguide, and below detection limits.

### 3.4.2 Raman Loss Modeling

From chapter 2, a loss measure $\alpha_R$ was assumed for Raman signal propagating along the waveguide (equation 2.10). Using the reflectivity profile of the cladding from section 3.4.1, an approximate value of $\alpha_R$ can be derived for modes at each Stokes frequency and wave vector. As an example, we analyze the Stokes signal generated at 700nm and propagating at 70° with respect to the core-cladding interface. In this example, the core width is chosen to be 100μm.

![Figure 3.12: Stokes signal reflecting of wall and continuing propagation down waveguide](image)

From ray optics perspective, after each bounce along the interface the signal reflected back into the core is found to be 0.999987 of the incident signal. A characteristic length $L_{1\text{dB}}$ can be calculated for each possible Stokes signal representing the propagation along the waveguide until the power is attenuated by a factor of 10 times or 1dB loss. In this example, $L_{1\text{dB},700\text{nm},70^\circ} = 274\text{m}$, corresponding to $\alpha_R$ of 0.00021 dB/cm.
To compare enhancement between various waveguides and their Raman enhancement potential, we come up with a figure of merit defined by equation 3.28:

\[
FOM_1 = \frac{\int_0^{90} \int_{633\text{nm}}^{847\text{nm}} e^{-\alpha d_\theta} d\lambda d\theta}{\int_0^{90} \int_{633\text{nm}}^{847\text{nm}} I d\lambda d\theta}
\]  

(3.28)

\(FOM_1\) assumes that all Stokes signals between 633nm and 847nm are generated with equal power and scattered equally in all directions between 0° and 90°. Since we are only concerned with the efficiency of Raman collection, \(FOM_1\) looks to measure the ratio of the collected signal power for a waveguide with length 1cm.

Comparing a variety of structures, Table 3.1 shows the \(FOM_1\) values for the Bragg stack corresponding to waveguides of different core widths.

<table>
<thead>
<tr>
<th>Structure</th>
<th>0.5um Bragg stack</th>
<th>7um Bragg stack</th>
<th>100 µm Bragg stack</th>
</tr>
</thead>
<tbody>
<tr>
<td>(FOM_1)</td>
<td>11.68%</td>
<td>35.66%</td>
<td>55.55%</td>
</tr>
</tbody>
</table>

Table 3.1: Comparison of \(FOM_1\) between BRW of three different core widths, all having a stack of 10 alternating layers

From Table 3.1 the 100µm Bragg stack exhibits the highest efficiency for Raman power collection. The trend for lower losses given larger core widths can be explained by two factors.

1. As the core width increases, the frequency bandwidth of the high reflectivity region increases, as observed in Figure 3.11.

2. As core width increases, the number of reflection events per centimeter, for a given propagation angle is reduced, and therefore the total power leaking out of the structure is lowered.


3.5 Hollow Core Bragg Groove Reflection Waveguide Structure

The utility of Bragg reflection waveguides for Raman spectroscopy has demonstrated the potential for high efficiency signal collection. Guiding occurs within the low index region of the waveguide, whilst both the fundamental mode and the scattered Raman signal can be confined by tuning the waveguide width and cladding layer thicknesses. In this section we look into applying this model to physical waveguide designs which can be practically fabricated using the processes and equipment available at the University of Toronto clean room.

The designs investigated in this thesis incorporate flip chip bonding of two silicon wafers to seal a hollow core. The flip chip bonding process will be discussed in detail in Chapter 5. To understand why these designs are favored, a quick digression into ARROW fabrication is necessary.

The ARROW structure designed by Barber et al. utilizes a very unique method for fabricating hollow core waveguides: sacrificial core etch. One problem with this method is that it has severe limitations on core size, as large core widths could lead to structural stress and eventual collapse of the waveguide. The second problem is that etching the sacrificial core layer is a slow process, and the process involves simultaneously etching and removing the dissolved material effectively, for which latter poses serious limitations on the waveguide length. The process reported by Barber et al. stated that maximum waveguide lengths that are achieved on any practical timescale are on the order of 1cm, which require an etch time of one week to complete. From the insights learned in section 3.4, core widths and waveguide length are directly related to Raman
enhancement, and propagation loss. For this reason, it was deemed necessary to investigate flip chip designs in order to realize tens of centimeter long waveguides having core size close to 100μm in width.

The design analyzed in the thesis, is a hollow core Bragg groove reflection waveguide (BGRW) with cross-section shown in Figure 3.13. This design was chosen as the thickness and refractive index quality of cladding layers could be easily controlled using standard deposition techniques.

![Figure 3.13: Cross-section of Bragg groove reflection waveguide structure, with close-up.](image)

The cladding layer thicknesses were calculated from expression 3.27 and 3.26 in the 1D Bragg analysis section. Equation 3.27 provides a good approximation to the TE fundamental mode effective index of a 100μm wide groove. The resultant effective index is 0.999995. Lumerical Finite Difference Eigenmode (FDE) solver produced a similar value, \( n_{\text{eff}} = 0.999967 + i6.56\times10^{-8} \) for the fundamental TE mode at a wavelength of 633nm. The reason why the 1D analysis performs reasonably well in this case is because the glancing angle is approximately 90° i.e., the mode propagation vector inside the core is parallel to the \( z^+ \) direction of propagation. Therefore, the mode hardly interacts with the transverse structure of the waveguide, and thus for a 1-D or 2-D cross section, the mode characteristics are not very different.
The loss associated with the imaginary component of $n_{\text{eff}}$ is primarily due to silicon absorption at 633nm, and is plotted as a function of core width in Figure 3.14.

![Figure 3.14: BGRW (a) Numerical loss extraction for varying core sizes, and cladding layers. (b) mode profile for 100μm core width waveguide](image)

From Figure 3.14 it can be deduced that the confinement of the fundamental mode is significantly lowered for a groove structure having four or more cladding layers. As the number of layers increase, confinement is enhanced and lower loss is obtained. The relationship observed between higher core width and lower propagation losses is supported with the analysis from section 3.3.2. The loss for the 100μm wide waveguide is extracted to be 0.0556 dB/cm. This design was fabricated during the course of the thesis and the process details are discussed in chapter 5. Table 3.2 compares the simulated loss with the ARROW structure and other air core waveguides reported in literature.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss dB/cm</td>
<td>0.0556</td>
<td>1.1</td>
<td>1.3x10^{-7}</td>
<td>1.63x10^{-6}</td>
</tr>
</tbody>
</table>

Table 3.2: Comparing theoretical losses of various air core waveguide structures.
It should be noted that the loss measures for the ARROW structures are limited only due to fabrication limitations. The loss reported of 1.1 dB/cm was for a waveguide with core dimensions, 24μm x 9μm. The ARROW paper reported similar trends of lower propagation loss for larger core dimensions. However, as mentioned at the beginning of section 3.5, these large core structures cannot be fabricated due to structural stresses, and the high potential for core collapse, and were therefore not included in the table above.
4 Photonic Crystal Fiber Aerosol Sensing

4.1 Introduction

This chapter examines the use of the hollow core photonics crystal fiber (HC-PCF) for aerosol sensing. In particular we look at examining household aerosols such as Lysol, mosquito repellent, and WD-40. Lysol in particular is of special interest because it contains ethylene glycol ethers, much like many other air fresheners. This chemical is also found in some chemical warfare gases including mustard gas. Equation 4.1 and 4.2 show the chemical reaction and composition of ethylene glycol and mustard gas by-products respectively[62].

\[
\text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O} \rightarrow \text{HO-CH}_2\text{CH}_2\text{-OH} \quad 4.1
\]

\[
\text{SCl}_2 + 2 \text{C}_2\text{H}_4 \rightarrow (\text{Cl-CH}_2\text{CH}_2)\text{S} \quad 4.2
\]

The \( \text{CH}_2\text{CH}_2 \) glycol compound is a bond formation found in both molecules. Due to the common molecular composition, Lysol aerosol serves as a good indicator for future detection and
identification of chemical warfare agents such as mustard gas.

Past work regarding Raman spectroscopy of aerosols have been limited to trapping aerosol particles on a fine-mesh filter, and directly measuring the Raman signal from the surface. However, this technique was not applied to any standard aerosols found commercially and cannot be used for comparison.

4.2 Aerosol coupling into Hollow Core-PCF

4.2.1 Coupling methods

Coupling of the aerosol particles into the PCF is a non trivial challenge and two different test methods were created to compare coupling efficiency via the Raman signal. The first coupling setup is shown in Figure 4.1, where the aerosol straw is directly connected to the fiber via a Plexiglas unit. The connector has a decreasing annular radius that directs the aerosol flow into the PCF.

![Figure 4.1: PCF Plexiglas connector unit with aerosol straw output.](image)

The second coupling method involves spraying aerosol into an air pump, with the pump outlet directly connected into a PCF. Figure 4.2 depicts the second coupling method.
This method allows us to simulate how detection in the field would be done. In practice, an air pump would be used to direct and concentrate ambient particulates into the sensing device.

### 4.2.2 Aerosol size distribution

Typical particle size distribution from aerosol sprays are shown in Figure 4.2.

**Figure 4.2**: Coupling aerosol particles into PCF via an air-pump.

**Figure 4.3**: Typical aerosol particle diameter distribution for hair sprays[63]
Comparing this with the PCF core diameter of 10um, the majority of particles greater than 10um will not be able to enter the channel, and can even end up blocking the channel and prevent further aerosol particles from coupling in. To estimate the number of particles that enter the core, the curve in Figure 4.2 is integrated for percentage of particles falling below 10um in diameter. The gives the total percentage of aerosol spray particles which are compatible with PCF core size, approximated to be 30%. Additionally, the aerosol stream strikes the entire facet of the fiber, of which the core only makes up 1% in area. The combination results in an estimated 0.3% of total aerosol particles entering the fiber core. Understanding what phase the aerosol particles are in inside the core is also a big question. The coalescence of the aerosol particles inside the fiber or aggregation could lead to larger particles or droplet formation of liquid phase aerosols. In method two, there is a continuous air stream directed into the fiber, along with the aerosol particles. Using this method, it is predicted that the amount of particle coalescence or droplet formation inside the PCF is substantially reduced. The next section examines the Raman measurements of the aerosols using these coupling methods.

4.3 Aerosol Raman Measurement

The Raman measurements in this section utilized a 633nm helium-neon source along with a 800nm center bandgap frequency HC-PCF with characteristic loss profile shown in Figure 4.4.
Figure 4.4: HC-PCF 800 loss dependence on wavelength[64]

Figure 4.5 and 4.6 shows the Raman spectra of Lysol and WD-40 aerosols, sprayed into the fiber as per the first coupling method in Figure 4.1.

![Raman spectra](image)

**Figure 4.5:** Lysol Raman measurement by directly coupling aerosol spray into PCF Low exposure setting (10-20sec)
Figure 4.6: WD-40 Raman measurement by directly coupling aerosol spray into PCF Low exposure setting (10-20sec)

Figure 4.5 highlights the Lysol peaks common to ethylene glycol modes in red. For reference the ethylene glycol spectra measured using the PCF is given in Figure 4.7.
The fact that similar modes were found gives reason to believe that detection and identification of similar compounds found in mustard gas is possible. A thorough literature search was conducted to compare and confirm Raman spectra of various household aerosol measurements, but no such reports were found. It should be noted that the large hydrocarbon peaks centered around 3000 cm$^{-1}$ in Figure 4.5 and 4.6 are indicative of hydrocarbon remnants from aerosol compressed gases. This can be compared against previous gas phase Raman measurements of propane [78] shown in Figure 4.8. The experiment employed HC-PCF in the forward scattering method to obtain the spectra.
This region compares well with the PCF measurements in Figures 4.5 and 4.6. Some of the gases are found in the material safety data sheet (MSDS) of most aerosol sprays and serve as the pressurized gas which propels the liquid phase aerosol particles into the atmosphere. The mode and peak assignments shown for each measurement can be used in determining the chemical structure of the aerosol particles. Comparing the peaks of Lysol aerosol to WD-40 there are distinct differences in peak location and relative intensities. These are the characteristics that are abundant in Raman spectroscopy, which allow for simultaneous detection and identification of analytes. What is interesting about these measurements is that the PCF bandgap lies between wavenumbers 2894.56 cm\(^{-1}\) to 4033.08 cm\(^{-1}\), and this leads us to question how modes below 2000 cm\(^{-1}\) are so prominent. One possibility is that aerosols are indeed, coalesced into liquid phase droplets and thereby also provide TIR guidance due to higher core refractive index. The measurement summary including the signal to noise ratio for each measurement is presented in
Table 4.1.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Peak Intensity average (Counts)</th>
<th>Signal/Noise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lysol spray</td>
<td>15,651</td>
<td>1.5</td>
</tr>
<tr>
<td>WD-40</td>
<td>36,420</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 4.1: SNR and peak intensity summary for PCF direct aerosol coupling measurements

The values are normalized with respect to fiber length and exposure time of each measurement.

The Lysol measurement using the second setup via the air pump is shown in Figure 4.9

Figure 4.9: Lysol Raman measurement by coupling aerosol spray via air-pump into PCF. High exposure setting (200sec)
Figure 4.10: Mosquito repellent Raman measurement by coupling aerosol spray via air-pump into PCF. High exposure setting (200sec)

Under low exposure settings (10-20 sec) nothing other than the background silica modes could be observed for low wavenumbers. With high exposure (200 sec) the hydrocarbon region showed similar activity to spectra obtained with method one. Since nothing was seen below 2000 cm\(^{-1}\) it is believed that method two did not promote liquid phase aerosol coalescence. With the absence of TIR guidance, Raman modes below 2000 cm\(^{-1}\) were not confined in the waveguide. The fact that the pump also introduces a continuous air stream leads to particle dispersion and impedes droplet formation. The signal to noise comparison for each of the measurements is given in Table 4.2.
<table>
<thead>
<tr>
<th>Analyte</th>
<th>Peak Intensity average (Counts)</th>
<th>Signal/Noise</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lysol spray</td>
<td>1,750</td>
<td>0.003</td>
</tr>
<tr>
<td>Mosquito Repellant</td>
<td>2,250</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**Table 4.2:** SNR and peak intensity summary for PCF aerosol coupling via air-pump measurements

The intensity and SNR values, of the spectra obtained from method two, are reduced by at least an order of magnitude. This is attributed to the dilution of aerosol particles within ambient air, and reduced droplet formation limiting TIR guidance. Mitigating the dilution of the aerosol particles within the air stream is an important consideration. One solution is to incorporate aerosol compactors\[68,79,82\]. Compactors separate incoming air stream and aerosol particles of various sizes, and weight. By segregating and collecting particles with diameter on the order of tens of microns, aerosol particles can be effectively isolated and detected.

In Chapter 6 we compare the SNR and peak intensity values of the aerosols using the Bragg groove reflection waveguide.
5 Fabrication of Hollow Core Waveguides

5.1 Introduction

The Bragg groove waveguide design from Chapter 3 was intended to utilize standard silicon planar fabrication processes and equipment available at the University of Toronto Nanofabrication Centre (TNFC). Hollow core waveguides built using these processes must meet several important criteria to create an enhanced Raman sensing system, that can be further developed to fully realized lab-on-chip devices. Reasonable lengths greater than 1cm must be reached to enable enhanced sensing of analytes on the order of nano-molar concentration. In chapter 7 adapted designs of the groove waveguide will be discussed to explain how extended effective interaction lengths on the order of meters can be achieved on a single chip. This can potentially increase the platform sensitivity by a factor of 100. The inner surface of the waveguide must be made smooth in order to minimize light scattering inside the waveguide. Mode scattering could amount to higher propagation losses and reduced interaction length. Roughness at the core-cladding interface can further lead to local effective index changes along
the length of the waveguide. The varying effective index corresponds to a pseudo-grating structure that could scatter the mode in various directions[65]. Additionally the dielectric cladding layers of the waveguide must be uniform and controlled in order to achieve high Stokes signal confinement.

There are general methods for fabrication of hollow core structures. One method, direct bonding, consists of forming a trench on a substrate, then sealing the trench with another substrate, by thermal bonding [66,67]. Electrostatic sealing, facilitated by use of anodic bonding, has been applied for bonding between silicon and borosilicate glass substrates [68,69]. The process relies on the transfer of charged ions between the two substrates creating a hermetic seal. These methods becomes extremely difficult when the middle layers are dielectric and can lead to significantly reduced bonding area and strength[70]. Successful bonding between few dielectric layer stacks of nitride and oxide of a few tens of nanometers have been reported by Thomas et al. [70], but extending this to a stack of ten or more layers is extremely difficult, and bonding strength is greatly reduced in the process. Wafer bonding techniques such as anodic or direct bonding require wafer surfaces with a nanometer scale roughness and very few non-uniformities, meaning structures having large topographic variance cannot be reliably sealed. Waveguide designs incorporating these bonding processes are limited in hollow core dimensions and have severe restrictions on the top and bottom cladding thicknesses. This is not ideal for Bragg waveguide fabrication, where the number of layers directly controls the loss characteristics of the waveguide.

A second fabrication technique employs a sacrificial core layer, around which the rest of the structure is grown. The core acts as temporary scaffolding allowing for a complete structure to be
fabricated on a single substrate without requiring flip-chip bonding to seal the structure. Fabrication difficulty with this technique is encountered during the core etch process. Long etch times for even 1cm long waveguides lasting a week is reported by Barber et al. [36]. This limitation is the product of poor etchant diffusion through the narrow waveguide core, and the inefficient removal of dissolved sacrificial material inside the channel. These challenges make fabrication of waveguides longer than 1cm impractical. The designs are also constrained to core widths below 28um and heights below 9um [37] due to induced mechanical stress ensued when dissolving the sacrificial core.

This process described in this thesis employs an alternate wafer bonding process relying on an adhesive intermediate layer to provide a robust seal of the hollow core groove, and is compatible with large core sizes and cladding thicknesses. This chapter will give a detailed overview of the entire fabrication process. The application of the waveguide to Raman spectroscopy and sensing is the key innovation and will be described in the next chapter.

### 5.2 Process Overview

Waveguides were made with 100mm diameter silicon wafers having <100> crystal orientation to facilitate anisotropic v-groove etching. Using PECVD processes the Bragg cladding layers of alternating oxide and nitride films were deposited on the top and bottom substrates, shown in Figure 5.1.
An SU-8 negative photo-resist adhesive layer is spun on the top wafer, and thereafter the two substrates are bonded under higher pressure and temperature. The bond between the substrates at the end is strong enough for the device to be cleaved using a dicing machine.

**5.3 KOH etching**

V-groove etching[71] is a wet-etching process, developed as a robust packaging technique. The structure serves as an inset channel to secure and align various optical and electrical components. V-groove etching uses KOH diluted solvent to etch crystalline silicon along the <111> plane. The etch rate is highly selective depending on the crystal orientation, and some silicon planes etch slower than others creating the characteristic v-groove shape. Typically silicon <111>
planes tend to etch relatively slower than other orientations, while the \(<110>\) plane etches at a faster rate, and the \(<100>\) plane etches at an intermediate rate.

Depending on the shape and size of the exposed silicon and its crystal orientation, many different etch patterns can be created.

![Figure 5.2: KOH etch results for crystalline \(<100>\) silicon using variety of masks [71]](image)

The etch rates are dependent on both the KOH solution concentration and temperature.

The surface roughness is also dependent on these parameters as shown in Figure 5.3.

![Figure 5.3: Roughness profile for varying KOH solution temperatures and concentrations[71]](image)
During the course of this thesis four different KOH temperatures were examined for v-groove surface characterization. Figure 5.4 compares grooves wet-etched at 50°, 60°, 70°, and 80° to visualize surface properties.

![Figure 5.4: KOH 15% etch results using rectangular etch mask for temperature (a) 50°, (b) 60°, (c) 70°, (d) 80°. Etch time was 4 hours for each groove structure.](image)

All grooves had similar dimensions and were left in the KOH solution for 4 hours. It should be noted that since the etch rate is higher for higher temperatures that some of the grooves were left in the solution even after the v-groove shape was established. The roughness is more exaggerated as the temperature is increased, and one major factor for this is that any swing in temperature during the process has a large impact on the etch rate, hence if the hot plate has high variability, or the temperature controller has a slow feedback mechanism, this could severely affect the
uniformity of the etch. This effect is substantially mitigated by operating at temperatures close to 50°C.

The aim of the design was to achieve a 100um wide v-groove with low surface roughness. To limit the surface roughness while ensuring an etch time of a few hours, KOH solution with 15% concentration set at 50°C Celsius was used. The etch rates for the different crystal orientations and materials for these conditions are listed in Table 5.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>KOH etch rate (15% weight, 50 degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;100&gt;</td>
<td>13.97 μm/hour</td>
</tr>
<tr>
<td>&lt;110&gt;</td>
<td>21.19 μm/hour</td>
</tr>
<tr>
<td>&lt;111&gt;</td>
<td>0.315 μm/hour</td>
</tr>
<tr>
<td>Silica PECVD</td>
<td>40 nm/hour</td>
</tr>
<tr>
<td>Silica thermal oxide</td>
<td>14 nm/hour</td>
</tr>
<tr>
<td>Silicon Nitride PECVD</td>
<td>30 nm/hour</td>
</tr>
<tr>
<td>Silicon Nitride LPCVD</td>
<td>--</td>
</tr>
</tbody>
</table>

**Table 5.1:** KOH etch rates for crystalline silicon, and dielectric films[71]

The choice of etch mask is very important. Experiments conducted over the course of the thesis included PECVD silica, and thermal oxide. The challenge with PECVD oxide is that the layer density is very low, and varies with position along the surface. This leads to pinhole formations followed by rapid mask degradation after 2 hours. To last the entire 4 hour etch length was not possible. Thermal oxide provided a suitable mask alternative, with higher selectivity to KOH as shown in Table 5.1. Figure 5.5 shows a comparison between KOH grooves using PECVD oxide and thermal oxide mask.
Figure 5.5: (a)V-groove etch using thermal oxide mask showing clear etch boundaries, (b) v-groove etch using PECVD oxide, shows non-uniform edges, (c) multi-groove structure

It can be seen in Figure 5.5(b) that the PECVD oxide has many variations in groove width, along the channel. This is due to the mask thickness not being uniform and pin holes exposing silicon where it was not meant to. Figure 5.5 (c) displays an array of v-grooves, etched using thermal oxide mask, on a single chip. The multi-groove configuration can be useful for many applications. By filling each groove channel with an array of analytes, multi-analyte batch sensing can be conducted. A second application involves coating each groove with a unique antibody, such that efficient labeled fluorescence or SERS sensing techniques can be devised. Eventually in chapter 7, an adapted multi-groove pattern will demonstrate how the multi-channels can be joined to create a longer waveguide for Raman enhancement.
5.4 Plasma Enhanced Chemical Vapor Deposition

5.4.1 Chamber properties

During fabrication of semiconductor devices, multiple deposition steps may be included in the process, many of which are conducted by Plasma-enhanced chemical vapor deposition (PECVD). Common dielectrics deposited with this technique are silicon dioxide, silicon nitride, and polycrystalline silicon. A diagram of a basic PECVD reactor is shown in Figure 3.2. The PECVD chamber introduces reactant gases such as Silane, ammonia, and nitrous oxide, which combine at low pressures ranging between 300 to 1000 mTorr, at the substrate surface. Substrates are placed on a heated platen which is operated typically between 250\(^\circ\) and 300\(^\circ\) C. There is also an RF energy source used to excite the gases into a plasma state and facilitate the various reaction dynamics. These factors all play a role towards film conformality, refractive index, and density.

A typical reaction that occurs incorporating silane (SiH\(_4\)) and nitrous oxide (NO\(_2\)), and its formation of silica (SiO\(_2\)) is given in equation 5.1.

\[
\text{SiH}_4 + 2\text{N}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2 + 2\text{N}_2 \tag{5.1}
\]
A diagram of a typical PECVD chamber is given in Figure 5.6.

![Diagram of a PECVD chamber](image)

**Figure 5.6:** PECVD deposition chamber, showing schematic of gas flow, RF generator, vacuum pump hose, heated platen, wafer, and Plasma region [40]

There are four gases utilized by the TNFC PECVD reactor. The gases are controlled by mass flow controllers (MFC’s) and excited by the RF power supply with corresponding 13.56 MHz automatic tuner. The recipes that run inside the chamber are manually controlled with user defines gas flows, pressure, temperature, and RF power levels. Table 5.2 shows the process gases used for the Bragg groove structure.

<table>
<thead>
<tr>
<th>Gas name</th>
<th>Gas composition</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH$_3$</td>
<td>Nitrogen source for SiNx deposition</td>
</tr>
<tr>
<td>Silane</td>
<td>SiH$_4$(5%)/N$_2$(95%)</td>
<td>Silicon source for all film deposition</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N$_2$O</td>
<td>Oxygen source for SiO$_2$ deposition</td>
</tr>
<tr>
<td>Tetrafluoromethane</td>
<td>CF$_4$(92%)/O$_2$(8%)</td>
<td>Chamber clean</td>
</tr>
</tbody>
</table>

**Table 5.2:** PECVD gases used during deposition, with chemical composition, and purpose
For the purposes of this thesis all cladding structures consisting of alternating layers of silicon oxide and silicon nitride were deposited using PECVD techniques, at 300° platen temperature. In the next section, film conformity and thickness variations are studied.

5.4.2 Film Conformality

Films grown using PECVD techniques are not exactly isotropic, and this leads to different deposition rates for horizontal and vertical surfaces. The Bragg groove structure can be separated into a slanted groove, and planar surfaces for which two different recipes are used to ensure correct thicknesses. The v-groove structure is made up of two slanted side walls angled at 57° with respect to the deposition vector. The degree of anisotropy depends on the reactor geometry and recipe pressure used. At higher pressures near 1000 mTorr, there are more collisions between reactants which scatter the molecules in all directions. The result is a more isotropic deposition than observed with lower deposition pressure. At higher pressures, ratio of horizontal to vertical surface deposition rate was measured to be between 1.2 and 1.6. The exact ratio corresponding to v-groove deposition was measured to be 1.4. Hence, in the recipe, deposition times used for the v-groove surface was multiplied by a factor of 1.4. Table 5.3 gives the recipe details of oxide, nitride films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas 2 Flow (SiH₂/N₂)</td>
<td>170</td>
<td>sccm</td>
</tr>
<tr>
<td>Gas 3 Flow (N₂O)</td>
<td>710</td>
<td>sccm</td>
</tr>
<tr>
<td>RF Power</td>
<td>30</td>
<td>W</td>
</tr>
<tr>
<td>Pressure</td>
<td>1000</td>
<td>mT</td>
</tr>
<tr>
<td>Growth Rate</td>
<td>60</td>
<td>nm/m</td>
</tr>
</tbody>
</table>

Table 5.3: PECVD oxide deposition recipe and growth rate
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas 2 Flow (SiH₄/N₂)</td>
<td>500</td>
<td>sccm</td>
</tr>
<tr>
<td>Gas 3 Flow (NH₃)</td>
<td>75</td>
<td>sccm</td>
</tr>
<tr>
<td>RF Power</td>
<td>30</td>
<td>W</td>
</tr>
<tr>
<td>Pressure</td>
<td>1000</td>
<td>mT</td>
</tr>
<tr>
<td>Growth Rate</td>
<td>12</td>
<td>nm/m</td>
</tr>
</tbody>
</table>

Table 5.4: PECVD nitride deposition recipe, and growth rate

5.4.3 Film Characterization

The deposited layers were measured for two critical properties, thickness and refractive index. Having each fall within design tolerances, ensures that the cladding structure will exhibits high reflection for desired wavelengths and angles. Due to chamber geometry, the RF power, and gas distribution may not be consistent at all sample positions leading to variations in both, layer thicknesses, and refractive indices. The quality of the deposited films were checked using ellipsometry.

Of the two deposited films, nitride deposition turned out to be the more challenging process. Nitride deposition is a slightly thermodynamically unfavorable process [10] often resulting in silicon oxy-nitride rather than nitride. Many initial nitride deposition trials often led to low refractive index measurements near 1.47-1.5 from ellipsometry, caused by the oxy-nitride formation. The main factor for this is residual oxygen absorbed on to the chamber wall and residual oxygen gas flow, which reduces the nitride refractive index. It was found that conditioning the chamber with a long nitride run lasting 15 min, before stack deposition, helps by providing a protective layer. The layer covers any oxygen absorbed on to chamber walls. Also
by stopping the nitrous oxide flow, which is used in silica film growth, significant increase in measured refractive index was observed.

One of the other main factors effecting nitride deposition is the non-stoichiometric nature of PECVD nitride, resulting in a ratio that differs from traditional Si$_3$N$_4$ ratio, and is designated by SiN$_x$ indicating that the ratio of the two chemicals is unknown. The ratio of the two chemicals is very important in determining the refractive index, and can be controlled by the relative flow rates of Silane and ammonia. As the flow ratio skews in favor of silane, the film silicon ratio will increase, thereby increasing the refractive index[85]. Figure 5.7 plots the refractive index for PECVD nitride layer for varying ratio of silane to ammonia flow rates.

![Figure 5.7: PECVD nitride refractive index dependence on silane:ammonia flow rate](image)

From previous reports[72], typical flow ratios reported ranged between 1 and 1.3, corresponding to refractive indices near two. Unfortunately with these flow ratios the desired index was not reproducible with the Oxford Plasma Deposition machine. One explanation is that the silane
source used is actually diluted 5% with nitrogen gas, instead of the typical helium. This added nitrogen could skew the film ratio.

The design required a nitride refractive index of 2.0. The measured refractive index for silane-ammonia process ratio of 6.5, ranged between 1.97 and 2.05 from ellipsometry. This variability falls well within the allowable tolerances of the design. The oxide film was similarly measured to have an index of 1.45 to 1.46, also within acceptable tolerance levels.

5.4.4 Film Uniformity

To characterize the thickness uniformity across the sample, the ellipsometer was used to measure thicknesses at five random positions for five different chips. The variability in film thickness was measured and also modeled to understand the effect on the reflection profile of the Bragg stack. Figure 5.8 and 5.9 plots the single layer film thicknesses of each of the samples.

![Nitride deposition thicknesses](image)

**Figure 5.8:** PECVD nitride variability. Thickness measurements are constant within chip area, and show more variability between chips. Black line represent ideal constant nitride thickness of 91.1 nm. Chips are on average 2cmx2cm in area.
**Figure 5.9:** PECVD oxide variability. Thickness measurements are constant within chip area, and show more variability between chips. Black line represents ideal constant oxide thickness of 151.7 nm. Chips are on average 2cm x 2cm in area.

From Figure 5.8 and Figure 5.9, it was observed that nitride thickness varied by 7%, and oxide thickness uniformity was within 4%. Figure 5.9 shows SEM images of the full stack structure for two different chips, showing the fabrication variability.

**Figure 5.10:** SEM image of entire Bragg structure for two chips. (a) Has layer thickness: oxide (141nm) and nitride (102nm). (b) Has layer thickness: oxide (147nm) and nitride (95nm).
The dark bands correspond to SiO$_2$ layers, and the light bands correspond to SiN$_x$ layers. The contrast between the layers are a result of stain etching the stack cross-section in buffered oxide solution for three minutes. To understand the effect of the thickness variation on the stack Reflectivity, Figure 5.11 plots the profile for the two deposited structures shown in Figure 5.10.

![Reflection profile for two different 10 layer quarter wave stacks](image)

**Figure 5.11**: Reflection profile for two different 10 layer quarter wave stacks (a) Has layer thickness: oxide (141nm) and nitride (102nm). (b) Has layer thickness: oxide (147nm) and nitride (95nm).

Visually, the reflection profiles show only minor differences. Quantitatively, we can calculate the FOM$_1$ defined in chapter 3 to understand the variability of the waveguide collection efficiency. Structure 1, shown in Figure 5.8 (a) has FOM$_1$ = 53.65%, and structure 2, shown in Figure 5.8 (b) has FOM$_1$ = 54.3%. Comparing the FOM$_1$'s the enhancement deviations due to fabrication variability is marginal.
5.5 SU-8 adhesive bonding

5.5.1 Overview

After depositing the top and bottom structure with the Bragg layers, SU-8 2007 negative tone photoresist was spun on the top layer. This provided a relatively uniform and thick adhesive coating that could be used to bond the two substrates. The parameters of notable interest are the spin speed, post bake temperature, bonding pressure, and bonding temperature used in this process. As a common theme among all photoresists, the spin curve, Figure 5.12, modeling the resist thickness versus the spin rate of the sample is of great importance, as it plays a big role in film uniformity and edge bead formation.

![Figure 5.12: SU-8 2000 series spin curve. Spin speed of 3000 RPM corresponds to 7um SU-8 2007 layer thickness[73]](image)

Bonding between the top and bottom structures requires a flat SU-8 adhesive layer. As such, the top sample on which the SU-8 film was spun had a slightly larger area than the bottom (v-
groove) substrate. In this manner, the edge beads forming along the edges of the spun sample would lie beyond the bonding area.

5.5.2 SU-8 spin deposition

To prepare the top sample for SU-8 coating, standard clean processes SC-1 and SC-2 were run, removing all organics from the surface. Some reports also mention simple acetone wash is sufficient [45] for adhesive bonding. The clean step is to ensure that the SU-8 is in fact spun directly onto the sample surface. The sample is then prebaked using a hot plate at 130°, for 10 min to make sure all moisture and hydroxyl bonds are removed from chip surface.

Picking the correct SU-8 thickness is a compromise between having enough adhesive thickness to take into account surface unevenness of the top and bottom cladding structures, while not going too thick as to deviate significantly from hollow core groove design. The SU-8 was first spun at 500 rpm for 15 sec with acceleration of 14 rpm per second, and then quickly ramped up to 3000 rpm for 45 sec with acceleration of 30 rpm per second per second. The initial 500 rpm spin rate was to make sure that all the SU-8 resist was spread along the sample surface and was not aggregated at the center, and the second spin step was meant to even out the layer thickness to 7μm over the entire surface.

The sample was then placed on top of a hot plate for post bake of 65° Celsius for 15 min to planarize the surface, followed by quick ramp up to 95° and hold for 10 min to evaporate any remaining solvents at the surface.

5.5.3 Bonding

To finally bond the top and bottom substrates and seal the groove, careful steps must be taken with respect to temperature and applied pressure. Groove filling caused by SU-8 reflow is a
possibility during the bonding process. Firstly, after keeping the top planar substrate with spun-on adhesive at 95° (from the post bake step), the temperature is ramped down to 75° on the hot plate. Once the temperature reaches 85° the v-groove substrate is flipped and placed on top of the heated sample. Using a small roller to go over the samples serves to make contact over the entire surface between the two substrates. The roller is used continuously over the entire area until temperature is finished ramping down 75°. The sample is then transferred to hot plate set at 60°, and then left for one hour with 1 kg weight on top of bonded substrate for curing. The bonding temperature is set purposefully to take advantage of the phase changes of SU-8. 95° C is near the glass transition temperature of SU-8. At this temperature SU-8 is in a liquid phase and can re-flow easily. If bonding was attempted at this point, adhesive would flow and fill the groove due to contact pressure as shown in Figure 5.13.

![SU-8 photo-resist filling hollow groove structure. High temperatures >900° are conducive to SU-8 reflow](image)

**Figure 5.13:** SU-8 photo-resist filling hollow groove structure. High temperatures >900° are conducive to SU-8 reflow

Figure 5.13 is an optical microscope image taken of an initial SU-8 bonding attempt made using silicon groove substrate and borosilicate glass. Glass was used to understand the filling and planarization tendency of SU-8 near glass transition temperature. It is important to understand that the postbake step is very important in removing resist solvents, such that during temperature
ramp down below the glass transition point the resist can harden, with reduced reflow, providing a tight seal.

At 60°C the SU-8 layer is hardened and takes on a more solid phase, and very little SU-8 can move thereafter. This ramp down process was optimized after many trials for minimal reflow and sufficient contact between groove substrate and adhesive within the ramp down time.

![Image](image_url)

**Figure 5.14:** Minimum reflow observed at bonding temperature below 85°C

Even with the optimized process, there were still some attempts where SU-8 filled parts of the groove, shown in Figure 5.14, and this can lead to deviations from predicted loss values. This will be examined in chapter 6. One major advantage of this technique is that SU-8 is spun on the planar top substrate and no alignment is required with the bottom substrate during the entire process.

### 5.6 Sample Dicing

Once the substrates are bonded, the sample is strong enough for dicing. The dicer used is the Disco Dicer 35A60 instrument with maximum blade RPM of 30K and water jet cooling.
capabilities. The dicer is used in order to achieve a flat facet of the Bragg groove waveguide, and to be able to efficiently couple light into the device. Since the dicing blade is not recommended to cut beyond 700um thick sample in one pass, two passes were programmed for sample dicing with combined thickness of 1um. The first pass was set to a height of 300um, while the second pass was set to 700um creating a clean cut of the cross section. The blade was set to 30K RPM to achieve maximum facet smoothness. The thickness of the blade was 30um wide and did produce jagged edges due to blade twisting during the cut. The resulted in some facet unevenness as evident in Figure 5.9.

Figure 5.15: Dicing of (a) BGRW with 115um core width, (b) Silicon-silicon trench waveguide 95 μm core width. Minor SU-8 reflow can be observed in the trench waveguide.

As can be seen, although the facet has minor aberrations, the groove is intact and can be directly coupled to an analyte via a suitable pump.
6 Bragg Reflection Waveguide Characterization

6.1 Overview

This chapter focuses on testing the fabricated Bragg waveguide chip for propagation loss, and Raman enhancement. Comparison of the acquired spectra using the waveguide is particularly interesting since unlike the hollow core PCF, there is no TIR mode confinement and therefore any enhancement is primarily due to bandgap confinement.

6.2 Waveguide Loss Characterization

The propagation loss was found using the cut-back methodology. The setup is shown in Figure 6.1.
The chips used in the experiment were all fabricated together using a batch wet etching, and film deposition process. This reduces any measurement error associated with fabrication variability. Chips with multiple lengths were measured for total output power using a silicon power meter. The equation relating input power to output power is given by [74]:

$$P_{output} = CC' e^{-aLT_{set-up}} P_{in}$$  \hspace{1cm} (6.1)

The input and output waveguide light coupling terms $C$, and $C'$ depends on the level of alignment and focus of the objectives and mirrors used in the setup. $T_{set-up}$ is the inherent loss of the system that are generated from laser output, and mirror surfaces. For all chips measured, the mirror and objective stages were adjusted in an iterative process until the measured power output at the detector was maximized, corresponding to optimal alignment and focus of the system. Since this process was undertaken for all measurements, the product of input, output coupling terms, and $T_{set-up}$ can be assumed constant among the entire set of chips measured. This leaves the waveguide length as the only varying term in equation 6.1 between experiments. Taking the logarithm of equation 6.1 gives a linear power relation with respect to waveguide length.
\[
\ln(P_{\text{output}}) = \ln(CC'T_{\text{set-up}}P_{\text{in}}) - \alpha L \\
= y_0 - \alpha L
\]

Where \(y_0\) is the \(y\)-intercept of the log output representing the loss of a zero length waveguide just having input and output coupling losses. Figure 6.2 plots the measured log power output versus waveguide length.

![Graph](image)

**Figure 6.2:** Log power output measured for Bragg groove waveguides of different lengths

Least squares regression allows us to approximate the plot with a line of best fit, where the line slope is the loss term and the constant term represents the product of input and output coupling loss. The loss factor measured is 0.17 dB/cm and is higher than the numerically predicted 0.05 dB/cm from Chapter 3. Higher losses can be attributed to three reasons:

1. Scattering losses along the waveguide due to rough edges and interfaces.
2. SU-8 adhesive that may have flowed into the core, interfering with laser propagation.
3. Refractive index and film thickness variations along the length of the waveguide can change the local effective index. This could lead to a pseudo-grating structure in the direction of the waveguide scattering the mode light.

From earlier analysis conducted in chapter 5, the cladding thickness tolerances proved to have minor effect on waveguide loss. The bulk loss can therefore be attributed to SU-8 reflow into the groove channel, and scattering losses.

Table 6.1 compares this loss value to other experimental values including ARROW structures and omni-guide Bragg fibers.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Bragg groove waveguide</th>
<th>Arrow waveguide</th>
<th>HC-PCF</th>
<th>Bragg Fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss dB/cm</td>
<td>0.17</td>
<td>2.6</td>
<td>0.0015</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Table 6.1:** Comparison of the measured Bragg waveguide loss with other hollow core waveguides. The arrow waveguide is the only other on-chip waveguide loss provided. The fiber based devices have far superior loss values in comparison.

The Bragg groove device has the lowest measured propagation mode loss among on-chip air core waveguides known to date, making it an ideal component for integration with lab-on-chip devices.

Light output at the output of the waveguide was captured by an optical camera, shown in Figure 6.3.
The mode takes on the characteristic triangle shape seen in Chapter 2. Due to the size of the waveguide core, the output light could not be adequately focused, and mode dispersion can be observed.

6.3 Raman Spectroscopy Characterization

6.3.1 Measuring Raman Enhancement

The fabricated devices were tested for Raman enhancement on a variety of liquid and aerosol analytes. Two types of on-chip waveguides were tested:

1. Bragg groove reflection waveguide (BGRW), with 5 alternating layers of silicon nitride and oxide thin films.

2. Silica groove waveguide (SGW), having the same structure as the Bragg waveguide, but now having just one cladding layer of 3μm thick oxide, used as comparison benchmark.

All measurements using the PCF device, used 8cm long fibers to maintain consistency between experiments. The measurement setup is depicted in Figure. 6.4.
6.3.2 Silica Groove Waveguide Characterization

The hollow core waveguide and fiber are filled with the liquid analytes via capillary action. The Raman spectra for liquids measured using the SGW and PCF are shown in Figure 6.5.

**Figure 6.5:** (a) Comparison of Toluene (n=1.6) Raman spectrum between silica groove waveguide and HC-PCF device (b) Raman spectrum of glycerol (n=1.46) obtained using silica groove waveguide. All spectra were captured using low exposure times (10-20 sec)
In Figure 6.5(a), the silica groove waveguide is used to measure the Raman spectra of Toluene with refractive index of 1.6. Since the liquid core is of greater index than the surrounding silica cladding, TIR guidance is expected to confine the pump as well as some of the Raman modes within the core, increasing the interaction length. As expected, the signal shows similar enhancements with the corresponding PCF measurement. Figure 6.4 (b) plots the glycerol measurement using the same silica groove device. As can be seen, the glycerol peaks are barely noticeable or observed. This is expected, since glycerol has a refractive index of 1.46, similar to silica. In this configuration, very little of the Raman modes are expected to be confined inside the core by TIR guidance. The small glycerol peaks are likely collected signal within the focus depth of the objective lens, having an interaction length of just a few microns. It should also be noted that the peak located at 520cm\(^{-1}\) generated from the silicon substrate, is almost at saturation point (65x10\(^3\) counts). This confirms that there is very poor mode confinement inside the groove core, and most of optical power is leaking into the silicon substrate. The SNR for the bare silica groove chip is calculated to be 0.2 for the glycerol measurement.

**6.3.3 Bragg Groove Reflection Waveguide Enhancement**

The Bragg waveguide and PCF Raman measurements for glycerol, water, and IPA are shown in Figure 6.6.
Conversely, the Raman spectra taken using the BGRW shows a greatly attenuated silicon peak for water, and no discernible peak for glycerol or IPA. This is further evidence that the pump light is well confined to the hollow core region with minimal leakage into the substrate. Table 6.2 compares the spectra in Figure 6.6 between the Bragg groove and PCF devices for peak intensities and signal-to-noise ratio, normalized for interaction length and exposure time.
Table 6.2: Comparison of the measured Bragg waveguide Raman enhancement with HC-PCF measurements for measured liquids. All values are normalized for device length and exposure times. $FOM_2$ represents the product of SNR and average peak intensity.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Avg Peak Intensity PCF (Counts)</th>
<th>SNR fiber</th>
<th>$FOM_2$ PCF</th>
<th>Avg Peak Intensity on-chip (Counts)</th>
<th>SNR on-chip</th>
<th>$FOM_2$ on-chip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>4364.5</td>
<td>24</td>
<td>104748</td>
<td>11551</td>
<td>5.8</td>
<td>66995.8</td>
</tr>
<tr>
<td>Water</td>
<td>17551</td>
<td>20.4</td>
<td>358040.4</td>
<td>48000</td>
<td>7.92</td>
<td>380160</td>
</tr>
<tr>
<td>IPA</td>
<td>6000</td>
<td>10.6</td>
<td>63600</td>
<td>21087</td>
<td>4.25</td>
<td>89619.75</td>
</tr>
</tbody>
</table>

Although the Bragg groove waveguide shows significant SNR enhancement over the silica groove waveguide of almost 30 times, the SNR is still not comparable to PCF having SNR almost 3.33 times larger on average. The SNR takes into consideration the spectra baseline typically attributed to fluorescence, and is identified as a noise source, limiting the detection of Raman peaks. That being said, the fluorescence intensity changes with each analyte and can theoretically also be used as a detection and identification marker. As a compromise, the FOM in table 6.2 is the product of the normalized peak intensity with the SNR and is a holistic representation of device enhancement. With this metric, the Bragg groove waveguide and PCF devices are comparable in performance, even though the propagation loss of the Bragg waveguide is higher. One possible explanation is the significantly larger core size of the groove waveguide (10x larger than the PCF) which also serves to increase the total overlap area between the pump and the analyte, increasing the amount of scattered light.

### 6.3.4 Aerosol enhancement

It should be noted that the PCF used in these experiments mainly relies on TIR guidance, as the liquid core is of higher refractive index than the bulk cladding and is not indicative of the
enhancements that can be measured for low index analytes such as aerosols.

In the next set of experiments a BGRW was used to acquire the Raman spectra of household aerosols Lysol and mosquito repellent. Figure 6.7 plots the obtained aerosol spectra.

Figure 6.7: Raman spectra of (a) Lysol and (b) Mosquito repellent using Bragg groove waveguide. All measurements taken at low exposure setting (10-20sec)

The measurements were conducted by spraying the aerosol into an air pump, connected to the facet of the Bragg groove waveguide, similar to the setup used for measuring aerosols using the PCF in Chapter 4. All measurements using the on-chip waveguide were taken at low exposure levels (10-20 sec). The on-chip aerosol spectra now exhibits modes below 2000 cm$^{-1}$, which were not seen using the PCF. This is consistent with the PCF bandgap which only resides at wavenumbers well above 2000 cm$^{-1}$. Using the HC-PCF, Raman modes were only observed when aerosol droplets were thought to have formed along the core walls enabling TIR guidance. The bandgap of the groove waveguide was designed to collect light ranging the full extent of the spectra, from 633nm to 830nm. This enables guidance of Raman modes in the spectral range of
100 cm$^{-1}$ to 4000 cm$^{-1}$ wavenumbers. The spectra comparison between the PCF and on-chip groove aerosol measurements are presented in table 6.3.

![Table 6.3: Comparison of the measured Bragg waveguide Raman enhancement with HC-PCF measurements for measured aerosols. All values are normalized for device length and exposure times. FOM$^2$ represents the product of SNR and average peak intensity](image)

The intensity and SNR values are all normalized for confocal hole size, magnification, interaction length, and laser power. The SNR values obtained using the Bragg groove chip are at least an order of magnitude larger for both analytes. This demonstrates the enhancement provided by bandgap devices to sense low index analytes such as gases and aerosols. Next steps of design and fabrication involve improving the confinement and loss characteristics of the waveguide in order to achieve higher SNR values, and perform effectively as early warning detectors in the field.

### 6.3.5 Fabrication Variability

This section looks into how the Raman spectra and enhancement changes between different chips. It is expected that the refractive index and the deposited cladding thicknesses may vary considerably between different samples. This is due to the variability of the PECVD process over wafer position. As discussed in Section 5.3, the asymmetric geometry of the deposition chamber leads to gradients in the gas flows and pressures within the chamber. This can lead to variability in Bragg layer thickness and refractive index as a function of wafer position. Individual chips
fabricated have dimensions 2cm x 1cm or smaller, and it is expected that the deposition process elements remain constant within a single chip area. Additionally the bonding process may also lead to some SU-8 resist flowing into the groove core. This could contribute to deviations from predicted enhancements. This is why observing fluctuations in measured Raman spectra between individual chips gives added insight into the processing variability and fabrication tolerances. Figure 6.8 plots Raman spectra of IPA obtained from three different Bragg waveguide chips.

Two of the chips are of similar length, while the third is significantly shorter. Using the relation between Raman enhancement and waveguide length given by equation 2.15, longer waveguides are expected to measure higher back scattered power. This is evident by simple visual analysis of the spectra obtained with the 0.4 cm long waveguide in comparison with the higher intensity spectra obtained using both the 1.6cm and 1.7cm long Bragg waveguides. Figure 6.9 plots the predicted and measured peak intensities for the aforementioned waveguides.

**Figure 6.8: Raman spectra of IPA for three different Bragg waveguide lengths**
Figure 6.9 compares the average peak intensities normalized to the longest waveguide in both the predicted and experimental case. The deviation between the measured, and predicted values of the peak intensities represents the fabrication variations in our process. The deviations from predicted enhancements are observed to be within $\pm 15\%$. As mentioned earlier, this deviation can be primarily attributed to SU-8 bonding conformity, and deposition variability.
7 Conclusion

7.1 Summary Of Achievements

Sensing platforms have seen a big thrust towards lab-on-chip platforms, providing significant sensitivity and unprecedented portability, opening up opportunities in many industries. This thesis focuses on Raman spectroscopy as an optical detection and identification technique.

Raman spectroscopy probes the native vibrational modes of an analyte, used to unambiguously distinguish molecules from one another. As the method does not rely on external markers such as fluorescing labels or antibodies, it opens the door for in-situ sensing, where it becomes possible to observe native reactions and chemical dynamics of a system. Although Raman spectroscopy has garnered much interest over the last decade for biological sensing, its low scattering cross section and reduced sensitivity makes it unsuitable for early warning detection of hazardous chemicals and contaminants requiring nano-molar sensitivities [79].
This thesis examined the design and utility of on-chip hollow core Bragg structures to enhance the total Raman signal collected and measured. Design of the Bragg waveguide involved optimizing the reflectivity profile of the cladding, to confine both the pump mode and Stokes scattering modes within the waveguide. The cladding structure which consists of alternating silicon oxide, and nitride layers, greatly extends the light-matter interaction length thereby generating more Raman signal than typically possible. The BGRW incorporates a large hollow core groove structure with cladding layers deposited right within the groove. Cross section is shown in figure 7.1. This groove design was chosen, as it greatly simplifies many of the fabrication steps involved.

![Figure 7.1](image)

**Figure 7.1:** (a) Bragg groove waveguide cross section, showing alternating layers of oxide and nitride cladding. Red region is silicon substrate region. Deep blue region is air. (b) Close up of Bragg stack cladding

Fabrication of the BGRW utilized the processing facilities and equipment available at the Toronto Nanofabrication Centre (TNFC). Considerable effort was taken during the process to optimize many of the individual steps with regards to surface smoothness and film quality. During the silicon groove wet etch step, the optimal temperature and concentration of the KOH solution was determined to be 50°C at 15% KOH by weight. The resulting silicon surface was
smooth such that ensuing cladding layers could be evenly deposited. The deposition step itself involved tuning the flow ratio of the various gases in order to achieve high quality oxide and nitride films which fell within design tolerances. The bonding process developed also played a crucial role in creating a robust seal for the waveguide structure.

Once fabrication was completed, the waveguides were characterized for propagation loss, and Raman enhancement factor. The propagation loss for a 633nm laser source coupled into the hollow core Bragg waveguide was determined experimentally to be 0.17 dB/cm, using the cut-back method. This is the lowest propagation loss value measured among on-chip air core waveguides to date.

Raman measurements were carried out on a variety of liquid and aerosol analytes, showing comparable enhancement with PCF devices for liquid phase measurements, and much higher enhancements for aerosols. The sensitivity limits of the BGRW waveguide were measured with sequentially diluted forms of glycerol solution. The BGRW measurement was benchmarked against direct micro-droplet measurement on glass slide. Figure 7.2 plots the resulting signal-to-noise ratios for the two methods.
From Figure 7.2, it can be seen that at each stage of dilution, the Raman SNR obtained using the Bragg waveguide is at least an order of magnitude higher than the glass slide measurement. Furthermore, using the glass slide approach, glycerol solutions below 0.6 Moles/liter results in no distinguishable signal at all. From Figure 7.2, it is apparent that the sensitivity limit of the Bragg waveguide is approximately on the order of mill-Moles per liter. As mentioned at the start of the chapter, for a sensing platform to be used as an early warning detection device, nanomolar detection sensitivities must be achieved[79]. The next section looks at additional enhancement techniques to approach this sensitivity limit.

**Figure 7.2:** Measured signal-to-noise ratio for diluted solutions of glycerol, comparing Bragg groove waveguide, and micro-droplet measurement.
7.2 Future work

7.2.1 UV excitation

In this thesis, the main excitation wavelength used was centered at 633nm. The Raman cross section has a $\lambda^{-4}$ dependence and by switching to a UV source operating near 254nm the cross section and measured power can be increased theoretically by two orders of magnitude. In addition to higher cross section, energy contained within incident photons are generally in the range of material bandgap, allowing the analyte to excite to higher electronic energy bands. This is also known as resonance Raman and the process is depicted in Figure 7.3.

![Figure 7.3: Quantum representation for non-resonance, resonance, and fluorescence optical scattering methods[38]. S0 and S1 are ground and first order electronic bands.](image)

By virtue of exciting the analyte into a higher electronic state, the resonant Raman cross section is enhanced by a factor of $10^2$-$10^6$[75]. This can lead to increased sensitivity for low concentration liquids and gases. One disadvantage of resonance Raman is that fluorescence background can be significantly higher than with traditional Raman, and this could lower the
signal-to-noise ratio of the measurement. The effects of UV enhancement must be investigated to understand these effects.

### 7.2.2 Lower propagation loss

From Chapter 3, the numerically extracted loss for a 100μm wide Bragg waveguide core is determined to be 0.0556 dB/cm. The losses are primarily dominated by silicon absorption at 633nm wavelength. By increasing the number of cladding layers the propagation loss can be lowered by reducing the mode leakage. For a 100um width waveguide designed to operate at 254nm pump wavelength the reflectivity profile for the Bragg stack is shown in Figure 7.4.

![Figure 7.4](image.png)

**Figure 7.4:** (a) Mode profile of 1-D Bragg waveguide for corresponding 100um core width Bragg waveguide, operating at 254nm. Yellow and green bars represent nitride and oxide cladding layers respectively, (b) Reflectivity profile for ten alternating layers of nitride ($n_1=2$, $d_1=36.7$ nm) and oxide ($n_2=1.46$, $d_2=60.5$ nm) alternating stack. The white area of the reflection contour represents reflectivity < 0.99.

The reflection profile exhibits high reflectivity for Raman scattering angles between 60°-90° from 254nm to 282nm optical wavelengths. This frequency range corresponds to Raman wavenumbers; 0cm\(^{-1}\) to 4000cm\(^{-1}\).
The theoretical mode loss for the 100μm wide Bragg waveguide, calculated from cladding reflectivity from Figure 7.4(b), is 0.0016 dB/cm. The losses due to material absorption are not accounted for and must be investigated for UV wavelengths.

### 7.2.3 Increased interaction length

Chapter 2 discussed the crucial role that the interaction length plays in overall Raman enhancement. By extending the length of the waveguide channel, the overlap between the analyte and laser mode is increased giving rise to more scattering events. Figure 7.5 plots the theoretical dependence of the back-scattered measured power versus Bragg waveguide length operating a 254nm wavelength.

![Figure 7.5](image)

**Figure 7.5:** Enhancement factor versus waveguide length for: 10 layer, 100um core width, Bragg waveguide operating at 254nm pump wavelength.

Figure 7.5 demonstrates that increasing the waveguide to 5 meters can increase the total measured power by two orders of magnitude. Of course it would not be practical to fabricate a 5 meter long waveguide on a silicon wafer, and this would deviate from the whole notion of
portability. To overcome this, adapting a looped waveguide structure allows us to fit a 5 meter long waveguide inside a 3cmx3cm silicon wafer sample, as depicted in Figure 7.6.

![Figure 7.6: Looped configuration of Bragg waveguide (top view) helping to conserve chip area](image)

Using an adapted configuration of combined straight, and bent Bragg waveguides allows for longer interaction lengths while satisfying the portability requirement. The loss of the straight waveguide configuration has been extensively modeled and simulated in this thesis, and similar investigation into bent waveguide must be conducted. Based on the bend losses, including coupling and mode propagation losses, the effective enhancement will have to be re-evaluated. That being said, the Bragg cladding exhibits high reflection for a broad range of propagation angles at the 254nm pump wavelength, and this can help reduce the measured losses around bends. The Bragg layer thicknesses can also be modified exclusively at bend location, in order to minimize losses.

### 7.2.4 Nano-Molar sensitivity

The next iteration of the platform hopes to combine the enhancements resulting from both UV resonance Raman, and increased waveguide length.

Figure 7.7 shows the incremental sensitivity improvements for each of the enhancement
features, showing how this work can be extended to approach nano-Molar sensitivities. These improvements are non-trivial and further investigation into design and fabrication feasibility is required.

![Graphical representation of the platform sensitivity](image)

**Figure 7.7:** Graphical representation of the platform sensitivity, showing enhancements measured during Bragg waveguide measurements, switching to UV pump source, and looped waveguide configuration

In conclusion, Bragg groove reflection waveguides exhibit promising characteristics which can be used for low index guiding, and sensing applications of various liquids and aerosols.
Appendix A

Sample Matlab Script

A.1 1-D Bragg Reflection waveguide profile script

%set waveguide parameters
lambda = 0.633E-6;
nc = 1;
n1 = 2;
n2 = 1.46;
tc = 50e-6;
m1 = 0; %mode order of cladding material 1, zeroth order set m1=0
m2=0; %mode order of cladding material 2, zeroth order set m2=0

%sweep through x-axis
for idx1=1:length(tc)
    kc = pi/tc(idx1);
    neff(idx1) = (nc^2 - (lambda/2/tc(idx1))^2)^0.5;

%calculate transverse momentum vectors
    k0 = 2*pi/lambda; %converting from microns to meters
    k1 = k0*(n1^2-neff(idx1)^2)^0.5;
    k2 = k0*(n2^2-neff(idx1)^2)^0.5;
    d1(idx1) = (pi/2+2*m1*pi)/k1;
    d2(idx1) = (pi/2+2*m2*pi)/k2;
    LAMBDA(idx1) = d1(idx1)+d2(idx1);

%profile params
    sigma = k1^2/(k1^2-k2^2);
    C1 = (tc(idx1)/2 + pi*kc^2*sigma*(k1+k2)/(2*k1^3*k2))^(-0.5);
    C2 = -kc/k1*C1;

    if(idx1==500)
        idx1=500;
    end
counter=1;
%calculate transverse electric field
for idx = 0:0.01e-6:tc(idx1)/2+lambda*100;
    if(idx<=tc(idx1)/2)
        Ey(idx1,counter) = C1*cos(kc*idx);
    else
        n = floor(((idx-tc(idx1)/2)/LAMBDA(idx1));
        if((idx-tc(idx1)/2)>=n*LAMBDA(idx1) && (idx-tc(idx1)/2<n*LAMBDA(idx1)+dl(idx1))
            Ey(idx1,counter)=C2*(-k2/k1)^n*sin(k1*(idx-tc(idx1)/2-n*LAMBDA(idx1)));
        else
            Ey(idx1,counter)=C2*(-k2/k1)^n*cos(k2*(idx-tc(idx1)/2-n*LAMBDA(idx1)-dl(idx1)));
        end
    end
    counter=counter+1;
end
Ey(idx1,:) = Ey(idx1,:)./max(abs(Ey(idx1,:)));

idx = 0:0.01e-6:tc(idx1)/2+lambda*100;

%%plotting E field and waveguide structure
figure();
hblue= plot(idx*1e6,Ey);
uistack(hblue,'top')
hold on
numLayers = lambda*100/LAMBDA(idx1);
limits = ylim;
counter=1;
for idx2=1:numLayers
    hred(counter)=rectangle('Position',
    [1e6*(tc(idx1)/2+LAMBDA(idx1)*(idx2-1)), limits(1),1e6*(dl(idx1)),limits(2)-limits(1)], 'FaceColor', [1,1,0]);
    uistack(hred(counter),'bottom')
    counter = counter+1;
    hred(counter)=rectangle('Position',
    [1e6*(tc(idx1)/2+LAMBDA(idx1)*(idx2-1)+dl(idx1)), limits(1),1e6*(d2(idx1)),limits(2)-limits(1)], 'FaceColor', [0,1,1]);
    uistack(hred(counter),'bottom')
    counter = counter+1;
end
xlabel('distance from core [μm]','FontSize',14)
ylabel('Normalized E field Amplitude','FontSize',14)
set(hred, 'EdgeColor', 'none')
end
Appendix B

Lumerical FDE Simulation

B.1  **100um wide Bragg Groove Reflection Waveguide**

We would like to understand the various modes of the BGRW. Figure B.1 plots the first three mode profiles with their propagation loss. In trying to understand whether the waveguide will be in single mode or multi-mode operation, the loss values can give a lot of insight. Looking at Figure B.1 the first order symmetric mode has the lowest loss, 0.057 dB/cm. The next lowest mode operation is the first order anti-symmetric mode having propagation loss of 0.182 dB/cm. These are both single mode operation, although the loss ratio is 1:3 between the two. The next lowest loss mode is the second order anti-symmetric mode with having characteristic loss of 2.6 dB/cm. The loss ratio with the lowest loss propagation mode is 1:45. Therefore it can assumed that this waveguide will naturally filter out multi-mode waveforms, and can be thought of as a single mode waveguide.
Figure A.1: Comparing the lowest three propagation modes of the BGRW. The loss ratio between the multi-mode waveform and the lowest mode waveform is 45:1.
Appendix C

ReporteR Portable Raman Measurements

C.1 Aerosol measurements

This section examines the enhancement that can be obtained by coupling the portable Raman system, shown in Figure C.1, with a HC-PCF device.

Figure C.1: SciAps ReporteR Portable Raman machine[77]

The Raman spectra obtained from Lysol air spray, and mosquito repellent is shown in Figure C.2. What is visually apparent from the spectra is the large background modes that exist at low wavenumbers. The background is what is picked up by the PCF silica cladding material, by aligning the portable Raman laser beam with the core of the PCF. The fact is, the laser spot size of the portable Raman instrument is not focused by an objective, and hence the collimated source
has a beam waist size of 30μm. This is 3x greater than the PCF hollow core diameter, and therefore Raman signal from the cladding region is also collected.

![Figure C.2](image)

**Figure C.2:** Raman spectra obtained from (a) Lysol, and (b) Mosquito repellent, using the portable Raman machine coupled to the HC-PCF.
References


