ENHANCEMENT OF SENSING CAPABILITIES AND FUNCTIONALIZATION OF OPTICAL MICRORESONATORS

A Dissertation in
Electrical Engineering
by
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Submitted in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

August 2017
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ABSTRACT

Optical microresonators have been demonstrated to provide a large enhancement in electric field by containing a resonant mode in a very small volume. This resonant enhancement is proportional to the quality of the resonator, which for microspheres has been demonstrated to be on the order of $10^{10}$. These devices can be leveraged to greatly improve light-matter interaction and for this reason the theoretical background of optical microresonators is discussed in the second chapter. This includes the use of COMSOL Multiphysics to model the mode structure and scattering from different resonator geometries. The second chapter also contains details on the fabrication and experimental design of optical microresonators. This includes the fabrication of fiber tapers for evanescent wave coupling into the devices.

Once the theoretical framework for utilizing resonators as tools for enhancement has been established in the second chapter, we progress to the discussion of the microbubble geometry and its potential for use as an on-chip sensor system. Topics covered include design, fabrication, and theoretical analysis of the mode structure in this geometry. Modal interaction with a liquid filled microbubble is demonstrated. Additionally, the use of microbubble resonators as highly accurate temperature sensors is demonstrated experimentally and theoretically.

In chapter 4 we investigate the use of silica microspheres as sensing devices; specifically, using them for the purpose of sensing nano-particles and chemicals in incredibly minute quantities. In this section microresonators are demonstrated to provide enhancement to Raman scattering from nano-scale particles. This configuration retains the traditional sensing methods of resonators by observing mode shifting and splitting in the resonance spectrum, while adding in a label-free sensing ability to determine material composition on adhered micro and nanoparticles.

The fifth chapter discusses the characterization of a new class of materials known as two dimensional materials (2D materials). Typically made from single atomic sheets of transition metal dichalcogenides, they are called two dimensional due to their incredibly small thickness. Monolayers of metal dichalcogenides offer large values for optical nonlinear susceptibility and can be used to generate highly efficient nonlinear optical phenomena. This chapter seeks to understand and describe the capabilities of these materials in a context of eventually integrating them into optical microresonators to create a new class of silica-based miniaturized nonlinear optical devices.

The final chapter in this dissertation covers the proposed and in-progress work related to those topics already covered in previous chapters. This includes direct growth of transition metal dichalcogenides onto microsphere resonators to create narrow linewidth microscopic lasers. Another novel photonic device consists of a single mode optical fiber etched to expose the core onto which a monolayer of 2D material is adhered. This presents the capability to create a simple photonic device which can easily be integrated as a discrete optical component capable of producing guided photoluminescence or extremely high second harmonic generation. Finally, spectral holography is discussed as a potential tool to record the phase information of light traveling through optical microresonators, adhered particles, and directly grown 2D materials.
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ACKNOWLEDGEMENTS

This dissertation represents years of work and collaborations with many fine researchers. The person most responsible for my success is my doctoral advisor Dr. Zhiwen Liu. His continued passion for teaching and understanding all of the intricacies in the research contained here is infectious. His patience and instruction were key to my growth as a researcher, and I simply cannot thank him enough for all he has done for me.

Next I would like to thank everyone who worked alongside me in the Ultrafast and Nonlinear Optics group at The Pennsylvania State University. Dr. Perry Edwards, Dr. Ding Ma, Dr. Nikhil Mehta, Dr. Corey Janisch, Chenji Zhang, Yizhu Chen, Atriya Gosh, William Murry, Josh Noble, and Cheng-Yu Wang your discussions and feedback have been invaluable throughout the years. All of your different experiences and backgrounds have allowed me to approach problems from new and unique directions. All of my interactions with you have enriched my time as a researcher here, and for that I thank you.

Additionally, I would like to thank the long list of professors and students outside of the Ultrafast and Nonlinear Optics group that I have collaborated with. Getting the chance to work with other like-minded individuals across the country was invaluable to the completion of the work presented here. At Penn State, Dr. Terrones’ research group provided the 2D materials as well as constructive feedback and frequent insights into material physics. I would especially like to thank Dr. Mauricio Terrones, Dr. Ana Laura Elias, Dr. Kazunori Fujisawa, Zhong Lin, Ethan Kahn, and Tianyi Zhang for all their help in the fabrication and the lengthy discussions about two dimensional materials. I would also like to extend my thanks to the Micro and Nanoscale Devices Group run by Dr. Srinivas Tadigadapa. Their expertise and assistance in micro and nanoscale fabrication helped to advance the work on microbubble resonators in new and very exciting ways. I would like to extend my thanks to Dr. Srinivas Tadigadapa, ChenChen Zhang, Eugene Freeman,
and Vedant Sumaria for their extensive work in microbubble fabrication, and the many hours spent analyzing these devices and thinking of new way to utilize them. Finally, I need to thank Dr. Lan Yang and her research group in the Micro/Nano Photonics Lab. I learned an incredible amount through extensive correspondence with Dr. Yang and Steven Huang, and the work on Raman sensing in microresonators would have been even more challenging.

I would also like to extend my thanks to Dr. Zhiwen Liu, Dr. Iam-Choon Khoo, Dr. Chris Giebink, Dr. Qiming Zhang, and Dr. Lasse Jensen for their advice, expertise, and assistance in preparing this manuscript. They were invaluable in helping me organize so much work in a coherent and thoughtful manner.

Additional thanks are due to the National Science Foundation. Funding for various projects throughout my time as a student allowed me to focus on learning and growing as a scientific researcher. Lastly, I would like to thank my family and friends for their unfailing support over the years. The amount of encouragement and assistance I have received over the years is incredible. Without each and every one of you I would not have been able to complete this work and succeed in any measurable way. Thank you all from the bottom of my heart.
Chapter 1
Introduction

Whispering gallery mode resonators have been of interest since their original discovery in certain architectural designs. Indeed, the name is derived from the ability for sound wave to propagate in a confined and low-loss manner around the circumference of certain rooms. Mathematical analysis of the whispering gallery was proposed by Lord Rayleigh in the 1910s to describe the acoustic phenomena inside of St. Paul's Cathedral [1]. Recently, studies of these types of structures and their unique properties has been performed in the optical domain. The ability of these devices to confine light in a stable and continuously circulating manner offers the possibility of high power densities inside of the device and thus enhanced optical nonlinearities and interaction with matter [2]. In ultra high Q resonators, the Q factor can be up to $10^{10}$ [3, 4], and the internal electric field buildup can be up to five orders of magnitude which allows for incredibly responsive interaction between light and matter. It is this property that makes them invaluable for the study of micro and nano-sized materials.

Chapter 2 will introduce the foundation for analyzing the interaction between light and nanomaterials in or on an optical microresonator. This includes the modal structure of light in a WGM as well as the useful metrics for evaluating the quality of a resonator. It will detail how resonators, eignenmodes, and Q factor are modeled in the finite element method of COMSOL Multiphysics.

Chapter 3 will discuss a new type of optical microresonator. Silica microspheres were first noted for their ease of fabrication and extremely high Q factor [5]. However, microspheres lack the ability to be produced in arrays on-chip. We seek to produce a WGM resonator which is
both scalable in fabrication, and still allows for modal interaction with the surrounding environment. Our solution to this is the use of a geometry known as a microbubble which was first fabricated from a silica capillary [6]. These type of devices consist of a hollow core which can be filled with materials of interest, and a thin layer of silica which forms the wall of the bubble. In such a device the modes can be confined to the wall which will expose a much larger portion of the wave, or the mode can propagate in the interior of the bubble if a suitably high refractive index material is used for filling. A further improvement to the microbubble system is to move away from single resonator fabrication and into scalable arrays. Functionalities such as highly responsive temperature and magnetic field sensing can be designed into these microbubble systems by observation of resonance mode shifts. The possibility of creating coupled waveguides and resonators on the same chip is a way towards creating a lab-on-a-chip technology which can function accurately and be fabricated with common silicon processing techniques.

In Chapter 4 we use optical microresonators to study the interaction between light and matter. Optically sensing nanoparticles and nanostructures is traditionally extremely difficult due to their size being on the order of or smaller than the wavelength of the visible spectrum. Current particle detection methods using microresonators rely on perturbing the mode within the resonator though a change in refractive index. These techniques can show the presence and even detect the size of a nanoparticle, but supplies little information about the type of material. To overcome this problem, we leverage the capabilities of optical microresonators to strongly enhance the interaction of light and matter [7]. One popular method of optically characterizing materials is the use of Raman scattering, originally discovered by C. V. Raman in 1928. It is a process by which scattered light is shifted by an amount of energy equal to that of a vibrational mode in the material. Thus each material has a unique Raman spectrum, which can be used to identify it. Experimentally, this is an incredibly weak signal compared to the linear Rayleigh scattering, and the amount of Raman signal scattered decreases with the cross section of the material. Here then,
the enhanced interaction between a circulating whispering gallery mode (WGM) of a microresonator and a particle offers a solution. One application of optical microresonators is to leverage the field enhancement produced by ultra high quality resonators to be used for sensing and determination of particles via enhanced Raman scattering.

Chapter 5 is devoted to the functionalization of optical resonators and photonic devices using 2D materials. Two dimensional (2D) materials are a relatively new class of matter that was first discovered with graphene [8]. These 2D materials are called such since they consist of a single or few number of atomic layers. They have been investigated recently for their novel properties which differ drastically from the bulk form. The study of graphene eventually led to the discovery of other atomically thin materials such as transition metal dichalcogenides (TMD) [9]. While incredibly thin, few layer number TMDs exhibit strong photoluminescence and second order optical nonlinear properties which make them suitable for creating new and powerful devices. We have used the extraordinary nonlinear capabilities of these materials to image and characterize unique structures via second harmonic generation. The exceptionally small depth of 2D materials makes them an excellent candidate for integration with our optical microresonator systems, to impart new functionalities.

The goal for these devices is to combine the whispering gallery mode resonators with the unique properties of nanomaterials in order to create novel devices on a microscopic scale. Many nanomaterials such as quantum dots and two dimensional materials offer fluorescence without the drawbacks of traditional organic dyes. The addition of two dimensional materials such as tungsten or molybdenum sulfide layers to the surface of high Q optical microresonators would allow for the generation of new frequencies of light, and novel optical devices.
Chapter 2

Resonator Fundamentals

Before we can examine in depth the potential for microresonators as sensors, we should examine the nomenclature and fundamental physics of these cavities.

2.1 Cavity Mode Equations

The Helmholtz equation is the fundamental method by which we can describe the resonant system inside a microsphere or microbubble. Equation (2.1) is the wave equation in Cartesian coordinates

\[ (\nabla^2 + k^2 n^2)\psi = 0 \]  \hspace{1cm} (2.1)

where \( k \) is the spatial angular frequency defined as \( 2\pi/\lambda \), \( \lambda \) is the wavelength, \( n \) is the refractive index, and \( \psi \) is the amplitude of the wave. This can be solved for either a TE (\( \vec{E} \parallel \hat{\theta} \)) or TM (\( \vec{H} \parallel \hat{\theta} \)) case with either the electric field or magnetic field being represented by \( \psi = \psi_r(r)\psi_\theta(\theta)\psi_\phi(\phi) \). When transformed into spherical coordinates, equation (2.1) becomes

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2 \psi}{\partial \phi^2} + n^2 k^2 \psi = 0 \]  \hspace{1cm} (2.2)

Equation (2.2) when solved using the separation of variables method supplies information regarding the spatial distribution of the electric field inside the resonator. This method of solving
the equations leads to a series of relationships between the electric field components involving
total integer constants

\[ \psi_\phi = \frac{1}{\sqrt{2\pi}} \exp(\pm im\phi) \quad (2.3) \]

\[ \frac{1}{\cos(\theta)} \frac{d}{d\theta} \left( \cos(\theta) \frac{d}{d\theta} \psi_\theta \right) - \frac{m^2}{\cos^2(\theta)} \psi_\theta + \ell(\ell + 1)\psi_\phi = 0 \quad (2.4) \]

\[ \frac{d^2}{dr^2} \psi_r + \frac{2}{r} \frac{d}{dr} \psi_r + \left( k^2 \cdot n \cdot (r)^2 - \frac{\ell(\ell + 1)}{r^2} \right) \psi_r = 0 \quad (2.5). \]

Where \( \psi_\phi \) is the azimuthal field, \( \psi_\theta \) is the polar field, and \( \psi_r \) is the radial field. Notice that in the
spherical coordinate case, there is a reliance on the integers \( m, \ell, n \), which are the azimuthal,
polar, and radial mode numbers respectively. These directions are illustrated in figure 2-1 as the
\( \phi, \theta \), and \( r \) vectors. The azimuthal and polar numbers are related by the allowable range of \( -\ell \leq m \leq \ell \). The eigenfunctions in equations (2.4-2.5) have solutions which are the generalized Legendre
Polynomials, which are represented using Spherical Harmonic functions and Bessel functions. In
the radial direction, this simplifies to Bessel functions on the interior of the resonator and Hankel
fields (due to the radiative losses into an infinite system) in the exterior.
2.2 Q factor and Buildup factor

One of the key metrics in evaluating the usefulness of a resonator is the Quality (Q) or Q-factor. This is essentially a merit of how ideal the mode is; the higher the Q the lower losses are present in the resonating mode. Increasing the Q of a resonator is no trivial task, as everything from material absorption, surface scattering, intrinsic or Rayleigh scattering, and mode tunneling serve to reduce the effective Q-factor of a resonator. One method of defining the Q-factor is through the ability to store energy for a number of electric field oscillations inside the resonator [10].

\[
Q_0 = \frac{\omega E_{\text{stored}}}{P_{\text{diss}}} = \omega \tau \quad (2.6)
\]

Here, \( \omega \) is the oscillation frequency in the resonator and \( \tau \) is the photon lifetime; in a physical sense, \( \tau \) can be thought of as the photon or wave lifetime in the resonator. Besides the ability to store energy, the microresonator also acts in a similar fashion to the prototypical Fabry-Perot etalon, allowing only wavelengths which result in a multiple of \( 2\pi \) phase shift around the
resonator to circulate. In a different but equally valid approach, the Q-factor can be defined as a function of the resonance spectrum [11]

\[ Q = \frac{\omega}{\Delta \omega} = \frac{\lambda}{\Delta \lambda}. \quad (2.7) \]

This identifies the Q-factor as the frequency selectivity of the resonator, where \( \Delta \omega \) and \( \Delta \lambda \) are the frequency and wavelength width of the resonance. This is typically defined as the full width at half max (FWHM) of the resonance. If we consider round trip time in a resonator, we can relate it to the Finesse of a cavity through the following equations.

\[ Q = \frac{\omega_0 T_R}{2\pi} F \quad (2.8) \]

\[ Q = \frac{\omega_0 L_{\text{eff}}}{2\pi c} F \approx mF \quad (2.9) \]

Here \( T_R \) is the round trip time in a resonator, \( n_{\text{eff}} \) is the effective refractive index in the resonator, \( F \) is the finesse of the cavity, and \( m \) is the azimuthal mode number. The quality is then related to the finesse through the azimuthal mode number. The Q-factor is typically thought of in terms of the resonance peaks associated with a device; specifically it is the ratio of the center frequency to the resonance width. The finesse is the ratio of the free spectral range (FSR) to the resonance width; this then provides information about the sharpness of each resonance relative to the space between each one. Physically, the Q-factor represents the number of optical cycles before the energy decays to 1/e of the original value, and the finesse represents the number of round trips inside the cavity before the same amount of decay occurs. Due to the spatial confinement of light occurring in a microresonator, there exists another useful property of well-designed devices: the intensity buildup factor. The amount of intensity buildup occurring in a resonator which is coupled to an external waveguide (typically a tapered optical fiber) is given by equation (2.10) below [10].
The buildup factor relies on the coupling rates of $1/\tau_0$ and $1/\tau_{ex}$ which are the inverse of the resonator and coupling waveguide lifetimes, as well as the FSR of the resonator. The rightmost side of equation (2.10) shows that a large value for the $Q_0$ of the microresonator results in a massive buildup of the intensity, this is particularly beneficial since most of the nonlinear phenomena studied require large values for the electric field in order to become noticeable.

### 2.3 Mode Volume

Another important metric for microresonators is called mode volume. This is typically defined as the volume that would be occupied by the mode if all of the energy were distributed evenly at the peak value. The simplest way to describe it is related to the energy density which is defined as

$$w_e(r) + w_m(r) = \frac{1}{2} \varepsilon \bar{E} \bar{E} + \frac{1}{2\mu} \bar{B} \bar{B}$$  \hspace{1cm} (2.11)

which is the sum of the electric and magnetic field energy density. $E$ is the electric field, and $B$ the magnetic field. This effective volume can then be calculated as

$$V_{\text{mode}} = \frac{\int (w_e(r) + w_m(r)) dV}{\max(w_e(r) + w_m(r))} = \frac{\int \varepsilon(r)|\bar{E}(r)|^2 d^3r}{\max(\varepsilon(r)|\bar{E}(r)|^2)}$$  \hspace{1cm} (2.12)
Now that the fundamental behavior of a microresonator can be understood, we will shift our attention to modeling the behavior of various resonators.

### 2.4 Finite Element Modeling

Modeling of optical microresonators and the modal electric fields can be accomplished through use of finite element solvers such as COMSOL. Finite element methods are particularly powerful for solving boundary interactions for which the wavelength of operation is much smaller than the geometry of the device. A silica microsphere of radius 30μm will support a large number of modes which require fine detail along the surface boundary but which can be computationally expensive to extend to the entire defined area. This can be overcome through the use of adaptive meshing techniques which are available in many commercial FEM software.

To start our modeling of whispering gallery modes we begin with the simplest case, a silica microsphere. In the 2D case we look at the cross section, and introducing an axial symmetry around the center of the sphere serves to simplify the simulation. WGM behavior is analyzed by solving for eigenfrequencies in the following manner

\[
\nabla \times \mu_r^{-1} (\nabla \times \mathbf{E}) - k_0^2 \begin{pmatrix} \varepsilon_r - \frac{j \sigma}{\omega \varepsilon_0} \end{pmatrix} \mathbf{E} = 0
\]

\[
\lambda = -j \omega + \delta
\]

\[
\mathbf{E}(r, \varphi, z) = \tilde{\mathbf{E}}(r, z) e^{-j m \varphi}
\]

This assumes that the eigen frequency, defined in COMSOL as lambda ($\lambda$), is complex valued. Additionally, the azimuthal dependence of the electric field is assumed to vary as $e^{-j m \varphi}$ where $m$ is the azimuthal mode number and $\varphi$ is the azimuth angle. A good estimate for $m$ in solving
computationally is \( m = \left( \frac{2\pi rn}{\lambda} \right) \) where \( \lambda \) is the wavelength of light in vacuum, and \( n \) is the refractive index of the resonator.

![Figure 2-2 A microsphere with radius 25μm surrounded by air. The meshing is finer around the boundary between the microsphere and air.](image)

Meshing is a critical parameter, as under sampling the space will lead to numerical errors and over sampling will result in unreasonable computational requirements. It is advised to select a mesh which has a maximum element size of 1/25 the wavelength in the required area, and such that the mesh does not change in shape with varying frequency. An example of a fundamental WGM for a 25μm radius silica microsphere is shown in figure 2-3.
Figure 2-3: A fundamental whispering gallery mode inside a silica microsphere

This corresponds to equations 2.3-2.5 with $m = \ell = 200$ and $n=1$. This is called a fundamental mode, where the mode path is closest to the equatorial plane.
Figure 2-4: A microsphere with $m = \ell - 2$. This is an example of a higher order mode, where the mode path extends farther along the polar direction.

Another important parameter of the WGM resonator that can be simulated is the Quality factor. This can be difficult to model in a realistic manner since accuracy depends on not only accounting for radiation loss from the curved interface of the resonator, but also on scattering defects and material absorption. Despite these difficulties, an estimate can be found by evaluating the radiation pattern of the mode in the simulated space. Specifically, a lower bound on the $Q$ can be defined as [12]

$$Q \geq \left( \frac{8 \pi f}{c} \right) \frac{\iiint |E|^2 dV}{\iint |E| dS}$$  \hspace{1cm} (2.13)

which in the 2D axisymmetric representation can be reduced to

$$Q \geq \left( \frac{8 \pi f}{c} \right) \frac{\int \left[ (E^r)^2 + (E^\theta)^2 + (E^z)^2 \right] r dr dz}{\int \left[ |E^r|^2 + |E^\theta n_r - E^z n_z|^2 \right] r dl}$$  \hspace{1cm} (2.14).

The above equation assumes that a perfect electrical conductor borders the simulation space. This is necessary to enforce boundary conditions in solving the eigenmode equations, but can result in standing waves which significantly lower the estimated value of the $Q$. This involves utilizing the postprocessing feature in COMSOL, where each integral can be evaluated separately. An upper bound on the $Q$ can be determined by utilizing so-called Perfectly Matched Layers (PML) which serve to absorb any radiating energy and eliminate standing waves in the solution. Utilizing the PML will result in the eigenfrequency being complex valued. The upper bound on the $Q$ is then

$$Q \leq \frac{9R(f)}{2 \Im(f)}$$  \hspace{1cm} (2.15)
Extending the modal analysis into 3 dimensions requires exponentially increasing computational power, and becomes increasingly nontrivial with more complicated device geometries. This can be avoided by generating wedges or portions of a full 3 dimensional geometry, and then revolving the solution to illustrate a complete device. For example, the solution in figure 2-4 is a 2D slice of the full 3D solution. By revolving the 2D solution and varying the solution as eqn 2.3 (i.e. a cosine function) we can generate a 3D solution from a less computationally expensive 2D one. Now that the fundamentals of FEM modeling are covered, we can move to the experimental conditions necessary to fabricate, characterize, and utilize optical microresonators.

### 2.5 Fabrication of Optical Microresonators

In order to fabricate microsphere or microbubble microresonators, or an optical fiber taper used to couple light into these resonators, the initial step is to fabricate an optical fiber taper. First, a fiber is stripped and cleaned before mounting between two fiber clamps. A hydrogen torch is brought below the fiber, softening the fiber between the two clamps. The clamps are then pulled apart using computer controlled linear actuators. While pulling the fiber, the transmission of the fiber is monitored to determine when the pulling process is completed. The single mode fiber transitions to a multimode fiber as the core thins, and then, as the thickness of the fiber approaches the wavelength of the light, the fiber transitions back to a single mode fiber. Fibers used to couple light into microresonators are pulled to approximately 1μm, whereas fibers used to create microresonators are pulled between 10μm-20μm to create a thicker stem for the final resonator.
Figure 2-5: Fiber tapering experiment. Actuators pull fiber clamps as a hydrogen torch melts the optical fiber.

To finish fabricating microspheres, the fiber taper is mounted in a CO\textsubscript{2} laser setup. A CO\textsubscript{2} laser is focused by a ZnSe lens (f = 10cm) and then reflected by a mirror mounted in an adjustable piezoelectric scanning head. The mirror is electronically adjusted until the fiber taper begins to melt. Then the laser power is increased to melt the fiber, and surface tension pulls the melted portion back on itself, creating a microsphere.
Figure 2-6: Microsphere fabrication setup. a) CO$_2$ laser is focused by a ZnSe lens onto the fiber taper. b) As the laser melts the fiber taper, surface tension forms a sphere. Simultaneously the sphere and fiber are rotated with a stage to ensure symmetry.

### 2.6 Experimental Measurement of Q

Determining the Q-factor of the fabricated resonator is done through analysis of the transmission of an external cavity diode laser through a section of tapered optical fiber coupled with the resonator. The fiber is tapered to a diameter of $\approx 1 \mu$m which allows the evanescent portion of the propagating light to be coupled into the microresonator. A large value for Q results in a sharp decrease in transmission at that laser wavelength, and can be defined as

$$Q = \frac{v}{\Delta v} = \frac{\lambda}{\Delta \lambda}$$

which in a transmission curve equates to the ratio of center frequency to the full width half maximum of the curve [13]. As this is a single pole resonance, the transmission curve is Lorentzian in shape. Fitting a curve to the data and extracting the width is equal to the
full width half maximum measurement. The voltage sweep size was calibrated using a scanning Fabry-Pérot interferometer, with the 10V scan range equivalent to 22 GHz of $\Delta \nu$. Utilizing the voltage and frequency conversion, the resonator for which the transmission curve is shown below was calculated to have a Q value of $1 \times 10^7$. Although the demonstrated limit in the literature for Q is $10^{10}$, this is much more difficult with a shorter wavelength laser (760nm compared to 1550nm). The primary limitation on Q for our fabrication method is surface roughness and optical scattering. A shorter wavelength laser is much more sensitive to surface defects and hence values of $10^7$ or $10^8$ are quite good for our system.

Figure 2-7 An oscilloscope capture of a fiber taper transmission curve. The purple ramp curve is a voltage control which modulates the laser diode wavelength. The yellow curve is photodiode
voltage from the optical fiber taper. The bottom image shows a magnified section of the transmission curve to illustrate the width of the mode.

Figure 2-8  A computer controlled scan of the same modes as the figure above. Note the thermal broadening of the modes on the right side of the scan due to high intracavity power during the slow downwards voltage scan.

While the fabrication of resonators with high Q is repeatable and the value of Quality often can be inferred from visual inspection, care must be taken to measure each device in the manner described above before modifying it to use in spectroscopic or other sensing applications, as even nanoscale surface defects can drastically alter the performance.
Chapter 3
Optical Microbubble Resonator

WGM based sensors have attracted a significant level of interest since they afford an extreme level of sensitivity [14], i.e. large perturbations of the mode shape or location can be attributed to nanoscale changes in the resonator. Changes in cavity geometry, and refractive index contrast between the cavity and surrounding medium perturb the resonance characteristics of the confined optical modes and can be used for sensing applications. Optical microresonators have been created in several different geometries, from the microsphere [2, 15] to microdisk and microtoroid resonators [16, 17]. Two kinds of sensor configurations have been realized to date: (i) on-chip devices consisting of microdisk and microring resonators [16] and (ii) microsphere [18] and microbubble [6] resonators realized by using glass blowing and reflowing techniques from glass fibers and capillaries. Each of these geometric configurations has different strengths, for microspheres they are the ease of fabrication and the number of available modes, for microdisks and microtoroids the ability to manufacture many in parallel on a silicon chip leads to high repeatability. Typically, the microtoroid and microdisk configurations have smaller mode volumes for a given Q factor, resulting in greater electric field buildup inside the cavity [19].

However, a new class of optical microresonator has been developed in recent years which maintains the higher number of available modes of a microsphere while also reducing mode volume like a microdisk or microtoroid. Often the large number of modes in a microsphere is detrimental, however the microbubble offers an additional dimension of confinement to the modes which makes it a midpoint between the capabilities of the microsphere and microdisk resonators. This new resonator type is called a microbubble resonator (MBR) [6]. These new resonators consist of a silica shell and hollow core fabricated by microscopic glassblowing techniques [20, 21]. Because of the hollow design, these resonators can be utilized as a sensor for
a multitude of detection tasks such as temperature sensing, gas sensing, and biosensing [22-24]. The integration of closed spherical shell structures on chip can allow for the realization of WGM based in-line biochemical sensors where the analyte fluid interacts with the optical resonance through the inner surface of the shell – a configuration first described in capillaries as the optofluidic ring resonator (OFRR) [25]. Unlike the microdisk and microring resonators, the optofluidic ring resonator configuration has the advantage of directly integrating the resonator directly to the analyte delivery microfluidic column [26]. These resonators are limited in their Q factor due to the cylindrical geometry of silica capillaries, and so to overcome this limitation we look at the MBR.

3.1 Microbubble Resonator Types

The main use of a microbubble resonator is the electric field interaction with the interior environment. WGM confinement can be adjusted by altering the wall thickness, or even the material refractive index. Thick-walled MBR or high index material results in tight containment of the electric field, limiting the ability to probe the surrounding material. Conversely, a low refractive index facilitates extension of the mode profile beyond the confines of the resonator medium allowing for the optical radiation to interact with the surrounding medium and thus allowing for sensor designs with exceptionally high sensitivity – albeit at the expense of the $Q$-factor. OFFRs offer the ability to easily integrate a resonator with a gaseous or liquid analyte, but the wall thickness requires etching from a pre-formed capillary. In order to have more control over the diameter and wall thickness, a different technique must be employed.

The first microbubble resonators were fabricated from silica capillaries using glass blowing techniques [6, 27]. This consists of applying both internal aerostatic pressure and an external heat source. Originally, this heat source consisted of a CO$_2$ laser operating at 10.6μm
directed at the capillary from opposite sides simultaneously. This is desirable due to the fact that silica melting only occurs at the location where the laser strikes the capillary and is absorbed. By choosing the location carefully along the length of the capillary where the glass is heated, different shapes of bubbles can be formed. Locations close to the sealed end produce single-input bubbles [27], while those farther from the end produce double-input bubbles. This process is self-limiting due to the fact that it is laser absorption based, i.e. when the glass thickness becomes smaller less material exists to be heated by the laser. More precisely, the heating of a microbubble is proportional to the wall thickness, but the convective cooling is dependent on surface area. Because of this thermodynamic equilibrium between the silica and surrounding air is reached at a certain threshold of wall thickness and the bubble will stop expanding. An example of this technique is shown in figure 3-1b, where instead of using counterpropagating laser beams, a single beam is directed at the capillary and the entire glass structure is rotated symmetrically.

A second method of manufacturing microbubbles is to use a microscopic heat source. Optical fiber fusion splicers utilize a plasma arc cause by high voltage discharge across electrodes to melt silica and fuse fibers together. This has been demonstrated as a suitable method for fabricating microbubble resonators [28]. This method relies on heating the air around the silica, and is controlled solely by the amount of current through the plasma arc. An example of this method of fabrication is shown in figure 3-1a.

The current work with optical microbubble resonators have demonstrated effective capabilities as sensors in microfluidic applications [22, 23, 29], but each device must be custom made with large variations between individual MBRs. An improvement on these resonators could be made if we can combine the repeatability of traditional silicon processing techniques with the advantageous form factor of the microbubble. Recently, glass blowing techniques have been demonstrated to create hemispherical and toroidal structures from glass and fused silica on a chip [30, 31]. These structures consist of glass microbubbles with thicknesses in the range of 0.1 μm –
10 μm and can be used as WGM resonator structures. This method produces consistent MBRs with high Q factor with the potential for on-chip applications. Figure 3-1(c-d) shows on-chip MBR in repeatable arrays, fabricated by Chenchen Zhang in Dr. Srinivas Tadigadapa's laboratory.

![Microbubble resonator fabrication approaches](image)

Figure 3-1. Microbubble resonator fabrication approaches a) MBR fabricated from silica capillary using a fiber fusion splicer. b) MBR created using single CO\textsubscript{2} laser and rotation stage. c) single on-chip MBR showing high sphericity. d) Array of on-chip MBRs

### 3.2 On-Chip Fabrication

All microbubble resonators in this chapter were fabricated by Chenchen Zhang of the Micro and Nanoscale Devices Group, directed by Dr. Srinivas Tadigadapa at Penn State. The
described procedure was reported elsewhere [32]. The following discussion follows closely from [32].

The glass microbubbles were fabricated on 500 µm thick silicon substrate. First, circular features are patterned using positive photoresist and the silicon is etched 250 µm using deep silicon etching process to realize cylindrical cavities as shown in Figure 3-2(a). Second, Corning® 7740 borosilicate glass wafer is optionally patterned with smaller circles than on silicon using positive photoresist and 4 µm of nickel was electroplated as an etch mask. After removal of the photoresist in acetone, the borosilicate wafer was etched to a depth of t₁ µm with a modified ICP-RIE smooth and fast high-aspect ratio glass etch [33]. Thereafter, the nickel, chrome and gold layers are stripped from the borosilicate wafer using wet etchants resulting in a cross-sectional profile as shown in Fig. 3-2(b). The etched silicon and optionally etched borosilicate glass wafer were aligned to result concentric circular pattern and anodically bonded at a pressure of 1.35 atmosphere (1026 Torr) at 400 °C. Silicon-glass bonded cavity is formed as seen in Figure 3-2(c). The bonded wafer is diced into chips and the borosilicate layer of the bonded chip is thinned down to a total thickness of t₂ µm from the un-etched side in 49% hydrofluoric acid as shown in Figure 3-2(d). The chip was then heated on a silicon nitride ceramic heater to a temperature of 775 °C in a vacuum oven maintained at 0.13 atm (100 Torr) for 45 seconds and was rapidly cooled down to ambient temperature. The borosilicate glass softens and begins to expand into a spherical shell under the pressure differential between the sealed cavity and the outside created by the high temperature[30]. The blown glass microbubble is schematically illustrated in Figure 3-2(e).
Figure 3-2. (a) Silicon wafer is patterned and plasma etched 250 µm to define circular pits (b) Borosilicate glass wafer is optionally patterned and plasma etched to define $t_1$ µm circular features (c) Two wafers are aligned and anodically bonded. (d) Borosilicate wafer is thinned down to $t_2$ µm in hydrofluoric acid. (e) Glass microbubble is blown at 775 °C in a vacuum oven.

3.3 Microbubble WGM Resonance

The position of the equatorial plane of the glass microbubble is critical to obtaining WGM optical resonance. The modes are localized at the equatorial plane and are sustained only when the equatorial plane is above the substrate. In our initial experiments, the etched silicon was heated at ambient pressure to result in hemispherical bubbles. In these devices no optical resonance was obtained since the wave is coupled into the substrate and is consequently dissipated. This situation is remedied by changing the rapid thermal anneal step in vacuum rather than at ambient pressure. The vacuum during the glass blowing step raises the pressure difference relative to the cavity pressure, thus enhancing the expansion of microbubble volume to develop spherical structures with equatorial planes above the substrate. The sphericity of blown glass microbubbles quantifies the relative height of the equatorial plane to the glass substrate regardless of bubble sizes. Sphericities close to unity indicate that near-spherical glass microbubbles are achieved in our work. The result of relatively smaller sphericities in some fabricated
microbubbles is explained by the observation of lateral glass expansion at the bubble-base resulting from glass reflow during blowing process. The visible bubble-base lateral expansion is believed due to excessive glass material in blowing process and can be eliminated by reducing the thickness of bonded glass layer. Microbubbles are cleaved after optical characterization and the sidewall thicknesses were measured with SEM at the equatorial plane of the microbubbles. With the thickness reduction of the undeformed glass layer from 100 µm to 50 µm, the sidewall thicknesses of blown bubbles reduce from 6.7 µm – 8.6 µm to 1.1 µm – 2.2 µm. The plasma etching of the glass substrate followed by the subsequent blanket etching results in a thin region which essentially blows into the spherical microbubble structure. Based on the volumetric redistribution of the glass in this region into the spherical shell, the microbubble wall thickness can be estimated and agrees well with the measured thicknesses ranging from a few hundred nanometers to 1 µm. Furthermore, since the optical mode is confined to the equatorial plane, if a microbubble was overblown and was split open on the top, so long as the remaining structure maintains a spherical contour, WGM resonance was clearly observed at the equatorial plane. Thus, wafer level glass blowing can be tailored to achieve glass microbubbles of various sizes and wall thicknesses with ultra-smooth wall morphology for obtaining optical resonances.

The experiment set-up used for characterizing optical resonance in the glass microbubble is shown in Figure 3-3 (a). The excitation source consists of a tunable 760 nm laser (Thorlabs, TLK-L780M). The laser tuning was driven via a triangle wave at 10 Hz and corresponds to 15 GHz shift from the center wavelength of 760 nm. This is then evanescently coupled to the resonator via a tapered optical fiber. The fiber taper was fabricated with a hydrogen torch placed in the middle and then pulled at a constant rate from both ends. We control the polarization of the incident laser with a fiber polarization controller in order to optimize coupling efficiency. After passing through the resonator and fiber taper, the transmitted light was monitored using a photodiode (Thorlabs DET36A). Resonant modes in the equatorial plane of the glass microbubble
form dips in the transmission spectrum. The full width at half maximum (FWHM) of the transmission dips indicates the Quality factor. Figure 3-3 (b) shows an optical micrograph of a MBR with a mode in which the light is confined to the equatorial plane of the bubble. Figure 3-3 (c) shows less than 10 resonant modes observed in the transmission spectrum within the 15 GHz frequency span due to small bubble diameter and thin sidewall thickness. A quality factor of $4.7 \times 10^7$ is measured in the transmission spectrum with the calculated finesse of $2.2 \times 10^4$. It is interesting to note that equal-spaced resonance frequencies are observed in the transmission spectrum of Figure 3-3 (d), we will briefly discuss the reason for this.

Figure 3-3. (a) Schematic illustration of the experimental set-up for the measurement for the WGM resonance in glass bubbles. (b) Optical image showing the light confined to the equatorial plane of the microbubble from evanescent coupling of the light through the tapered fiber. (c) - (d) Transmission spectrum of optical microbubble resonators within 15 GHz frequency span.
The frequency spacing of 0.76 GHz between each peak is within one free spectrum range of 117 GHz. It was observed and explained by eccentric geometry induced azimuthal mode splitting [10]. The azimuthal mode splitting results from the removal of degeneracy of polar quantum number $\ell$ in the solution of spherical harmonic function. The analytical expression of azimuthal mode splitting is derived with perturbation method and given by [34]:

$$\frac{\Delta \omega_{\text{ecc}}}{\omega_{\text{nm}}} = -\frac{\varepsilon}{6} \left(1 - 3 \frac{m^2}{\ell(\ell + 1)}\right)$$

Where $\omega_{\text{nm}}$ is the resonance frequency of mode with radial mode number $n$, azimuthal mode number $m$, and polar mode number $\ell$. Eccentricity $\varepsilon$ is defined with the polar radii $r_p$ and equatorial radii $r_e$ by $\varepsilon = \frac{r_p - r_e}{R_o}$.

Hence the splitting between modes with successive azimuthal mode number is given by [10]:

$$\Delta \omega_{\text{ecc}} \equiv |\omega_{\text{nm}} - \omega_{n,n+1,1}| \approx \omega_{\text{nm}} \cdot \varepsilon \frac{|m| + 1/2}{\ell^2}$$

Here, $\omega_{nm}$ is calculated by COMSOL simulation where the microbubble is modeled as an ideal spherical shell with uniform wall thickness. With the assumption of observing the splitting of a fundamental azimuthal mode ($m \approx \ell \approx 3359$) in Figure 3-3d, the frequency spacing of 0.76 GHz leads to the corresponding eccentricity of $\varepsilon \approx 0.65$ % which matches the estimated sphericity of 0.9960 (i.e. 0.4% eccentric) for that microbubble well.

Table 3-1 contains some important parameters for a selected number of microbubbles. The $\Psi$ parameter refers to the sphericity of the microbubble, with values close to unity being highly spherical. In subsequent discussions, the microbubbles will be referred to by number corresponding to the table below.
<table>
<thead>
<tr>
<th>Bubble</th>
<th>Diameter (µm)</th>
<th>Ψ</th>
<th>Wall Thickness (µm)</th>
<th>Effective Refractive Index*</th>
<th>Highest Q-factor</th>
<th>Free Spectrum Range</th>
<th>Finesse</th>
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<td>6.7</td>
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<td>102 pm (54.4 GHz)</td>
<td>1.1×10³</td>
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<td>9.49×10²</td>
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<td>614</td>
<td>0.9319</td>
<td>8.6</td>
<td>1.45710</td>
<td>4.02×10⁶</td>
<td>199 pm (106GHz)</td>
<td>1.07×10³</td>
</tr>
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<td>2.2</td>
<td>1.45485</td>
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<td>192 pm (102GHz)</td>
<td>2.94×10³</td>
</tr>
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<td>1.4</td>
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<td>1.18×10⁷</td>
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<td>3.45×10³</td>
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<td>1.1</td>
<td>1.43647</td>
<td>4.68×10⁷</td>
<td>354 pm (189 GHz)</td>
<td>2.21×10⁴</td>
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<td>713</td>
<td>0.9915</td>
<td>0.3</td>
<td>1.35475</td>
<td>8.73×10⁶</td>
<td>171 pm (91 GHz)</td>
<td>1.99×10³</td>
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<td>1.0</td>
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<td>1.46×10⁶</td>
<td>302 pm (161 GHz)</td>
<td>5.88×10²</td>
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<td>1.54×10⁶</td>
<td>528 pm (282 GHz)</td>
<td>1.09×10³</td>
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</table>

*calculated by Comsol simulation of each glass microbubble with ideal spherical shell and uniform wall thickness

Table 3-1 Optical characteristics of blown microbubbles

### 3.4 Thermal Sensitivity of Microbubble Resonators

Optical resonant modes in whispering gallery mode resonators are achieved when the coupled light can constructively interfere with itself by completing an integer number of cycles for each revolution around the bubble equatorial circle. Thus, for a laser wavelength of \( \lambda \), the condition for whispering gallery mode resonance in a dielectric annulus of radius \( R \) can be...
expressed as \( m\lambda = 2\pi nR \), where \( n \) is the modal index of the fundamental WGM mode, and \( m \) is the integer number of azimuthal wavelengths [35]. Thus, WGM resonance frequencies depend on the size and refractive index of the resonator. A small change in the size or the refractive index can cause a significant resonance frequency shift. Since both the refractive index and the size of a spherical shell depend upon temperature due to thermo-optic and thermal expansion effects, a WGM resonator can be configured as a sensitive thermometer. Assuming a linear dependence of thermal expansion and refractive index for small temperature variations, these can be expressed as \( dR/R = \alpha dT \) and \( dn = \beta dT \); where \( \alpha \) and \( \beta \) are the thermal expansion coefficient and thermo-optic coefficient respectively of borosilicate glass. Taking a variation of the resonance condition, we can now express the fractional change in the wavelength as

\[
\frac{d\lambda}{\lambda} = \frac{dn}{n} + \frac{dR}{R} = \left( \frac{\beta}{n} + \alpha \right) dT
\]

\[\Rightarrow \frac{d\lambda}{\lambda dT} = \left( \frac{\beta}{n} + \alpha \right) (3.9)
\]

The sensitivity of the microbubble to temperature changes was experimentally measured. In the experiment, the glass microbubble chip was placed on the hot side of a Peltier cooler. The electric-thermal response of the Peltier cooler was pre-calibrated using a thermocouple. The frequency shift of the optical resonance mode relies on the thermally induced changes in both the refractive index of glass and the equatorial radius of the microbubble. The WGM resonance modes of microbubble 7 were monitored as a function of temperature. As seen in Figure 4(a), the resonance frequency of the \(~10^7\) \(Q\)-factor mode increases with increasing temperature. Fig. 4(b) plots the temperature induced linear resonance frequency shift of the on-chip glass microbubble and exhibits a thermal sensitivity of -1.81 GHz/K (5 pm/K). Assuming the frequency resolution of the measurement system to be 100 kHz at a \( Q\)-factor of \(10^7\) (22GHz scan range with 65,000 samples), the microbubble temperature resolution can be determined to be 55 \(\mu\)K. The thermal
induced resonance frequency response is also simulated in COMSOL. The thermo-optic coefficient of borosilicate glass at room temperature is found in the literature as $\beta = 3.41 \times 10^{-6}$/K [36, 37]. The refractive index $n$ of bulk borosilicate glass is $\sim 1.467$ at 750 nm wavelength [38]. Using the coefficient of linear expansion for borosilicate glass of $3.25 \times 10^{-6}$/K [38], the change in the radius $\Delta R$ thermal expansion can be estimated. The top line in Figure 3-4(c) simulates the temperature induced resonance frequency shift of microbubble 7 with the thermal expansion coefficient and optic-thermal coefficient described above. This model yields a thermal sensitivity of $-2.23$ GHz/K. However, it should be noted that linear thermal expansion may not accurately describe the thermal expansion of a 3-D spherical shell structure. And the bonded silicon substrate probably results in a silicon-glass thermal expansion coefficient (TEC) mismatch and leads to a smaller effective thermal expansion coefficient in the scenario. The bottom line in Figure 3-4 (c) simulates the temperature induced resonance frequency shift of a microbubble with effective thermal expansion coefficient of $2.19 \times 10^{-6}$/K and is close to the measured thermal sensitivity. Figure 3-4 (d) shows the measured thermal sensitivity of two microbubbles within a fine scan. It can be noticed that the temperature sensitivity is nearly independent of the size of the microbubble. This is in accordance with eq. (3.9), where the temperature dependence of wavelength shift in a WGM resonator is only a function of the equatorial plane wall thickness, effective refractive index, temperature dependent properties of glass and the wavelength. Based on effective refractive index in table 1 and effective thermal coefficient of $2.19 \times 10^{-6}$/K as discussed above and using eq. (3.9), the fractional change in wavelength per unit temperature can be calculated to be $\Delta \lambda / \lambda \Delta T = 4.707 \times 10^{-6}$/K, whereas the measured wavelength shift from the graph shown in Fig. 3-4 (b) is found to be $4.593 \times 10^{-6}$/K.
3.5 Liquid Filling Microbubble Resonator

WGM resonators with shell structure take the advantages of carrying aqueous sample and performing as liquid-core optical ring resonator (LCORR) [39]. In our work, the on-chip microbubble wall thickness dependent sensitivity of liquid-core microbubble resonator is predicted and experimentally examined. In the experiment, on-chip blown glass microbubbles were coated and protected with Crystalbond adhesive and the silicon substrate was etched and thinned in potassium hydroxide solution for 250 µm thick from backside to open an access to the
microbubble cavity. Then the coated crystal bonds were removed in acetone at 80 °C. With the open access to the microbubble cavity, the microbubble was filled with water in a vacuum chamber. The filled water was held inside the microbubble cavity under the atmosphere due to the surface tension at the small opening. The water gradually evaporated and eventually dried out in the microbubble spherical cavity. The water-filled microbubble 10 with wall thickness of 4.7 µm and a microbubble with a wall thickness of 6.4 µm were coupled with taper fiber and the modes were monitored and tracked as water dried out in the microbubbles. The transmission spectrum of the microbubble in Figure 3-5 (a) shows a blue-shift due to the decrease of effective refractive index as the water dries out in the microbubble cavity. Inset image in Figure 3-5(a) shows a zoomed image of a shifted resonate mode which indicates a frequency shift of 0.51 GHz and an increase of Q-factor from 2.51×10⁶ to 2.69×10⁶ as the core changes form water to air. Resonance frequency shift was hardly observed in the transmission spectrum of the thicker-walled microbubble. Wall thickness dependent sensitivity of liquid-core microbubble resonator is simulated as frequency shift of the first radial order fundamental TE mode. The shift between water core and air core of a 600 µm diameter microbubble resonator with different wall thicknesses are demonstrated in Figure 3-5b. Experimental measurement fits well with the theoretical simulation. The unapparent frequency shift of the thicker microbubble is believed to be due to the limitation of a ~10⁶ Q-factor mode. Modes of this width are difficult to use for resolving smaller frequency changes. A higher value for Q-factor allows for finer shifts in the resonant frequency to be detected. Figure 3-5 (c) and (d) show confined electric field in a 0.6 µm thick shell at fundamental eigen-frequency with water and air filled microbubble core respectively. The inset images in Figure 3-5 (c) and (d) plot the intensity of electric field in logarithmic distribution. Electric field is observed leaking into the water core in Figure 3-5 (c). Figure 3-5 (e) and (f) demonstrate the electric field of the fundamental mode is nearly identically confined inside the 8 µm glass shell with water and air filled microbubble core respectively.
Figure 3-5. (a) Transmission spectrum of resonate modes obtained from microbubble 10 with wall thickness of 4.7 µm. A blue-shift of the resonate modes was observed as the water-filled microbubble core dries out. Inset image shows 0.51 GHz frequency shift that observed from a 2.5×10^6 Q-factor mode. (b) Simulation predicts the frequency shifts between water-core and air-core microbubbles in 600 µm diameter with experimental achieved shell thicknesses ranging from 300 nm to 10 µm. (c)-(d) FEM solved fundamental TE mode confined in 0.6 µm microbubble shell with water and air core respectively. Inset images compare the electric field intensity in logarithmic scale in two cores and exhibits dissipation of electric field into water core in (c). (e)-(f) FEM solved fundamental TE mode identically confined in 8 µm microbubble shell with water and air core respectively. Comparing with eigen-frequency shifts between (c) to (d) and (e) to (f), larger frequency shift obtained from thinner microbubble shell indicates stronger interaction of the optical mode with the water.

The on-chip microbubble resonator has been shown to be highly useful as a temperature sensor. Additionally, we have control over the wall thickness, allowing for fine tuning of the mode profile in both the interior and exterior of the resonator. This provides an ideal platform for optofluidics and gas sensing. Previous work has been done to demonstrate the adjustment of WGMs in a resonator using stress or pressure [40, 41], and even electrical tuning using liquid crystals [42]. Even more research has been dedicated to producing frequency combs [43-49] and studying soliton and pulse formation [50, 51]. Microresonators have even be used to generate stable lasing modes [52, 53], and generate strong second harmonic generation [54, 55] when fabricated from a nonlinear medium. On-chip microbubble resonators possess the potential to integrate many functionalities through resonance tuning and selective filling of the hollow interior.
Chapter 4
WGM Microresonator Enhanced Raman Spectroscopic Sensing

The main advantage of these microresonators is the large buildup factor inside the device when coupled into a high Q mode. When these modes are contained close to the surface of the device, the interaction of the circulating mode with matter on the surface can lead to various methods of sensing with enhanced sensitivity. Chapter 3 discussed some of the ways in which the resonator structure is sensitive to changes through thermal effects, but the circulating electric field is also highly sensitive to perturbation by micro and nano-sized particles. Previously optical microresonators have been shown as incredibly sensitive to particles attached to the surface, generating mode splitting and mode shifting. These phenomena have been shown to be highly accurate, with less than 10% error in determining the size of adhered nanoparticles [56]. Even single viruses are detectable by using these techniques[57-59]. Additionally, the polarizability of the adherent can be determined, which allows for calculation of the refractive index. However, the determination of size and polarizability does not reveal exactly what material is adsorbed to the resonator. Raman spectroscopy can overcome this limitation and add supplemental capabilities to the optical microresonator sensing platform.

4.1 Raman Spectroscopy

Raman spectroscopy has developed as an invaluable tool for material characterization since its discovery by C. V. Raman in 1928 [60]. Spontaneous Raman scattering is an optical effect which arises from inelastic photon scattering. An incident photon strikes a material, and the inelastically scattered photon exhibits a different energy (and therefore wavelength) with the
difference being equal to a vibrational energy of the material carried as a phonon. The scattered photon with a lower energy is known as the Stokes signal. This is an incredibly infrequent event, as the scattering cross section for some particles is on the order of $10^{-30} \text{ cm}^2$ [61]. The reverse of the Stokes emission is also possible, where an incident photon receives additional energy equal to a phonon and is blue shifted. This is known as anti-Stokes Raman scattering, and occurs even less frequently than the Stokes case. A diagram of this process is shown in figure 5-1a. This process inherently reflects the vibrational energy of the material, resulting in an optical "fingerprint" that can clearly indentifies individual molecules and compounds. Various methods have attempted to overcome the low intensity of the spontaneous Raman scattering, such as surface enhanced Raman scattering (SERS) [62], and coherent anti-Stokes Raman scattering (CARS) [63]. CARS has been extended to holography and single-shot imaging, and offers many benefits for label-free biological imaging [64-66].
Figure 4-1. a) The Raman scattering process, with both Stokes and anti-Stokes processes shown. b) The measured CARS and spontaneous Stokes spectrum of Polystyrene measured in above reference [67].

4.2 Cavity Pumping and Frequency Locking

In order to probe ultra high Q cavities a laser with a very small linewidth is needed. We utilized a Thorlabs TLK-L780M kit laser which consists of an open gain chip in a Littman configuration. Lasers of this design typically achieve a FWHM of tens of kilohertz. Our laser in this configuration allows for two methods of adjusting the center wavelength, a coarse adjustment via actuator driving the mirror, and a fine adjustment controlled by a piezoelectric plate. A
schematic of our external cavity laser is shown in figure 4-2. In this manner we can move the laser wavelength from 750nm to 780nm precisely. The piezoelectric element allows for an open loop scan covering a laser frequency range of 22 GHz, which was verified using a scanning Fabry Perot interferometer (Thorlabs SA210). Further refinements are needed in order to prevent the laser from mode-hopping and achieving a smooth frequency sweep. To this end, we applied a current modulation waveform to the laser diode in conjunction to the voltage waveform which drives the mirror actuation. A schematic diagram of the laser frequency modulation electronics is shown below in figure 4-4.

Figure 4-2. A diagram of the external cavity laser. The emission from the diode is directed towards a grating and reflected back into the diode by a mirror. The laser frequency is adjusted by moving the mirror via an actuator and piezoelectric element. The laser output is the first diffraction order of the grating.
Figure 4-3. The red triangle indicates the voltage being applied to the piezo-electric element to shift the laser frequency. The dips in the photodiode voltage indicate resonances. Insufficient current correction applied to the laser diode results in the mode hop noted in the image. The asymmetry of the curve is due to thermal broadening as indicated.

In addition to correcting for mode hopping, it is also necessary to create a feedback loop to lock on to a given resonant mode and maintain the laser frequency on the resonance. This is complicated by the fact that ultra high Q resonators experience thermal expansion from the small amount of material absorption present in a resonant mode [68]. This thermal expansion results in a shift in the mode frequency. When on the frequency up-scan, the thermal shift moves the resonance down in frequency, opposite to the laser. In this case the mode is artificially narrowed. On the frequency down-scan the thermal shift of the mode moves in the same direction as the scanning laser frequency. This results in positive feedback and the mode shape is artificially broadened. A typical mode scan is shown in figure 4-3.
Figure 4-4 A block diagram of the electronics used to control our laser and resonator system. This involves a switchable state from constantly scanning over a range of 22 GHz to a computer controlled scanning or locking to a given frequency.

Frequency locking is difficult to do by hand with ultra-high Q resonances. For this reason we have designed a custom locking procedure which is computer controlled. The computer controls the piezo-actuator voltage and laser current modulation via the DAQ, and the resulting output of the system is analyzed by looking at the voltage from the photodiode. A change in the transmission results in a change of the photodiode voltage which is monitored by a lock-in
amplifier. The lock-in amplifier is driven at the same rate as the function generator. The transmission signal is analyzed and the slope of the curve at each point is reported to the computer, with higher values corresponding to a larger slope and a positive or negative value indicating direction. This allows the computer to determine how much and in which direction the laser frequency should move in order to lock to a resonant mode. This system allows for a single mode in the transmission spectrum to be locked to and the large buildup factor of the resonator to be utilized. In order to couple light into the resonator system we used a tapered optical fiber.

This was fabricated using the hydrogen torch method, which consists of heating an optical fiber and pulling both ends away from each other in order to draw the molten glass down to a smaller diameter. By monitoring the transmission with a photodiode and oscilloscope during the pulling process, we are able to achieve tapers with diameters on the order of the wavelength and up to 85% transmission. This process creates fiber tapers with large (5mm) lengths of exposed and by altering the location along the length of the taper, additional flexibility in coupling is realized. The system as designed allows for accurate mode locking of resonators with Q of up to $10^7$ easily.

### 4.3 Raman Enhancement in Microspheres

Having created a system capable of interrogating a microresonator and locking onto an ultra high Q mode, we now wish to add spectroscopic capability to our system. This is achieved by using Raman spectroscopy. The large buildup of field inside the resonator enhances the interaction between the laser and particle and also increases the total amount of Raman scattering signal generated. This is accomplished as shown in the figure below. The tunable laser is launched into single mode fiber (Corning sm600) and the polarization controlled with a fiber polarization controller. The scattered light is collected by a long working distance 50x objective.
lens (Mitotuyo 50x Plan Apo) and filtered with an 810nm long pass filter. This removes part of the laser pump and low wavenumber silica Raman signal, while allowing the particle Raman signal to pass to the spectrometer (PI Acton 2500i).

Figure 4-5. The pump laser light is guided by a single mode optical fiber and its polarization is controlled by a fiber polarization controller. The light is coupled to the resonator with a fiber taper and the transmission is recorded by a photodiode. The scattered light from the resonator/particle system is collected by a 50x LWD lens and the signal is reflected by a longpass filter in order to allow simultaneous signal collection and imaging with a CCD. The signal is further filtered by an 810nm longpass filter before being collected by the spectrometer.

The microsphere resonators were fabricated in two steps. First, we pulled a fiber taper using the same process as mentioned previously. After the pulling was completed and the fiber taper reached an appropriate diameter, the fiber taper was broken at the waist. One half of the taper was then moved to a rotational stage and irradiated by a CO$_2$ laser (Synrad 48-1 series). The fiber was rotated as the laser melts the thinned part of the fiber. The surface tension from the
liquid glass forms a microsphere. To ensure symmetry around the stem, the fiber is continuously rotated as the laser sweeps from the thinnest part to the thickest end. This ensures the silica sphere is centered on the fiber taper stem and a high quality resonator is formed. To deposit a particle on the surface of the resonator, 2μm PS microspheres were first deposited on a probe fiber taper. This fiber was then mounted on a 3-axis stage and brought into position next to the resonator. The probe taper was then brought to gently touch the resonator and the particle was brushed off the probe and onto the resonator. In order to ensure proper interaction with the mode of the resonator, the particle was deposited at the same height as the fiber taper. To couple light into the microsphere microresonator from a fiber taper, the resonator was mounted to a piezo-electric stage and brought close to the fiber taper. The resonator was then carefully positioned next to the fiber to be at critical coupling, allowing maximum coupling into the resonator.

Figure 4-6. a) side view of the resonator during particle deposition, including the fiber taper, particle, and probe, b) Top view of resonator during particle deposition, c) resonator modes
before particle deposition, d) the same modes after depositing a 2μm PS particle, exhibiting broadened resonant peaks.

Particle deposition lowered the quality of the cavity by inducing scattering, as can be seen in the figure 4-6. This indicates that the modes have a strong interaction with the particle and are thus useful in generating enhanced Raman scattering. Figure 4-7 shows the Raman spectrum of a polystyrene (PS) particle in different interrogation situations. Putting a particle directly on the fiber taper allows for a minimal amount of pump interaction and generated Raman signal. Scanning across multiple modes on the resonator shows some minor enhancement, but when locked to a resonant mode a much larger amount of signal is generated. Note that spectral features between 810 and 900nm are the silica Raman generated in the fiber and resonator. The small peaks at 970nm and 990nm are the Raman spectrum from the PS particle. As can be seen by the second image, the three peaks of the PS Raman spectrum are clearly visible at 2850 cm$^{-1}$, 2905 cm$^{-1}$, and 3050 cm$^{-1}$. These peaks are the Raman scattering peaks from the C-H bond within PS. This demonstrates that the microsphere resonator can be used to detect the Raman scattering from adhered particles, and offers approximately one order of magnitude enhancement compared to different scenarios of placing a particle directly on a fiber taper or on a resonator while the laser frequency is scanned across many resonant modes. The benefit of attaching a particle to the resonator is not readily apparent until the laser is locked to a mode and the electric field is allowed to build up inside the resonator. The buildup factor is determined by the quality of the resonator and calculated at critical coupling as [10]

$$B \approx \frac{Q_{ex} \lambda}{4\pi^2 n R},$$

where $Q_{ex}$ is the quality of the resonance, $\lambda$ is the resonance wavelength in vacuum, n is the refractive index of the resonator, and R is the radius of the resonator. Since spontaneous Raman
scattering is proportional to the number of photons incident on the material, the enhancement is also linearly related to the cavity buildup factor. This considers only the pump buildup, and if the resonator supports resonant modes at the Stokes wavelengths the resonant portion of the Raman signal can undergo the same enhancement as the pump. This has been demonstrated in reports of ultra-low threshold Raman lasing [17].
Figure 4-7. (a) shows typical Raman spectra when a particle is attached directly to the fiber taper, and then attached to a microsphere resonator while the laser frequency is scanned across resonant modes or locked to a resonant mode. The large peaks between 810-900nm are the generated silica Raman. (b) a zoomed in area of the PS Raman signal of interest.

Microsphere microresonators can have quality factors up to $Q = 1 \times 10^{10}$[3, 4], and for a typical resonator of $R = 25\mu m$ pumped at 760 nm, leads to a build-up factor of $B = 5 \times 10^6$. From the build-up factor we can see that Raman scattering should dramatically increase when a high $Q$ mode is locked to. In order to better quantify this enhancement we looked for the minimum integration time required for the Raman measurement.
Figure 4-8 shows that at 2 seconds of integration time it is possible to distinguish 3 PS Raman peaks. After just one half of a second the resonator system generated the same amount of signal as if the particle were placed directly onto the taper. This represents a 4x enhancement as
illustrated, as compared to the 10x enhancement of figure 4-7. This is most likely due to small experimental variations such as laser drift during frequency locking and movement of the fiber taper due to air currents. At low signal to noise ratios (SNR) it becomes difficult to accurately analyze the spectrum, and for this reason the data in figures 4-8 and 4-9 have been filtered with a Savitsky-Golay filter to minimize the effect of thermal noise and shot noise in the detector. This experiment utilized a relatively high pump power (8mW) inside the fiber taper in order to show the speed at which Raman spectra can be acquired. But this is not always desired, as thermal broadening and other mode shifting behaviors occur when the pump power is large. For this reason we decided to determine the lower bound on pump power in order to perform Raman measurement.
Figure 4-9: Low power Raman spectroscopy. a) Raman spectra for a pump power of 200μW. b) the generated PS Raman.
To investigate the low power behavior we purposely reduced coupling efficiency into the fiber and at the minimum detectable level of the photodiode attempted to acquire the scattered PS Raman signal. The results of this are shown in figure 4-9 where with only 200μW of pump power the three PS Raman peaks are visible. This was accomplished by locking the laser frequency to the resonant mode and integrating the signal in the spectrometer for 30 seconds. With a 100μm slit the corresponding resolution of our spectrometer was 0.25nm per pixel. As with the data in figure 4-8 the width of the PS Raman spectrum is due to two primary reasons, the first is the width of the slit. As the generated Raman signal is quite weak, a compromise must be made where a small slit increases the spectroscopic resolution, but also decreases the amount of gathered signal. The second reason for the width of the Raman signal is the instability of the laser. There is an unknown amount of electronic noise in the laser control circuitry which causes jitter in the laser frequency, and subsequently in the PS Raman scattering. Thus far, we have seen clear evidence that the cavity enhancement increases the amount of Raman signal generated. In order to evaluate the dependence on Q, we chose to degrade the Q factor of a resonator while simultaneously recording the amount of signal generated. This was accomplished by utilizing another silica probe and touching the side of the resonator with the probe at various points along the length of the probe. This varied the effective diameter of the probe and changed the amount of mode disturbance. In this manner we were able to degrade the Q by up to one order of magnitude as demonstrated in figure 4-10.
Figure 4-10. a) An optical image of the resonator, fiber taper, and silica probe. The arrows indicate various locations used to touch the resonator on the side opposite the fiber taper and degrade the Q factor of the resonator. b) A representative mode on the microsphere before being probed. c) The same mode as (b) after degradation with the silica probe.

As shown in figure 4-10, the Q of this mode was degraded from $1 \times 10^6$ to $6.8 \times 10^4$. The precision of this probing required use of oxygen plasma cleaning for the probe to remove any surface charging effects generated during the fabrication process. Additionally a piezoelectric stage was used to precisely position the probe along both its length and on the equator of the sphere. The results of the Q degradation experiment are shown in figure 4-11.
Figure 4-11: Dependence of Raman spectrum on Q of a resonator. a) Measured PS Raman spectra at various Q values from $9.5 \times 10^5$ to $2.8 \times 10^5$. b) The peak Raman value as a function of the Q factor.

As can be seen in figure 4-11, the Q was degraded by approximately 3x during the experiment. There are several reasons for this. In figure 4-10, the Q was modulated by a much larger amount since it was a new resonator without a particle on it. This means that the initial Q factor was much higher than in the experiment producing the data in figure 4-11. In the latter
case, the sphere have a PS particle on it which caused surface scattering to degrade the Q to the order of $10^5$. The 2852 cm$^{-1}$ PS Raman peak was chosen based on limitations of the silicon detector. As the Raman signal approaches 1µm in wavelength the sensitivity of the CCD decreases rapidly, such that even though the 3056 cm$^{-1}$ peak is the strongest, in figure 4-11 it appears the weakest. The signal vs Q factor plot appears approximately linear as is to be expected by the decrease in the cavity buildup factor. The discrepancy is most likely due to physical changes in the mode profile created by the large silica probe impinging on the equatorial mode.

While this work has demonstrated the potential for adding Raman spectroscopy to microresonator-based sensing, and the enhancement that these devices offer there are some issues which must be discussed. For a microsphere of 25µm radius and with a Q factor of $10^7$ we expect an enhancement of $5\times10^3$ which differs vastly from the data presented here. There are two main reasons for this. The first is the choice of resonator geometry. While microsphere resonators are simple to fabricate with high Q, they support a very large number of modes. This becomes problematic experimentally since higher order modes may have extremely high Q factors, but only weakly interact with the adsorbed particle. Since there is no direct feedback available on the mode shape inside the resonator, the only way to know if a resonance will produce the desired Raman signal is to lock the laser to the resonance and try it. This is incredibly inefficient, and for a sphere with tens or hundreds of modes in a free spectral range makes finding the resonance with optimal analyte interaction extremely challenging. This can be solved by choosing a geometry with a smaller number of supported modes such as the microbubble resonator, microdisk, or microtoroid resonator. The second reason for differing values of enhancement is the collection scheme as shown in figure 4-5. The experiment is oriented in such a way that the fiber taper, circulating optical mode, and adsorbed particle are all in a plane perpendicular to the signal collection microscope. This allows only Raman signal emitted in that direction to be collected, which significantly negates the enhancement of the resonator since optical signals circulating in a
whispering gallery mode will often not be scattered at a large angle from the circulating direction. A solution to this problem would be to rotate the resonator and taper such that the WGM lies in a plane parallel with the microscope. For more examples on the power of microresonators to enhance Raman spectroscopy see [69] and upcoming publications from the same authors. Yet an advantage of the current configuration is the strong suppression of the Rayleigh-scattered pump light.
Chapter 5
Two Dimensional Materials

The property that makes optical resonators useful for sensing applications, their ultra-high quality factor, also presents a hindrance for use in systems with large amounts of interaction with surrounding material. For example, as shown in figure 4-6, when a 5μm large sphere is attached to a resonator the Q is visibly decreased, and the mode pattern inside the device can be disturbed. If we wish to functionalize optical microresonators we must enlist the help of materials which exist on the nanometer scale and yet offer significant contributions to the optical properties of the device. This chapter will discuss methods to characterize and utilize these materials optically. None of the work presented here would have been accomplished without the help of the Terrones Research Group in the department of Physics at Penn State University in fabricating the samples of 2D materials and providing certain characterization steps. Additionally, the second harmonic raster scans shown in this chapter were completed in collaboration with William Murray of the Ultrafast and Nonlinear Optics Group at Penn State.

5.1 Two Dimensional Material Properties

So-called "two dimensional materials" typically consist of single crystalline layer of material approximately one nanometer in thickness. Initially discovered as graphene [8] these materials have developed significant interest of late. In this chapter we will discuss the subset of 2D materials consisting of transition metal dichalcogenides (TMDs) . These 2D materials have undergone extensive study in recent years due to the difference in their optical properties from
their bulk counterpart [70]. TMDs were first noted to possess nonlinear optical characteristics [71] weakly in the bulk form. However, when the number of atomic layers of these materials is decreased towards mono-layer, the electronic structure begins to change such that a direct band gap exists and strong photoluminescence is possible [72-74]. This photoluminescence is surprisingly strong and in WS$_2$, enhancement can be seen at the edges of few-layered pieces [75]. The electronic band structure shifts with the addition of more layers such that monolayers exhibit the strongest photoluminescence and the amount is non-measurable after approximately 10 layers. Although this decreases with layer number [74], it is less than precise for determining exact number of layers. Determining layer thickness is additionally non-trivial as the individual layer thickness is less than one nanometer, well beyond the diffraction limit for visible and UV microscopy. Direct layer height measurements require expensive tools such as an atomic force microscopes. However, as discussed in Chapter 4, Raman spectroscopy reveals chemical information that can otherwise be difficult to determine. By examining the Raman scattering of TMDs it is possible to precisely differentiate single and multiple layer regions [76]. This is a useful technique for evaluating the quality of growth, or in conjunction with the photoluminescence intensity is a useful metric for examining large exfoliated regions. There is still another optical property of transition metal dichalcogenides that can give us an extra tool for interrogating material properties.

5.2 Second Harmonic Generation in 2D materials

Only materials which lack centrosymmetry possess a nonvanishing second order nonlinear susceptibility under the dipole approximation[77]. This allows for sum-frequency generation, where two photons annihilate to produce a third photon equal to the sum of their individual frequencies. A special case of this is second harmonic generation, which occurs when
both frequencies are identical. Materials capable of second harmonic generation are most frequently crystals with non-contro-symmetric lattices. Typical nonlinear crystals such as KTP, BBO, and LiNbO$_3$ exhibit birefringence in addition to their nonzero $\chi^{(2)}$ term. This birefringence allows for excellent phase-matching between the fundamental pump and second harmonic signal over certain wavelengths, but also requires careful tuning of crystallographic direction and proper orientation of polarization. These nonlinear crystals have been the standard for many years, and are still in use today even in places such as the National Ignition Facility [78]. The two primary considerations for using these materials for SHG are the phase matching requirements, and the efficiency of the second harmonic material. The efficiency is a function of the second order susceptibility and the phase matching. In order to compare these traditional metrics to the new class of two dimensional materials, we need to first model the SHG process and derive a relationship that will allow for calculating the susceptibility from a measured quantity.

The relationship between SHG from a two dimensional material and input power for a pulsed laser through an objective lens was calculated in [79] as

$$\chi_s^{(2)} = \sqrt{\frac{\varepsilon_0 c^2 \lambda_0^2 P_{av1} R t_i (n_2 + 1)^2 (n_i + 1)^4}{32 N A^2 t_2 P_{av1}^2 \phi}}$$

When modeling the TMD as an infinitely thin sheet source. $R$ is the repetition rate, $t_i$ is the pulse width, $c$ is the speed of light, $\lambda_i$ is the wavelength, $n_i$ is the refractive index, $N A$ is the numerical aperture of the objective lens, and $P_{av}$ is the average power ($i=1$: fundamental, 2: Second Harmonic signal). This allows us to determine the nonlinear optical properties of a new TMD with a system such as that shown in figure 5-1. We relate this calculated sheet susceptibility to an equivalent effective bulk susceptibility as $d_{eff} = \chi_s^{(2)}/2T$, where $T$ is the monolayer thickness. This results in an effective bulk susceptibility of 4.5 nm/V for WS$_2$ [79]. The value of $d_{eff}$ for BBO is 1.6 pm/V found in [80], this is similar to values for other traditional nonlinear crystals. We can therefore see that WS$_2$ has a second order optical nonlinearity nearly three orders of
magnitude larger than that of traditional nonlinear crystals. This is also true for other TMDs such as MoS$_2$ and WSe$_2$ [71, 81]. In addition to their extraordinarily nonlinear properties, the extremely low thickness of these materials relaxes the phase matching condition, increasing the possible SHG bandwidth.

![Figure 5-1](image)

Figure 5-1. A schematic of the SHG measurement system. The femtosecond laser propagates through the filters and the objective lens (OL: Newport M-60x) to strike the sample and generate the second harmonic signal. The signal is reflected by the dichroic filter (DM 1: dichroic mirror 400-500nm reflect) and through the band pass (BP: 400-450nm) to the spectrometer (PI Acton 2500i). The imaging path for alignment consists of a white light source placed between DM1 and DM 2 and the pi-reflected signal is collected by the OL and reflected off the dichroic mirror 2 (DM 2: reflect 500-700nm) placed on a flip mount. The signal is then focused by the tube lens (TL: 300mm) onto the CCD.

An experimental setup to measure the second harmonic generation in TMDs is depicted in figure 5-1. It consists of a femtosecond pulsed laser (Spectra-Physics Tsunami, center wavelength ~ 810nm, pulse width ~ 100fs, 100MHz repetition rate, 800mW average power) propagating through an objective lens (Newport M60x, NA= 0.85). The second harmonic is collected by the objective lens and propagates towards the laser until directed to the spectrometer (PI Acton 2500i with liquid nitrogen cooled silicon CCD) by a dichroic mirror and filtered by a shortpass filter (Chroma ET470sp). A monochrome video CCD is used for sample alignment and imaging. To image, the laser is blocked by a broadband white incoherent light source, and the
dichroic mirror 2 serves both to filter the pump to wavelengths above the bandgap as well as direct the image signal towards the CCD.

An example utilizing the equipment from figure 5-1 is shown in figure 5-2. Two monolayers of WS₂ are shown in the optical micrograph at right. The second harmonic raster scan shows enhanced spatial details hardly visible in the optical image such as the nucleation site in the middle of the central triangle. This point is where the crystal began to grow from a single lattice point into the approximately 80μm per side triangle. The central nucleation point also typically contains extra sulfur residue leading to the higher than average signal present in the SHG image.

![Figure 5-2](image)

**Figure 5-2.** a) SHG raster scan of WS₂ monolayer triangles. b) An optical micrograph of the same triangles shown in (a).

In addition to its use in determining material properties, the second harmonic generation capabilities of TMD monolayers has proven to be surprisingly robust. The photoluminescent emission from TMDs can be suppressed by defects, choice of substrate, or addition of layers [82].
Additionally, the photoluminescent emission degrades over time with exposure to air [83]. The hexagonal monolayers of WS$_2$ shown in figure 5-3 are continuous atomic sheets and contain no grain boundaries. The alternating intensity pattern of photoluminescence is reminiscent of the international radiation symbol, and in figure 5-3a the contrast from light to dark section is approximately 3:1. The reason for this has been examined in [84] and determined to be due to atomic tungsten and sulfur vacancies in the regions of interest. In the above publication, the photoluminescence contrast was reported to be 30:1, indicating that the electronic band structure was altered enough to almost completely quench the emission and shift the Raman scattering by up to 0.3 eV. From examination of figure 5-3b we can see that the second harmonic intensity is uniform over the area of the hexagonal WS$_2$. 
The uniformity of the SHG over areas where significant atomic defects are present is a strong indication of these materials' robust nonlinear properties. This indicates that nonlinear devices constructed from TMDs are likely to retain their usefulness even if their linear optical response has degraded or been altered. Furthermore, the resistance of the nonlinear properties to change also suggests that applications such as cellular labelling or in-vivo SHG-based imaging may be possible.

5.3 Engineering 2D Optical Properties

We have determined that TMDs have both extremely large as well as robust second order nonlinear susceptibilities. However, in order to create new and useful devices we should have a way to adjust the optical properties as we see fit. Since crystallographic defects have been demonstrated to alter the photoluminescent properties, we should examine whether there is a correlation with the nonlinear properties as well. To determine if there is a relationship between defect density and second harmonic generation, we utilized the same focused ion beam technique presented in [85] to induce defects in the TMD.
Figure 5-4. The locations of various irradiation amounts on the TEM grid. Large values for Ld correspond to lower amounts of radiation. The monolayers indicated with red squares were analyzed for second harmonic generation. Photoluminescence image provided by Kazunori Fujisawa of the Terrones Research Group.

Figure 5-4 shows the sample prepared by controlled irradiation of gallium (Ga 3+) ions. By adjusting the speed at which the ion beam is scanned across the sample, greater or less ion damage can be induced into the structure. In the above figure, this corresponds to an average interdefect distance (Ld) ranging from less damage (large Ld) to more damage (small Ld). The sample was prepared by controlled CVD growth, and the resultant large number of monolayers was transferred to a carbon mesh TEM grid (Quantifoil, from SPI) for ion bombardment. The sample was provided by the Terrones Research Group and irradiation performed by Kazunori Fujisawa. As noted in [79], the suspended WS₂ produces significantly more second harmonic than those monolayers on a standard Si/SiO₂ substrate.
The effect of the carbon mesh on the SHG can clearly be seen in figure 5-5b as a suppression of the second harmonic generation resulting in the grid or checkerboard pattern. The addition of a carbon mesh suppresses second harmonic generation in those places that it touches the monolayer. The raster scan was generated using the same setup as shown in figure 5-1. To determine a correlation between crystallographic defects and second harmonic generation, we averaged several of the highest second harmonic signal points on each of the triangles indicated by the red squares in figure 5-4. The result of this is shown in figure 5-6.
Figure 5.6. Dependence of the SHG signal vs the average defect length from irradiation. The amount of defects appears to be linearly related with the average defect length created by gallium ion bombardment. As the average defect length decreases, less of the original crystal structure is maintained, resulting in a reduction of SHG. The decreasing trend towards the bottom left of the graph is most likely due to the severity of crystallographic degradation. At this point the physical structure is so disrupted that the Raman peaks begin to lose their shape and the electronic band structure is drastically altered [85]. Combined with the knowledge from the previous section, we now have a way to engineer the optical properties of two dimensional materials. Specifically we have a method to controllably pattern the nonlinear properties of TMDs. Our final goal in this chapter is to demonstrate a method for introducing 2D materials to optical microresonators in order to create novel devices.
5.4 Integrating 2D materials with optical microresonators

We can now work towards the fabrication of a new class of optical devices which leverage both the ultra high Q factor of microresonators and the large photoluminescence and second order optical nonlinearities inherent in two dimensional materials. First reports in the literature have already demonstrated that the addition of a microdisk resonator to a monolayer of WS$_2$ can generate an excitonic laser [86]. This work however relies on carving a microdisk out of the substrate material rather than direct transfer or growth onto a high-Q resonator. We aim to achieve both of these approaches while achieving the highest possible Q. This in turn will reduce the laser pumping threshold, as well as give access to intracavity SHG.

There are two paths towards this goal. The first is via direct growth. Using either chemical vapor deposition (CVD) or physical vapor deposition (PVD), we wish to grow monolayers of TMD on the surface of high-Q optical microresonators. The second approach is to use a dry transfer method, where a grown monolayer is transferred to the surface of a resonator without damaging either the resonator or the TMD. The first method is the more interesting of the two, as it provides the potential for scalability and parallel processing, whereby multiple resonators can be functionalized simultaneously. The potential drawback is that this is a much more complicated process than growing monolayers on the surface of a silicon/silica wafer. The dry transfer technique allows for the quickest way forward, individual devices can be manufactured quickly with a high confidence of success.

The first approach involves the direct growth method. This was performed by Ethan Khan of the Terrones Research Group at Penn State. As jumping directly from wafer growth to a 3D geometry was met with a great deal of difficulties, we examined the growth behavior on a simplified but still three dimensional geometry, silica fibers. Initially this consisted of standard 125μm diameter single mode fiber, but was expanded into including silica capillary of 300μm and
210μm diameter. As strain has been demonstrated to have a significant effect on the optical properties of monolayers[87, 88], we utilized an atomic force microscope to investigate the amount of strain in our growth on silica fibers. Two examples of growth on a fiber is shown in figure 5-7.

Figure 5-7. AFM images of direct TMD growth on silica fibers a) The phase imaging mode of the AFM showing the TMD growth in strong contrast. b) the same growth in (a) illustrating strong adhesion to the surface of the silica fiber despite the strong curvature. c) a 2D plot of the height of a monolayer growth showing strong internal defects. d) the same growth as in (c) showing in a 3D plot illustrating despite the large defect structure, the growth is still conformal. AFM images taken by Simin Feng

The images in figure 5-7 illustrate that the growth method produces conformal monolayer growth on a curved surface. After this confirmation, the next step is to produce direct growth onto a working optical microresonator. Besides the additional difficulty of surface curvature, monolayer
growth on a microresonator must be extremely clean in order to preserve the high Q that makes the device useful.

An example of resonator behavior after growth is shown below in figure 5-8. The optical image shows the tapered optical fiber delivering light to the resonator from the left. The bright reflection on the left side of the sphere is from unguided residual light from the tapering process. Due to the finite amount of transmission in the fiber taper, some light is not contained in the fiber and instead propagates unguided along the taper. Small surface defects and deposits appear as glowing points as they scatter light from the internally circulating mode. The transmission spectrum in figure 5-8b shows there are several modes within a 22GHz range that still remain after the growth process. The mode indicated by the arrows has a Q factor of $5 \times 10^5$, which is more than 2 orders of magnitude greater than that in the literature capable of producing a laser [86].
Figure 5-8 a) An optical transmission micrograph of a silica microsphere with WS2 monolayer growth on the surface. b) The transmission spectrum of the microsphere in (a). The designated mode has a Q factor of $5 \times 10^5$. c) Modes of a representative microsphere prior to the growth process, the Q factor for the central mode is $7.5 \times 10^6$ indicated by arrows. d) The same modes from the microsphere in (c) after the growth process. The Q is $4.9 \times 10^4$.

Although both monolayer growth, and the presence of resonant modes were confirmed in the microspheres no cavity interaction was observed in the photoluminescence spectrum of the devices. We will discuss possible reasons for this below, but for now let's move to another approach to functionalizing resonators with 2D materials.
The dry transfer technique involves taking a grown monolayer and removing it from the substrate with a dissolvable layer of Poly methyl methacrylate (PMMA). This is then pressed onto a Polydimethylsiloxane (PDMS) stamp. This stamp is then gently pressed against the resonator, and the 2D material remains on the surface when the PDMS is removed. This technique was developed in [89], and was performed by the Terrones research group. In an effort to streamline this process, a microscope dedicated for this transfer process was designed and constructed by the author with an undergraduate student, however samples transferred with this equipment are not depicted here. Figure 5-9 below shows the result of two different attempts to transfer TMDs to microsphere resonators.

![Figure 5-9](image)

Figure 5-9. a) Optical micrograph of a microsphere resonator with transferred exfoliated MoSe2 flake. b) Optical micrograph of a microresonator with exfoliated WSe2 flake. Transfer and images were provided by Kin Fai Mak research group c) and d) PL images of microsphere resonators with grown WS2 triangles.
Figure 5-9 illustrates some of the current attempts at transfer and growth of TMDs onto silica microresonators. Physical transfer techniques appear to produce cleaner results on the resonator surface, but are more likely to cause serious scratches or damage to the resonator if performed incorrectly. Current CVD growth techniques produce consistent results, but with additional surface defects cause by powder deposits and chemical precursors.

So far, the photoluminescent emission when pumped by a combination fluorescence/Raman microscope system does not indicate any filtering effect expected from the whispering gallery modes of the resonator. This indicates that although we have both a relatively high Q factor, and direct TMD growth with photoluminescent emission, the two are not coupled strongly together. Another potential reason for that is our choice of resonator geometry. Microspheres were chosen due to their ease of fabrication and high Q factor as compared to microtoroids or microdisks. Microsphere resonators support WGMs in any great circle around the device. The modes measured by our pump and fiber taper system only shows those modes corresponding to the equatorial plane determined by the fiber taper, identical to those excited by the setup in figure 4-5. In reality, there are a great many more modes supported by the entire sphere for which omnidirectional surface emission from an adhered monolayer may couple into. Thus when examining the PL spectrum, there is almost certainly cavity filtering occurring, but it is unresolvable by any commercial spectrometer. To avoid this problem, there are at least two possible solutions. The first is to both pump and collect from a tapered optical fiber. This ensures that only a small subset of modes in the sphere will couple back into the fiber, showing the cavity-PL interaction we expect to see. Another method is to utilize a different geometry which has a much smaller number of supported modes. This could be either a much smaller microsphere, a microbubble, microdisk, or microtoroid resonator. Further work in this direction would likely produce excellent results and higher quality devices.
Chapter 6
Future Work

This dissertation has covered the enhancement of light and matter interaction in optical microresonators. In chapter 2 the fundamental properties of whispering gallery mode resonators were explored, as well as how we can model the light distribution in such systems. In chapter 3 we discussed a new type of resonator system with highly accurate temperature sensing capabilities. The microbubble system also has the potential for surpassing capillary-based optofluidic sensing schemes, and even as a gas or molecular sensor. Into chapter 4 we discussed the capability of resonators to directly enhance light-matter interactions through the increased emission of Raman scattering. This added a further capability to resonators as optical sensor systems. Recent discovery of two dimensional materials suggests that additional capabilities such as photoluminescence and second order nonlinear properties can be added to our silica based fiber and resonator systems. In chapter 5 we discussed the properties of TMDs and how we characterize their linear and nonlinear properties. Finally we also note that these materials support robust SHG and the amount of which can be engineered to fit our designs. The last remaining step is to integrate these incredible materials into optical microresonator systems to create a new class of devices with strong optical nonlinearities which are traditionally absent from these materials.

6.1 Second-order Nonlinear Optical Fiber

Silica optical fiber has uses in almost every facet of commercial and research photonics. Dopants are frequently used to modify the refractive index and even produce gain, as in the case
of embedded erbium ions. However, none of these dopants overcome the fact that silica has no second order nonlinear susceptibility. Our solution to this is to utilize the unique shape of the so-called "D-side" fiber, which consists of a standard single mode optical fiber which has been etched or polished to remove the cladding and expose part of the core. These samples were prepared by Dr. Dong Wang and Professor Yong Xu of the Center for Photonics Technology at Virginia Tech. When looked at in cross section, it is easy to see why the fiber is called this. We wish to utilize the evanescent portion of the guided mode to interact with a chosen TMD over a long interaction length enabled by the fiber optical waveguide. Previous work in this area have utilized the linear optical properties of TMDs to create saturable absorbers and produce modelocked lasers [90, 91]. Our proposed device would instead become a component which can be used to add second order nonlinearity to a fiber-based system which previously had none.
Figure 6-1. a) The mode profile of a typical 800nm single mode optical fiber with diameter 125μm. b) the same mode as (a) zoomed to show the profile around the core/cladding interface. c) A fiber has been polished to expose part of the core resulting in the characteristic "D" shape of the fiber. d) The exposed core of the D fiber alters the mode and exposes the evanescent portion of the wave at the air/core interface.

Figure 6-1 illustrates the difference between a standard mode fiber and a D side fiber. As an incremental step towards the fabrication of our device, we first tested the TMD transfer process on an un-polished single mode optical fiber. This consisted of creating a thin layer of PMMA through spin coating, which was then pressed onto the grown monolayer-substrate chip. Once attached in this manner, the PMMA/monolayer film is pressed onto the optical fiber and
then baked at 200 °C. Finally, an acetone bath removes the PMMA and the monolayers are transferred directly to the desired fiber. The results of this process can be seen in figure 6-2.

![Image](image.png)

Figure 6-2. Broadband and Fluorescence optical micrograph of the WS2 monolayers transferred to the surface of a sm600 optical fiber. The TMD triangles are adhered across the bend of the fiber, and demonstrate the adaptability of the transfer process. The TMD monolayer transfer and images courtesy of Tianyi Zhang of the Terrones Research Group.

The results show that the transfer technique achieves good adhesion to the curved surface of the 125μm diameter optical fiber. The fluorescence imaging in figure 6-2b shows edge enhancement as expected [75], and relatively small amounts of damage to the monolayers. Once applied to the polished D fiber, strong evanescently coupled nonlinear processes (i.e. SHG) can be incorporated to many future photonic systems.

### 6.2 Spectral Holography

Previous experiments have shown the sensitivity of optical microresonators to small refractive index changes [24, 59], but holography offers the chance for additional sensing capabilities. Using the same external cavity tunable diode laser as discussed in chapter 2, we will
create a one dimensional interference pattern which can record the phase of our laser as it travels through the resonator system.

Holography is a powerful tool first discovered by Gabor [92]. This technique allows for the capture of both an optical wave amplitude and its phase by means of recording an interference pattern. In two dimensions this can be used to recreate the spatial profile of objects, or to investigate the phase profile of the wave as it propagates through a medium [93]. A two dimensional hologram is created from the spatial interference of two propagating waves, usually denoted as signal and reference beams. The interference pattern captures changes in the phase due to interaction with some matter. Spectral holography is called such due to the interference pattern being recorded in the spectral domain [94]. Originally this was accomplished by two propagating femtosecond laser pulses overlapping in time and an interference resulting from the temporal overlap of spectral components [95]. To generate a spectral hologram one pulse is delayed by an adjustable amount of time such that the pulse traveling through a medium arrives at the same time as the delayed one. In this way with a pulse containing a broad spectrum, the full profile of the chromatic properties of an incident object can be recovered from the hologram. Spectral holography has been used to investigate properties of waveguides [96], and Bragg gratings [97] among other devices. A diagram of our system in shown in figure 6-3.
Figure 6-3. A block diagram of the spectral holography experiment. The external cavity diode is coupled into single mode fiber and split into signal and delay paths. Each path is polarization controlled by a fiber polarization controller. The combined light propagates through an optical fiber taper and resonator system. The interference pattern is measured by a photodiode and displayed by an oscilloscope.

The interferometer consists of the external cavity laser coupled into a single mode fiber which is then split into a signal and delay path. Each of these optical paths consist of spooled fiber and polarization is controlled through fiber polarization controllers. The photodiode at the end of the fiber measures the intensity output. As the frequency of the laser is changed, the photodiode records the change in transmission due to interference of the laser propagating through different lengths of fiber. By sweeping the laser frequency over the range of 22 GHz, the photodiode records an interference pattern as a temporal change in intensity. The polarization controllers allow the ability to change each path of the laser to either TE or TM polarization. In this manner we maintain the ability to investigate the transmission profile of resonant systems (i.e. resonance locations in a microsphere) as well as superimpose a spectral hologram. The spectral hologram captures the phase phase response of the transmission spectrum of the
resonator system, and the fringe spacing of the hologram is determined by the delay line. The recorded intensity at the photodiode is described by the equation

\[ |S(\omega) + R(\omega)|^2 = |S(\omega)|^2 + |R(\omega)|^2 + S^*(\omega)R(\omega) + S(\omega)R^*(\omega) \]

where S is the signal and R is the reference beam. The signal beam has a phase delay equal to \( \frac{2\pi n}{\lambda} L \) where L is the length of the delay line, which determines the fringe spacing in the spectral hologram. As opposed to traditional broadband spectral holography, we utilize an external cavity laser diode with tunable frequency. For a fixed delay line, the laser frequency is changed and the interference of the signal and reference are recorded by the photodiode.

A representative interference pattern is shown below. The fringes of the pattern are too finely spaced to be visible over the typical laser scan range of 20GHz. The slope in the interference pattern is due to the current correction applied to the laser diode.
Figure 6-4. An interference pattern obtained using the system shown in Fig 6-3. The top image shows the full 20 GHz frequency sweep. The bottom image shows the indicated region zoomed in so that the interference fringes are visible.

One of the major obstacles to overcome here is the noise from the laser electronics. Figure 6-4 shows the asymmetry of the interference pattern due to noise. Ideally the fringes should be an evenly spaced sinusoid, the variations in periodicity indicate the presence of noise in the laser frequency. This added noise makes phase reconstruction difficult as it lowers the signal
to noise ratio. Additional experimental difficulties lie in resolving the extremely fine fringes of the interference pattern. Figure 6-5 shows the interference pattern over several high-Q modes in a silica microsphere.

![Graph showing interference pattern](image)

**Figure 6-5** The transmission spectral-hologram of a high Q resonator. The fringes are extremely fine. This is necessary in order to resolve the phase profile across a resonance peak, but it adds experimental difficulties. It requires a large number of sampling points (65,000) and due to the memory limitations of our oscilloscope only extremely high Q modes fit inside the acquisition area. The modes shown above have a FWHM of approximately 50MHz, which equates to a Q factor of almost $10^7$. Once the experimental difficulties are overcome, we expect that spectral holography will become a useful tool for examining the effect of TMDs on systems such as microresonators or even the D side fiber.
Appendix A

Compressive CARS Holography

This appendix contains a paper previously published in Optics Express. The citation for which is found as reference [98]. For this work, my contributions included co-authorship of the text, as well as the generation of figures and data. The other co-author, Dr. Nikhil Mehta helped extensively with the text and mathematical formulation.

A-1. Introduction

Holography has been adapted to many uses since its invention by Gabor [92], due to the ability of the interference pattern to encode both amplitude and phase onto a recording medium. With the inception of digital holography, the ability to numerically analyze holograms has given rise to many new tools for generating and analyzing holograms numerically. Direct digital propagation of a hologram can be useful for estimating the behavior of the signal at different positions along the propagation direction, but direct inference of a volumetric estimate is ill-posed as proved in [99]. This is due to the fact that a three dimensional estimate obtained in that manner is not unique, and that the recorded hologram can be the result of many different object and wave interactions. This is traditionally overcome by recording multiple holograms along different axes as in the case of diffraction tomography [100].

CARS holography offers the benefits of chemical identification from Raman spectroscopy and the spatial resolution of holography in one nonlinear process. As demonstrated in [65, 66, 101], by probing a sample coated with a material which has a nonzero $\chi^{(3)}$ nonlinear susceptibility with both a pump/probe and stokes beam from a pump laser and OPO (optical parametric oscillator) respectively, a resonant four wave mixing occurs with the anti-stokes
radiation. The anti-stokes signal interferes with the reference beam from the OPO and creates a hologram containing information about the $\chi^{(3)}$ distribution. The ability to tune the stokes beam from the OPO is one of the main advantages of this technique, since it allows for chemical selectivity based on the material being imaged.

Compressive sensing is a relatively new technique which relies on the sparsity of real signals to overcome traditional limitations in image and data reconstruction. In the case presented here, compressive refers to the inference of a three dimensional volume estimate from a single two dimensional hologram. If the volume is especially sparse, implementation of more aggressive algorithms can allow for increased noise suppression and decreased computation time. By combining compressive sensing with holography, the amount of time spent gathering signals is drastically reduced, as the majority of the work involved is in processing a single hologram. The marriage of compressive sensing and CARS holography creates a large improvement in signal and image quality in addition to label-free microscopy.

**A-2. Theory**

**A-2.1 CARS**

A brief overview will be presented here, for more information see either chapter 10 of [102] or [65]. CARS holography is a nonlinear four wave mixing process which relies on the interaction of two incident laser beams denoted by their angular frequency as pump $\omega_p$ and stokes $\omega_s$.

**A-2.2 Compressive Sensing**

Compressive sensing is a method of utilizing multiplexer encoders to record sparse measurements which will allow accurate reconstruction of the original signal from incomplete or
inaccurate measurements. This has been demonstrated by [103] and [104] in seeming defiance of the traditional limits posed by Shannon in [105]. More details and examples of compressive sensing applications can be found in [106], but the basic equations for this application are shown below. The restricted isometry property (RIP) forms the foundation of compressive sensing and shows that a measurement matrix $H$ satisfies sparsity for a signal $f$ that is $S$ sparse if the following conditions are met,

$$
(1 - \delta_S) \| f_T \|_2^2 \leq \| H_T f_T \|_2^2 \leq (1 + \delta_S) \| f_T \|_2^2,
$$

(1)

where $T$ is the set of indices over which $f$ and $H$ are sparse, and $\| \cdot \|_2$ is the Euclidean norm. The coherence function is defined as

$$
\mu_1(H, \Psi) = \sqrt{N} \max_{1 \leq m \leq M} \max_{1 \leq n \leq N} | \langle h_m, \psi_n \rangle |,
$$

(2)

where $h_m$ and $\psi_n$ denote the $m$-th row of $H$ and the $n$-th column of $\Psi$, respectively. If $M$ satisfies

$$
M \geq C \cdot \mu_1^2(H, \Psi) \cdot S \cdot \log N,
$$

(3)

and the other RIP conditions are met, then [103] and [107] have shown that the original signal can be reconstructed with a high degree of accuracy by solving

$$
\theta_e = \arg \min_{\theta} \| \theta \|_1 \text{ such that } g = Hf_e = H\Psi \theta_e,
$$

(4)

Ideally a low value of coherence between the measurement and the projection basis is desired. Equation (4) illustrates that if a measurement is sparse, then the reconstruction of the original function $g$, in this case the 3D volumetric data, can be obtained as long as the measurement is sparse on the projection basis $\Psi$ and undergoes an $l_1$ minimization.

### A-3. Method

The method for solving the inversion problem and arriving at the denoised object scattering field is similar to that in [108] and [109] with the major difference being that the
recorded hologram is of off-axis rather than inline or Gabor style. Brady [108] describes a Gabor hologram in the context of decompressive inference in the following manner,

\[ \tilde{g} = G_{2D} QBf, \quad (5) \]

where \( B \) is the block diagonal matrix with elements that are discrete 2D Fourier transforms, \( G_{2D} \) is the inverse 2D DFT, and \( Q = [P_1 P_2 \cdots P_{N_z}] \) with \( [P_i]_{m1m2} = e^{i\Delta x_k} e^{i\Delta y_l} e^{-i\frac{m_1^2 m_2^2}{2} \Delta x_k \Delta y_l} \). Here \( \Delta \) refers to the discretization of both the detector in the form of pixel pitch, and the axial resolution determined by the feature size being investigated. The individual matrices in \( Q \) then can be seen to be the phase accrued from the detector plane to each \( z \) “slice” of the 3D volumetric data. In a Gabor hologram, there is a real constraint that needs be applied to equation (5) but as the hologram discussed in this document is off-axis, the real constraint can be dropped. The result is then

\[ g = G_{2D} QBf = Hf + n, \quad (6) \]

where \( n \) is additive noise. Equation (6) is similar in form to (4), thus by minimizing the L1 norm of (6) the inversion problem is solved. While the detector used to collect the hologram only supplies intensity data, the use of off-axis measurements allow \( f, g \) and \( H \) from equation (6) to be complex valued. Thus, by performing the initial steps of filtering the DC component and one sideband from the Fourier transform of the hologram and using the resultant complex valued image generated by the inverse Fourier transform as the starting measurement data, the complex valued scattering field can be found.

Utilizing the algorithms proposed by [110-112] specifically, the TwIST algorithm was convenient for performing the required minimization. By minimizing the objective function described in [110] and shown here as

\[ f(x) = \frac{1}{2} \| y - Kx \|^2 + \lambda \Phi(x), \quad (7) \]
the original 3D signal can be recovered. In equation (7) $y$ is the known observation, $x$ is the recovered signal (until minimization is complete this is merely an estimate), $\Phi$ is a regularizer function, and $\lambda$ is a regularizer weighting parameter. If the regularizer invoked is applied in the total variation domain along with the denoising function specified by [112] the TwIST algorithm can sufficiently minimize the objective function, which directly corresponds to the requirements of equation (4). The choice of regularizer and denoiser functions is critical, and the standard has been to perform these actions in the total variation domain. However, due to the point-source like nature of the CARS signal which is further reduced by the self-focusing nature of the microspheres, regularization and denoising directly in the $l_1$ domain is possible. The direct $l_1$ minimization is performed by utilizing a hard thresholding denoiser and the direct $l_1$ norm of the vectorized dataset. The results of the objective function minimization are discussed in the next section.

A-4. Results

A-4.1 Suspended Microspheres

![Figure A-1: Result of numerical backpropagation. The 9 microspheres are visible, but are occluded by out of focus wave contributions.](image-url)
Figure A-2: Applying decompressive inference to the hologram in the Total Variation domain results in clearer images with the diffraction patterns almost entirely eliminated.

Figure A-3: Use of the direct $l_1$ minimization removes all unwanted noise, effectively reducing the volumetric data to only that of the microspheres.

Besides the obvious results shown above, in which noise is drastically reduced, computation time also benefits greatly. Due to the nature of compressive sensing, and the complex computations required to compute the object field estimate during each iteration, using a
simplified $\Psi$ function greatly increases the speed at which a result can be obtained. In this case, a reduction in computation time of two orders of magnitude was achieved.

As demonstrated in figure A-4, the choice of value for $\lambda$ in equation (7) is vital, as it controls the weight given by the algorithm to direct $l_1$ minimization. There is a critical value for $\lambda$ where the most information is preserved locally while minimizing noise; this is found through trial and error by examining the object features. Placing too much weight on the $l_1$ minimization results in figure (4-a), while putting too much weight on the MSE minimization results in figure (4-b). Overbiasing towards the $l_1$ norm results in a loss of useful information due to the fact that local features are kept at the expense of larger data context. This is demonstrated in figure A-4a where the feature in the top left corner is accentuated, and several other microsphere contributions are eliminated.

![Figure A-4: (a) the results of an overly large value for $\lambda$. (b) the results of a value of $\lambda$ which is too small.](image)

**4.2 HeLa Cell**

As demonstrated in [66], CARS holography can also be useful in bio-imaging due to the selective nature of the CARS signal, and its ability to be tuned to a wavelength corresponding to different features inside of a biological sample. CARS holography is superior to
direct CARS imaging since it requires only a single exposure to capture all of the phase and amplitude information required to digitally propagate through different planes in the z direction.

Figure A-5 shows the result of digital backpropagation and figure (6) shows the result of applying compressive sensing to the object volume estimate.

![Images](image1.png)

Figure A-5: at left, shows the result of digital propagation of a recorded HeLa cell hologram. At right, shows the result of volume data estimation from the TwIST algorithm

5. Conclusion

Applying the principles of compressive sensing to CARS holography offers many benefits. The ability to computationally acquire volumetric data from a single 2D hologram offers a vast improvement over the other methods of tomographic reconstruction including diffraction tomography. The compressive sensing technique allows for more time to be spent on the back end computationally rather than at the front end of the holographic process by collecting multiple holograms. The ability of CARS holography to encode material specific information in the interference pattern eliminates the need for labeling materials, as their individual CARS signal will be shifted in wavelength and will only appear in the final image when the shift is accounted
for. This has proven to be a robust technique which eliminates almost all unwanted noise and provides far more information than standard holographic techniques alone. For \( l_1 \) sparse objects such as \( \chi^{(3)} \) distributions in microspheres, this method of compressive sensing is greatly advantageous.
Appendix B

Development of opto-electronic fiber device with multiple actuating nano-probes

This appendix contains a paper published previously in Nanotechnology. The citation can be found as reference [96]. This author's contributions include modeling the photonic crystal fiber in COMSOL. This includes the calculated dispersion in the fiber, as well as the electromechanical properties of the carbon nanotube probes.

B-1. Introduction

The field of fiber optics has witnessed significant advances owing to the pioneering work of Russell and coworkers which has led to the development of micro-structured optical fiber,[113-115] in particular photonic crystal fiber (PCF). An important advantage of PCF over conventional optical fiber is the ability to precisely engineer the optical modal properties by designing the shape, size and distribution of the air holes. The recent active scientific interest can be attributed to the fact that the properties of PCF can be altered by incorporating special materials in its air holes. Indeed, the choice of material(s) and selective filling of air holes offer additional degrees of freedom which vastly expand the scope of PCF based optical devices and their applications. Of particular interest here is the fact that electrically conductive media, such as metals, may be filled in the PCF structure to design novel devices and sensors. For example, Sazio et al. demonstrated unique all-in-fiber active photonic devices [116, 117] by filling silicon and germanium within the air holes. Recently several applications based on filling metals in PCF have been reported [118-122]. Furthermore, surface plasmon polariton sensors based on metallic filling of PCF has also been the focus of active research [123, 124].

Metal filled PCF devices feature the ability to conduct electricity as well as guide optical waves. Furthermore, nanotubes or nanowires can be incorporated within metal filled PCF such that each nanoprobe may be individually controlled. This points to the exciting potential of
developing an integrated opto-electronic fiber platform which is capable of simultaneous
electrical and optical interrogation and probing at the nanoscale. Key to developing such a
platform is the ability to repetitively and reliably fill metal into the air holes of the PCF
selectively without damaging its structural integrity or its optical wave-guiding functionality.
Towards that end goal, here we report on the fabrication and characterization of a novel fiber
based opto-electronic nanoprobe engineered by selectively penetrating metal electrodes in PCF
and by attaching nanotubes individually to each electrode. We present methods to create any
desired configuration of such electrodes and show the feasibility that the attached nanotubes can
be actuated through electrostatic force by controlling the voltages applied to the electrodes. In
other words, the PCF serves as scaffold for an electromechanical nanoprobe as well as an optical
waveguide. This unique aspect of our device differentiates it from existing single tip
nanomanipulators [125-128] and two arm nanotweezers [129-132].

The paper is organized as follows: we begin by presenting the techniques we have
developed for fabrication of the proposed opto-electronic nano-probe, including selective filling
of metal electrodes in PCF and precise attachment of individual nanotubes to them. We then
report results of optical characterization of our device using spectral holography to quantify the
group velocity dispersion of the metal-filled PCF. Lastly we discuss the potential
electromechanical functionality of the device by demonstrating the feasibility of electronic
actuation of the attached nanotubes, and comparing the observed movement with numerically
simulated deflection.

**B-2. Results and Discussion**

**B-2.1 Selective filling of PCF:**
Selective penetration of foreign material especially metals in air holes of PCF has led to design of novel fiber devices optimized for particular applications. A wide variety of techniques have been demonstrated to achieve selective filling. Some of the early techniques for infiltrating metal involved carefully inserting thin metal wires directly into specific fiber air holes [133] and using vacuum suction [134] to draw molten material into the fiber.

Huang et al. leveraged non-uniform air hole sizes in their multistep injection-cure-cleave technique to demonstrate selective filling of larger diameter holes with a UV curable polymer by applying external pressure [135]. Another technique based on varying size of air holes involves use of fusion splicer to collapse smaller holes and leave open larger holes for filling [136, 137]. Borrowing on the technologies developed in the field of microelectronics, a novel technique based on use of high pressure chemical vapor deposition was developed to successfully demonstrate filling of semiconductors and metals to form functionalized microstructured optical
fiber (MOF) devices [116, 138]. It has also been shown that the conventional stack and draw procedure can be adapted to fabricate PCF with appropriately positioned stack of metal rods around the core, instead of penetrating the PCF post fabrication [139]. Vieweg et al. have shown selective filling of PCF in arbitrary pattern by targeting and sealing individual air holes using a focused pulsed laser to polymerize a photo-resist covering those holes, so that the unsealed holes are available to be filled [140]. Another method utilizes side access to the air holes through the fiber walls created using focused ion beam, so that the process of selective filling does not occlude optical access to the PCF facet [141]. In our technique detailed below, we selectively pattern the PCF facet by targeted application of UV curable optical glue to individual air holes, followed by pumping molten metal in the open holes under high pressure. In fact, variants of the technique of using pressure differential to pump or draw molten metal into PCF has been reported by several researchers in the past [118, 119, 122, 142-144]. Our procedure does not require the air holes to be of varying size, and is not influenced significantly by fluidic properties of the liquid phase metal. It does not involve milling/splicing/arcing or other steps which may cause damage and alter the optical properties of the PCF. This ensures that the fiber can guide light and electricity along its length and perform both electrical and optical probing as envisaged above. We demonstrate our procedure, illustrated in Fig. B-1, by filling multiple individual holes in more than 15 inch long endlessly single mode PCF (SC-PCF, Blaze Photonics ESM-12-01) with low melting point metal. The fiber has a 12 µm solid silica core surrounded by hexagonal array of 3.68 µm air holes in cladding region. The pitch of cladding holes is 8 µm. As shown in Fig. B-1(1), initially the three holes to be infiltrated are each sealed by local application of a drop of UV-curable optical glue (NOA-81) under an optical microscope using a fiber taper maneuvered with a three-axis stage. Upon curing, the selectively blocked facet of the PCF is immersed into NOA-81 which draws the glue into all but the blocked holes at least 5-6 mm deep via capillary action (blue column in Fig B-1 (2) and (3)). Further UV curing of the penetrated optical glue, followed by
cleaving the PCF close to the facet creates the required PCF template with only the three holes exposed (Fig. B-1(3)) as desired. The PCF template is then mounted within a home-made high pressure pumping system for pumping molten metal through it. In particular, the patterned facet of the fiber is held in place in a chamber using polydimethylsiloxane (PDMS) (Dow Corning Sylgard 184 and curing agent 10:1 ratio). The chamber is topped off with Ostalloy 158 (eutectic solder alloy of 50% bismuth, 26.7% lead, 13.3% tin and 10% cadmium, having melting point 70 °C) and is placed inside an oven which is maintained at a temperature above the melting point (approximately 100 °C). The inset in Fig. B-2(a) shows the cutout of the chamber with the fiber facet sunk in the alloy. The other facet of the fiber is held outside the oven at room temperature as shown in Fig. B-2(a). After the temperature within the oven equilibrates, compressed nitrogen gas at pressure of about 500 psi is used to pump the molten alloy through the unblocked holes of the patterned fiber, until the molten alloy leaks through from the other end which is seen as a shiny blob in the image in Fig. B-2(b). This indicates penetration of the metal along the entire fiber length and typically takes a few minutes for our nearly 15 inch long fiber. It has been reported that pumping liquefied metal by applying pressure often causes air gaps along the length of the filled metal due to the difference in the thermal expansion coefficient of the metal and silica [118, 119]. In contrast, our technique of maintaining the distal end of the fiber at room temperature causes the leaking alloy to solidify into the shiny blob which then acts as a plug to seal the channel and avoid any voids as the alloy stays compact while cooling down under constant pressure. The selectively filled fiber is seen in the scanning electron microscope (SEM) image in Fig. B-2(c) with arrows pointing to alloy-filled holes. We have successfully fabricated several dozens of such long selectively filled PCF containing multiple 3.68 μm sized alloy electrodes with high yield. We further confirmed the electrical continuity of each filled electrode by measuring the resistance between the two ends at the fiber facet by using a pair of tungsten probes as illustrated in Fig. B-2(d). A 4cm long piece of the filled fiber electrode typically has
measured d.c. resistance of 1657Ω. Based on the reported conductivity of the alloy of 2.320 x 10⁶ S/m, the computed resistance of 1621Ω agrees well with our measured d.c. resistance. We note that following this method, we have also successfully patterned PCF with indium electrode which melts at higher temperature of 156.6 °C.

**B-2.2 Nano-tube attachment:**

As stated earlier, the proposed opto-electronic nanoprobe is designed to allow electromechanical probing at the nanoscale in addition to functioning as an optical waveguide. It is well known that carbon nanotubes (CNT) have several unique electronic and mechanical properties which make them suitable for this purpose. Multi-walled CNT (MWCNT) may be either metallic or semiconducting with a variable band-gap based on their chirality and diameter. CNTs can carry high currents without heating and are stiff and exceptionally strong [145]. Owing to their properties, CNT has been used in variety of applications as tweezers or probes [128, 130, 146-148]. In this section, we discuss our results with two different techniques of attaching CNT to the selectively filled PCF for fabricating our device.
Figure B-2: Pumping molten alloy through patterned PCF. (a) Schematic of oven showing a PCF held in a chamber. The inset shows cutaway of the chamber in which patterned pcf is held using PDMS and sunk in bath of alloy. (b) Filled PCF under 500 psi showing alloy leaking out as shiny blob from the other end held outside the oven at room temperature. (c) SEM image of a PCF with 3 holes filled with alloy. (d) Setup for checking electrical continuity and typical resistance of filled electrode (1657 ohms).

We note that the non-planar, circular geometry and small, uneven cross section of the patterned facet of the PCF precludes the use of conventional photolithography based techniques for fabrication of our device. Additionally, the small dimension and high aspect ratio of CNT poses unique challenges for achieving targeted attachment of individual CNT to each filled electrode while ensuring their correct alignment. Hence, we explored and developed two separate techniques for attaching individual CNT to each filled electrode of the fiber - (a) laser welding,
and (b) focused ion beam (FIB) and electron beam assisted deposition. Laser assisted fabrication of PCF and infiltration of MOF has been previously demonstrated as a useful technique, and so this approach was used first [149]. In the laser welding technique, a laser beam is steered to focus on the electrode using a 20x long working distance objective. To prepare the CNT sample, we sonicate a dispersion of CNTs (PECVD MW-CNT from NanoLab Inc. 200nm in diameter and about 20 µm long) in DI water in ultrasonic bath (Tru-Sweep 275DA, Crest Ultrasonics), and air-dry a small drop of the dispersed solution on a glass slide. A single CNT is then fished from the glass slide sample under a microscope using a fiber taper and is maneuvered to a PCF electrode using multiple 3D stages while the laser is incident, as shown in Fig. B-3(a). The schematic in the inset illustrates the process from the top view. The laser power is increased very carefully until the filled electrode melts only slightly due to absorption of laser energy to reflow and locally weld the CNT. A gentle tug on the delivery taper is enough to detach it from the welded CNT leaving it electrically welded with the electrode as shown in Fig. B-3(b). The same procedure is repeated for attaching each CNT to the electrode. It is important to monitor and control the laser power carefully since the heat may melt an adjacent electrode as well and may cause the CNT attached to it to re-align incorrectly or even detach.
Figure B-3: Laser welding process for CNT attachment. (a) Side view image of CNT just prior to being laser welded to alloy filled pcf. Inset shows the schematic top view illustrating the fiber taper used for delivery. (b) Laser welded CNT.

The increased risk of device failure associated with the laser welding method prompted us to investigate another technique for picking and targeted bonding of individual CNT using FIB. In this method, the CNT dispersion is air-dried on a TEM lacie carbon grid (Electron Microscopy Sciences LC-200 Cu). The CNT lying on the carbon mesh is attached using FIB assisted platinum deposition (FEI Helios NanoLab 660) to a fine tungsten probe (tip size ~500nm) (7.7 pA at 30 kV) with the CNT aligned correctly (Fig. 4(a) and 4(b)). It may be necessary to mill individual synapses of the carbon mesh which may be adhered to the CNT as the nanotube is lifted off the grid. The tungsten probe carrying the CNT is then navigated near the filled electrode and the CNT is bonded with the alloy using electron beam assisted tungsten
deposition (3.2 nA at 2 kV) (Fig. B-4c). After CNT attachment the probe is milled at its tip to release it from the CNT. We note that the fiber is coated with iridium (Emitech K575X) prior to using FIB to avoid charging under ion beam. In this way, we have fabricated many devices by sequentially attaching multiple individual CNT symmetrically around the solid core of the PCF to individual electrodes. Figure B-4d shows the ion beam image of such a typical fabricated device. We found that the yield of device fabrication was significantly improved using FIB owing to the controlled assembly in our pick and bond technique.

Figure B-4: FIB assisted CNT attachment. (a) CNT lying on lacie carbon mesh is bonded to 500 µm tungsten probe tip via Pt deposition. (b) CNT liftoff. Part of carbon mesh can be seen adhered to the CNT. Individual synapses need to be milled for ‘clean’ liftoff. (c) Sequential targeted attachment of CNT via e-beam assisted tungsten deposition. (d) Ion beam image of a three-arm device.

B-2.3 Device characterization:
In order to investigate the performance of the proposed opto-electronic nano-probe we performed both numerical simulation and experimental measurements to characterize the group velocity dispersion and electromechanical actuation. We first measured the refractive index and extinction coefficient of Ostalloy 158 by using a rotating compensator spectroscopic ellipsometer (M-2000, J.A. Woollam Co.). The alloy sample is an approximately 200 µm thin disk (shown in inset of Fig. B-5a that was prepared by melting a small drop of alloy over a glass slide and letting it reflow as it solidified on the slide. The disk was then carefully flipped over so that its smooth and un-oxidized underside is face-up and consistent ellipsometric data was measured in reflection geometry at multiple angles and from several locations on the disk. Figure B-5a plots the averaged refractive index and extinction coefficient over 600-1400 nm range obtained from the ellipsometric measurement.
Figure B-5. (a) The average refractive index and extinction coefficients of Ostalloy 158 obtained via ellipsometry of the inset sample, (b) simulation of the typical optical mode field for the unfilled PCF, (c) the mode field when three of the most center air holes are filled with Ostalloy

B-2.3.1 Group Velocity Dispersion

Using the experimentally measured conductivity of Ostalloy and the dispersion for silica modeled using the standard form of the Sellmeier equation,
\[ n^2 - 1 = \frac{0.6961663\lambda^2}{\lambda^2 - 0.0684043^2} + \frac{0.4079426\lambda^2}{\lambda^2 - 0.1162414^2} + \frac{0.8974794\lambda^2}{\lambda^2 - 9.896161^2} \]

and coefficients from [150]. We simulated the eigenmodes and effective mode index \( n_{\text{eff}}(\omega) \) of the selectively filled PCF in COMSOL. Figure B-5 (b-c) shows the simulated field distribution of the fundamental mode within the core of the bare as well as selectively filled PCF. The presence of the electrodes in close vicinity of the core along the entire length of the fiber slightly distorts the mode field distribution as can be seen in Fig B-5c. The group velocity dispersion of the PCF can be computed using \( D(\omega) = -\frac{\lambda}{c} \frac{d^2 n_{\text{eff}}(\omega)}{d\lambda^2} \). In this way by simulating the effective index for both the bare as well as selectively filled PCF, we numerically obtained the dispersion curve for each from 1.1 \( \mu \)m to 1.3 \( \mu \)m.

We also used spectral holography to experimentally characterize the group velocity dispersion of both the bare and selectively filled PCF. Spectral holography is a sensitive and linear optical technique to measure the relative spectral phase of the complex optical field [151]. For spectral holography a supercontinuum source with a broad spectrum (600-1600 nm) is generated via four-wave mixing by propagating sub-ns pulses at 1064 nm in a nonlinear PCF (SC-5.0-1040). The reference arm of the Mach-Zehnder interferometer shown in Fig. 6(a) consists of the supercontinuum beam delayed using a delay line. The ‘object arm’ consists of the PCF under test. By appropriately adjusting the delay line to obtain consistent and good quality fringes over the 1.1\( \mu \)m - 1.3\( \mu \)m wavelength region, we detect the spectral hologram of the field at the output of the PCF using an optical spectrum analyzer (Ando AQ-6315E). The spectral hologram can be modeled as

\[ |S(\omega) + R(\omega)|^2 = |S(\omega)|^2 + |R(\omega)|^2 + S^*(\omega)R(\omega) + S(\omega)R^*(\omega) \]

where \( R(\omega) \) is the reference field and \( S(\omega) \) denotes the output field from the PCF. Typical recorded spectral hologram is shown in Fig. 6(b). The spectral hologram contains information of the spectral phase in its interference fringes. Hence to extract the spectral phase, we compute the Fourier transform of the hologram and digitally filter the appropriate sideband. The inverse Fourier transform of the filtered
sideband yields the complex spectrum $S(\omega)R'(\omega)$. (See reference 131 for more details.) In order to remove the contribution due to the presence of other optical components in the ‘object arm’, we additionally obtain the spectral hologram in the absence of the fiber, and thereby calibrate the transfer function of the ‘object arm’. Taking the ratio of processed sideband terms of these two measurements, we can acquire the complex transfer function containing both the amplitude and the phase information of the selectively filled PCF. Fig. B-6(c) shows the typical relative spectral phase of the filled PCF. We believe that the noise in the relative spectral phase can be attributed to the fact that the low melting point Ostalloy is observed to exhibit plasticity during the measurement when exposed to focused laser light. This may lead to variation in the optical path in the object arm of the interferometer. Since the group velocity dispersion is obtained from the 2nd order derivative of the relative spectral phase, we smoothen the measured phase by fitting a curve with a 3rd order polynomial in Matlab. Finally we compute the group velocity dispersion values for D [ps/nm/km] by taking into account the length of the fiber used in the measurement. Thus following this procedure we experimentally obtained the dispersion parameter plot for both the bare (unfilled) and selectively filled PFC. Figure B-6(d) shows the comparison of the numerically simulated (solid lines) and experimentally obtained (dotted lines) curves for D for both such fibers. It also plots the manufacturer supplied data for D for the unfilled fiber (black line). Our results show that the selective metal filling does not damage the waveguiding properties of the unfilled PCF. In other words, the optical channel and electric channel in our device can be accessed without affecting the performance of each other. However we do note that the transmission efficiency of the selectively filled PCF can be significantly lower than the unfilled fiber, especially when the holes being filled are immediately adjacent to the central core [122].
Figure B-6: Group velocity dispersion for nano-probe with 3 filled electrodes. (a) Mach-Zehnder setup for spectral holographic measurement. (b) Typical recorded spectral hologram (c) Measured relative phase, and 3rd order polynomial fit, (d) estimated dispersion parameter for unfilled pcf (red dotted) and fabricated device (blue dotted). Corresponding COMSOL simulated dispersion for unfilled pcf (blue red line) and modeled device (solid blue line) are also plotted for comparison. The black curve is dispersion parameter for bare fiber as specified by manufacturer.
B-2.3.2 Electromechanical characterization

The ability to control the motion of multiple nanoprobe tips allows the possibility to mechanically interact with the sample under study as well as interrogate the sample electrically and optically. A basic requirement of such a nanoprobe device is the ability to actuate the probe tips to open and close them. Our proposed opto-electronic nano-probe consists of multiple CNTs attached to each filled electrode in the selectively filled PCF. To investigate this

Figure B-7. Electro-mechanical deflection of fabricated nano-probe. (a) Montage of 3 sequential frames from a video recording CNT deflection. The dotted line shows the trace along which intensity is plotted in (b) and (c). The markers in (c) indicate pixel positions of the ‘tip’ of the lower CNT in each frame.
ability in our device, we experimentally measured the deflection of the CNT tips by applying variable potential difference of up to 40V between the pair of electrodes. In particular, a pair of tungsten electrodes was positioned in place using three-dimensional precision stages in order to contact the two electrodes exposed at one facet of the filled PCF (without CNTs). We highlight the fact that each electrode was independently tested for its electrical continuity by measuring its d.c. resistance as mentioned earlier (see Fig. B-2d). The tungsten electrodes were connected to a signal generator to apply a manually variable dual polarity dc voltage (±20V) or generate a pure tone sine wave of ac amplitude 40V. Thus the CNTs connected at the other facet accumulated charges of opposite polarity and varying density as the voltage was varied and bent towards each other in response to attracting charges. We recorded a video of this motion of the CNTs on a CCD camera. Figure B-7(a) shows a montage of three frames in sequence from the recorded video in which the CNT deflection is visible. The observed range of nano-tube deflection was small. To help visualize the deflection, Fig. B-7(b) plots the line trace of the image along the line marked in each frame. We observe a deflection of the tip of the nanotubes of 2 to 3 pixels (note the pixel numbers in the magnified Fig. B-7(c)). The deflection is more pronounced in the lower CNT than the upper (in the frame). Accounting for the magnification of our imaging system, this corresponds to approximately 260 nm to 392 nm deflection.

To investigate the relatively small deflection of the nano-tubes, we numerically simulated the bending of the CNTs in a model of the fabricated device. We utilized the MEMS module of COMSOL Multiphysics to solve the coupled physical model based on structural mechanics and electrostatics. This involves modeling the CNT as an electrically conductive and linearly elastic material by specifying its physical parameters including density (ρ), Young's Modulus (E) and Poisson's ratio (ν). With the exception of the resistivity, which was measured experimentally, the physical properties of the CNT were chosen to be in between those of graphite and multi-walled
CNTs. These values are $\rho=2300 \text{ kg/m}^3$, $E=1.28 \text{ GPa}$, and $\nu=0.35$ respectively. The choice of Young's Modulus was most critical as this parameter varies several orders of magnitude (TPa to GPa) based on the number of walls and diameter of the CNT [152, 153]. We therefore chose the values noted above as being between those of bulk graphite and small MWCNTs. The length and diameter of the CNT in the simulations were chosen to be 20 $\mu$m by 200nm as an average of those used in the experiments. The accumulation of charge on the tips of the CNT in response to applied potential difference between the electrodes was verified through two different methods. Two dimensional simulations were performed, in which CNTs are embedded in a silica substrate and suspended in air. The first simulation was conducted in the time domain to verify the accumulation of charges at the tip rather than at an arbitrary point along the length of the tubes. Figure 8(a) plots the change in the space charge density at the tip of the CNT for ±20V applied to the electrodes. The charge accumulation at the tip follows the input triangle wave as expected. While only the magnitude of the charge accumulation at the tips is plotted, it was verified along the length of the probes to be greatest at the free ends. The second simulation was to verify that the deflection is a function of the instantaneous electrostatic force acting on the CNT tips as a result of charge accumulation. The bending of the CNT in response to the charge accumulation though a MEMS simulation in the steady state condition is illustrated in Fig. B-8(b-c). Fig. B-8(b) shows the CNT deflection as they are bent towards each other. The nonlinear displacement at the tips of the CNTs as a function of applied voltage in the simulation verifies that the deflection is due to electrostatic forces. Both the time dependent and steady state simulations thus indicate that accumulation of charge density at the CNT tip drives the electromechanical deflection of approximately 670 nm upon application of ±20V as shown in figure B-8(c). There is a reasonable agreement between the electro-mechanical deflection of the tip observed experimentally and that obtained from simulation. We highlight that a key difference between the PCF based opto-electronic nano-probe presented here and several devices reported in the literature is that the CNTs in our fabricated device are
spatially situated ~24 µm apart due to the use of PCF with 12 µm core, whereas most devices reported in the literature feature a separation of <2 µm [146-148]. This is the main reason why the deflection observed in the tips of the CNTs is less compared to typical performance reported on nanotweezers. We verified this inference by simulating more closely spaced CNTs with identical properties in COMSOL, which indeed shows a significant bending effect as the CNT separation is reduced. We believe that using a PCF with a smaller core size as the platform for filling and attaching the CNTs will result in improved performance. Another approach to improve the CNT deflection is to taper the fiber at one end so that the separation between the CNTs is much smaller.

Figure B-8: Numerical simulation results. (a) charge distribution at the tip of a CNT when a -20V ramp wave is applied to the terminal, (b) charge distribution along two CNTs with ±20V applied. The deflection of the CNT is indicated by the red line which marks the original position, (c) the tip displacement as a function of voltage applied to the electrodes within the PCF.

B-3. Conclusion:
We have introduced a novel hybrid optoelectronic nanoprobe device based on a selectively filled PCF. Our selective filling method involves use of UV curable optical glue to seal all PCF holes except the ones intended to be filled and then pumping molten metal under high pressure. We have demonstrated the method by filling electrically continuous electrodes made of a low melting point alloy as well as using indium metal. Furthermore, we presented two techniques for precise and targeted attachment of individual carbon nanotubes to each filled electrode, namely laser welding and pick and bond using FIB and electron beam assisted deposition. Our device can guide light and conduct electricity to potentially allow both optical and electronic probing capability to interrogate a nanoscale sample held in place by the attached nanotubes. Towards this aim we characterized the optical waveguiding property and movement control of the attached nanotubes by estimating the group velocity dispersion and the electrically actuated deflection of the CNT tips both experimentally and numerically, which agree well with each other. The concept of functionalizing a PCF to tune its properties by incorporating foreign materials in the air holes has led to the evolution of optical fiber as platform for fiber-integrated opto-electronics. On the other hand, development of electrically actuated nanotweezers has been recognized as an important step towards assembling complex nanostructures, and as an enabling technology for realizing nano-electro-mechanical and nano-robotic systems. While the device we have fabricated and presented here is elementary, it embodies the concept of combining fiber-based opo-electronic sensor with nanotweezers in a single package. We believe that this forward looking hybrid feature makes our device unique and warrants further development and research.

Acknowledgement: The authors acknowledge the support from the National Science Foundation (Grant # 1128587).
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