ARROW-Based On-Chip Alkali Vapor-Cell Development

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ARROW-Based On-Chip Alkali Vapor-Cell Development

John F. Hulbert

A dissertation submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

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ABSTRACT

ARROW-Based On-Chip Alkali Vapor-Cell Development

John F. Hulbert
Department of Electrical and Computer Engineering
Doctor of Philosophy

The author presents the successful development of an on-chip, monolithic, integrated rubidium vapor-cell. These vapor-cells integrate ridge waveguide techniques with hollow-core waveguiding technology known as Anti-Resonant Reflecting Optical Waveguides (ARROWs). These devices are manufactured on-site in BYU’s Integrated Microelectronic Laboratory (IML) using common silicon wafer microfabrication techniques. The ARROW platform fabrication is outlined, but the bulk of the dissertation focuses on novel packaging techniques that allow for the successful introduction and sealing of rubidium vapor into these micro-sized vapor-cells. The unique geometries and materials utilized in the ARROW platform render common vapor-cell sealing techniques unusable. The development of three generations of successful vapor-cells is chronicled. The sealing techniques represented in these three generations of vapor-cells include high-temperature epoxy seals, cold-weld copper crimping, variable pressure vacuum capabilities, indium solder seals, and electroplated passivation coatings. The performance of these seals are quantified using accelerated lifetime tests combined with optical spectroscopy. Finally, the successful probing of the rubidium absorption spectrum, electromagnetically induced transparency, and slow light on the ARROW-based vapor-cell platform is reported.

Keywords: John F. Hulbert, Aaron R. Hawkins, atomic vapor, vapor-cell, slow light, electromagnetically induced transparency, rubidium, electroplating, ARROW, indium, lab-on-a-chip, microfabrication, spectroscopy, waveguide, optic
I would like to dedicate my dissertation to my grandfather, Robert Eugene Hulbert, one of the greatest examples in my life and the first of many Hulberts dedicated to excellence in engineering.

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1 INTRODUCTION

1.1 Motivation

Alkali vapor-cells have been used extensively since the 1960’s in the study of light-atom interactions. As scientists came to better understand the underlying principles of such interactions and discover new optical phenomena, many device oriented applications have been theorized. Vapor-cell applications, both proposed and realized, include, but are not limited to, atomic clocks [1], communication system switches and buffers [2-4], single photon generators and detectors [5], gas phase sensors [6], nonlinear frequency generators [7], and precision spectroscopy instrumentation [8]. However, most of these applications have only been created in laboratory settings and the applications that have been deployed in real-world situations have not yet reached their full potential. What is the biggest obstacle? Vapor-cell size and integratability. Traditional vapor-cell systems are large, have many discrete components, and consume a large amount of power. To realize the full potential of vapor-cell-based technologies, the vapor-cells and supporting optics would best be miniaturized.

Imagine low-cost, low-power, monolithic, integratable, on-chip atomic vapor-cells used as atomic clocks allowing for precise GPS equipment in cell phones, small UAV’s, cars, automated farming equipment, and many more applications that have not been thought of yet. They could replace less accurate crystal oscillators (XO) as frequency generators in computing
and communication applications. Though fiber optics are ubiquitous in our current communications infrastructure, the benefits of optical communications are bottlenecked at every networking junction, or node, in which the optical signals are converted to electrical signals to allow for routing. Integrated vapor-cells could potentially alleviate these electrical bottlenecks by allowing the signals to be routed in the optical domain via all-optical communication buffers and switches. On-chip vapor-cells could also make the oft theorized quantum communication systems a reality as platforms for single photon generation, switching, and detection.

While the focus of my research was on developing an alkali vapor-cell, specifically rubidium, the vapor-cell technology outlined in this dissertation could readily be populated with many different types of vapors.

1.2 Current Vapor-cell Technologies

As previously discussed, the desire to create commercially viable devices using atomic vapor goes hand in hand with the drive to miniaturize the cells and integrate them in a compact photonic environment. Traditional methods of construction are limited in their scalability and versatility. This dissertation outlines my efforts in the creation of a monolithic, integratable silicon based on-chip alkali vapor (Rb) cell. To afford the reader a better understanding of my research I will outline some of the current vapor-cell technologies already in existence.

1.2.1 Bulk cells

As early as the 1960s scientists have utilized conventional atomic vapor-cells that I will refer to as ‘bulk’ cells [9]. These bulk cells are constructed entirely out of glass. The cells come in many shapes and sizes. However, bulk cells are generally shaped as cylinders with lengths on
the order of several inches or more and diameters of 1-2”. The two flat surfaces are aligned perpendicularly with the optical beam transmission path in order to decrease optical loss. The cells are created using glassblowing and a complex network of tubes, valves, and vacuums. The bulk cell is attached to the network via a narrow glass tube protruding from the cell and is evacuated to obtain the desired pressure (in the bulk cell we use, has a on the order of $10^{-5}$ Torr). An ampule of solid rubidium is connected to the vacuum tubing and heated, introducing vaporized rubidium into the cell. The bulk cell is finally sealed and separated by melting and twisting off the glass tube connecting the cell to the vacuum system. The bulk cell is then ready for optical experimentation.

These bulk cells are generally placed in large tabletop systems made with discrete optical components. Light is guided and focused into the cell using a system of free-space mirrors, filters, and lens. In some optical experiments multiple beams must propagate through the same tiny excitation volume inside the bulk cell, requiring complicated systems that are difficult to align. While these systems are nice for experimentation because of their highly configurable
nature and high-sensitivity, they are limited in their practical, device-oriented applications due to size and complexity.

![Image of a tabletop optical system.](image)

**Figure 1.2: Image of a tabletop optical system.**

### 1.2.2 Chip-scale vapor-cells

One of the most successful outcomes of the drive to miniaturize atomic vapor-cells has been pioneered at NIST [10]. The main goal at NIST was to create a miniaturized atomic clock, though the cells have other applications. The techniques and technologies developed have led to commercially available miniaturized atomic clocks that have already achieved exciting new capabilities in underwater exploration, UAVs, mobile communication, GPS navigation,
unmounted signal jamming, and small spacecraft [11, 12]. They can be as small as 1/30 the size and operate at 1/100 the power of conventional atomic clocks [12, 13]. They also demonstrate an accuracy improvement up to four magnitudes of order over traditional crystal oscillators while consuming 1/10 of the power [13]. One of the great strengths of this miniaturization approach is that it utilizes well-proven microfabrication techniques to efficiently create mass-producible, micro-sized atomic vapor-cells.

The NIST cell is made possible via a common MEMS-based fabrication technique known as anodic bonding (see Figure 1.3). Anodic bonding is commonly used to bond glass and silicon (Si) wafers together without the need for an intermediate bonding material. Anodic bonding requires the two bonding surfaces to be completely flat to ensure good uniform contact between the two surfaces. In the case of bonding a borosilicate glass wafer to a silicon wafer, the wafers would be clean and pressed together. The system would be heated to temperatures from 200 to 500 °C. Next a voltage on the order of hundreds of volts is applied across the wafers, the

![Figure 1.3: Illustration of anodic bonding procedure.](image-url)
cathode on the glass wafer, and the anode on the silicon wafer. The electrostatic potential across the wafers creates a migration of oxygen ions in the glass to migrate toward the silicon. At the interface they form an oxide with the silicon, bonding the two wafers together [14].

![Diagram of NIST chip-scale cell and fabrication procedure](image)

**Figure 1.4:** Illustration of NIST chip-scale cell and fabrication procedure [15].

NIST uses the anodic bonding to create a hermetically sealed vapor-cell (see Figure 1.4). This is done by first etching holes through a silicon wafer. These holes will form the hollow interior of the cell. The silicon wafer is then anodically bonded to an intact glass wafer, thereby creating a vapor-cell ‘preform.’ The holes are then populated with an alkali vapor, in this case cesium (Cs), one of two ways. The first is done by placing solid BaN₆ and CsCl in the preform cavities and then placing the preform in a high vacuum chamber. In the vacuum chamber the preform is heated to 120 °C which causes the BaN₆ to decompose into elemental barium (Ba) and nitrogen gas (N₂). Since the preform is in high vacuum, this leaves only elemental Ba and CsCl in the cavity. The vacuum chamber can then be backfilled with buffer gas to the desired pressure and the cavity is hermetically sealed by anodically bonding another glass wafer to the silicon. During the high heat of the bonding process, the elemental Ba reacts with the CsCl and
forms solid BaCl and elemental Cs. The second method employs the use of an oxygen-free chamber. Inside the chamber, liquid Cs is piped into the cavities. The preform is then placed in a bell jar where it is evacuated to the desired pressure and hermetically sealed with a glass wafer via anodic bonding. The wafer can then be cleaved into individual vapor-cells where the glass wafers form windows through which the vapor may be optically probed. The completed individual cells measure around 2 mm cubed.

In a fashion similar to NIST, a group of researchers at the University of Stuttgart have also made miniaturized vapor-cells using microfabrication techniques [16]. Their devices consist of cavities etched into the surface of a glass substrate with another glass substrate welded on top, the cavities forming the hollow vapor populated cell. The main advantage to this approach is the ability to create arbitrarily shaped and sized cavities, or even a network of interconnected vapor-cells depending on application requirements. While these cells successfully miniaturize atomic vapor-cell dimensions by using effective, well-proven fabrication procedures, supporting optics are still needed to guide and focus the light into and out of the cell.

1.2.3 Waveguide atomic vapor-cells

Another way some research teams seek to improve vapor-cell technology is to create a miniature vapor-cell that is also an optical waveguide. This allows for the decoupling of the optical beams’ spot size and its interaction length. In Gaussian optics [17, 18] the relationship between focal depth, \( \delta \), and beam width, \( w_0 \), is described as shown in Equation (1.1),

\[
\delta = \frac{2\pi w_0^2}{\lambda},
\]

where \( \lambda \) is the wavelength. As can be seen, the focal depth is proportional to the square of the beam width. Any increase in the focal depth results in an increase in the beam width and any
decrease in the beam width results in a decrease in the focal depth. The previously discussed atomic vapor-cells (bulk, NIST, and Stuttgart) all rely on free-space Gaussian beam optics in order to be probed. In vapor-cell applications that utilize optical nonlinear or quantum effects, it is desirable to have both a small beam spot size and a long interaction length (which in terms of Gaussian optics is the same as the focal length.) If the spot size is fixed, having a long interaction length is the only way to increase the excitation volume. Specifically, having a beam spot size similar to the absorption cross-section (as defined in Equation (1.2)) of the vapor being probed and a large optical depth \(\kappa\) (defined in Equation (1.3) where \(n\) is the atomic density, \(L\) is the interaction length, and \(\sigma\) is the atomic absorption cross-section) is necessary for low-level quantum interference effects and enhanced nonlinear effects [19-23].

\[
\sigma = \frac{3\lambda^2}{2\pi},
\]  
\[
\kappa = nL\sigma.
\]

As an example, let us consider the rubidium D2 transitions. The transitions take place at a wavelength of 780 nm which, using Equation (1.2), results in an atomic cross-section of 0.3 \(\mu\)m\(^2\). Therefore, for probing rubidium nonlinear effects, the beam waist radius would ideally be as close to \(\sim 0.3 \mu\)m as possible, which would correspond with an interaction length of 0.7 \(\mu\)m. The only way to maintain a small spot size and increase the interaction length is to create a vapor-cell that is also a waveguide. The beam spot size would then be confined to the waveguide dimensions throughout the entire length of the device. The interaction length would then only be limited by waveguide loss and acceptable device dimensions.
Generally, optical waveguiding is achieved by total internal reflection (TIR), a phenomena governed by Snell’s Law described in Equation (1.4) [17]. The law states that light can be confined in a material with an index of refraction (index) equal to $n_1$ surrounded by another material with an index of $n_2$ as long as $n_1 > n_2$ and the incident angle of the propagating light at the interface of the two materials is less than the critical angle, $\theta_{\text{crit}}$. Generally the higher index material is referred to as the core while the encapsulating, lower index material is called the cladding. Equation (1.5) defines the critical angle in terms of the two material indexes, $n_{\text{core}}$ and $n_{\text{clad}}$, as illustrated in Figure 1.6. If $\theta_i > \theta_{\text{crit}}$ then the light experiences TIR and continues to propagate in the core. However, if $\theta_i < \theta_{\text{crit}}$ then light will leak through the interface and propagate in the cladding, resulting in optical loss. If the waveguide is designed by properly utilizing TIR light can travel great distances exhibiting minimal loss. A great example of this is optical fibers used in the telecommunication industry that carry light signals for hundreds of miles.
\[ n_{\text{core}} \sin \theta_i = n_{\text{clad}} \sin \theta_t, \]  

(1.4)

\[ \theta_{\text{crit}} = \sin^{-1} \left( \frac{n_{\text{clad}}}{n_{\text{core}}} \right). \]  

(1.5)

What about situations where light needs to be confined in a low index media like air \((n=1)\)? Materials that exhibit an index of refraction less than 1 in the near-infrared and visible wavelengths are rare. In such cases, traditional waveguiding schemata that rely on total internal reflection are not applicable.

Figure 1.6: Illustration of total internal reflection and critical angle [25].

Figure 1.7: a) Illustrated transverse cross-section of hollow-core waveguide Bragg fiber and b) Scanning Electron Microscope (SEM) cross-section image of Hollow-Core Photonic Band-gap Fiber [25].
Creating a waveguide with a core comprised of atomic vapor (essentially air, hence \( n=1 \)) would be such a scenario. To successfully create integrated waveguide/vapor-cell devices, it is best to investigate other methods of optical confinement. One such method entails using interference-based cladding layers surrounding the hollow-core. This method utilizes periodic, partially reflective structures whose combined reflections interfere constructively. Each additional reflective cladding layer improves the confinement with total internal reflection achievable only by adding the partially reflective layers to infinity. The number of reflective layers added depends on how much loss is acceptable in the given application versus how many layers can be practically created before size and fabrication complexity become an issue. There are a number of ways these reflective layers can be created. Some reflective cladding layers are created using the Bragg reflection mechanism, which is created by combining different dielectric materials with unique indexes of refraction [26-29]. Another way the reflective layers are formed is with specially designed periodic geometric patterns [30-33].

Researchers at Cornell University and others have successfully created an integrated waveguide/vapor-cell device using hollow-core photonic band-gap fibers (HCPBF) [3, 19, 34, 35]. HCPCFs are fiber optic cables that confine light in a low-index hollow-core using interference-based reflective honeycomb shaped photonic structures built into the cladding as shown in Figure 1.7. The vapor-cell is created by connecting the two ends of the fiber to transparent cells connected to an active vacuum system and a rubidium source. Light is coupled into and out of the fiber through the vacuum cells on the end. These HCPCF based vapor-cells allow for small beam widths (several micron scale core radii) with interaction lengths that can easily be thousands of times longer than Gaussian optics would permit. However, the fiber is connected to bulky cells and an active vacuum system, making it difficult to integrate into a
miniature stand-alone device. There is still room for improvement in the field of miniature vapor-cells.
2 ARROW VAPOR-CELL APPROACH

This dissertation outlines a unique solution to integrated atomic vapor-cells. This approach combines the benefits of microfabrication seen in the NIST cells with the long interaction lengths achieved with the HCPBF vapor-cells. This is done by utilizing a planar, monolithic, integrated hollow-core interference-based waveguide platform known as an Anti-Resonant Reflective Optical Waveguide (ARROW).

2.1 Theory of Operation

The ARROW platform was originally developed at Bell Laboratories in 1986 [36, 37]. Like the HCPBF, light is confined in a hollow waveguide by reflective periodic structures surrounding the hollow-core. Unlike the geometric honeycomb patterns in the HCPBF, the ARROW utilizes paired layers of two different materials with unique, high-value indexes. In the ARROW platform created here at Brigham Young University (BYU), these pairs are created with silicon nitride (n=2.05) and silicon dioxide (n=1.46) [38]. Each nitride/oxide pair forms a highly reflective Fabry-Perot etalon that reflects most of the light back into the channel. By stacking these pairs together the loss is reduced by almost 70% with each additional pair. The nitride and oxide thickness have to be precise in order to create the constructively interfering
anti-resonant condition that causes the light to reflect back into the core. The thickness of the \( j \)th layer in the ARROW stack is defined in Equation (2.1),

\[
t_j = \frac{\lambda}{4n_j} (2M + 1) \left[ 1 - \frac{n_c^2}{n_j^2} + \frac{\lambda^2}{4n_j^2 d_c^2} \right]^{-\frac{1}{2}},
\]

where \( M \) is the anti-resonance order, \( n_j \) is the index of the \( j \)th layer, and \( n_c \) is the index of the core.

By carefully calculating the thickness of each ARROW layer (illustrated in Figure 2.1), a low-index core waveguide, albeit lossy, can successfully be designed.

![Figure 2.1: Illustration of a) generic ARROW interface b) longitudinal cross-section of hollow-core waveguide using ARROW cladding layers [25].](image)
2.2 Design and Layout

At the BYU Integrated Microelectronics Laboratory (IML) several teams work with integrated ARROW platforms. All these teams except mine utilize ARROW devices for liquid-core sensing experiments. Even though most liquids do not have indexes as low as air (for water $n=1.3$) they are still lower than most conventional waveguiding materials and as such liquid waveguiding experiments benefit greatly from the ARROW platform. Each of these teams have ARROW designs specific to the needs of their applications [39-43]. Even though the designs are similar and a lot of cross coordination goes into developing the ARROW platform, in this paper I will focus only on the designs used in gas-filled, or air-core, ARROW devices.

The BYU ARROW platform fully integrates solid- and hollow-core waveguides into one device [38, 44, 45]. This negates the need for traditional bulk optics and allows for the routing of optical signals on-chip, greatly reducing the size of the whole system. The ARROW design utilized in my research was referred to as the ‘s-mask’ design [see Figure 4.1]. This design consisted of a straight length of hollow-core 4 mm long with two perpendicular arms 2 mm long at each end pointing in opposite directions. This hollow-core design was called an ‘s-mask’ because of the general resemblance the hollow-core shape had with the letter ‘s’. Light is coupled into and out of the center 4 mm hollow-core length via solid-core ridge waveguides at each end. In our experiments the hollow-core is probed by coupling light into the solid-core ridge waveguide via fiber optic cable. The light then propagates down the solid-core waveguide into the hollow-core back into a solid-core waveguide and then is collected by a fiber optic cable that carries the signal to a photodetector. The end of each hollow-core arm is open to allow for (a) the sacrificial core material removal (more on this later) and (b) the introduction of gases.
The hollow-core cross-sectional dimensions are 12 µm wide by 5 µm tall. The hollow-core is surrounded by 3 silicon nitride/silicon dioxide etalon pairs, 6 layers in total. The 6 layer design was chosen as the ideal compromise between lowering optical loss and increasing fabrication complexity. The hollow-core has 4 sides. The top and the two side walls are surrounded by air whereas the bottom hollow-core surface rests on the silicon substrate. Due to silicon’s high index of refraction (n=3.5), this interface is the most lossy and the ARROW layers that separate the hollow-core from the silicon substrate, referred to as the ‘bottom layers’, are critical in decreasing the overall waveguide loss. This is not to say that the layers that form the top and sides of the hollow-core, referred to as ‘top layers’, are not important, but even when all the layers meet design specifications, the top layers will experience less loss than the bottom ARROW layers. Since the top layers and bottom layers interface with different media (top layer -> air, bottom layers -> silicon), it follows that they will have different stack designs [see Table 1].

Two different designs were used to create vapor-cells: planar ARROW design and self-aligned pedestal (SAP) ARROW design [46, 47]. The planar design placed the hollow-core on a flat silicon substrate. The SAP design raises the hollow-core 5 µm off the silicon substrate on a pedestal (see Figure 2.2). The planar design was used early in my research but was later replaced by the SAP because of its benefits. The first benefit is that the SAP design improves structural yield. Because of shadowing effects in our PECVD processes, the deposited films at the base of vertical structures form a seam. In the case of the planar ARROW design, this seam was formed at the bottom corners of the hollow-core. This seam formed a natural weak spot and was the cause of many structural failures. On the SAP design, the seam is formed at the base of the pedestal. In this case the side top layers have 5 µm of the pedestal side wall to adhere to,
thus allowing for better structural integrity. Out of the wafers that were fabricated for air-core applications during my investigations, the planar design saw a ~20% structural yield while the SAP design saw ~85% structural yield.

![Figure 2.2: Transverse cross-sections of hollow-core ARROW waveguides. a) Illustration of planar ARROW, b) Illustration of SAP ARROW, c) SEM of planar ARROW, d) SEM of SAP ARROW.](image)

The second improvement realized by the SAP design was improved optical loss. The combined top layer thickness of the planar design are over 75% of the total height of the hollow-core. This means that in reality the side ARROW layers of the hollow-core are not surrounded by air alone, but in fact, a significant portion is surrounded by top ARROW layers in the horizontal direction (see Figure 2.3). This caused a greater optical loss as some of the light was coupled into those top layers. However, the SAP design raised the hollow-core above the height of the top layers such that the sides of the hollow-core were surrounded by air, decreasing the optical loss [47]. While the SAP design introduced an extra level of complexity in the device
fabrication process, the improvements in structural yield and optical loss led to the retirement of the planar design in our experiments.

![Figure 2.3: Illustration of side wall optical loss for a) planar and b) SAP hollow-core waveguide geometries.](image)

The aforementioned solid-core waveguides that couple light into and out of the hollow-core are ridge waveguides, often referred to as ‘ridges’. Ridge waveguides are 3D, rectangular structures that protrude from a planar substrate. The light is horizontally confined to the region below the ridge due to a drop in the effective index of refraction on either side that is caused by the lower height of the material [48]. In our ARROW design, the ridge is etched into the thick top silicon dioxide layer and is confined below by the reflecting ARROW layers. To maximize coupling efficiency, the ridge width shares the same width as the hollow-core (12 µm) and the ridge height is half of the total top oxide thickness [49]. The ARROW optical mode FWHM area is 8.6 µm² [50]. The interface between the hollow-core and the solid-core waveguides is a major source of optical loss. First, the light has to pass through ARROW layers, and second, the seam at the base of the hollow-core caused by the shadowing effect mentioned earlier causes a sort of pinch-off loss effect on the light. Recently there have been some investigations into ways to reduce this loss [39].
2.3 Fabrication Processes and Terminology

A significant portion of this dissertation will reference common microelectronic fabrication processes performed in the BYU Integrated Microfabrication Laboratory (IML). This section will discuss and review important processes, machines, and terminology to provide the reader with a sufficient reference knowledge to follow the techniques proposed in this dissertation. For an in-depth discussion of the development of the ARROW fabrication process, I recommend reading the work of my colleague Evan Lunt [25].

2.3.1 Cleanroom

The IML is a cleanroom facility. A cleanroom is an enclosed facility where a low level of environmental contaminants is maintained. Such contaminants include chemical vapors, airborne microbes, dust, and other aerosolized particles. The process run in cleanrooms, such as micro and nano-scale fabrication and experiments would be catastrophically destroyed by the presence of even just one dust particle in the wrong spot. This environment is maintained by constantly cycling the air through filters to remove the contaminants. Many cleanrooms also maintain a positive pressure. This means any leaks between the cleanroom and the outside environment will flow outward, preventing the unfiltered outside air to flow in. Personnel who conduct operations inside the cleanroom don protective suits (sometimes called ‘bunny suits’), boots, gloves, goggles, and sometimes masks before entering. This clothing is not to protect the wearer but to protect the environment from the wearer. Without the protective clothing the wearer would introduce contaminants into the environment; dust from clothes and shoes, dried skin flakes, grease from hands, and aerosolized particle via the mouth and nose. Cleanrooms are classified by the amount and size of particles found in the air per unit volume. The BYU IML is
a class 10 cleanroom by Federal Standard 209E; this correlates with a class 4 via International Standards Organization TC 209 standard. This means that there are fewer than 10 particles per cubic foot. Most of the fabrication processes for our ARROW-based vapor-cells take place in this environment.

2.3.2 Photolithography

Photolithography, often shortened to ‘lithography’ or ‘photo’ within the microfabrication community, is a means to image a pattern onto a silicon wafer’s surface using photoresist (PR). Photoresist is a light-sensitive polymer-based material that can be applied in a viscous, liquid state onto the wafer that is later hardened via curing. The photoresist itself can act as a permanent part of the device structure or, more commonly, acts as a mask for the following processes. After the photoresist pattern is imaged onto the wafer, an inverse of the image can be etched into the underlying substrate by placing it in a chemical or by building on top of the surface by depositing a new material. By concatenating multiple lithographic patterns with other processes like etching and material deposition, complex geometrical patterns and structures can be created on the surface of the silicon wafer [51, 52].

Multiple ways exist to deposit photoresist, but in the IML we primarily use the spin-on method. The wafer is sealed to a chuck via a vacuum. A small pool of photoresist is poured onto the center of the wafer. The chuck is pre-programmed to spin at a certain speed (~100 to 6000rpm), acceleration, and duration. While the chuck spins, the centrifugal force spreads the viscous photoresist from the center to the edge, leaving behind a uniform layer of photoresist on the wafer. By changing the spin speed and duration, the final layer can be altered to have the desired thickness (within the physical limitations of the photoresist).
Next the wafer is placed in a mask-aligner machine to apply the desired image or pattern onto the photoresist. The image will be generated by using a specific ‘mask’ and UV light. A mask is a transparent glass slide with patterned metal one side. The mask is aligned to the wafer and the two are brought together. After alignment the wafer is ‘exposed’ that is, the aligned mask and wafer are placed under a UV light source. The UV light will expose all the photoresist that is not shielded by the metal patterns on the mask. The photoresist exposed to UV light will become chemically altered, resulting in its becoming either soluble or insoluble to a specific chemical solution called a ‘developer’. There are two main categories of photoresist; positive and negative. Positive photoresist starts insoluble and becomes soluble when exposed to UV light while negative resist starts soluble and becomes insoluble when exposed. The wafer is placed in the developer and the soluble photoresist is removed leaving behind the desired pattern. Often the developing process leaves behind organic residues on the exposed wafer surface. Quick ‘descum’ cleans in oxygen plasmas are almost always employed following photoresist development to provide a clean surface for the following processing steps. At this point the photoresist is either left to stand as part of the device structure or used as a mask for a subsequent etching or material deposition process. Except in rare cases, photoresist is generally used as the latter. If the photoresist was used as a process mask, the photoresist at some point is no longer needed and is removed, typically with a solvent or acid. Figure 2.4 illustrates the photolithographic process flow to create a pattern atop a silicon dioxide layer using a positive photoresist.
2.3.3 Wet etching

In microfabrication, etching is the controlled removal of material. There are two basic types of etching, wet etching and dry etching. Wet etching consists of placing a wafer into a liquid solution where a chemical will react with a given material removing it from the wafer. Dry etching refers to processes where material on the wafer surface is removed by exposing it to

---

Figure 2.4: Illustration of a basic photolithography process flow used to etch a pattern into a silicon dioxide layer.
reactive gases, bombarding particles, or combinations of both. We will briefly discuss both etching processes.

I will use wet etching to illustrate an importance concept in microfabrication referred to as ‘selective etching’. Selective etching forms the backbone of a masked etch process. The chemistry of a selective etch is specially designed to etch a target material while not (or at least very slowly) etching other materials present. This is often how photolithographic patterns are transferred from the resist to the underlying material. In this way the geometry of individual materials and layers present on the wafer can be individually dictated. For example, in Figure 2.4 step e) the oxide that was removed could have been removed using a Hydrofluoric (HF) wet etch. The wafer with the developed photoresist pattern in step d) would be placed in a HF etch bath. The photoresist protects the oxide underneath while the HF removes the oxide left exposed. The HF selectively etches only the oxide and does not etch the photoresist or silicon underneath allowing for the precise control of the device geometries.

One major downside to wet etching is that during the etching and follow-up rinsing process, the wafer will likely come into contact with water necessitating a dehydration bake afterwards. A dehydration bake is a bake done at a high temperature (some common temperatures being 120, 150, and 200 °C) with the goal being to remove adsorbed water from the wafer surface. The presence of water on the surface changes the surface properties and can adversely affect the adhesion of subsequent material depositions. The other disadvantage to wet etching (and arguably the most important), is that wet etches tend to be isotropic. A generalized definition of an isotropic etch is that the material etches in all directions whereas an anisotropic etch etches at different rates depending on the direction. An ideal anisotropic etch would only etch in one direction allowing for precise patterning. Figure 2.5 illustrates a potentially adverse
consequence of isotropic etching know as undercutting. Undercutting is horizontal etching that under cuts the protective mask layer. Undercutting is especially harmful in cases where the etch must be deep and the walls straight. It can therefore be advantageous to find an alternative to wet etching (a) if materials included on the wafer cannot withstand a high dehydration bake temperature, (b) to cut out the dehydration bake process and thus reduce the total process time, or (c) to limit the effects of undercutting. The alternative to wet etching is dry etching.

![Figure 2.5: Illustration of isotropic and anisotropic etching.](image)

### 2.3.4 Dry etching

The most common dry etching machines are called Reactive-ion etchers (RIE) or ‘plasma’ etchers. Plasma etching is the removal of material by exposure to a reactive plasma [53, 54]. Plasma is a collection of ionized matter in a state similar to gas. Plasma is generated by exposing a low-pressure gaseous mixture of chemicals to a high-energy RF field. This field
strips the molecules of their electrons and creates a gaseous ionic mixture, or plasma. Based on the machine configuration and recipe, different etching mechanisms may occur in a plasma etcher. All of these mechanisms are volatile, meaning the byproducts vaporize, thus removing material from the wafer. The active vacuum system then removes these byproducts from the chamber.

![Diagram showing four types of plasma etching mechanisms: chemical, sputtering, ion-enhanced energetic, and inhibited ion-enhanced.]

**Figure 2.6: Four types of plasma etching [25].**

As shown in Figure 2.6, there are four basic plasma etching mechanisms: chemical, sputtering, ion-enhanced energetic, and inhibited ion-enhanced. The chemical mechanism refers to when the plasma chemistry reacts with wafer surface forming a volatile by-product removing material from the wafer. This mechanism tends to be isotropic in nature and is a more selective etch, very similar to a standard wet. Sputtering comes about when an ion is accelerated toward the wafer surface by an electric field with enough kinetic energy to dislodge, or sputter, matter. Because of the directionality of the electric field this etching mechanism is anisotropic and less
selective in nature, i.e. it etches all of the materials present on the wafer. Ion-enhanced energetic etching is essentially the combination of both the chemical and sputter mechanisms. This combination results in an etch that is both isotropic and anisotropic. By altering the process parameters, often collectively called the ‘recipe’, the ratio of isotropic to anisotropic etching can be raised or lowered as needed by the application at hand. Inhibited ion-enhanced etching is the same as the last except as the etch progresses, material is deposited on the sidewalls to stop isotropic etching from progressing horizontally. The Bosch etch is a common form of inhibited ion-enhanced etching [55]. This method allows for deep anisotropic etching without the fear of undercutting. Understanding these basic mechanics of plasma etching and how they affect your design is an important part of becoming adept at microfabrication.

Figure 2.7: Diagram of basic parallel-plate plasma etcher [25].
A basic plasma consists of two parallel plates in a vacuum chamber. Gas is introduced into the chamber and an RF potential is put across the parallel plates to create a plasma. Figure 2.7 illustrates the basic design of a plasma etcher. All of the plasma etchers used in the IML for the creation of ARROWs use 13.56 MHz RF generators, a standard industry frequency.

Three plasma etchers in the IML are typically used in the creation of ARROW devices. The first of these is the Planar Etch II (PE2) by Technics, Inc. The PE2 is a very simple plasma etcher that is well described by Figure 2.7. Because of a lack of a voltage bias across the two RF plates there is no directionality in the plasma and therefore very little of a anisotropic component to the etch. As such the PE2 etch is a chemical etch and isotropic. In the IML the PE2 is used as an oxygen descuming or ashing machine. Wafers are placed in a non-directional oxygen plasma to clean surfaces of any photoresist residues leftover from development. Since the descum etch is meant to clean surface contamination and not remove any bulk material the durations are generally pretty short, anywhere from 30 to 90 seconds. This process is probably the most common and widely used plasma etch in the IML.

The second commonly used plasma etcher in the IML is the Anelva RIE (Anelva) by Anelva Corporation. The Anelva is a type of reactive ion etcher (RIE). The layout of this machine is very similar to Figure 2.7 except the top RF electrode is larger than the bottom electrode. The difference in size creates a bias potential across the two electrodes. The bias provides a directional sputtering component to the etch. This means that a RIE is capable of creating anisotropic etches. Even though there will always be an isotropic component to the etch, a specially designed recipe will minimize the effects such that the anisotropic etching component dominates. This allows for near straight-walled etches, especially for shallow etches. The Anelva was used to etch ridge waveguides into the ARROW surface and to open up the ends.
of the hollow-core waveguides. Both of these etches work by etching through the top ARROW layers comprised of silicon dioxide and silicon nitride. The Anelva was phased out of ARROW fabrication process after the arrival of a relatively new plasma etcher called the Trion.

The Trion ICP/RIE by Trion Technology is an inductively coupled plasma (ICP)-RIE hybrid etching system. The benefit of the Trion system over the Anelva, apart from having automated controls, is that it allows for greater control over the anisotropic to isotropic etch component ratio. The chamber is split into two regions. The first region is surrounded by a coil that inductively creates a plasma. The second region is the typical RIE parallel plate configuration that generates a DC potential to accelerate ions toward the wafer to provide the anisotropic etch profile. This dual configuration decouples the plasma density from the bias potential, thus allowing for greater control of the etch profile: in a traditional RIE system these two properties are linked. In terms of ARROW fabrication, it means that our ridge walls can be straighter and our etching times are faster.

![Figure 2.8: Illustration of wafer topography with a) a low aspect ratio and b) a high-aspect ratio.](image)

The Trion’s configurability also allowed for new processes and therefore new ARROW designs. One of these new designs was the self-aligned pedestal that was discussed earlier. This
design was enabled because of a deep silicon etch process run in the Trion. This process was
developed and patented by Robert Bosch and is known as the Bosch process [55-57]. This
procedure is known as a high-aspect ratio etch, where the aspect ratio is the height of a feature
over its width [see Figure 2.8]. A high-aspect ratio etch allows for deep etches with straight
walls and minimal to no undercutting. This means that the etch must be very anisotropic in
nature. This high-aspect ratio etch is achieved by alternating etch and passivation processes as
illustrated in Figure 2.9.

![Figure 2.9: Bosch etching process illustration.](image)

An etch process is run for a short time, and then a passivation process is run that deposits
a chemically inert material on the wafer. This coating is sometimes referred to as the etch
inhibitor film. Then an etch process starts again. The directional ion bombardment removes the
passivation layer on the horizontal surfaces and continues to etch while the vertical surfaces keep
the passivation layer, which prevents undercutting, or horizontal etching, from occurring. These steps are repeated until the appropriate etch depth has been reached, at which point the inhibitor and photoresist films are removed leaving behind a deep etch with straight walls.

Figure 2.10: Illustration of sacrificial etching used to create ARROW hollow-core. Perspective is a transverse cross-section of hollow-core waveguide.

Sacrificial etching is another important etching term. Sacrificial etching relies on selective etching but refers to the practice of using a sacrificial material as a temporary form to
allow the formation of a permanent structure. It can be thought of as falsework, like concrete forms, for the microfabrication world. Once the desired structure has been fabricated, the wafer undergoes a selective etching process that removes the sacrificial material and leaves behind the desired architecture. Sacrificial etching is especially prominent in microelectromechanical systems (MEMS) where structures and free-moving mechanisms are created. In our ARROW devices sacrificial etching is used to create our hollow-cores. A photoresist is deposited and defined using photolithography in the exact dimensions of the region we want to be hollow at the center of our hollow-core waveguides. The silicon dioxide/nitride walls and roof of the hollow-core are deposited over the photoresist ‘falsework’ and then the photoresist is removed, leaving behind a hollow-core waveguide as shown in Figure 2.10.

### 2.3.5 Material deposition

The previous section about etching revolved around processes that remove material from the surface of a wafer, but what if material needs to be deposited on the wafer? Two of the most common deposition methods are physical vapor deposition (PVD) and chemical vapor deposition (CVD). The PVD method relies on vaporized material condensing on the surface of the wafer while CVD is a chemical reaction between introduced gas-phase precursor materials and the wafer surface. Many different types of PVD and CVD machines and methods exist in the microfabrication industry, but I will only mention the two that are used in the IML in the creation of the ARROW platform: the electron beam PVD (EBPVD or e-beam) and the plasma enhanced CVD (PECVD).
Before we discuss the specifics of the IML deposition machines, let me introduce two important microfabrication deposition terms: uniformity and conformality (see Figure 2.11). Uniformity describes how uniform the process is across the surface of the wafer. If, for example, a process deposits silicon dioxide on a wafer and the oxide thickness in the center is the same as the oxide thickness at the edge, then the film is said to be uniform. If, however, there is a difference between the thickness at the center and at the edge than the film is non-uniform. The conformality of a process can be thought of as describing the uniformity of a process across the horizontal and vertical surfaces of the features on the wafer. Let us assume that there is a ridge etched into the silicon substrate of a wafer and we deposited silicon dioxide onto the wafer surface. If after inspecting the oxide thickness, we found that the thickness on the top of the ridge (horizontal surface) was the same as the thickness on the sides of the ridge (vertical surface), we would call the film conformal. If, however, the thickness on the top was different than the thickness on the sides, then the film would be non-conformal. I introduce these terms
now because they are important properties of deposition methods to be aware of. PVD processes tend to be directional, particles are emitted from a source and travel in a straight line to the wafer surface. This generally results in non-conformal coatings. Pure CVD processes allow wafers to sit in a gaseous ‘soup’ of chemicals that react on the wafer surface to form the film; this results in a more conformal film. Depending on the end applications, understanding the properties of the different processes can be critical.

The EBPVD at the IML is a Denton E-beam Evaporator by Denton Vacuum. A generalized illustration of an e-beam chamber is presented in Figure 2.12. A wafer is mounted to a rotating wafer mount known as a planetary, which is located at the top of a vacuum chamber. The source material, the material being deposited, is placed in a crucible at the bottom of the chamber. In the IML we routinely use carbon crucible liners since many different materials are deposited in the Denton e-beam. This negates the need for arduous post-run crucible cleaning, allowing for quick transitions from one metal to another. The chamber is evacuated to high vacuum, in our procedures < 5.5x10^{-6} Torr. High vacuum allows for a long mean free path inside the chamber. Mean free path is the average distance a particle can travel without a collision with another particle. A long mean free path is needed in PVD systems to allow for the evaporated particle to travel from source to target unperturbed. This allows for efficient, uniform, high-quality depositions. An electron beam is focused on the source material causing it to heat and evaporate. The evaporated material travels line of sight until coming into contact with the wafer surface where it condenses, coating the wafer. To improve the uniformity of the coating, the wafer is placed on a rotating axis called the planetary. The planetary rotates in the chamber to avoid any chamber/spatial-dependent irregularities in the metal vapor density profile.
There are two PECVD machines in the IML. One is dedicated to silicon dioxide growth and the other to silicon nitride. PECVD films are not the highest quality CVD films. Low-pressure CVD (LPCVD) process yields high-quality films. The difference is determined by how energy is put into the system to encourage the desired chemical reactions. LPCVD systems use high heat (600–900 °C) to create the chemical reactions while PECVD systems introduce energy via RF fields that create reactive ions. PECVD films are generally more porous and have higher defect densities leading to lower dielectric breakdown thresholds and less thermal stability than their LPCVD equivalents. Heating the wafer substrate to a high temperature is the better method; however, not all common microfabrication materials and device geometries can survive such high heat, and therein lies the main advantage to the PECVD process. They can be used to deposit thin films at low temperatures. The IML PECVDs are both custom-built models that
follow the same general design as outlined in Figure 2.13. One will notice that the design is similar to a plasma etcher, the main difference being in the plasma chemistry. Instead of the plasma containing chemicals that react with the surface, resulting in a volatile product, the chemistry is such that plasma precursors react with each other and the wafer surface to form an adhered solid. Also note that the RF field adds a directional component to the deposition process. This means that PECVD depositions tend to be less conformal than a ‘pure’ CVD process like LPCVD; however, the process recipe can be adjusted to change conformality of the film.

![Diagram of a generic PECVD machine](image)

**Figure 2.13: Illustration of a generic PECVD machine [25].**

This concludes the description of the common fabrication processes used in the IML. Other processing is available in the IML, but this section has covered the processes most commonly used in the construction of vapor-cell technologies. While these descriptions were
brief overviews, they should be sufficient to allow the reader to understand the processing and research outlined in the remainder of this document.

2.4 **ARROW Fabrication Process**

The following section will outline the typical fabrication process of a Self-Aligned Pedestal air-core ARROW. It is important for the reader to recognize that the presented process was the best-known process at the conclusion of my time at BYU. There have been many past iterations, and likely many future iterations, that differ in aspects that affect both the structural and optical yields and vary in their efficiencies. However, they have all been very similar in both design and function. Also, note that most illustrations representing ARROW waveguides in this dissertation are not to scale to allow for better visibility of device features.

![Fabrication Process Diagram](image)

**Figure 2.14: Steps 1 through 3 of SAP air-core ARROW fabrication process.**

Fabrication starts with a bare 100mm silicon wafer. The wafer is cleaned with a 20 minute soak in 90 °C Nanostrip as a general organic and metal clean, followed by a quick dip in
HF to rid the wafer of any accumulated oxide, followed by a deionized (DI) water rinse. The wafer is now ready for the bottom silicon nitride and silicon dioxide layers. The alternating layers are deposited using PECVD machines (see Table 1 for thicknesses). The bottom layers will form the optical ‘mirror’ in between the silicon substrate and the hollow waveguide. Because of the relative high index of refraction between the silicon and air these layers are arguably the most sensitive to any error in thickness or index. As such, depositions on test wafers monitoring the index of refraction and the deposition rate are run in between each layer to ensure the highest accuracy possible.

<table>
<thead>
<tr>
<th>Bottom ARROW Layers</th>
<th>Top ARROW Layers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Name</strong></td>
<td><strong>THK (nm)</strong></td>
</tr>
<tr>
<td>Oxide 1</td>
<td>920</td>
</tr>
<tr>
<td>Nitride 1</td>
<td>110</td>
</tr>
<tr>
<td>Oxide 2</td>
<td>184</td>
</tr>
<tr>
<td>Nitride 2</td>
<td>110</td>
</tr>
<tr>
<td>Oxide 3</td>
<td>184</td>
</tr>
<tr>
<td>Nitride 3</td>
<td>110</td>
</tr>
</tbody>
</table>

After the bottom layers have been deposited the next step is to form the sacrificial core that will form the hollow-core waveguide. In order to form a hollow-core surrounded by the ARROW layers a sacrificial material must be used to create a mold of the core. In our process we use a photodefinable epoxy produced by Microchem called SU-8 [58]. The main benefit of SU-8 is that it can withstand high temperatures without deforming or reflowing. One of the downsides of SU-8 is the relative long amount of time it takes to remove in comparison to most photoresists. The SU-8 is spun on and then defined as a 12 µm wide by 5 µm tall core as
previously mentioned using standard lithography techniques. Even though SU-8 does a remarkable job maintaining its shape at high temperatures, some deformation and shrinking are always expected when heating photoresists. To prevent any deformation while the top layers are grown and to provide a stable base until the top layers are strong enough to support themselves, the SU-8 must first be cured. Since the top PECVD layers will be deposited at a temperature of 255°C, the wafer with the defined cores are placed on a hotplate at the same temperature for 30 minutes and then cooled to room temperature. A quick O₂ plasma descum is recommended immediately preceding the cure to remove any residues left over from SU-8 development and to ensure a clean surface for future depositions.

Now come the steps that are used to create the SAP. As described earlier the underlying motivation of this step is to put the hollow-core waveguide up on a pedestal to improve optical loss. Since core dimensions are so small it is practically impossible to align the core to a previously defined pedestal. That is why the SAP method was developed by my colleague Evan Lunt, it uses the core itself as the etch mask that defines the pedestal. To properly etch the pedestal there are two regions we need to protect: the top of the SU-8 core and the areas where the ridge waveguides will be created in the future. While the SU-8 core could act as an etch mask by itself, it was found that the pedestal etch roughened the top surface. This surface roughness ultimately led to an increase in optical loss. As such, we coat the very top of the SU-8 core with a 100 nm coating of metal, generally either nickel (Ni) or chromium (Cr). The other consideration that needs to be made is that the ridge waveguides must be on the same plane as the hollow-core waveguide if they are to effectively couple light into and out of the hollow-core. As such the regions where the ridge waveguides will ultimately be placed are also protected with the metal etch mask during the pedestal etch.
The creation of the pedestal etch mask is a little different process than your standard photolithography step so I will briefly outline the process. The process is referred to as the “lift-off” process and is illustrated in Figure 2.16. First, photoresist is spun on and the regions where the ridge waveguides will be is patterned by full exposure to UV light. So far this is a standard photolithography process. Now comes the deviation. The entire wafer is lightly exposed to UV light for several seconds. This means that the patterned regions will develop quickly while the rest of the photoresist will slowly etch in the developer. The wafer is developed until a) the photoresist has been completely removed from the ridge waveguide regions and b) the photoresist across the wafer has been removed until just the top of the SU-8 sacrificial cores are exposed [see Figure 2.15 (S4)]. With the photoresist patterned and developed the exposed surfaces are cleaned with a quick oxygen plasma descum. Then 100 nm of metal (Cr or Ni) is deposited onto the wafer. We want the metal coating to be non-conformal to allow for better lift-off. The-lift off process relies on there being no metal on the side walls of the photoresist. When the wafer is placed in a dish of acetone the exposed photoresist sidewalls are etched away.
The acetone continues to remove the photoresist from under the metal until the metal is no longer attached to anything and is lifted off the surface.

![Illustration of lift-off sequence]

Figure 2.16: Illustration of lift-off sequence. a) Photoresist mask. b) Non-conformal metal coating deposited on wafer. Photoresist side walls exposed to acetone. c) Acetone has removed photoresist and “lifted-off” the metal.

Only the metal that was deposited on the exposed wafer surface is left unperturbed. The wafer is removed from the acetone bath and given a final clean with a fresh acetone and IPA rinse. This results in the metal mask seen in Figure 2.15 (S6). The bottom ARROW layers are removed from all unprotected regions using a standard fluorine based plasma etch following which a Bosch etching process is used to etch the silicon until the top of the SU-8 core is 10 µm higher than the surface of the silicon substrate as seen is Figure 2.15 (S7). The metal mask is
removed using metal etchant after which the pedestal formation is complete [see Figure 2.17 (S8)].

![Metal Mask Removed](S8)

![Top ARROW Layers Deposited](S9)

![Ridge Waveguides Etched](S10)

![Core Ends Exposed](S11)

**Figure 2.17: Steps 8 through 11 of SAP air-core ARROW fabrication process.**

The top oxide layers are then grown over the SU-8 core. These layers form the top and side optically confining surfaces in the hollow-core. My colleagues who fill the ARROWs with liquid can get reasonable optical confinement in the core with only a single, thick silicon dioxide film. This is because of the natural confining benefits of propagating light through water, with an index of 1.33, surrounded by air, with an index of 1 [39]. However, since in my air-core application we are essentially trying to confine light in air surrounded by air, it is critical to form the reflecting oxide layers on the top and sides as well. These top ARROW layers are again deposited using the PECVD machines. This application is really where PECVDs excel. Since we are depositing these layers over the SU-8 sacrificial core we cannot use other CVD processes which require high temperatures because this would destroy the SU-8. The PECVD allows us to deposit the silicon oxide and silicon nitride layers at a relatively low temperature of 255 °C, which is low enough to not adversely affect the SU-8. These layers are deposited in the same
fashion as the bottom layers except different thickness are used [see Table 1 and Figure 2.17 (S9)].

After the top layers are deposited, the solid-core (ridge) waveguides that couple light into and out of the hollow-core are formed. This is done by forming an SU-8 etch mask on top of all the layers using standard lithography steps. A ridge half the height of the top oxide is etched into the top oxide using a fluorine based plasma [see Figure 2.17 (S10)]. The SU-8 ridge etch mask is then removed using piranha.

At this point the hollow-core waveguide is still not hollow, the SU-8 sacrificial core is still inside. Also, the hollow-core region is completely enclosed. In order to a) etch the SU-8 core and b) have access to the hollow-core to allow for Rb population, the ends of the hollow-core channel need to be exposed. You will notice in Figure 2.17 that there are two branches coming off perpendicularly from the hollow-core waveguide. A 150 nm chrome etch mask is created to protect the hollow-core waveguide and ridge waveguides. Only the very tip of the hollow-core channel arms are left unprotected by the chrome etch mask. A fluorine plasma etch is used to remove the top ARROW layers and expose the hollow-core ends [see Figure 2.17 (S11)]. The chromium etch mask is removed using chromium etchant. Now that the SU-8 core is exposed we can remove it. The SU-8 sacrificial core removal is done with piranha (1:1 mixture of 98% H₂SO₄ and 50% H₂O₂) and usually takes about 1 week to complete [58]. An optical microscope can be used to ensure the complete removal of the SU-8 core. The wafer should then be thoroughly rinse and allow to soak in DI water for 24 hours to ensure the piranha has been flushed from the hollow-core to ensure no residues are left behind.

This point is what I will call the completion of the basic ARROW platform fabrication process. For my early ARROW based vapor-cells the wafer would be cleaved into individual
devices at this point. For our current devices there is still some additional processing needed before cleaving the wafer (this will be discussed in detail later). After the wafer is cleaved into individual devices, there still remains two hugely crucial steps of the ARROW vapor-cell construction: a) the introduction of rubidium (Rb) vapor to the hollow-core waveguide and b) the final hermetic seal to isolate the channel. The majority of this dissertation is devoted these topics and the details of post sacrificial core etching fabrication processes will be outlined in following chapters.
3 VAPOR-CELL OPTICS

During my time on the ARROW air-core team, we probed our vapor-cells for three main optical effects. These effects were rubidium spectroscopy, electromagnetically induced transparency, and slow light. The vapor is probed by passing a laser through the vapor-cell and then collecting the transmitted light in an optical detector. By analyzing the transmitted light one can observe the desired effects. In this chapter I will outline the theory behind the aforementioned optical effects.

![Simple diagram of a vapor-cell being optically probed](image)

Figure 3.1: Simple diagram of a vapor-cell being optically probed [24].

3.1 Rubidium

Our devices are populated with rubidium vapor. Rubidium is an alkali metal with an atomic number of 37. It is extremely malleable at room temperature and has a lustrous, silver-like appearance and a low melting point of 39 °C. Rubidium is found in two naturally occurring isotopes: $^{85}\text{Rb}$ accounts for 72% of rubidium in nature and $^{87}\text{Rb}$ for 28%. Rubidium has many characteristics that make it ideal in many applications. Alkali metal vapors, especially rubidium
and cesium, are ubiquitous in applications that utilize precision spectroscopy and optical quantum coherence effects. This is made possible because of the relatively long metastable lifetimes of applications mentioned in the introduction of this dissertation. Rubidium was chosen for our experiments because of its unique energy transition structure around 780 nm, a wavelength easily obtained via readily available commercial lasers. The rubidium ground state electron configuration in standard notation is given in Equation (3.1),

$$[1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6], 5s^1. \quad (3.1)$$

As can be noted in the electron configuration, the valence shell (located outside the square brackets) has only one electron. This results in an energy structure that behaves similarly to hydrogen; such atoms are often referred to as “hydrogen-like”. The alkali metals all naturally exhibit hydrogen-like energy structures. This hydrogen-like structure, coupled with the fact that the one valence electron is relatively distant from the nucleus, gives rise to one of the lowest electronegativities on the periodic table. As a general rule, electronegativity increases on the periodic table as you move toward the right-hand upper corner. Electronegativity describes the ability the atom has to attract an electron. A low electronegativity in rubidium means that the outer valence electron is weakly attracted to the atom. Therefore, the valence electron is easily excited and readily given up, making rubidium highly reactive and an attractive option for optical probing.

3.2 Spectroscopy

Electrons orbiting atoms can occupy only precise, periodic energy levels as describe by quantum mechanics. At these energy levels there are a specific number of states, each of which may be occupied by only one electron. These states are described by four quantum numbers.
The principal quantum number \( n \) describes the electron shell being occupied by the electron. The principle quantum number defines the energy level of the orbiting electron. The principle quantum number is the basis for the Bohr model of the atomic structure. The azimuthal quantum number \( \ell \) describes the angular momentum of the orbital. This is often referred to as the subshell. The magnetic quantum number \( m_\ell \) describes the orientation of the subshell, often referred to as an orbital cloud. The final quantum number \( s \) (spin projection quantum number or intrinsic angular momentum) describes the spin of the electron. As explained by the Pauli exclusion principle, no two electrons can have all the same four quantum numbers, or in other words, occupy the same state.

Electrons fill the orbital structure as described by the Aufbau principle and Madelung’s rule. Generally speaking, they fill the lowest energy level possible first. Electrons in filled shells tend not to react and are not easily excited from their current state. The outermost shell is called the valence shell and, if unfilled, typically contains the reactive and excitable electrons. Even though this is a generalization, it is an observable trend. As such, when talking about the atomic structure, most of the focus lies on the valence shell. The electron configuration of the valence shell can be abbreviated using the Russell-Saunders term symbol shown in Equations (3.2) to (3.7),

\[
(n)^M L_J, \tag{3.2}
\]

\[
M = 2S + 1, \tag{3.3}
\]

\[
L = \sum_i \ell_i, \tag{3.4}
\]
\[ S = \sum_i s_i, \quad (3.5) \]

\[ J = L + S, \quad (3.6) \]

\[ |L - S| \leq J \leq L + S, \quad (3.7) \]

where \( M \) is the multiplicity, \( S \) is the total spin angular momentum, \( L \) is the total orbital angular momentum, and \( J \) is the total angular momentum (which falls within the range of Equation (3.7)). Also note that in Equation (3.2) the total orbital angular momentum is in spectroscopic notation (0=S,1=P,2=D,3=F…). Applying Hund’s rule, the ground state of rubidium can be represented in Russell-Saunders term symbol notation as \( 5^2S_{1/2} \) since \( S = 1/2, L = 0, \) and \( n = 5 \).

While in some atomic models all the electrons occupying the same orbital are said to be degenerate, meaning they all have the same energy levels, this is an approximation. In actuality, each state has its own unique energy level. The first source of energy level difference comes from interactions between the electrons occupying the different suborbital. Electrons with lower angular momentums interact more closely with the nucleus while the nucleus-electron interactions of higher angular momentums are partially obstructed by the presence of electrons in orbitals with lower angular momentum. As a result the energy level of an electron generally increases the higher the angular momentum, or the higher the suborbital. There are two other sources of energy level differences in the different electron states. These are referred to as fine energy level splitting and hyperfine energy level splitting. These correlate with the fine and hyperfine structures observed in atomic spectroscopy. Fine energy level splitting is caused by the interaction between the spin and angular momenta of an orbiting electron. Hyperfine splitting is caused by the interaction between the magnetic moment of the electron created.
because of its spin and the magnetic moment of the nucleus, generated by the total nucleus spin. As the names suggest, the hyperfine structure energy splitting happens on a smaller scale than the fine splitting, about four orders of magnitude less.

Since there is only one electron in the valence shell of the ground state of rubidium, located in the 5s subshell, there is no fine splitting (\(\ell=0\)). However, the first excited suborbital from the ground state of rubidium occurs in the 5p orbital, which does exhibit fine splitting. This fine structure splitting can be denoted using term symbols. In the 5p suborbital \(L=1\), \(S=1/2\), and \(n=5\). This allows for two \(J\) values of 1/2 and 3/2. Therefore the first two energy levels to which the ground state electron may be excited are \(5^2P_{1/2}\) and \(5^2P_{3/2}\).

The hyperfine splitting of fine structures is denoted by the total atomic angular momentum \(F\) defined in Equations (3.8) and (3.9),

$$ F = J + I, \quad (3.8) $$

$$ |J - I| \leq F \leq J + I, \quad (3.9) $$

where \(I\) is the total nuclear angular momentum. Since the composition of the nucleus for \(^{85}\text{Rb}\) and \(^{87}\text{Rb}\) are different, they have different values for \(I\), 5/2 and 3/2 respectively. Possible values for \(F\) are all integers that fall in between the range defined by Equation (3.9). As such the \(^{85}\text{Rb}\) ground state splits into \(F = 2 \& 3\), the \(5^2P_{1/2}\) line splits into \(F = 2 \& 3\), and the \(5^2P_{3/2}\) line splits into \(F = 1, 2, 3, \& 4\). For \(^{87}\text{Rb}\), the ground state splits into \(F = 1 \& 2\), the \(5^2P_{1/2}\) line splits into \(F = 1 \& 2\), and the \(5^2P_{3/2}\) line splits into \(F = 0, 1, 2, \& 3\). The transitions from the ground state to the \(5^2P_{1/2}\) and \(5^2P_{3/2}\) energy levels are known as the Rb D1 and D2 lines, respectively. Figure 3.2 depicts the Rb D1 and D2 transitions in detail [59, 60].
Figure 3.2: Rb D line energy structure.

The absorption of light by the electron configuration in an atom gives rise to a unique spectrum for each element. The electromagnetic energy of incident photons is transferred to orbiting electrons, thus promoting them to a higher energy level. However, not all promotions, or transitions, are allowed. Such promotions are governed by quantum selection rules [61]. The energy difference between two states in dipole-allowed transition dictates the wavelength of light needed to excite an electron. The relation between the energy and wavelength of a photon is given by the Plank-Einstein equation outline in Equation (3.10) [62],

$$E = \frac{hc}{\lambda}$$  \hspace{1cm} (3.10)

As a beam of light propagates through a medium, such as atomic vapor, the light is absorbed as described by the Beer-Lambert law. This relationship, written in the gaseous media form, is shown in Equation (3.11) [17, 63],

49
\[ T = \frac{I}{I_0} = e^{-\sigma l N}, \]  

(3.11)

where \( T \) is the transmission through the media, \( I_0 \) is the input intensity, \( I \) is the output intensity, \( \sigma \) is the absorption cross-section of an individual particle, \( l \) is the distance traversed by the light, and \( N \) is the particle density (particles/volume) or, in our case, the atomic density. For our lifetime tests we monitor the atomic density. Beer-Lambert’s law can be manipulated to allow for the calculation of the atomic density of a Rb vapor-cell as seen in Equation (3.12). When optical probed, the dips in the transmission output will coincide with the wavelengths where light was absorbed because of the matchup with the energy needed to promote an electron to another state.

\[ N = -\frac{1}{\sigma l} \ln \left( \frac{I}{I_0} \right). \]  

(3.12)

The absorption cross-section for Rb around the D2 lines can be approximated using Equation (1.2) and a wavelength of 780 nm, which yields a value of 0.3 \( \mu m^2 \) [20]. However, in reality each specific transition has its own precise cross-section. These values can be obtained by using in-depth models and/or tabulated experimental results [59, 60].

In an ideal scenario one should be able to see a dip in optical transmission for each of the allowed hyperfine transitions while probing the Rb D2 lines. However, during basic spectroscopy the individual transitions are not separately resolvable because of a phenomenon called Doppler broadening. The Doppler broadening causes multiple individual transition absorption dips to merge together, forming one large transmission dip. Doppler broadening is caused by the random motion of atoms in the vapor. When an atom has some or all of its velocity vector parallel with the probing beam’s propagation axis, either with or against, the
beam’s wavelength is longer or shorter from the atom’s perspective. It is similar to the relative speeds of cars on a freeway. For example, two cars are driving down a freeway, the first at 5 mph and the second at 10 mph. When they are driving in the same direction, from the first car’s perspective, it seems that the second car is only driving at 5 mph, less than its actual speed. When they are driving toward each other, the second car, from the first car’s perspective, seems to be traveling at 15 mph, which is faster than its actual speed. In a similar manner, the relative wavelength of the probing light increases and decreases with the direction and velocity of the moving atom. Atoms that are moving in the same direction as the light see the wavelength as ‘red-shifted’ while atom’s traveling against the direction of propagation see the light ‘blue-shifted’. As such, the atoms in motion along the axis of light propagation absorb light with wavelengths on each side of the center wavelength, causing a Gaussian-shaped absorption profile. The motion of the atoms in a vapor can be described by a Boltzmann probability velocity distribution shown in Equation (3.13) and the resulting Doppler width is described in Equation (3.14),

\[ P(V_x) = \exp \left( -\frac{MV_x^2}{2k_BT} \right), \]  

\[ \Delta \omega_d = \frac{\omega_0}{c} \sqrt{\frac{8k_BT}{M}}, \]  

where \( k_B \) is the Boltzmann constant, \( c \) is the speed of light, \( T \) is the temperature, \( M \) is the atomic mass, \( \omega_0 \) is the center transition frequency, \( x \) refers to the direction of the beam propagation, and \( V_x \) is the x component of the atom’s velocity. Note the Doppler broadened linewidth’s
dependence on temperature. This is an important factor to consider in experiments that will be described later.

Pressure broadening is another important consideration in atomic spectroscopy [64]. Like Doppler broadening, pressure broadening also causes an increase in the absorption dip linewidth of the transition spectrum. This broadening is caused by the presence of other particles. When two particles collide, the energy structures are perturbed, causing slight increases or decreases in the transition energies. If an absorption transition takes place at this time, a photon of a wavelength different from the center transition wavelength will be absorbed, which causes a broadening in the spectrum. The more of these collisions that take place, the more likely an atom with an altered energy structure will absorb light at a wavelength other than the center frequency, causing the spectral broadening. There are two ways that such collisions can increase. The first is an increase in temperature, which causes the particles to move about and increases the frequency of collisions. The second is an increase in pressure, which by definition means an increase in the particle density, making collisions more probable and frequent. Pressure broadening is described by a Lorentzian distribution with the resulting linewidth broadening described in Equation (3.15),

\[ \Delta \omega \approx \frac{n \sigma}{\pi} \sqrt{\frac{2k_B T}{M}} \]

(3.15)

where \( n \) is the number of atoms per unit volume and \( \sigma \) is the collision coefficient.
Figure 3.3: Effects of pressure broadening between two second-generation minicell Rb spectra. One minicell was evacuated to ~1 mTorr (blue line) while the second was evacuated to 2 Torr (green line). a) Rb D1 line absorption spectrum. b) Plot showing the increase in linewidth due to the higher pressure. Also shows the increase in the linewidth due to temperature.

While the effects of pressure broadening never go away completely, by evacuating the cell to a low pressure the effects can become negligible when compared to other broadening sources such as Doppler. Notably, the cell pressure \( P \) can be related to the number of atoms as shown in Equation (3.16) [64],

\[
n = \frac{P}{k_B T}
\]  

(3.16)

One common method used to resolve the individual transitions by eliminating (for the most part) the effects of pressure and Doppler broadening is called saturation absorption spectroscopy (SAS) [65-67].

3.3 EIT

As mentioned earlier, many potential applications are based on nonlinear optical effects observed in atomic vapor-cells. One such effect that serves as a ‘gateway’ to such devices is
electromagnetically induced transparency (EIT). In short, EIT creates a narrow transparent window in a normally opaque absorption dip based on quantum coherence phenomena [68]. Alkali metals are particularly well suited for quantum-coherence-based experiments because of the relatively long metastable state lifetimes in the electronic energy structures, another reason we have chosen to use rubidium. EIT is possible only in specific three-level atomic structure configurations. As seen in Figure 3.4, there are three possible configurations: vee, ladder, and lambda.

![Figure 3.4: The three EIT configurations a) lambda, b) vee, and c) ladder.](image)

Significantly, the $|1\rangle$ to $|2\rangle$ transition is dipole forbidden (i.e., no transition is allowed) and state $|2\rangle$ must be metastable (relatively long lifetime.) In this dissertation we shall focus on the lambda configuration, which is a commonly probed structure in the rubidium D2 lines. The rubidium D2 line lambda EIT configuration used in our experiments is illustrated in Figure 3.5.
The $|1\rangle$ to $|3\rangle$ transition corresponds with the $^{85}\text{Rb } 5^2S_{1/2}(F=2)$ to $5^2P_{3/2}(F=3)$ transition and the $|2\rangle$ to $|3\rangle$ transition corresponds with the $^{85}\text{Rb } 5^2S_{1/2}(F=3)$ to $5^2P_{3/2}(F=3)$ transition.

![Diagram of Rb D2 line EIT experiment](image)

Figure 3.5: Rb D2 line EIT experiment. a) Lambda state configuration illustration. b) Lambda configuration shown in D2 line structure. Coupling laser in red and probe laser in green.

Since EIT is a quantum-based effect, it is described by using quantum mechanics. The approach outlined in this dissertation is referred to as the ‘dressed state’ approach [69]. We start off with the unperturbed Hamiltonian of the three-level lambda system, $H_0$. Then we apply two electromagnetic fields to the system, each tuned to near resonance of one of the two allowed transitions. The laser tuned to the $^{85}\text{Rb } 5^2S_{1/2}(F=3)$ to $5^2P_{3/2}(F=3)$ transition is called the coupling beam, and the laser tuned to the $^{85}\text{Rb } 5^2S_{1/2}(F=2)$ to $5^2P_{3/2}(F=3)$ transition is called the probing beam. The resulting perturbed system can be described by the Hamiltonian shown in Equation (3.17),

$$H = H_0 + V_1 + V_2,$$

(3.17)

where $V_k$ represents the system’s interaction with the incident electric field caused by the coupling and probe beams and is described in Equation (3.18),
where $\Omega_k$ is called the generalized Rabi frequency or Rabi coupling. The Rabi frequency $X_{ij}$ describes the coupling between an electromagnetic field and the atomic transition. It is the frequency of oscillation for an atomic transition and is proportional to the transition dipole moment $\varrho_{ij}$ and the amplitude of the applied electric field $E_0$ as shown in Equation (3.19). The generalized Rabi frequency is essentially the Rabi frequency with the detuning in the applied electric field taken into account. Detuning is the difference between the frequency of the transition and the frequency of the applied electric field. The generalized Rabi frequency is described by the following series of equations,

$$V_k = \hbar \Omega_k,$$  

$$\Omega_k = \sqrt{|X_{ij}|^2 + \Delta_k^2},$$  

$$\Delta_k = \omega_{ij} - \omega_k,$$  

where $\omega$ is frequency and $\Delta_k$ is the detuning. The $ij$ subscript denotes the transition the term relates to. In this case, $ij = 31$ refers to the $|1\rangle$ to $|3\rangle$ transition and $ij = 32$ refers to the $|2\rangle$ to $|3\rangle$ transition. The subscript $k$ denotes which applied electric field the term relates to. The applied electromagnetic fields are tuned to a specific transition, so while $k$ may correlate with a certain transition, it does not denote a property of that transition. In this dissertation $k = 1 = p$ correlates with the transition $ij = 31$ while $k = 2 = c$ correlates with the transition $ij = 32$.

To simplify the solution of the Hamiltonian, the rotating wave approximation (RWA) is employed. The RWA neglects terms with rapid oscillations. This approximation assumes that
the electric fields affecting the system are at or near resonance and that their intensities are small. The resulting solution is represented in

\[
H = \begin{bmatrix}
0 & 0 & \Omega_p \\
0 & -2(\Delta_1 - \Delta_2) & \Omega_c \\
\Omega_p & \Omega_c & -2\Delta_1
\end{bmatrix}.
\] (3.22)

The resulting eigenstates of this Hamiltonian are quite complex. To simplify them we will describe them in terms of the ‘mixing angles’ \(\theta\) and \(\phi\) shown in Equations (3.25) and (3.26), respectively. The mixing angles are in turn described using the single-photon and two-photon detuning shown in Equations (3.23) and (3.24), respectively. We will also assume two-photon resonance where \(\Delta_2 = \Delta_1\).

\[
\Delta = \Delta_1,
\] (3.23)

\[
\delta = \Delta_1 - \Delta_2,
\] (3.24)

\[
\theta = \tan^{-1}\left(\frac{\Omega_p}{\Omega_c}\right),
\] (3.25)

\[
\phi = \frac{1}{2}\tan^{-1}\left(\sqrt{\frac{\Omega_p^2 + \Omega_c^2}{\Delta}}\right).
\] (3.26)

Making the above substitution the eigenstates can be written in the following way,

\[
|a^+\rangle = \sin \theta \sin \phi |1\rangle + \cos \phi |3\rangle + \cos \theta \sin \phi |2\rangle,
\] (3.27)

\[
|a^0\rangle = \cos \theta |1\rangle - \sin \theta |2\rangle,
\] (3.28)

\[
|a^-\rangle = \sin \theta \cos \phi |1\rangle - \sin \phi |3\rangle + \cos \theta \cos \phi |2\rangle.
\] (3.29)
The eigenstates in their current form describe a phenomenon called coherent population trapping (CPT), which is closely related to EIT. CPT is a quantum-coherence phenomenon in which a ‘dark state’ is created that does not allow for an atom to absorb or emit photons, essentially trapping the electrons. Examining the equations shown above reveals that the state represented in Equation (3.28) has no component of state $|3\rangle$, making it a dark state since there is no opportunity to make a transition. Also, the dark state relative energy is stationary at zero while the states represented in Equations (3.27) and (3.29) can shift up or down by an amount $E^\pm$. Notably, this shift can be moved by changing the intensity of the coupling and probe beams,

$$E^\pm = \frac{\hbar}{2} \left( \Delta \pm \sqrt{\Delta^2 + \Omega_p^2 + \Omega_c^2} \right). \quad (3.30)$$

To achieve EIT from this point, all that has to be done is to alter the probe and coupling beams. We alter them such that $\Omega_p \ll \Omega_c$, which makes $\sin \theta \to 0$ and $\cos \theta \to 1$. Also, the probe beam is tuned to resonance such that the single-photon detuning goes to zero. The eigenstates can then be further simplified to the following,

$$|a^+\rangle = \frac{1}{\sqrt{2}}(|3\rangle + |2\rangle), \quad (3.31)$$

$$|a^0\rangle = |1\rangle, \quad (3.32)$$

$$|a^-\rangle = \frac{1}{\sqrt{2}}(|2\rangle - |3\rangle). \quad (3.33)$$

As seen in Equation (3.32) the ground state becomes similar to the dark state in CPT from which excitation cannot occur. This results in a transmission window in the absorption peak that was previously opaque, as illustrated in Figure 3.6.
3.4 Slow Light

While EIT is itself an interesting phenomenon the real potential applications arise from the condition EIT creates, a condition called slow light [68, 69, 71]. Slow light refers to the ability to slow down, and even stop, the speed at which an optical signal propagates.

The ability to slow down an optical signal comes about because of the unique relationship between frequency and index of refraction around the $|1\rangle$ to $|3\rangle$ transition under EIT conditions. In order to understand slow light we must first derive an equation that describes the index of refraction in the quantum system encountered during EIT. We will do this using the density operator and a density matrix to describe the system. The density matrix describes a multi, or mixed, state system as a collection of probabilities that the system will be found in a certain state. A density matrix can be set up describing the three-level lambda configuration with the two perturbing electric fields, coupling and probe. After making the same assumptions that we
made in section 3.3 the $|1\rangle$ to $|3\rangle$ transition density operator can be solved, yielding Equation (3.34) [68],

$$
\rho_{31}(t) = \frac{i\varrho_{31}E_0\rho e^{-i\omega pt}(\gamma_{21} + i\Delta)}{2\hbar\left[(\gamma_{31} + i\Delta)(\gamma_{21} + i\Delta) + \frac{\Omega_c^2}{2}\right]},
$$

(3.34)

where $\gamma$ is the coherence decay rate and $\phi$ is the phase of the dipole matrix element. The density operator can then be related to the complex polarization using Equation (3.35),

$$
P(z, t) = 2qpe^{i[\omega t - kz + \phi(z,t)]}.
$$

(3.35)

The susceptibility, $\chi$, can then be related to the polarization using Equation (3.36),

$$
P = \varepsilon_0\chi E_0,
$$

(3.36)

where $\varepsilon_0$ is the permittivity. By using Equations (3.34) through (3.37) and the Kramers-Kronig relations, the real and imaginary components of the susceptibility can be shown as Equations (3.37) to (3.39),

$$
\chi = \chi' + i\chi'',
$$

(3.37)

$$
\chi' = \frac{N_a|\varrho_{31}|^2\Delta}{\varepsilon_0\hbar Z}\left[\gamma_{21}(\gamma_{31} + \gamma_{21}) + \left(\Delta^2 - \gamma_{31}\gamma_{21} - \frac{\Omega_c^2}{4}\right)\right],
$$

(3.38)

$$
\chi'' = \frac{N_a|\varrho_{31}|^2}{\varepsilon_0\hbar Z}\left[\Delta^2(\gamma_{31} + \gamma_{21}) - \gamma_{21}\left(\Delta^2 - \gamma_{31}\gamma_{21} - \frac{\Omega_c^2}{4}\right)\right],
$$

(3.39)
where \( N_a \) is the atomic density and \( Z \) is described in Equation (3.40),

\[
Z = \left( \Delta^2 - \gamma_{31} \gamma_{21} - \frac{\Omega_C^2}{4} \right)^2 + \Delta^2 (\gamma_{31} + \gamma_{21})^2. \tag{3.40}
\]

The complex index of refraction, \( n_{cx} \), describes how light interacts with the medium through which it travels. The real component is the index of refraction while the imaginary component contains the absorption coefficient. The complex index of refraction is a function of the susceptibility as shown in Equations (3.41) and (3.42),

\[
n^2_{cx}(v) = 1 + \chi(v), \tag{3.41}
\]

\[
n_{cx} = n + i\alpha. \tag{3.42}
\]

Putting all this together, we can solve for the index of refraction and the absorption coefficient of Rb vapor under EIT conditions as shown in Equations (3.43) and (3.44),

\[
n = \left\{ \left[ \frac{(1 + \chi')^2 + \chi''^2}{2} \right]^\frac{1}{2} + (1 + \chi') \right\}^\frac{1}{2}, \tag{3.43}
\]

\[
\alpha = \left\{ \frac{[(1 + \chi')^2 + \chi''^2]^{\frac{1}{2}} - (1 + \chi')}{2} \right\}^{\frac{1}{2}} \text{sgn}(\chi''). \tag{3.44}
\]

The speed at which light propagates through media is inversely proportional to the index of refraction. Equation (3.45) defines the phase velocity, \( v_p \), of light traveling through a medium with an index of refraction, \( n \). Phase velocity is the speed at which the phase of the electromagnetic wave travels. Notice that if the light is traveling in a vacuum (\( n=1 \)), then the phase velocity is the speed of light. However, as the index of refraction increases, the phase velocity decreases. If the goal is to stop or slow light in a waveguide by radically decreasing the
phase velocity, a medium with low absorption and an extremely large index of refraction would have to be found. Practically, this sort of medium is hard to find. The phase velocity describes the velocity of only one wavelength component of the propagating light as described in equation (3.45). The index of refraction is generally a function of wavelength; in other words, the index of refraction for a medium will change depending on the wavelength of the propagating light. In reality, optical sources create light that are made up of a range of wavelengths. When a signal is created by modulating the light it may be assumed that the modulation is spread across all wavelengths in the propagating beam. Since the index of refraction is a function of wavelength, some components of the modulation will travel faster than other components. The group velocity describes the speed at which this spectrum of wavelengths travels as a group. The group velocity is different from the phase velocity; the phase velocity describes the speed at which a single wavelength is traveling whereas the group velocity describes the speed at which a modulated signal spread across a spectrum of wavelengths travels. In the slow light experiments described in this dissertation, it is not the phase velocity of light that is being slowed but the velocity at which a signal ‘riding’ the light is traveling. In other words, it is the group velocity that is being slowed [72, 73].

\[ v_p = \frac{c}{n} \]  

Equation (3.45)

The group velocity can be slowed more easily than the phase velocity because it depends on more than just the index of refraction. Equations (3.46) and (3.47) show that, as well as being inversely proportional to the index of refraction, the group velocity is related to the index rate of change versus frequency,
\[ v_g = \frac{c}{n_g}, \]  
\hspace{1cm} (3.46)

where,

\[ n_g = n - \omega \frac{dn}{d\omega}. \]  
\hspace{1cm} (3.47)

If a medium can be created with a very steep slope in the index of refraction with respect to wavelength, the group velocity can be drastically decreased. Such a medium is created in Rb vapor during EIT. Equation (3.43) describes the index of refraction of Rb vapor under EIT conditions. Plotting this equation as a function of frequency yields Figure 3.7. Notice the steep slope about the center frequency; this is precisely the environment needed to slow down the group velocity of light. If a signal is modulated onto the probe laser, that signal velocity will decrease while propagating through the Rb vapor, thus successfully creating ‘slow light’.

A unique relationship exists between the absorption coefficient and the index of refraction of a medium. The Kramers-Kronig relations describes the relation between the real and imaginary components of a complex number. Equation (3.42) shows that the complex index of refraction is comprised of the index of refraction (real) and the absorption coefficient (imaginary). Thus, via the Kramers-Kronig relations, the index of refraction and absorption coefficient of a medium are related. If one is altered, the other is as well. Books that describe the slow light phenomenon often state that it is the unique absorption profile of EIT that leads the steep slope in the index of refraction. While that claim can be a little misleading (it is a “chicken or the egg” scenario), it is important to note that they are related.
Figure 3.7: Graphs representing the response of [ a) & b) ] transmission and [ c) & d) ] refractive index with [ a) & c) ] the coupling laser turned off and [ b) & d) ] the coupling laser turned on [70].
4 RUBIDIUM INTRODUCTION AND SEALING

The largest obstacle in creating on-chip vapor-cells was the introduction and sealing of rubidium into the hollow waveguides on the ARROW platform. The techniques employed by the other vapor-cell technologies discussed earlier were not applicable to my research due to the unique requirements of the ARROW platform. Many of their applications feature robust planar geometries, similar materials, or are never separated from an active vacuum supply. The ARROW platform presents a unique set of requirements currently not found elsewhere. For example, the sealing surface is not planar because of the protruding, 3D nature of the hollow-core over which a seal must be made (see Figure 4.1). The fragile waveguides cannot withstand the harsh environments created in many popular sealing techniques. High heat, pressure, stress, agitation, and vibrations can all lead to broken devices. A new and versatile Rb introduction and sealing technique was needed in order to successfully create a viable on-chip vapor-cell.

A list of requirements was created to guide research efforts. This list evolved over time as new information was gathered. The final version of the list of necessary requirements is as follows: First, we must be able to evacuate the cell to an optimal pressure (which may differ for each application). Second, all materials used must not react with Rb. Third, the technique must allow for sealing dissimilar materials with non-planar geometries. Fourth, the seal must be long-lasting. Fifth, the cell must be able to withstand a reasonable and repeated range of change in the operation environment (i.e., temperature cycling). Development of the process was often done in
steps, focusing on an individual or subgroup of requirements at a time to isolate problems encountered. As such our development was separated into several ‘generations’.

![Diagram of ARROW vapor-cell geometries](image)

**Figure 4.1:** Illustrated a) top down view and b) 3D angled view of ARROW vapor-cell geometries. Red arrows illustrate the optical path of probing beam during optical experiments. [Note: (1) The ARROW illustration in b) is a simplified illustration of the ARROW platform that highlights the solid-core and hollow-core waveguide regions without detailing the rest of the device topography. Refer to Chapter 2 for a more detailed account of ARROW device structure. (2) Though the dimensions are labeled please note that they are not to scale.]

After considering a variety of approaches and matching them to our capabilities, we chose a generalized approach of introducing and sealing rubidium into the ARROW vapor-cell was decided upon (see Figure 4.2). The following outlines our generalized approach. A 3D hollow reservoir is attached over the hollow-core waveguide on the ARROW device. The reservoir is then populated with rubidium and the top sealed. When the top seal is made, the hollow-core waveguide and reservoir are connected to form a hermetically sealed, isolated cell
where the rubidium is free to migrate from the source, located in the reservoir, into the hollow-core waveguide where the vapor then interacts with probing light sources. With this general approach set in place, my efforts focused on how to attach the reservoir, how to seal it, and what to make it with.

![Illustration](image)

**Figure 4.2:** Illustration a) top down view and b) angled 3D view of general Rb introduction and sealing approach.

### 4.1 Glovebox

Since rubidium is a highly volatile element that reacts with both oxygen and water the rubidium population and final sealing processes are done in a glovebox with a maintained inert
atmosphere. For the first-generation vapor-cells we maintained a helium atmosphere in the glovebox. However, shortly after we began development for the second-generation vapor-cells, we switched to a nitrogen atmosphere, which is easier to maintain than helium. The glovebox is connected to a bottle of nitrogen which keeps the glovebox slightly pressurized so that any leaks flow in the outward direction, not inward. Devices in the glovebox are manipulated by placing one’s arms into two vias with thick rubber gloves. The devices are loaded into the glovebox via a transfer tube. The devices are placed into the transfer tube which is then sealed shut. A vacuum evacuates the tube into the ~1 mTorr range. Then the tube is backfilled with nitrogen to match the pressure inside the glovebox. I generally run this evacuation/backfill cycle twice before opening the transfer tube to the glovebox. This effectively purges the tube of oxygen and moisture and allows for the safe transfer of materials into the glovebox.

There will always be a small amount of oxygen and moisture introduced into the glovebox during each transfer. A purification system using desiccant beads continually pulls oxygen and moisture out of the glovebox atmosphere. Over time the desiccant beads will become ‘saturated’ and will lose their effectiveness at purifying the atmosphere. For this reason the desiccant beads need to undergo a regenerating or ‘purging’ process periodically depending on glovebox usage. The beads are heated to high temperatures which releases the oxygen and moisture. The system containing the beads is under vacuum during the regeneration process which removes the molecules released by the beads. At the last stage of the heating process forming gas flows through the beads purging the system of any remaining oxygen and moisture. A properly maintained and utilized glovebox allows for the safe handling of rubidium and ensures that pure, un-oxidized rubidium is introduced into our vapor-cells.
4.2 Introduction to Minicells

Using ARROW devices as the primary platform to test rubidium introduction and sealing methods was not a viable option at the time this research was conducted. ARROW devices (especially during the early years of my research) were very time consuming to make, had low yields, and inherently have many failure modes. One wafer took about 1 month to complete and each contained 32 ARROW devices. The ARROW-based vapor-cell yield can be split into three categories: the structural yield, the optical yield, and the sealing yield. The structural yield refers to the number of devices that have intact solid waveguides, hollow waveguides, and solder pads. After a device is deemed structurally sound, it is optically tested. Light from a laser tuned to the desired wavelength is coupled into the device. If an output signal is detected then the device passes inspection, however if no output is detected then the device has failed and is discarded. The final yield point is the sealing. The device must withstand the reservoir attachment,
rubidium introduction, and sealing processes. After the device undergoes these processes it is tested by probing the atomic spectrum. If such a spectrum is observed than the device has a confirmed presence of rubidium and the device is successfully completed and is ready for use.

Since there are so many fail points and since fully functioning ARROW devices are relatively rare and run at a high cost to the researcher, it was not viable to use them in high-volume experimentation. Also, it is hard to identify the cause of failure on a complicated device with so many possible fail points. If, for example, a rubidium-loaded and sealed ARROW failed to produce a spectra, what caused it? Was there a micro crack in the hollow-core invisible to optical inspection? Was there blockage in the channel preventing rubidium vapor from filling the core? Did the Rb react with some material in the device? It can be very difficult to narrow down the causes of all possible failures given the limitations in metrological and investigative means. For me the answer was to set up experiments and platforms that isolated potential problems, either individually or in small distinguishable combinations. Much of this failure mode isolation is done using carefully designed experiments, but unique testing platforms also played a big role in my research.

To aid in the development of rubidium introduction and sealing methods, I employed vapor-cell devices dubbed ‘minicells’ en masse as cheap, quickly-fabricated testing platforms. Throughout my time on the slow light research team minicells came in many shapes and sizes, but in general they consist of an optically translucent base topped with the current sealing method in question. For example, the most common minicell by far has been a 2 mL glass chromatography vial topped with a short length of refrigeration copper tubing; see Figure 4.4. These minicells allow for great versatility in our approach to vapor-cell development. Tests can be inexpensive and provide larger sample sizes than the ARROW platform would allow for at
this time in its development. Not only that, but with a device so simple, many failure-mode unknowns are removed since there are fewer possibilities of failure.

![Figure 4.4: Illustration of a generic glass vial minicell.](image)

4.3 **First-generation Vapor-cells**

Early on in our development the idea of using epoxy to attach a reservoir to our ARROW devices presented itself as an attractive option. Since the epoxy was semi-solid, it would easily attach two dissimilar geometries while providing a hermetic seal. Epoxy is also an extremely gentle process. With epoxy the fragile hollow-core channels would not experience high heats, vibrations, or mechanical stress. Epoxy was also relatively quick and easy. After the sacrificial core was removed in the last step of the ARROW fabrication process, the vapor-cells were ready for epoxy reservoir attachment. No other processing was needed. Indeed, because of these benefits, we expended much time and effort into finding the perfect epoxy for the job. Two of the three previously mentioned vapor-cell ‘generations’ utilized epoxy.

The first sealing technique tested was an ‘all epoxy’ approach. The minicell created to test this approach was a glass tube glued to a glass slide. The vapor-cell was loaded into the
glove box where it was populated with Rb. The reservoir was then sealed by filling the top portion of the tube with epoxy. After curing the epoxy with heat/UV/time depending on the epoxy type, the vapor-cell was brought out of the glovebox and was ready for optical testing. This approach was never successful, possibly because during the curing process the epoxy was outgassing materials that were reacting with the Rb. This hypothesis came about after visually watching the Rb changing color and form in a supposedly inert atmosphere.

The second attempt still involved epoxy, but the epoxy was used to seal the base of the reservoir to the chip only. The reservoir was attached to the cell and the epoxy was allowed to fully cure before placing it into the glovebox and loading it with Rb. The Rb was then sealed by placing a rubber cap over the top of the reservoir. The hope was that the rubber cap would provide a hermetic seal around the top of the reservoir. When this method failed to produce successful results, a third attempt was made. We believed that perhaps the rubber cap was not providing a tight seal. We devised a new approach in which mechanical pressure around a rubber seal would provide a better seal. To that end a stainless steel threaded standoff was employed as the reservoir. The stainless steel reservoir was glued to a vapor-cell, cured, and loaded with Rb. The cell was sealed by placing a rubber gasket on top of the reservoir and then tightening a screw into the reservoir. The head of the screw tightened against the rubber gasket providing a tight, hermetic seal between the screw head and the reservoir.
The screw-and-gasket approach became what we now call our first-generation vapor-cell. Most of the experimentation was done with minicells but the screw and gasket approach was experimentally applied to the ARROW platform as well.
Figure 4.6: Illustration of first-generation ARROW loading. a) Attach reservoir and seal open end. b) Load solid Rb into reservoir. c) Seal reservoir with screw and gasket. d) Ready for optical testing.

This was done utilizing an individual ARROW device cleaved from a wafer that had completed a processing similar to the processing outlined in Section 2.4 (the only difference being there was no pedestal on our first-generation devices). The ARROW device/chip was then cleaned with acetone followed immediately by an isopropyl alcohol (IPA) rinse. The reservoir components were cleaned in a like manner. After the cleaning, the stainless steel standoff was attached to the chip with the hollow-core opening in the center of the reservoir using a generic “5 minute” epoxy. The epoxy was then allowed to cure. At this point the chip was taken into a glovebox where ~0.5 g of Rb is loaded into the reservoir using the tip of a metal syringe needle. The gasket was placed over the top of the reservoir and sealed shut with the stainless steel screw. The device was then ready for optical testing. An ARROW vapor-cell that is populated with Rb and sealed is referred to as a ‘loaded ARROW’. Even though a minicell using the first-generation sealing technique was never successfully observed to yield an atomic spectrum, this method did produce the first Rb spectrum probed on a single ARROW vapor-cell platform [66]. However, a first-generation device never again yielded successful results.
During our first-generation experiments, helium gas was being used as the inert atmosphere. A successful first-generation ARROW vapor-cell relied on the eventual escape of the helium atmosphere leaving behind a vacuum. Helium gas, a single He atom, is very small and difficult to contain. As such the helium gas could escape out of the cell via the rubber gasket while the gasket prevented other larger gasses from passing, either in or out. If a vapor-cell is not at a low pressure, collisional/pressure broadening can cause all of the absorption peaks to blend together making the spectrum unresolvable [64]. Waiting for the eventual escape of the helium gas was a very random and uncontrollable method of creating an atomic vapor-cell that was never successfully repeated. As such, a more consistent and controllable second-generation was sought.

![Figure 4.7: a) First absorption spectrum on ARROW platform. b) Photo of first-generation ARROW device.](image)
I should mention that most of the first-generation seal development was done by my predecessor, Don Conkey. I came on the project team toward the end of that period. I was, however, involved in its development. The rest of the development presented in the dissertation represents development conducted by myself.

4.4 Second-Generation Vapor-cells

After the importance of minimizing pressure broadening in absorption spectroscopy was fully understood, the goal was to develop an attachment process in which the vapor-cell pressure could be controlled. At this point we had switched our minicell bases from glass tubes glued to a glass slide to 2mL glass chromatography vials. One idea was to seal the top of these vials with a self-sealing membrane cap and then evacuate the vial by inserting a small needle attached to a vacuum. However, these tests were unsuccessful. More tests isolated the fail mechanism as a reaction between Rb and Teflon materials used in the construction of the membranes.

4.4.1 Copper cold-welds

While we were searching for other options, a fortuitous discussion with researchers at NIST suggested that copper metal did not react with Rb. After learning of this possibility, I sought to capitalize on the malleable nature of copper to create a seal. In the refrigeration industry, copper tubing is commonly filled with coolants and then sealed via crimping [74-76]. The general idea was to use a short length of copper tubing, often referred to as a ‘stub’, to act as the Rb reservoir in place of the glass and stainless steel reservoirs we used earlier. The base of
the stub would be glued to the chip with epoxy while the top of the reservoir could be crimped closed after populating with Rb, see Figure 4.8.

At first I tested a variety of electrical based crimpers and pliers to seal the minicells. However, none of these worked. Further research revealed the specific name of the copper seal used in the refrigeration industry. The crimps are actually called ‘cold-welds’ [77]. We purchased some special cold-weld pliers from CHA Industries that were specifically designed to form a hermetically sealed crimp in copper tubes up to 3/8” in diameter. The pliers exert sufficient force on the metal to fuse it together much like other welding methods but without the heat. Traditional metal welding techniques require high heat which would destroy our heat-sensitive ARROW devices. During the cold-weld, the metal gets so thin that the metal separates

---

Figure 4.8: a) Illustration and b) photo of second-generation minicell evacuation and cold-weld process. C) Photo of complete second-generation minicell.
down the center of the crimp. Sometimes, if the metal doesn’t separate on its own, gently bending the crimp back and forth is needed to make the final separation. The other reason we used copper tubing was because it could be attached to a vacuum while creating the final seal. This allowed for the precise control of the vapor-cell pressure. To this end a vacuum line was routed into the glove box.

![Figure 4.9: Cutaway illustration of minicell fabrication and loading sequence. a) Copper stub epoxied to glass vial. b) Rb-loaded into minicell. c) Minicell attached to vacuum via medical tubing and evacuated. d) Copper stub is cold-weld sealed and ready for optical testing.](image)

After acquiring the cold-weld pliers I set about creating successful second-generation minicells, see Figure 4.9 for illustration of process flow. To create a second-generation epoxy cold-weld minicell, the individual components were cleaned with acetone followed by IPA rinse.
The copper reservoirs were cleaned with sulfuric acid, rinsed with DI water, then dried with IPA. The sulfuric acid removes any copper oxide building and under etches any surface contaminates. The copper stub was then attached to the top of the glass vial with epoxy. This was done by inserting a 3/16” copper tube into the top portion of the previously mentioned glass vial and sealing the stub to the vial with epoxy. There were some experiments that utilized similarly constructed minicells except they used 1/8” and ¼” copper stubs, but the vast majority of the epoxy experiments utilized 3/16” copper tubing. The epoxy was allowed to cure before undergoing a 120 °C dehydration bake for 2 hours. Then, in the glovebox, Rb was loaded into the reservoir after which the end of the reservoir was attached to a vacuum system via a short length of thick-walled medical tubing. Once the desired pressure was reached, ~1mTorr for most of my experiments, the copper reservoir was cold-welded shut and separated from the vacuum system. After taking the loaded vapor-cell out of the glovebox, I generally used some more epoxy to encapsulate the cold-weld edge. The tip of a cold-weld on a copper tube is very thin, very sharp, and very fragile; thus the extra epoxy was used to protect the seal.

4.4.2 Quantifying seal performance

Once I developed this method, it became very easy to probe Rb atomic spectra in a minicell. In fact, it was very rare for a minicell not to yield a spectrum when tested. This allowed for more in-depth testing on our cells. While creating all of my previous minicells, I could visually observe that different epoxies and materials would cause some sort of reaction with the rubidium. Some materials were worse than others, but I had no quantifiable metric with which to test the performance of the different materials. Now that I had developed a consistent controllable fabrication method with the copper cold-weld seal, I could test and compare the performance of different epoxies.
In the first round of epoxy performance testing I used a type of accelerated lifetime testing called a ‘heat-cycle test’ or sometimes referred to as a ‘ramp test’. The idea behind accelerated lifetime testing is to put the cell through a harsh environment to simulate a long-term aging process in a short amount of time. This is sometimes also referred to as a premature aging process. The heat-cycle test used with our minicells heated the cells up to 80°C and then cooled them back down to room temperature three times. One cycle was referred to as a heat ramp. The atomic density was monitored during the cycling process. The atomic density at the start of the test was compared to the atomic density at the end from which a percent drop was calculated. The minicells with the smallest drop in atomic density were deemed the better choice.

Figure 4.10: Graph showing heat-cycle test for an epoxy minicell (ID# N6).

Before testing the different epoxies, I first conducted an experiment to verify the compatibility of Rb with the copper tubing and the sealing capability of the cold-weld seal. In
testing the second-generation sealing method, I divided the test into two parts. The first is the seal between the Rb reservoir and the body of the vapor-cell. The second part is the final separation and sealing of the Rb reservoir from the external environment. Before testing the sealing of the reservoir to the vapor-cell body, I wanted to ensure that the copper cold-weld seal was not the weak point. To that end I needed to employ a minicell where the only materials exposed to the Rb were copper and glass. To create such a minicell I did some research into epoxy-less glass-to-metal seals.

Epoxy-less metal-to-glass seals are fairly ubiquitous in vacuum technologies. Because of the relatively malleable properties of copper, epoxy-less glass-to-copper seals are among the most common metal-to-glass seals. Our epoxy-less copper-glass minicells used a seal called the “Houskeeper” seal [78-81]. To create a Houskeeper seal, the end of copper tube is feathered and borated to form a boron oxide on the copper that will promote a stronger bond to the glass. A glass tube and the copper tube are then heated and fused together. The ductile feathered end of the copper compresses as the glass tube shrinks around it while cooling. This process creates a strong, hermetic seal between the glass tube and the copper tube without any other materials. I located a company named Larson Electronic Glass that specialized in these seals and commissioned a custom order of what we dubbed ‘Houskeeper minicells’. Specifically, I asked for a ¼” copper tube to ¼” glass tube seal where the glass tube was melted closed at the opposite end as seen in Figure 4.11. We tested Houskeeper minicells using both heat-cycle tests and long-term heat exposure tests in which a Houskeeper minicell was stored at 90°C for two weeks. Both tests showed no appreciable drop in the atomic density; we therefore concluded that (a) Rb is compatible with copper and (b) the copper cold-weld seal forms a hermetic seal. The next step was to create a good seal between the copper reservoir and the vapor-cell body.
After the successful tests of the copper cold-weld seal, the epoxy seal was evaluated. Many epoxies were tested during the development of our second-generation vapor-cell. For many of the epoxies tested--such as generic “5” or “60 minute” epoxy, UV curable epoxies, and silicone-based epoxies--failures were immediate and catastrophic and did not merit further investigations. After doing some research and corresponding with industry experts at a variety of different epoxy companies, I compiled a list of high-performance epoxies that would be best suited for our application. These generally had some combination of desirable attributes such as resistance to chemicals, water-proof, impervious to high-temperatures, and NASA certified low-outgassing. The list of best performing epoxies follows: Aremco-Bond 2310, 3M Scotch-Weld 2216, M.E. Taylor Engineering Conductive Silver Epoxy, Dow Corning 732, Epotek 353ND, and Loctite E-30CL. Three or more copper cold-weld minicells were created using each of these
epoxies and were allowed to cure according to their instructions. Each cell underwent the previously mentioned heat-cycle test. As seen in Figure 4.12, the Aremco-Bond 2310 (2310) epoxy had the longest life out of all the other epoxies.

![Figure 4.12: Second-generation minicell epoxy performance.](image)

### 4.4.3 ARROW specific obstacles

After qualifying the Aremco 2310 epoxy on the minicell testing platform, construction of ARROW-based vapor-cells using Aremco 2310 epoxy began. Applying the sealing techniques on a chip scale came with its own unique challenges. One of the most challenging parts of attaching a reservoir to an ARROW device was the alignment. All of the features are very close together, leaving little room for error since the critical dimensions of the device are 10s of µm in size and the reservoir is a 3/16” copper stub. Up until this point the reservoirs were attached by hand. However, this led to a high degree of device fallout because of human error. As was previously mentioned, each die came at a high cost, and we wished to mitigate the losses. For
this purpose I created some attachment stages. These stages could hold a reservoir over a chip. There were some fine-tuning adjustment capabilities as well as rough adjustments. For example, one such stage consisted of an alligator clip attached to a copper wire mounted on an old microscope stage [see Figure 4.13]. The copper wire could be manipulated to level and center the reservoir. After centering the reservoir with a dry run, the microscope stage could raise the reservoir to allow for the application of the epoxy. Then the stage was lowered onto the vapor-cell and held in place until the epoxy was hardened. Many stages that performed the same essential function as described were devised and created during my research; they greatly improved attachment reliability.

![Figure 4.13: Example of a reservoir mounting stage.](image)

Another problem encountered with attaching the copper reservoir to the chip utilizing epoxy was wicking. When epoxy came into contact with the micro-sized ridges formed by the hollow-core waveguide, a clear, non-viscous, solvent-based component of the epoxy would wet to the surface, and capillary forces would wick it along the outside walls of the hollow-core [see
Figure 4.14. This clear epoxy byproduct would dry and harden alongside the hollow-core, forming a film.

Figure 4.14: a) Transverse hollow-core cross-section and b) ARROW S-mask top-down views of epoxy wicking problems encountered with second-generation ARROW vapor-cells.

Since the material was clear, it was often difficult to observe using normal optical microscopes. Fluorescing particles were mixed into the epoxy and fluorescence-based microscopy techniques were utilized to track the migration of wicking epoxy. Often the epoxy would wick all the way to the waveguiding portion of the hollow-core, creating a high-loss region and killing the optical mode. The other wicking problem occurred when the wicking
material migrated toward the hollow-core opening. The epoxy would wick into the channel and block the Rb from entering the hollow-core waveguide. While we experimented with a handful of different mechanisms to block wicking, we found that heating the epoxy at 65°C for 5 minutes before applying it on the ARROW platform made the epoxy viscous enough to minimize the wicking effect.

4.4.4 Cell wall passivation

During our investigations for a second-generation seal we also searched for other ways to improve our ARROW vapor-cell performance. Interactions between the cell wall and Rb atoms can have a negative impact on vapor-cell performance. The atoms can adsorb to the wall surface, effectively dropping the atomic density of the cell, which in turn decreases the optical depth. Depending on the surface properties these Rb atoms can stay adsorbed to the cell walls even when using optical and thermal desorption techniques. Not all negative cell wall interactions are caused by adsorption. Even atoms that have only short collisions or get too close to the wall can suffer from spin decoherence, which greatly limits the efficacy of many non-linear optical experiments like EIT and slow light [34]. While cell wall interactions are a problem in all vapor-cells, they are greatly exacerbated by small cell dimensions. To minimize cell wall interactions, the cell surfaces must be passivated.

The walls of larger vapor-cells are often passivated with a paraffin coating via evaporation [9]. However, the small, enclosed nature of our hollow-core waveguides does not allow for paraffin coatings. Instead, we use self-assembling monolayer coatings to passivate the cell walls [82-85]. Currently, we create this monolayer by using the organosilicon compound octadecyldimethylmethoxysilane (ODMS). The advantageous aspect of using ODMS to passivate the cell walls is that it can be delivered in liquid form. As the ODMS solution flows
through the hollow-core channel, ODMS molecules attach themselves to hydroxyl bonding sites on the silicon nitride walls. At one end of the long ODMS carbon chain exists a silicon atom with two methyl and one methoxy group attached to it. The methoxy branch is the key to the molecules attachment to the hydroxyl bonding site. The methoxy groups breaks off from the ODMS chain and bonds with the hydrogen atom from the silicon nitrides’ hydroxyl bonding site to form methanol. The silicon atom on the ODMS molecule then attaches to the available oxygen atom on the silicon nitride surface to form a siloxane branch [see Figure 4.15]. This reaction continues to take place, thus forming the monolayer one molecule at a time at the various hydroxyl bonding sites across the surface.

![Figure 4.15: Illustration of ODMS bonding to silicon nitride [24].](image)

The passivation process is begun by carefully mixing the solution that will ultimately deliver the ODMS molecules to the hollow-core walls. The solution must be mixed by hand immediately before application since the solution does not last much longer than a day. Cross contamination is of great concern in this process, especially the inclusion of more water than the recipe calls for; this can greatly reduce the solution’s lifetime and increase precipitation and
clogging. The process is as follows: In beaker (A) mix 0.5 mL of HCl with 6.024 mL of DI water. In beaker (B) mix 0.197 mL of the solution in beaker (A) with 24 mL of tetrahydrofuran (THF). Then in beaker (C) mix 0.25 mL of ODMS into 31.8 mL of THF. Then mix 0.18 mL of the solution in beaker (C) into beaker (B). Then filter 2.0 mL of the solution in beaker (B) and mix with 25 mL of cyclohexane in beaker (D). Filtering the solution from beaker (B) in this step is important since the formation of large organic precipitates in the passivation solution will greatly increase the likelihood of hollow-core channel clogging. I recommend using sub-micron level filters that can withstand strong solvents. I recommend 0.5 µm PTFE filters. The solution in beaker (D) should become slightly cloudy after mixing. Continue mixing the solution in beaker (D) for 5 minutes after which it will be ready for device application [85].

I first attempted to apply the ODMS solution to ARROW devices by simply submerging the chips in the solution for about 20 minutes and relying on capillary action to fill the channel. I then rinsed the chip in pure cyclohexane followed by DI water. However, I had a chronic problem with clogged hollow-core channels. By flowing dyes through the channels and observing them with optical microscopes I could identify locations (especially corners) where foreign material (presumably ODMS precipitates) tended to build up. Via subsequent experimentation I discovered that this buildup occurred because the ODMS solution was not properly flushed out of the channel. Since the channel was already full of ODMS solution when the chip was rinsed with cyclohexane, the cyclohexane did not flow through the channel via capillary action. While being rinsed in the cyclohexane, the ODMS solution was being purged from the channel only via diffusion, which, given the dimensions of the ARROW channels, happens at a very slow rate. Since the channels were not being completely purged of the ODMS
solution during the rinse, when the device dried the solvent evaporated, leaving behind deposits of ODMS in the channel, which caused clogging.

My solution to the clogging was to involve a pressure differential across the channel during the rinsing process to actively push the ODMS out of the channel while simultaneously pulling fresh cyclohexane into the channel. The basic technique is to never let the channel dry while it still contains the ODMS solution. To do this, a copper (Cu) stub reservoir is attached to each end of the channel. A vacuum is connected to one of the reservoirs via a rubber hose to create a pressure of ~70 mTorr in that reservoir. The other reservoir is filled with the ODMS solution and the channel quickly fills with the solution because of capillary action. After that, the vacuum maintains a slow but steady flow of ODMS solution from the filled reservoir to the reservoir attached to the vacuum. This flow is allowed to continue for 30 minutes to allow for the ODMS monolayer to fully form.

During this time the reservoir is always kept full of the ODMS solution such that the channel does not dry. After 30 minutes of ODMS flow, the remaining ODMS is removed from the reservoir and the reservoir is then immediately filled with pure cyclohexane. Since the channel is already full, the cyclohexane is introduced into the channel only at the flow rate caused by the pressure differential. The time it takes for the ODMS to be completely purged from the channel while simultaneously being filled with pure cyclohexane is 2 hours. During this time the reservoir has to be monitored to ensure that it never dries. After rinsing the ODMS application procedure is complete. Figure 4.16 illustrates the ODMS application procedure.
Figure 4.16: Cutaway illustration of ARROW channel ODMS coating procedure.

A test was devised to quantify the effect that ODMS had on the surface energy of silicon nitride when compared to other coatings. This test was conducted utilizing dyne pens. A dyne is a unit of force and dyne/cm is the unit traditionally used to measure surface tension. Dyne pens are a series of pens filled with liquids, each with a known surface tension. The surface energy can then be tested by applying a thin layer of the liquid from a dyne pen and monitoring the time it takes for the liquid to bead. Ultimately, the surface energy is said to be the same as the surface tension of the liquid in the pen with lowest dyne/cm value that beads in under two seconds. For example, if the liquids in 60 and 50 dyne/cm pens bead in under 2 seconds but the liquid in a 40
dyne/cm pen takes 5 seconds, the surface would be said to have a 50 dyne/cm surface energy. The results seen in Table 2 show that ODMS does in fact decrease the surface energy of the silicon nitride, but not as much as a paraffin coating (HDMS is not a practical solution due to its limited adherence time). This discrepancy could have to do with a (theoretically) incomplete coverage of the ODMS coating as discussed in the following paragraph. That being said it should be mentioned that during my time in the Slow Light group, the only Rb-loaded ARROWs that were successfully probed for optical effects (i.e., absorption spectrum, EIT, and slow light) had an ODMS coating as applied by the previously described methodology.

Table 2: Demonstration of the effect various coatings have on PECVD silicon nitride surface energy [24].

<table>
<thead>
<tr>
<th>PECVD Nitride surface energy</th>
<th>Uncoated</th>
<th>ODMS</th>
<th>HMDS</th>
<th>Paraffin</th>
<th>Surpass 4000</th>
<th>Ultratol Dynamic</th>
</tr>
</thead>
<tbody>
<tr>
<td>dynes/cm</td>
<td>60</td>
<td>50</td>
<td>40</td>
<td>40</td>
<td>&gt;60</td>
<td>&gt;60</td>
</tr>
</tbody>
</table>

Pure silicon nitride (Si$_3$N$_4$) does not contain any hydrogen or oxygen. However, in practice PECVD silicon nitride films contain impurities, many of which incorporate hydrogen and, to a lesser extent, oxygen. Therefore, passivation of silicon nitride surfaces using ODMS relies on the existence of hydroxyl impurities. This means that ODMS coverage of silicon nitride will not be a complete or uniform coating because of the small amount of available hydroxyl groups since, one would hope, impurities are rare in the surface composition. This is especially true when comparing ODMS coverage on a material such as silicon dioxide that has more oxygen in its composition. While ODMS has been shown to successfully alter the surface
properties of PECVD silicon nitride, there are other methods that could be employed to improve the monolayer coverage. First, an extremely thin layer of silicon dioxide could be deposited on the silicon nitride walls of the hollow-core channels such that it has effectively no impact on the optical properties of the channel but provides more hydroxyl bonding sites for the ODMS. The second method would be to switch from ODMS to another organosilicon compound with better self-assembling monolayer properties such as octadecyltrimethoxysilane (OTMS). OTMS is very similar to ODMS except it has three methoxy branches coming off the silicon atom at the end of the carbon chain instead of one. This means that not only can the OTMS molecule bond with hydroxyl groups on the silicon nitride surface, but the other methoxyl branches can bond with the methoxyl branches of adjacent OTMS molecules to form crosslinking siloxane chains. These cross-linked OTMS molecules can effectively ‘blanket’ the silicon nitride surface without the need for each OTMS molecule to be independently bonded to the silicon nitride surface. The OTMS blanket will have periodic anchor sites wherever available hydroxyl groups exist. It might be worthwhile for future researchers to look into this possibility.

4.4.5 Second-generation loaded ARROWs

All of this learning was applied to the successful and repeated creation of second-generation ARROW vapor-cells. This generation utilized devices that had undergone the full SAP process flow outlined in Section 2.4.
The chip was cleaned with an acetone and IPA rinse. The reservoirs are made with 3/16” copper stubs that are cleaned with a 15 second dip in a H₂SO₄:H₂O (1:2) mixture, rinsed with DI water, and then dried with IPA. After the chip and all components were cleaned, a copper stub reservoir was epoxied over the hollow-core openings, one at each end. For our first-generation devices we only needed one reservoir, but in order to apply ODMS two reservoirs are needed. The epoxy is allowed to fully cure. Then ODMS is applied as outlined in the previous section. After the ODMS rinsing procedure one end of the hollow-core is seal by applying a dab of epoxy right over the opening at the base of the reservoir. The completed chip then undergoes a 2 hour dehydration bake at 120 °C. Following the bake the chip is loaded into the glovebox, Rb is place in the non-sealed reservoir, attached to the vacuum, evacuated, and cold-weld sealed.

Figure 4.17: Illustration of second-generation ARROW vapor-cell fabrication and loading sequence.
Figure 4.18: Illustrations of second-generation ARROW vapor-cell. a) Top down view. b) Side cutaway view of reservoir. c) Angled 3D view.
The development of the second-generation vapor-cell construction techniques culminated after the successful observation of Rb atomic spectrum, EIT, and slow light on multiple ARROW devices [50, 86]. While the second-generation vapor-cells did prove successful in easily controlling the pressure and repeating the results, they suffered one major setback, short lifetimes. After an ARROW vapor-cell was heated to 80°C, for the optical tests it would only last for several hours. I conducted in-depth lifetime experiments to better understand the failure [87]. Those experiments are presented in section 7.2. We concluded that the Rb was reacting with the epoxy causing the atomic density to decrease over time. Not only was the atomic density dropping, but the cells suffered from pressure broadening because of either a byproduct of a chemical reaction or the outgassing of common epoxy byproducts (i.e. carbon monoxide, water). Thus began the search for a long-lasting third-generation vapor-cell sealing technique.

Figure 4.19: Photo of second-generation ARROW vapor-cell.
5 PURSUITING THIRD-GENERATION SEALING TECHNIQUE

While the epoxy used in the second-generation vapor-cells had many benefits such as its relatively simple application and gentle nature, its short lifetime made it a non-viable solution. We had already spent a lot of time and resources searching for the best performing epoxy and even that was not enough. As such, we switched gears and started looking for other materials with which to form a seal. In our search, we tried to look for materials that maintained the benefits of epoxy but that were compatible with Rb. Our third-generation sealing technique still utilized the copper reservoir and the cold-weld seal, but my efforts were focused on finding a new, non-epoxy method to seal the copper reservoir to the vapor-cell.

5.1 Wax

Sealing techniques that did not require extensive surface preparation were investigated first because of the inherent cost/time benefits. While investigating vapor-cells construction methods, I learned that many vapor-cell walls passivated with a coat of paraffin [88-92]. My conclusion from this discovery was that paraffin was compatible with Rb. This led me to investigate the possibility of using wax as a sealant.

To create a vapor-cell, I dipped the copper reservoir in molten wax to coat the bottom edge with wax. It was critical to apply as little wax as possible since an excess of wax would cover the opening into the hollow channel. The wax-coated stub was then lowered onto a heated
vapor-cell body. A dab of wax was also placed over the second opening to fully encapsulate the hollow-core waveguide. The joint was allowed to cool and was then ready for loading.

My first investigation utilized generic paraffin wax. I could not successfully create functional minicells with the wax because the wax did not create a stable seal. It suffered from adhesion problems and was very weak mechanically. Also, the wax completely melted at 50 °C and softened at 40 °C, which made heat-based optical testing difficult. The rubidium in the vials always oxidized. I was not sure if the Rb was reacting with the wax or if the wax was not creating a hermetic seal for one of the above reasons.

While researching for different kinds of wax, I encountered Crystalbond crystal-wax wafer-mounting adhesives. These products are used to mount wafers to another substrate while being relatively easy to remove. I tested Crystalbond 555 HMP, 509, and 590. These wax-like wafer adhesives (often referred to as ‘crystal wax’) were applied exactly like the paraffin wax; however, their melting temperatures were 66°C, 120°C, and 150°C respectively. The crystal wax definitely created strong hermetic seals. However, the Crystalbond 509 and 590 reacted fairly quickly with the Rb. After one day at room temperature the Rb was completely oxidized. The Crystalbond 555, however, fared much better than the other crystal-wax varieties. A series of minicells made with Crystalbond 555 were analyzed using the heat-cycle tests. Since the Crystalbond 555 melts at a temperature of 66°C the peak temperature in the cycle tests was only 60°C compared to the usual 80°C. At this lower temperature the crystal wax performed fairly well, exhibiting, on average, a 19% drop in atomic density.
Even though the crystal wax performed adequately at lower temperatures, I still abandoned this approach because it was evident that the minicells still failed over time. Even though the 19% drop in density seems like a huge improvement at first, one must remember that this result is at a temperature 20 °C lower than the other tests. This makes a big difference. We can reasonably assume that the performance would have decreased significantly if the material was able to tolerate those higher temperatures. I was not looking for another solution that would last as long as the Aremco 2310; I was looking for a solution that did not react at all with the Rb. The limitation in heat made testing the platform awkward and on ARROW devices, wax suffered from the same wicking problem that originally plagued epoxy-based ARROW vapor-cells. While it was an interesting investigation, I sought another solution.
5.2 Glass Frit

Since glass and copper metal were known to be compatible with Rb, sealing techniques using only these materials were investigated. While the geometries of our ARROW platform would not allow us to use an epoxy-less technique like the Houskeeper seal, I examined other glass-to-metal sealing techniques.

One such technique ‘welds’ metal to glass using a material known as glass frit, or glass solder. Glass frit is a powder of glass precursor granules on the order of 60 µm or less. This glass powder can be combined with a solvent or organic liquid binder to form a paste-like substance to allow for easy application and forming. Later the glass frit paste is heated to a high temperature where the binder bakes out and the glass granules fuse together to form polycrystalline glass. The glass formed during this process can form strong hermetic seals; in fact, glass soldering is a common practice in vacuum technology.

While there exists a wide variety of glass types, glass typically melts at very high temperatures between 500 °C to 1200 °C. Typical borosilicate glass (i.e. Pyrex) has a softening point of 820 °C. These temperatures are much too high for most microfabricated devices, so special low-temperature glass frit compositions were designed to create glass that can melt at temperatures as low as 200 °C to 450 °C. This is done by combining the glass with special additives. One of the most common low-temperature glass compositions is leaded borosilicate glass. These low-temperature glass frits are commonly used in the MEMs industry. Glass frit bonding is commonly used for wafer bonding and device encapsulation [93, 94].

After running heat tests on ARROW devices we discovered that temperatures above 275 °C destroyed the delicate hollow-core structures of our ARROW devices. We therefore tried to create minicells at 275 °C to mimic the temperatures we would use on the ARROW vapor cells.
However, at that low of a temperature the glass frit just barely fused together, but the resulting glass was brittle and porous. In order to create strong, hermetic seals higher temperatures had to be used. The high temperature requirement was incompatible with our ARROW vapor-cells, and we terminated our glass frit investigations.

5.3 **Metals and Anodization**

With the failures of the previously described sealing techniques, the next logical step in the research path was solder. Solder was not ideal because it generally involves a lot more surface preparation, with an increase in cost and a decrease in yield. I had a great deal of data that indirectly suggested that Rb was reactive with many of the more common soldering metals. I designed a test to better quantify Rb’s compatibility with common elements and materials used in silicon-device fabrication. I wanted the test to isolate individual materials and minimize other potential failures to get a clear signal of the material’s compatibility with Rb. At this point in our research only copper and glass were known to be compatible with rubidium. For this purpose I turned to Houskeeper minicells. Since I had already tested the long-term performance capabilities of the Houskeeper minicells, if I populated them with foreign materials I could reasonably assume that any degradation of the atomic density was caused by a reaction with that material. As such I made a list of materials I wanted to test and then loaded a sample of that material in an empty Houskeeper minicell. The minicells were then populated with Rb, evacuated, sealed, and tested via the heat-cycle method. The results of the Houskeeper tests can be seen in Figure 5.2.
5.4 **Ultrasonic Solder**

One of the more salient performances in the Houskeeper tests shown in Figure 5.2 was indium (In) metal. Looking into indium a little more I discovered that it is a fairly common solder in the electronics industry and has a melting point of only 156 °C. Another interesting fact is that it is wettable to bare silicon/silicon dioxide without any surface preparation. This immediately caught my attention as I viewed indium as a solder with potential epoxy-like simple application properties. After more research and communication with industry experts, I learned that for a silicon dioxide to metal joint it was recommended to use special indium solder alloys. These specially made alloys are designed to enhance the wettability and strength of pure indium. These solders are especially recommended for use with an ultrasonic soldering iron. The ultrasonic vibrations break up surface oxides, liquefy the solder, and promote the migration and
filling of micro fissures, ensuring good wetting to the substrate. The exact make-up of these solders are protected as trade secrets. We bought two types of indium-based solders, S-Bond Alloys from S-Bond Technologies and Cerasolzer from MBR Electronics.

We set up minicell experiments to test the ultrasonic indium-based solder alloy performance. Previously, we had been using only 3/16” OD copper tubing. The top surface of the glass vials used to make our minicells had an inner diameter close to 1/4” and an outer dimension of 7/16”. This meant that we could not directly attach the copper stubs to the top surface of the minicells. With the epoxy and wax this was not a problem because the copper stubs could be inserted into the glass vial opening and a seal created around the stub. However, for the solder to work we needed two flat surfaces to come together. My first workaround was to solder a copper plate to the top of the glass vial, drill a small hole in the copper plate, and then solder a copper stub around that hole. The second attempt was to take 1/4” copper stubs and flare the bottoms to create a wider base that matched the glass vial dimensions. We called these “flared” minicells. Figure 5.4(b,c) illustrates these two configurations. All of the ultrasonic solder tests were done utilizing these two methods. Figure 5.3 illustrates the ultrasonic solder process. The solder was applied to each surface of the seal separately with the heated ultrasonic
soldering iron. Then the two surfaces were brought together, heated with a hot air gun to re-melt the solder, and agitated via gentle rotations or ultrasonication to break the solder oxides and join the pieces together.

The results show that the ultrasonic solders performed at least as well if not better than epoxy minicells. On average Aremco 2310 epoxy minicells maintain 60% of their atomic density after a heat-cycle test whereas s-bond maintains a density in the mid-to-low 70% range. Cerasolzer was comparable to the s-bond results with the plate geometry, but was lower than Aremco 2310 levels with the flared geometry. This puzzles me especially because I did not observe the same trend in the s-bond geometries. My first guess is that the flaring of the copper stubs was done by hand so they did not have precise geometries leading to poor seals or more solder surface area with which the Rb could react.

Surface area can have a large impact on device lifetime. If the Rb is reacting with a certain material, the greater the surface area of that material, the faster the device fails. When comparing test results it is important to factor in the difference in surface area. Up until this point copper cold-weld minicell surface areas were constant since they all were created with the same geometry, a small diameter copper stub inserted into the glass vial. When I started to use solders other geometries had to be explored. This meant that a valid comparison of solder with a previous material, say Aremco 2310, required running new tests with the new geometry. While at this point in the development I was content with making generalized comparisons between two methods, you will notice in future sections as I fine tune my methodologies I take greater care in maintaining geometries. Figure 5.4 compares the second-generation geometries with the two ultrasonic minicells.
The favorable ultrasonic minicell performance led to the creation of ultrasonic solder ARROW vapor-cells. The fabrication process was similar to that with the minicells. The solders were ultrasonicated separately onto the base of the copper reservoir and onto the ARROW surface. The copper stub and the ARROW chip were aligned and brought together on an attachment stage made out of a drill press. They were heated for 30 minutes, at which point any
solder oxides formed were broken by agitation via rotating the drill head. After loading Rb into ARROW vapor-cells created with this method and optically probing them with no success, we performed some failure analysis to find any problems. What we found was that the ultrasonication during the soldering was breaking the fragile hollow-core structure over which we had to form a seal [see Figure 5.6 (c)].

![Figure 5.6: a) Top down illustration of the two ARROW ultrasonic soldering techniques. Also, transverse cross-section of copper reservoir seal over hollow-core b) without ultrasonication and c) with ultrasonication.](image)

We performed multiple experiments in which we created a berth of varying sizes around the hollow-core channel where we did not ultrasonicate the solder. While these experiments successfully kept the hollow-core intact, they revealed that locations that were not ultrasonicated did not create hermetic seals [see Figure 5.6 (b)]. While non-ultrasonicated solder did mechanically attach the copper stubs to the silicon dioxide surface, it did not create a hermetic
seal. In fact, the holes in the seal were so big that the reservoirs did not even hold water. After performing various other experiments, we concluded that solder had to be ultrasonicated to form a hermetic seal to silicon dioxide, but ultrasonication destroyed the ARROW hollow-core features.

5.5 Metal Solder Pads

5.5.1 Tin solder pads

During the beginning of the second-generation development, while still investigating epoxy seals, a short investigation of solder seals was conducted. The general idea was to metalize the ARROW surface and employ a solder to attach the copper stub to the ARROW. In this attempt I used deposited tin (Sn) as the metal soldering surface and tin/lead (Sn/Pb) solder. This initial choice was made due to the ubiquitous nature of tin/lead solder in the electronics industry and the good wettability between tin and tin/lead solder. Copper, an obvious choice for a solderable surface, was not used because of the lack of an immediately available copper deposition process. Two major concerns arose with the ARROW metallization process. First, both the solid and hollow-core ridges could not have any metal on top of them or they would cease to waveguide. Second, there could not be any metal surrounding the hollow-core channel openings or the solder, especially within the confined space of the reservoir, would wet to the metal surrounding it and seal the channel shut. The metalized surface had to be confined to the region directly under the reservoir seal. To this end, I developed a mask that formed metal rings or ‘donuts’ that circled the hollow-core openings. We dubbed this the ‘donut mask’ or the ‘donut process’. These rings allow for metal solder attachment of the copper stub, while
confining the solder to locations that do not disturb the overall functionality of the ARROW device.

Figure 5.7: a) Top down illustration of tin donut solder pads. b) Cross-sectional view of tin donut ARROW vapor-cell.

The rings are deposited using the lift-off technique described in section 2.4. The process is started with an ARROW wafer that has completed the entire SAP ARROW fabrication process outlined in section 2.4. Photoresist is spun on the wafer and patterned using standard photolithographic techniques. The photoresist is patterned such that the entire wafer is covered with photoresist except for a donut pattern around the two hollow-core openings. After the photoresist has been developed, it is rinsed in DI water and then placed in an oxygen plasma to
‘descum’ the surface where the tin will be deposited. To further clean and prepare the surface, the wafer is then dipped in a HCl:H₂O (1:1) mixture for 30 seconds followed by another DI water rinse. Next, the wafer is loaded into the e-beam PVD machine where 1 µm of tin is evaporated on the surface. PVD processes tend to be non-conformal in nature which is certainly true of the e-beam process in the IML. Since the solder will only wet to the metal solder pad and not silicon dioxide, the metal deposition process must deposit the metal on the horizontal AND vertical surfaces to ensure a hermetic seal. Figure 5.8 illustrates need for conformal depositions when creating solder pads.

Figure 5.8: a) Top down look at ARROW geometry b) Non-hermetic seal caused by non-conformal metal solder pad deposition. c) Hermetic seal due to conformal metal solder pad deposition.
To ensure a conformal coating during this deposition process the wafer is attached to an electric spinning mount which is in turn mounted to the spinning planetary in the e-beam machine. This double rotation mechanism ensures a uniform and conformal coating. The wafer then undergoes the lift-off process. Lift-off processes generally rely on non-conformal coatings which allows for the acetone to get under the metal. Since we needed the coating to be conformal, the lift-off process takes longer. Instead of exposed sidewalls the acetone has to find cracks and fissures in the tin coating. However, due to the stressed nature of metal films and the relatively poor adhesion of metal on photoresist, these cracks are prevalent enough to allow for successful lift-off. Finally the copper reservoir is attached using tin/lead solder, flux paste, and an electronics soldering iron.

This attempt at solder reservoir attachment was plagued with problems almost from the beginning. First, the machine used to generate the mask had trouble generating the shapes used in the mask design software. This meant that only a quarter of the mask was actually usable. Second, tin adhesion was a big problem. Very often the tin donuts would peel off because of a combination of poor adhesion and the relatively high-stress of 1 µm layer of tin deposited using our EBPVD system. Third, even the tin donuts that did not peel off would quickly be consumed via diffusion into the Pb/Sn solder, leading to the stubs falling off shortly after attachment. With these problems and the relative ease of using epoxy as the attachment medium I abandoned the solder route during the second-generation seal investigations. No successful vapor-cells were created using this technique. However, I did learn a lot during this process that was of great help during the development of the third-generation seals.
5.5.2 Chromium-nickel solder pads

After the failed ultrasonicated solder experiments, more in-depth investigations with metalized solder pads were conducted. After doing some research on metallization of silicon dioxide, I found that chromium has excellent adhesion properties with silicon dioxide [95-97]. As such, a thin layer of chromium is often employed as an adhesion-promoting intermediate layer between silicon dioxide and many metals such as gold, aluminum, nickel, copper, silver, etc. At this time the most convenient method for metal deposition was the e-beam PVD. Because of contamination concerns copper was not a deposition possibility. As such I looked to nickel as the soldering surface. According to my research, nickel had good adhesion to chromium and is commonly used as a soldering surface and Sn diffusion barrier for copper surfaces [98, 99]. Indium and copper also form a fragile and brittle intermetallic layer. Indium solder experts employ nickel as a diffusion barrier between the indium and copper. A typical solder industry standard is that barrier metals should be at least 50 µinches (1.3 µm) long [100]. Since I was planning to experiment with Sn-based solders as well as indium solders, the chromium/nickel solder pad seemed the ideal base to our soldered Rb reservoir sealing approach.

I immediately started fabricating soldered minicells. I deposited 250 nm of chromium directly followed by 250 nm of nickel on the top surface of the glass vials. I then deposited 1.3 µm of nickel on the bottom surface of a copper tube. Instead of using flared ¼” copper tubing like we did with the ultrasonic solder minicell tests, we switched to 3/8” copper tubing that fit perfectly to the glass vial soldering surface without any tampering. Note that we still used 3/16” copper tubing with the ARROW devices. The vials and copper tubes were heated and joined together using solder. To clean the surfaces and promote solder wetting we utilized flux #4-0A by Indium Corporation. The solders that I tested were 100% indium metal solder and eutectic...
tin/lead alloy solder, both of which have low melting temperatures of 157 °C and 183 °C respectively. There were three main problems I encountered with this initial solder method. First, the nickel e-beam deposition on the copper stub was not adhering. Second, the solder was not wetting to the copper stub or minicell vial surface very well. Third, stubs would often seem well attached to the solder pads at first, but then would randomly topple at later times.

Adhesion of the e-beam deposited nickel layer to the copper stub was almost non-existent. The metal was powdery and could be wiped off with a swipe of a finger. In an effort to improve nickel adhesion to the copper stubs, I ran a set of annealing experiments to promote the growth of a thick nickel-to-copper intermetallic layer. One limitation that I encountered was the lack of a proper annealing setup. Annealing furnaces generally should have the capability of supplying the desired atmosphere. Metal annealing should usually be done in a forming gas (80% nitrogen, 20% hydrogen) to inhibit oxide growth. While the IML does have such annealing furnaces the introduction of copper into these furnaces is prohibited due to its high diffusibility and doping characteristics. The presence of copper would potentially ruin other research. A high-temperature, copper-friendly oven was found, but it did not have atmospheric control capabilities. I concluded it would be good enough for initial proof-of-concept tests. I made batches of 3 e-beam deposited nickel-coated copper stubs and then loaded them into the furnace for different durations at multiple temperatures. Table 3 shows the results of these tests. At high temperatures the nickel layer oxidized, becoming powdery and easily falling off. At low temperatures the nickel kept its silver coloring but was easily removed during tape tests. I found that the optimal temperature and duration was 300 °C for 40 min. At this setting, the nickel turned a sort of bronze color very similar to the color of copper-nickel alloy samples I had
obtained. After conducting these tests I found that properly annealed nickel-coated copper stubs did not suffer from poor adhesion.

Table 3: E-beam deposited nickel-coated copper annealing test results. (a) Tape test: 1 no nickel was removed, 7 all nickel was removed. (b) Nickel coloring/oxidization: 1 silver, 4 bronze, 7 black.

<table>
<thead>
<tr>
<th>Time in Furnace (min)</th>
<th>Temperature (°C)</th>
<th>240</th>
<th>180</th>
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<td>a)</td>
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<td>5</td>
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<td>b)</td>
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The second problem encountered was that the indium solder was not wetting to the copper stubs or to the top of the glass vials used for minicells. With some effort we could get a good mechanical attachment between the stub and vial, but since it was not wetting there were always small holes in the joint that prevented us from achieving a hermetic seal. I ran some experiments on other surfaces. I noticed that the indium solder wetted just fine to the metal donuts on ARROWs and on some metalized glass slides. I came to the conclusion that surface roughness was the cause of our problems. To create flat soldering surfaces I used 150 grit (100 µm) sandpaper from the engineering shop. The 100 µm scale gauge created by the sandpaper were creating ridges that the surface tension of the indium solder could not overcome, thus preventing it from wetting properly to the surface; see Figure 5.9. The solution was tiered polishing. The surface was flattened with the 150 grit sandpaper, which was then polished by a succession of ever finer grit sandpaper: 400 grit, then 1200 grit, and lastly 6000 grit (2 µm).
After properly polishing all soldered surfaces, solder wetting problems were never encountered again. Note that this problem is not encountered on ARROW devices due to the polished nature of the silicon wafers.

![Diagram showing solder wetting on rough vs. smooth surfaces.](image)

**Figure 5.9: Solder doesn't wet to a) rough surfaces due to surface tension but does wet to b) smooth surfaces.**

The last problem encountered with our first attempt at metalized solder pads was the delayed toppling of the copper stubs. Right after fabrication the soldered seal seemed strong, but after a seemingly variable amount of time the copper stubs would pop off. I noticed that when the stubs toppled they took all the solder and the metal off the silicon dioxide surface. “Scotch tape” adhesion tests on the chromium-nickel solder pads showed good adhesion between the metal and silicon dioxide [101]. After doing some research I concluded that the total thickness of 500 nm of metal was too thin for soldering. The intermetallic layers between indium and nickel was thicker than 500 nm and the intermetallic layer formation was consuming the solder pads and destroying the chromium to silicon dioxide attachment. The solution was to create thicker layers of metal. However, thicker layers of chromium and nickel were not achievable with e-beam deposition. Previous experiments with depositions on our ARROW devices have shown that, with our e-beam process, chromium depositions over 300 nm thick and nickel depositions over 400 nm had a very high probability of peeling because of the high intrinsic
stress typical in evaporated chromium and nickel. So even when pushing the limits of the e-beam deposition process we could only achieve a total thickness of 700 nm on our solder pads, which was not enough. Indium Corporation recommended a minimum thickness of 1.3 µm for a nickel surface when utilizing indium solder [100]. It was at this point that I started to look for other metal deposition options, the most promising being electroplating.

5.6 Electroplating

Electroplating, or electrodeposition, is a commonly used metal deposition method that was developed in the early 1800s. The deposition occurs in an ionic solution in which metal cations are reduced on a conducting surface to form a coherent metal coating. In its most basic form, an electroplating system consists of a current source attached to an anode and a cathode submerged in an ionic solution. Current travels from the anode to the cathode via cations in the ionic solution. The anode is made of the metal you want to deposit and the cathode is the surface you want to deposit on. The anode replenishes the ionic solution with metal cations as the metal deposits on the cathode. Let us take copper electroplating as an example. As the current flows through the system, copper atoms on the anode give up two electrons (i.e., oxidation) and dissolve into the ionic solution as Cu$^{2+}$ ions. The Cu$^{2+}$ ions associate with SO$_4^{2-}$ anions in the solution and migrate to the cathode. At the cathode the Cu$^{2+}$ accepts two electrons (aka reduction) and bonds to the surface. Notice that the deposition amount is directly related to the total amount of current that passes from anode to cathode. In the case of copper, one atom of copper is deposited for every two electrons that flow from cathode to anode.
5.6.1 Electroplating simple geometries

When I decided to use electroplating to solve my metallization problems, the BYU IML had no documented electroplating procedures or equipment setup. To get an electroplating solution actualized, I first visited some colleagues in the chemical engineering department here at BYU. In their research they were electroplating nickel onto some of their devices. Even though our applications were not the same, they provided me with some reference materials, a nickel electroplating recipe, and introduced me to a potentiostat that could provide a constant current source. Their electroplating recipe seemed to be a modified Watts nickel plating solution. It consisted of 20 g of nickel sulfate, 23 g nickel chloride, and 30 g of boric acid with water added to make a total volume of 0.666 L. They suggested that the maximum current be 90 mA and the minimum 10 mA. The larger the total surface area being electroplated the closer the current
could be to 90 mA while the smaller the surface area the closer to 10 mA the current should be. The reaction that takes place for nickel deposition is essentially identical to that of the copper example earlier. In this case, however, the ionic solution is comprised of Ni$^{2+}$ cations associated with SO$_4^{2-}$ anions.

Calculating the electrodeposition time needed to achieve a given thickness is relatively straightforward. First you calculate the total mass, $m$, by multiplying the total volume of metal that you want to deposit, $V$, by the density of the metal, $\varrho$.

$$m = \varrho V.$$ \hfill (5.1)

Then you convert the total mass to total moles, $M$, by dividing the mass by the metal’s standard atomic weight, $W_S$, which can be considered as having units of g/mol,

$$M = \frac{m}{W_S}.$$ \hfill (5.2)

Then you calculate the amount of charge, $Q$, needed to deposit the metal using Equation (5.3),

$$Q = e \cdot L \cdot N \cdot M,$$ \hfill (5.3)

where $e$ is elementary charge, $L$ is the Avogadro constant, and $N$ is the number of electrons needed to reduce one atom of metal at the cathode. For nickel, the cation being reduced at the cathode is Ni$^{2+}$, therefore $N = 2$. The final step is to calculate the time, $t$, by dividing the total charge by the current, $I$, that is being supplied during the electroplating process,

$$t = \frac{Q}{I}.$$ \hfill (5.4)

Utilizing the electroplating solution and deposition process outlined above, I ran some preliminary tests on flat pieces of copper metal. Table 4 contains the results of these
experiments. The thickness was measured using a profilometer. Table 4 shows that the thicknesses were within 10% of their target value. This error was likely due to noise in the thickness measurements caused by surface roughness on the copper sheeting used as the substrate. Figure 5.11 shows an example of a profilometer measurement demonstrating the surface roughness. For our process, the 10% error was made acceptable by targeting a thicker layer than needed. While these tests were initially merely for proof of concept they proved to be so successful that they were soon employed for the metallization of solder contact points on minicells and ARROW devices alike.

Table 4: First nickel electroplating recipe thickness test results.

<table>
<thead>
<tr>
<th>Measured Thickness (µm)</th>
<th>Target Thickness</th>
<th>1 µm</th>
<th>2 µm</th>
<th>3 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td></td>
<td>1.06</td>
<td>1.84</td>
<td>3.06</td>
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<tr>
<td>Test 2</td>
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<td>2.18</td>
<td>2.92</td>
<td></td>
</tr>
<tr>
<td>Test 3</td>
<td></td>
<td>2</td>
<td>3.01</td>
<td></td>
</tr>
<tr>
<td>AVG</td>
<td></td>
<td>1.06</td>
<td>2.01</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 5.11: Sample profilometer output showing surface roughness in first Ni electroplating experiment.
To create a metal solder pad on a glass vial or ARROW device, the surface was ‘seeded’ by depositing 250 nm of chromium followed by 250 nm of nickel. This conductive metal seed layer was connected to the cathode of the potentiostat and placed into the electroplating solution. Pure nickel ribbon was attached to the anode of the potentiostat and placed into the electroplating solution. When the current was turned on the nickel ions would flow from the ribbon and deposit on the seeded solder pad. The same was done with the copper stubs to deposit a 3 µm diffusion barrier layer of nickel; however, no seed layer was needed since copper is metal. After the electroplating was finished, the soldering method discussed earlier was employed to create durable, hermetic seals between the copper Rb reservoirs and the vapor-cell body.

Figure 5.12: Photographs of a) original electroplating setup, b) electroplated Ni layer on 3/8” copper stub, c) vial with e-beam deposited Cr/Ni seed metal prepped for electroplating, and d) ARROW chip prepped for electroplating with e-beam deposited Cr/Ni seed metal patterned into 3rd gen donut solder pads.
One concern I had was whether or not the sidewalls of the ARROW hollow-core were coated with metal in the donut metal solder pad region. I discussed this concern in section 5.5.
and Figure 5.8 illustrates why sidewall coverage is important for hermetic solder seals. I had some of our chips that had been patterned with donut metal solder pads get SEM reviews to verify sidewall coating. These chips had received the standard 500 nm of Cr/Ni seed layers and 3 µm of electroplated Ni. Figure 5.13 shows that the PVD metal coating process I created was indeed conformal enough to allow for a complete electroplated Ni coating. With that concern overcome I was assured that my ARROW solder seals would be hermetic.

![Figure 5.14: Photo of third-generation indium minicell with black dust at bottom.](image)

Since the results published in Figure 5.2 showed that rubidium reacted noticeably with tin and lead (Pb), I decided to use pure indium solder with my first electroplated solder minicells. Initial tests looked very promising. Heat-cycle tests showed that minicells made with indium solder only dropped in atomic density by several percent. This was a huge improvement over Aremco 2310 minicells. However, I noticed that if a minicell was stored for a couple of days at high temperature, a fine black dust started to accumulate at the bottom of the minicells. This
accumulation of dust would increase until all the rubidium in the vial was consumed, at which point the atomic spectrum disappeared. The black dust was a by-product of a slow chemical reaction between rubidium and indium that could not be detected in the short duration of a heat-cycle test. At this point I knew I had to do two things: (a) develop a test to investigate long-term performance of minicells and (b) continue searching for a long-lasting sealing method. Chapter 7 discusses the long-term test I developed and its results in detail. This chapter will continue the narration of the development of a long-lasting seal.

5.6.2 Electroplating complex geometries

The failure of pure indium solder led me to begin investigating radically different sealing approaches. While conducting some research and brainstorming some solutions I came up with the following idea: I should stop looking for sealing materials compatible with rubidium and look instead for a way to coat incompatible materials with a compatible material. My list of compatible materials at this point was pretty short: glass, copper, and nickel. Even though the list was short, I had just learned a new way to deposit nickel, electroplating. My idea was to create solder minicells and then passivate the solder joints by coating them with nickel.

I created a series of experiments to test the adhesive properties of electroplated nickel on indium and tin/lead solder. I brought back tin/lead solder as an option because if I was going to passivate the surface it did not matter what solder I used. I found that electroplated nickel adhered well to tin/lead solder but wrinkled and fell off of indium solder. My hypothesis is that the relatively high-stress of deposited nickel easily warped the surface of the extremely malleable indium. I started making some minicells with tin/lead solder with nickel passivation coatings. However, I soon noticed a problem: the glass vials were cracking just under the tin/lead soldered joint. Sometimes the cracking would occur during cooling after the soldering
process and other times the vials would crack days later after a slight jolt. ARROW devices created with tin/lead solder would consistently shatter, even during careful handling. The conclusion I came to was that the joint was stressed because of the different thermal expansion coefficients of the materials involved, resulting in extreme sensitivity to mechanical shock. We conducted some experiments to identify the lowest soldering temperature possible (thereby reducing the thermal expansion delta between the glass and copper) and different cooling schemes, but the breaking never went away. For the tin/lead minicell lifetime data presented later in this dissertation, I coated the top of the glass vial with Aremco 2310 epoxy to prevent cracking. Ultimately though, I moved away from the tin/lead solder because the fragile nature of the ARROW devices could not withstand a high-stress joint.

When soldering with indium I never experienced any stress-related breakage on minicells or ARROW devices. For that reason I wanted to continue with indium solder. The problem was that nickel did not reliably electroplate onto indium. While considering my options I discovered that copper was in fact arguably one of the most commonly electroplated metals. As such I decided to develop copper electroplating capabilities in order to experiment with indium solder joints. I did some research and found a commonly used copper sulfate electroplating solution that was very similar to the nickel electroplating solution. The recipe consisted of 225 g/L of copper sulfate (CuSO₄·5H₂O) mixed with 65 g/L of sulfuric acid (H₂SO₄). After running preliminary tests with the same currents used with the nickel electroplating process, I found that copper showed good adhesion with indium solder.

I also experimented with electroplating copper onto tin/lead solder. While the tin/lead solder showed decent copper electroplating properties at first, high-temperature tests revealed that over time the copper film had a tendency to peel off. I looked back at some of my old nickel
onto tin/lead electroplating experiments and found that they exhibited the same tendency to peel over time. This peeling effect was accelerated by the introduction to heat. During my electroplating research I found some material suggesting that lead has an immediate adverse reaction with most electroplating solutions even with no current applied. This reaction creates a thin film over the lead metal that does not exhibit good adhesion properties. This can be overcome by using a modified electroplating solution and a surface preparation step known as ‘brining’. However, since the tin/lead solder was having stress breakage issues, I did not feel that a deeper investigation warranted the time it would take.

Figure 5.15: A electroplating process with low throwing power will deposit more metal on the closer surfaces.

While my initial foray into electroplated solder passivation layers proved promising, two major problems hindered my progress. The first was ‘throwing’ problems and the second was current density issues. ‘Throwing power’ is a term used to describe the ability that an electroplating process has to plate metal evenly on surfaces both close to the anode as well as far.
Electricity likes to find the path of least resistance. In all materials the greater the distance the electrons have to travel the higher the resistance. This concept is exacerbated the higher the resistivity of the material. In the case of electroplating, the electroplating solution, although conductive, has a higher resistivity than the target metal surface. This means that the ions will tend to migrate toward the parts of the cathode that are spatially closer to the anode, finding the path of least resistance.

A variety of solutions exist to overcome throwing problems in a process. One is to modify the throwing power of a recipe. This can be done by changing the concentration of ions in the solution, effectively decreasing the resistivity of the solution. Also, to a certain point, the current density in a recipe can be increased. This increase in current density effectively saturates the bonding sites at the nearest points of the cathode, allowing for a higher amount of current to continue on to farther parts. Arguably the best way to overcome throwing power issues is to cleverly plan out the geometry of the electroplating system. One solution is to place the anode far away from the cathode, thus making any difference in distance between the various points of the cathode small compared to the overall distance. Introducing multiple anodes is another possible solution. Another clever work-around is to place non-conductive obstacles between the nearest points and the anode to increase the path an ion would have to travel to the near parts while leaving the distances to other farther locations unchanged [102-105].

While electroplating solder pads onto minicells and ARROWs, we did not find throwing power to be a big issue. It is true that care had to be taken when electroplating multiple devices at once to ensure that the separate devices were placed equidistant from the anode to prevent thickness variation, but overall those were uncomplicated and fully exposed planar geometries. However throwing power became more critical in the process of trying to passivate/coat the
reservoir solder seal. In this case, the location I wanted to deposit metal was the bottom inside surface of a relatively long and narrow conductive tube. Throwing power became a significant source of error in plating thicknesses. In the first electroplating system I built, I placed the anode next to the opening of the copper tube. This resulted in most of the metal being deposited on the outside and end of the tube with some metal deposited on the inside of the tube but only for a short distance. In other tests the outside of the tube was electrically isolated by wrapping with non-conductive tape. This setup did not work either. Even though all the metal was deposited on the inside of the tube, it deposited only for a short distance from the entrance. In other words, the metal ions were unable to reach the very end of the copper tube where the metal was really needed. The distance the current needed to travel down a relatively narrow conductive channel was too great. The metal was plating to the sides before it could reach the end.

![Figure 5.16: Throwing power problems when trying to electroplate a coating of a metal (M1) onto the inside solder surface of a minicell. The metal plates on the end of the minicell copper stub and does not reach the solder surface.](image-url)
The final solution to my throwing problem was to effectively mask both the outside of the tube and most of the inside of the tube except for the very end where the solder joint was located. I called this process “targeted electroplating”. For the minicells a Teflon tube was milled such that the outer dimension was the same as the inner dimension of the copper tube. This was placed in the copper tube until it stopped just short of the solder joint. The anode was then placed down the center of the Teflon tube and was only exposed to the cathode copper tube at the very end, right next to the soldered joint.

Figure 5.17: Using a Teflon insert to mask areas where no coating of a metal (M1) is needed. Now only the inside solder surface receives a metal coating. This is called ‘targeted electroplating.’

For the ARROW copper-stub reservoirs, the same general solution was used except that because of the smaller size, a milled Teflon insert was not practical. Instead, a nickel wire acting as the anode was wrapping in heat-shrink tubing with only the very end exposed. In this case the
walls of the copper tube are exposed to electroplating solution the entire length of the tube, but it is the anode that is electrically protected, except for the very end. Even though the electroplated/not-electroplated dividing line will not be as sharp as in the case of the minicell, because of the relative short distances, the error introduced by the extra surface areas being plated will be pretty small and easily made up for by increasing the time or total surface area in the recipe calculations. These setups have been observed to provide adequate targeted electroplating depositions in our difficult geometries.

Two other important sub-categories of throwing power are micro-throwing capability and leveling capability. These two parameters are sometimes used interchangeably in literature, although these related concepts are not the same. Micro-throwing power refers to the difference in the thickness of the plated metal at the top of a micro-sized fissure or crack versus the bottom. Though similar in concept to throwing power, micro-throwing power refers generally to micro distances rather than macro distances. Micro-throwing power can be affected by the plating-solution chemistry and current densities being employed. Leveling power is the ability a recipe has to fill in cracks, level micro peaks, and smooth out any other micro-sized unevenness on a surface. Leveling generally can be done only via the introduction of special organic compounds. These organic molecules are attracted to the relative high electric fields located at any peaks or edges. While they do not adhere to the cathode surface, they do inhibit or ‘get in the way’ of metal deposition at those sites, thus allowing depressions to fill in faster than peaks grow. Ultimately, for our applications the leveling ability is not that important, but the micro-throwing power is important. Our application does not require a smooth or shiny surface, which is what the leveling power helps achieve. We do need to make sure that the entire surface is adequately covered, even cracks and fissures. A small exposed area will allow for the Rb to penetrate into
the solder and react. I have observed such reactions over time and while the reaction at first starts as a small dot from a small fissure or hole in the electroplated protective coating, the metal will start to peel back as the Rb reaction expands and consumes the solder underneath until all of the Rb or solder is consumed and the electroplated metal is completely removed. As such, I took this into consideration and chose only electroplating solution recipes that had been proven to have good micro-throwing properties.

The second major problem encountered with solder passivation electroplating was current density. I had noticed early on that during the nickel electroplating process little bubbles would form on the cathode surface. The bubbles would prevent metal from plating underneath them as shown in Figure 5.18. This caused little holes in the metal plating. These holes were not big problems for solder pads because the solder could seal around them just fine. However, even the smallest hole could be catastrophic in a solder passivation layer. As mentioned in the previous paragraph I have observed the Rb react with solder exposed in a hole only 10s of µm wide. Over time the reaction causes the metal to peel back until more and more solder is exposed and the minicell fails. I learned through more investigations that these bubbles could be caused by high current density during the electroplating process. While increasing the current during an electroplating process in general increased the deposition rates, there is a limit. The limiting factor is the maximum current density allowed by the solution. The concentration of ions in the solution plays a large role. As the concentration increases, the number of ions in proximity to the cathode and anode surface area goes up; thus also increasing the maximum allowable current for a given surface area as well. If the current ever exceeds the amount of available ions currently adjacent to the anode and cathode surfaces, side reactions will occur. A common side reaction in these electroplating solutions is the formation of hydrogen gas and unwanted oxides.
on the metals from water molecules. Often the other ions in the solution will start to deposit at higher current densities as well, the sulfate ions for example. It is therefore important to make sure that your electroplating current is not higher than what the surface areas and solution can support. In the case of the nickel bubbles, I was pretty confident they were hydrogen gas bubbles and were caused by having too high of a current density. Having high current densities can also cause surface roughness problems and the formation of metal peaks and valleys. In order to eliminate the holes in the nickel electroplating solution I set up some experiments to find the best current densities for my processes.

![Diagram of hole formation in electroplated metal on solder caused by the accumulation of gas bubbles.](image)

Figure 5.18: Hole formation in electroplated metal on solder caused by the accumulation of gas bubbles.

There is another important variable in the current density discussion. Not only is the ionic concentration important but so is the ionic flow. Current is charge over time. Current
density is current over a surface area. Therefore, current density can be written as charge over time and surface area. So the current density can be increased two ways: (a) increase the amount of charge per surface area--i.e., increase the ionic concentration or (b) increase the amount of charge per unit of time--i.e., increase the speed at which ions arrive at the surface. Since there are physical limits to the amount of ions that can be dissolved in a given volume of water, increasing the ionic concentration is not always an option. Therefore, if higher current densities are desired (i.e., faster deposition rates), the ionic flow to the surfaces must be increased. Under normal conditions the current density is limited by the diffusion rate of the ions through the solution. In industry, electroplating systems have heated vats with large pumping systems that cycle huge volumes of the ionic solution every second. Both the heat and increased flow allow for higher current densities. Because of the small and awkward geometries of the surfaces involved in our vapor-cells, neither the heat nor increased flow was very realistic. As such I set about to find the ideal current density for our solution recipes at RT and no flow.

For the Watts nickel electroplating recipe, I used the recommended current density range of 3 to 11 A/dm², the typical value being 4.3 A/dm² [103]. This was, however, based on operating temperatures between 44 to 66 °C with mechanical agitation. Since I was looking for a current density to use at RT with no agitation, I knew I would have to use lower current densities. The copper sulfate recipe I found had more useful recommendations; in situations where agitation and high temperatures were not feasible, the current density range for optimal performance was 3.7 to 5.4 A/dm² [103]. I chose 4.6 A/dm² as the copper electroplating current density for my procedures. In order to independently verify the copper current density performances and to find the optimal nickel current density, I ran a series of electroplating experiments. I wrote some MATLAB code to help determine the optimal electroplating
parameters. The code requires the metal type, the surface area of the anode and cathode, the desired thickness to be deposited, and desired current density. The code then outputs the current the process should be run at and the total time of deposition. This is done by finding the lowest surface area between the cathode/anode and multiplying it by the current density. This provides the optimal current setting. Equations (5.1) to (5.4) are then used in conjunction with the current, metal type, and desired thickness to calculate the total time of deposition.

In my investigation, I ran current density skew with multiple tests at each current density. The target thickness in these experiments was 3 µm. Table 5 shows the results of the tests. I should note that because of the relatively imprecise methods available to me for measuring the surface areas of the test surfaces, thickness error margins on the order of 15% were expected. Creating tests with higher resolution would have been more costly, and that type of error margin was completely acceptable for the trends I was investigating. For the copper tests, the target current density of 4.6 A/dm² showed great performance, not only in the thickness results but also in the reduction of surface irregularities and the promotion of a smooth, uniform surface. At the lower current density the copper did not plate over the entire surface. It only plated in random patches. At the higher current density the copper plating was a lot rougher and only two-thirds as thick as the target. During the high current density plating process bubbles were forming so fast that it looked like the solution was boiling. I concluded that the reduction in thickness was a direct result of a percentage of the current being consumed in unwanted side reactions since the recipe could not support the higher current density. The results matched theory.

For the nickel experiments, I was actually trying to tune into an optimal current density for our experiments. The thickness for each setting was matched with the target (taking into account our error margin) but the really telling metric was the existence of holes in the metal.
The bubbles formed during nickel electroplating processes with high current density stayed attached to the surface and prevented electroplating at their locations, creating holes in the deposited film. My goal was to find a current density at which this did not happen. Table 5(b) shows the measured hole depth for the different current densities. It is important that the observer does not take the hole depth at face value. The profilometer needle used to make these measurements has a relatively large triangular tip that cannot probe deep holes with micron scale dimensions. Therefore, it cannot be assumed that a hole with, for example, a measured depth of 0.58 µm does not in fact penetrate through the entire film thickness. This test was designed specifically for a there/not there hole resolution. The existence of any bubbles/holes points to an unwanted side reaction. It is interesting to note, however, that as current density decreases so does the measured hole depth; at the very least, a reduction in hole dimensions correlated with a reduction in total bubble size, which in turn points to a reduction in the unwanted side reaction rate. Returning to the main point of the investigation, I found that at a current density of 0.43 A/dm² the formation of bubbles completely stopped. Therefore, from this point out a current density of 0.43 A/dm² was used in my nickel electroplating experiments.

<table>
<thead>
<tr>
<th>Measured THK (µm)</th>
<th>Current Density (mA/dm²)</th>
<th>Current Density (mA/dm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.46  4.6  46</td>
<td>0.43 0.86  2  4.3</td>
</tr>
<tr>
<td>Test 1</td>
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<td>Measured THK (µm)</td>
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<td>Test 3</td>
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<tr>
<td>AVG</td>
<td>N/A  3.24  1.9</td>
<td>N/A  0.58  0.98  2.2</td>
</tr>
</tbody>
</table>

Table 5: Electroplating current density experiment results. (a) Copper thickness (THK) vs. current density. (b) Nickel thickness and hole depth vs. current density.
While creating a solution flow large enough to allow for a significant increase in current density was impractical, no solution flow could have a negative impact on the process. It is impossible to create an electroplating process with absolutely no side reactions. While one can minimize unwanted reactions, over time they can build up and deteriorate the electroplating solution. Also, impurities introduced into the solution from the devices as they go in and out of the electroplating solution can build up over time. These impurities effectively reduce the copper ion density and even more seriously can start to incorporate into the deposited films. I was worried that the small volume to surface area ratios in our minicells and ARROW reservoirs would cause this deterioration to occur rapidly.

Figure 5.19: a) Cross-section looking down minicell stub and b) system-level cutaway view of minicell targeted electroplating process with electroplating solution flow capability. The ARROW vapor-cells uses a similar system but on a smaller scale.
As such I looked into ways to constantly cycle the electroplating solution through our devices during the electroplating process. I decided to use a small fountain water pump. The pump provides a positive pressure flow of electroplating solution through a series of small tubes. Earlier I talked about the steps I took to ensure target deposition on the solder joints with a Teflon insert and heat shrink plastic tubing. In the case of the minicells, I replaced the old metal anodes with 1/8” nickel or copper tubing fed through the Teflon insert described earlier. The metal tube is then hooked up to the pump using plastic tubing. The metal tube then acts as both the anode and the input of the flowing electroplating solution. Small grooves were milled into the sides of the Teflon insert to provide a return path for the electroplating solution [see Figure 5.20].

Figure 5.20: Photo of targeted electroplating system with solution flow capability.
In the setup, the minicell does not even have to be submerged. The ARROW reservoirs were done in a similar manner but because of the smaller dimension we used 1/16” metal tubing as the anode/pumping tube. As before, the copper tubing is wrapped in heat-shrink tubing to provide both electric isolation and targeted deposition. Since dimensions prevent us from creating a milled spacer like the Teflon insert, special care had to be taken to mount the tube in the center of the reservoir to ensure even deposition. At this point I had overcome all the major electroplating difficulties and was able to electroplate targeted, smooth, and uniform metal coatings on the reservoir solder joints.

5.7 Final Fabrication Summary and Process Flow

Combining all of the techniques that I investigated in the previous chapters I was able to successfully construct a long-lasting minicell [106]. While section 7.3 goes into the details of the accelerated lifetime tests that demonstrate this, the long-lasting minicell was created with indium solder coated with electroplated copper. The previous chapters told the story of the long road (and many detours) I took to create a long-lasting on-chip Rb vapor-cell. There were many iterations of the devices. In the last section of this chapter I will clarify and outline the final methodology. The next couple of chapters focus on the tests used to determine this result.

5.7.1 Third-generation minicell fabrication

The successful third-generation minicell was made using a 2 mL glass vial and 3/8” copper tubing. The glass vial and copper tubing undergo a sanding and buffing process to ensure flat and smooth soldering surfaces. This buffing process can leave quite a bit of residue behind. The glass vials and copper stubs are scrubbed with a cotton swab in an acetone bath then rinsed
with IPA. The entire glass vial is cleaned in a HCl:H₂O (1:1) mixture for ~1 minute followed by a DI water rinse. The top of the glass vial is further prepared for metal deposition by being submerged in buffered oxide etchant (BOE) for ~30 seconds. Following a final DI water rinse the glass vials are loaded into the e-beam PVD where 250 nm of chromium followed by 250 nm of nickel is deposited onto the surface. To ensure a thick soldering surface 3 µm of nickel is electroplated on top of the 500 nm seed layer is deposited in the e-beam. The electroplating procedure used in outlined in section 5.6.2.

Next the copper stubs are prepared for the fabrication process. First they are scrubbed with a cotton swab in an acetone bath followed by an IPA rinse. Then the they are further cleaned with a 15 second dip in a H₂SO₄:H₂O (1:2) mixture, rinsed with DI water, and then dried with IPA. The polished end of the copper stub which will be used as the soldering surface has 3 µm of nickel electroplated onto the surface.

The vial and the stub are now ready to be brought together. The glass vial and the copper stub are both brought to a temperature of ~200 °C utilizing a combination of a hotplate and a soldering iron. A ring made of indium solder is place on the top of the glass vial. Using a mounting stage the copper stub is set atop the glass vial/indium solder at which point the flux is applied. The heated flux clean off any native oxides on the metals at which point the indium wets to all of the metal surfaces and forms a hermetic seal. The cell is then allowed to slowly cool to RT. The flux used in the soldering process leaves a residue on the minicell that requires a lot of cleaning to remove. First the minicell is rinsed and scrubbed in DI water. Then it is soaked in 55°C acetone for 15 minutes, scrubbed again in the acetone with a cotton swab, then rinsed with IPA. Then, the inside of the cell is cleaned with 48% HF for 5 seconds followed by an immediate rinse in DI water. This HF dip removes metal oxides and a layer of the glass
surface taking any surface contaminates with it. After the clean steps, the inside surface of the indium soldered joint has 3 µm of copper electroplated onto it using the copper electroplating process described in section 5.6.2. After which the minicell is again rinsed with DI water, dipped in 48% HF for 5 seconds, then rinsed in DI water for one final time. After a 2 hour 120 °C dehydration bake the cell loaded into the glove box where the Rb is introduced, the cell evacuated, and the copper cold-weld seal formed.

Figure 5.21: Cutaway illustration of third-generation minicell fabrication.
5.7.2 Third-generation ARROW vapor-cell fabrication

In order to apply the indium solder method to the ARROW vapor-cell platform additional processing steps are needed for the ARROW wafers than was required for the 1st and second-generation ARROW vapor-cells. To build a third-generation ARROW vapor-cell a wafer must first undergo the SAP ARROW processing described in section 2.4. At this point a metalized surface is still lacking for the solder process. To allow for soldering we create metal donut-shaped solder pads around the hollow-core openings exactly like the process outlined in section 5.5 except instead of depositing tin, we deposit 250 nm of chromium followed by 250 nm of nickel. Once the chromium/nickel donut rings have been deposited on the surface the wafer can be cleaved into individual devices. To ensure the metal is thick enough for soldering, 3 µm of nickel is electroplated on to the donut soldering pads using the electroplating process outlined in section 5.6.2. The reservoirs are again created using 3/16” copper stubs. These copper stubs are polished, scrubbed in DI water, cleaned in acetone, and rinsed in IPA. Then they are further cleaned with a 15 second dip in a H₂SO₄:H₂O (1:2) mixture, rinsed with DI water, and then dried with IPA. The polished end of the copper stubs which will be used as the soldering surfaces have 3 µm of nickel electroplated onto the surface.

The ARROW chip is placed on a hotplate with a vacuum chuck while the copper stubs are placed onto the solder pads and held there with a dual-stub mounting stage. Because the solder procedure would melt any previously soldered joints both of the reservoirs must attached at the same time. The chip and copper stubs are heated to ~200 °C. Once heated, the soldering process takes place more or less like a normal solder procedure. Flux is applied and a short length of solder is touched to each joint which melts and wicks into the joints creating hermetic seals.
Figure 5.22: Cutaway illustration of fabrication and loading process for third-generation ARROW vapor-cell.
The chip is then allowed to slowly cool to RT. The chip is then allowed to soak in DI water for 24 hours, followed by a 30 minute soak in 55 °C acetone, followed by an IPA rinse. Because of our thin ARROW layers and the aggressive silicon dioxide etching properties of 48% HF, we could not use the HF dip utilized with our minicells. Instead, we use sodium hydroxide to clean the ARROW vapor-cell. Sodium hydroxide aggressively attacks any flux residuals and removes the oxide from the copper walls. It also slowly etches silicon dioxide so care should be taken to minimize the exposure time. The ARROW vapor-cell is then rinsed with DI water. After the cleaning steps, the inside surface of the indium soldered joint has 3 µm of copper electroplated onto it using the copper electroplating process described in section 5.6.2. After which the ARROW vapor-cell is again rinsed with DI water, cleaned in sodium hydroxide, then rinsed in DI water for one final time. After a 2 hour 120 °C dehydration bake the cell is loaded into the glovebox.

The loading of the third-generation ARROW vapor-cell is slightly different than the loading of the second-generation cell. Though there were two reservoirs to help with the ODMS process in the second-generation devices, a dab of epoxy was used to seal one end of the hollow-core while the cold-weld crimp was used to seal the second. Since we no longer use epoxy to seal our devices both ends of the hollow-core must be sealed using a cold-weld for our third-generation ARROW vapor-cells. This is done by loading Rb into one of the reservoirs evacuating that reservoir and making a cold-weld seal. After making the cold-weld, the outside atmosphere will start to leak into the sealed reservoir via the hollow-core channel. However, due to the small dimensions of the channel the leak happens at an extremely slow rate. If the second reservoir is evacuated and sealed with a cold-weld within a couple minutes the increase in
pressure in the first reservoir will be negligible. After the cold-weld has been formed on both reservoirs the vapor-cell is now complete and ready for optical testing.

Figure 5.23: Illustrations of third-generation ARROW vapor-cell. a) Top down view. b) Side cutaway view of reservoir. c) Angled 3D view.
6 RUBIDIUM SPECTROSCOPY

6.1 Need for BYU Optical Testing Platforms

We collaborate in our research with an applied optics sister team at the University of California, Santa Cruz (UCSC). At BYU, for the most part, we investigate novel methods of device fabrication and then ship our devices to UCSC where they perform the optical experiments for which the devices are created. The UCSC teams have also traditionally been in charge of device optical yield testing. For the liquid core ARROW teams this is not a difficulty since most of the liquid reservoir attachment and filling is straightforward and performed at UCSC before the final experimentation. However, for my air-core research the attachment process is very involved, complicated, and requires equipment located at BYU. As such our chips make multiple trips back and forth between BYU and UCSC. After the chips finish the cleanroom fabrication steps they are cleaved and sent to UCSC where they are tested for optical throughput. The good chips are sent back, after which we attach the reservoirs, load with Rb, and seal. The devices are then sent to UCSC for final testing. Historically, many of these devices fail; either they completely optically fail or they fail to produce a Rb spectra. In order to pinpoint the root cause of device failure we need an increase in failure mode resolution. Can we identify a certain fabrication step that is causing the failure mechanisms? As an example it was just mentioned that the reservoir was attached to the chip and loaded before sending it back to
UCSC. If the device fails to produce a mode what caused the failure, the reservoir attachment or the Rb loading? We need to test devices in between unique fabrication steps. Sending the chips back and forth between UCSC and BYU after every step is not a viable solution. Each time a device is shipped, a higher probability of damaging the device exists. It was also economically and temporally inefficient.

Probing the Rb spectra in minicells also suffered from long distance testing at UCSC. Minicells are created quickly and in large batches. The time delay in shipping and waiting for test results protracted the iterative process of minicell development.

Because of these drawbacks it became a strategically important goal to develop waveguide and minicell optical testing capabilities, both for optical loss and Rb spectroscopy. One of the first forays into developing these capabilities at BYU was calculating waveguide loss with scattered light imaging [107].

6.2 Borrowed Spectroscopy System

The capability to test waveguide loss was a marked improvement for our failure analysis capabilities. However, I was specifically interested in generating the capability to do Rb spectroscopy here at BYU to be able to quickly verify the viability of Rb vapor-cells and to be able to perform cell lifetime tests without third-party involvement. After expressing these wishes to Dr. Hawkins, we decided to move forward in this direction. First we sought out any existing spectroscopy systems here at BYU that we could use for a while; from there we could make a more informed decision about whether getting our own setup would be a good use of our resources. I sought assistance among a handful of professor from the BYU physics department. In the end, Dr. Scott Bergeson agreed to help us and let us use his lab for our experiments. The
spectroscopy skills and knowledge I learned via his coaching were a critical part of my minicell development success, for which I am most grateful.

The laser used was a Del Mar Trestles Finesse Tunable Ti:Sapphire laser with a MSquared Solstis SRX cavity. The detectors are Thorlabs DET36A. These detectors were connected to a National Instruments (NI) BNC2090 break-out-box which was in turn connected to a NI PCI-6030E 16bit data acquisition (DAQ) card. Since my experiments involve multiple samples at several temperatures I wanted to be able to probe the maximum number of devices at once. The DAQ card was capable of reading 8 differential channels. One channel was dedicated to provide a power baseline while a second channel would monitor a bulk cell spectra for reference. This left 6 channels to be used for testing the actual devices.

Figure 6.1: Diagram of 1st Rb Spectroscopy setup at Dr. Bergeson’s optical lab.
I conducted a new epoxy lifetime experiment as well as my first indium experiments with this spectroscopy system. These experiments were successful in that I learned of indium’s slow reaction with Rb. However, the data gathered during this time was exhibiting unusual lifetime responses. The resulting spectra were noisy and had unusual erratic up-and-down shifts in day-to-day atomic density and linewidth measurements. I found some major problems that were affecting the accuracy of my tests: small absorption signal to probe intensity ratio, ghosting, and saturation intensity.

The detectors capture the optical signal and convert it into a current. This current was then dropped across a resistor, creating a voltage signal that the DAQ captures, see Figure 6.3. Therefore as the probing beam intensity increases, all things being equal, the voltage at the DAQ increases. As the voltage increases the resolution of the DAQ decreases. This is because the DAQ has a finite amount of capture points, 16 bits. The 16 bits are spread equally across the
DAQ’s voltage range. The higher the voltage range the more spread out these points are, thus resulting in a lower voltage resolution. Also, the noise in the DAQ system scales with the voltage range increase. This can be a problem because the spectral absorption signal amplitude does not scale with an increase in the probe signal intensity. In simple terms, the optical media has a finite number of atoms in it and thus will effectively reach a limit in the amount of light it can absorb. When the intensity of light is on the same order of magnitude as the amount of light the medium can absorb, the absorption dips can clearly be seen in the signal captured by the DAQ. As the probe intensity increases, the amount of light being absorbed becomes a smaller and smaller percentage of the total light being collected at the detector. This transfers over to the voltage signal at the DAQ. This can result, for example, in a 1 mV absorption signal riding a 10 V probe signal where the DAQ resolution is only 100 µV. This would result in only ten points of voltage resolution for the absorption signal. Additionally, the noise of the DAQ system is at the very least on the same order as the resolution which means the noise becomes very significant. For these reasons it is beneficial to keep the probe intensity as low as possible.

Figure 6.3: Simple diagram of original detection circuitry. The detector load resistors and DAQ capacitance form RC circuit that causes ghosting between channels.
The second problem that can arise is ghosting. This is a common problem with multiplexors (MUX). Though the DAQ has multiple inputs, it is only reading one input at a time. It scans through all the channels at a speed designated by the user using a MUX. The MUX has an internal capacitance (C) and when it combines with input channels load resistor (R) it forms an RC circuit. The RC circuit stores charge in the capacitor and releases the charge over time. The circuit will discharge 63.2% of its original charge after time $\tau$ and 99.3% of its charge after $5\tau$ where $\tau = RC$. If your sampling speed is too fast then the multiplexor will move from one channel to the next faster than the capacitor can discharge. This means at the second channel the voltage level will be affected by the previous voltage level, which can lead to a ‘ghost’ signal from the first channel on the second channel’s signal. During my first experiments, ghosting led me to believe that a failed minicell was still functioning because the spectrum from the previous minicell’s channel was leaving a ghost spectrum on the second channel. Ghosting can be solved by decreasing the load resistor or decreasing your sampling rate. However, this can lead to a trade-off scenario because sometime you need high sampling rates and if your incoming current signal is very small you need a large resistor to create a larger voltage signal for the DAQ.

A third problem encountered was caused by surpassing the Rb saturation intensity. The saturation intensity is defined as the probe intensity when excited electrons are equally likely to decay by stimulated emission as they are to decay by spontaneous emission. In a nutshell this is stating the obvious, the presence of the probe beam is altering the atomic structure that we are trying to observe. Though this will always be true, it is especially true at intensity levels near or above the saturation intensity. If an adequately low-intensity probe beam is used the effects on the atomic system can be negligible. Just how low the probe beam intensity needs to be depends
on the applications accuracy needs. A common probe intensity target for many general purpose spectroscopy applications is a magnitude of order lower than the saturation intensity. For my experiments, which are probing the $^{85}\text{Rb} \ 5^2S_{1/2}(F=3) \rightarrow 5^2P_{3/2} (F=2,3,4)$ absorption peak, the saturation intensity is 1.6 mW/cm$^2$ and a probe intensity one magnitude of order less would result in less than a 3% error between the observed optical depth and the actual optical depth [63].

![Figure 6.4: Optical power calculations for Dr. Bergeson's spectroscopy system.](image)

To get a better understanding of the intensity levels in the spectroscopy system in Dr. Bergeson’s lab, I used a Thorlabs PM100A optical power meter. The beam was sized to a diameter of 2 mm using an iris. The incoming beam was 14 mW. After passing through the beam sampler the power was 115 µW, experiencing 0.82% transmission. After passing through a well-aligned minicell made with a 2 mL glass vial, the signal dropped 20% to 92 µW; this is the optical power that is incident upon the signal detector. Assuming equal loss at each interface, the transmission of each pass through the minicell is 89.5%; therefore the optical power inside the minicell is 102 µW.
Also assuming a uniform beam intensity profile we can use this information to calculate the probing beam intensity inside the minicell as shown in Equation (6.1),

\[
I_{\text{minicell}} = \frac{P_{\text{optical}}}{A_{\text{beam}}} = \frac{102 \, \mu W}{\pi (1 \, \text{mm}^2)} = 3.2 \, \frac{mW}{cm^2}.
\] (6.1)

This means the intensity levels being used in the physics lab were double the saturation intensity, which, as mentioned earlier, can adversely affect the accuracy of the spectroscopy experiment. For more reliable testing results I needed to create a spectroscopy system where the DAQ and laser intensity levels could be modified to clear up the previously mentioned problems. Up to this point Dr. Bergeson and his students had graciously allowed us to use his lab and equipment. Even though they were very accommodating, in order to run the experiments with the consistency and in the quantities needed, we needed our own spectroscopy system.

6.3 BYU Spectroscopy System

6.3.1 Free-space optical system design

The BYU system was designed to have two capabilities: (1) to perform spectroscopy in macro-sized devices (i.e. minicells) and (2) to perform spectroscopy experiments on our ARROW platform. For the case of the minicells, we designed it to simultaneously test three channels. See Figure 6.7 for final system layout. The first component purchased was the photodiode laser. The photodiode was a PH780DBR040T8 by Photodigm, Inc. The laser diode (LD) is controlled using a ThorLabs ITC4001 LD/thermoelectric cooler (TEC) controller, HP waveform generator, and a LabVIEW script. The LD is designed especially for Rb D2 line precision spectroscopy. The wavelength is both temperature and current dependent. In our case, the center wavelength of our spectrum is adjusted by altering the diode temperature and a bias
current. After using the spec sheet provided by Photodigm and some experimentation, I found the center of the Rb D2 lines at a temperature of 15.88 °C and a bias current of 90 mA. The HP waveform generator then creates a 17 Hz, 14 mA peak-to-peak sawtooth signal on the 90 mA bias current. This 14 mA peak-to-peak current variation results in a 12 GHz spectral range in the output wavelength. Notably, while varying the current supplied to the photodiode varies the wavelength, it also varies the beam intensity.

![Illustration of final spectroscopy free-space optical system.](image)

The beam emerges from a rectangular waveguide in the diode laser and as such propagates with elliptical profile with two beam divergence angles: $\theta_\parallel = 6^\circ$ and $\theta_\perp = 26^\circ$. A Thorlabs C230TME-B 4.51 mm lens was purchased to collimate the beam. The focal length of 4.51 mm was chosen mostly due to physical limitations of the photodiode package on which the lens could be placed. The resulting beam waist can be calculated by solving Equation (6.3) for
In the parallel direction the beam radius would be 1.16 mm and in the perpendicular direction the radius is 5.37 mm. However, the lens itself only has a radius of 2.25 mm. Therefore, after this point the beam is approximated as an elliptical Gaussian beam with radii of 1.16 and 2.25 mm. After the collimator lens the light is guided with two adjustable mirrors that form a ‘periscope’ that allows for the beam to aligned at any height, in any direction. The periscope directs the beam into a 30mm cage system fitted with an iris, neutral-density filter, beam splitter, and objective lens. The iris enables better aligning capabilities and the ability to control the beam width. The 55:45 beam splitter is used to generate two separate beams. The reflected beam is directed to a free space optical spectroscopy setup for bulk cells and minicells and the transmitted beam for micro waveguide spectroscopy in our ARROW devices.

\[
\theta = \frac{\lambda}{\pi \omega_0}, \quad \tag{6.2}
\]

\[
\tan \theta \cong \frac{W}{f}, \quad \tag{6.3}
\]

\[
\omega_0 \cong \frac{\lambda}{\pi \tan^{-1} \left(\frac{W}{f}\right)}. \quad \tag{6.4}
\]

The beam that passes through the beam splitter is collected in an objective lens attached to the end of the cage system. The objective lens allows the beam to be coupled into our micro-sized ARROW waveguides whose solid-core waveguides mode sizes are approximately 3 µm in the vertical direction and 6 µm in the horizontal direction.

Beam-intensity calculations were done to ensure that the beam intensity was at or below 160 µW/cm². The power level can be controlled two ways in the optical setup. The first is to change the power output of the laser. In our case, with the Photodigm diode laser, the output
power can be altered by dropping the current supplied to the diode. However, for our spectroscopy setup, the diode current is how we control the laser wavelength. Also, the current can be altered only in a limited range before either damage is done or the laser stops lasing. So the second best option is to employ neutral-density (ND) filters. Neutral-density filters are made with an absorptive material designed to reduce the intensity of light that passes through it. There are a wide variety of ND filters, each with their own unique transmission vs. wavelength properties. Preliminary calculations are run to know what ND filter to use. The Photodigm laser diode we purchased has an operating power of 40 mW. So per the outlined design, the incident beam will first pass through a 1 mm diameter iris. The beam shape before the iris is an ellipse with $r_1$ and $r_2$ equal to 1.16 and 5.37 mm, respectively. Assuming a uniform beam intensity profile, passing through the iris would decrease the beam power as shown in Equation (6.5),

$$P_{\text{iris}} = \frac{A_{\text{iris}}}{A_B} P_B = \frac{\pi(0.5 \text{ mm})^2}{\pi(1.16 \text{ mm})(5.37 \text{ mm})} \cdot (40 \text{ mW}) = 1.6 \text{ mW}. \quad (6.5)$$

The beam then passes through a 50:50 beam splitter and a 1% beam sampler before arriving at the vapor-cell. This leaves an 8 µW optical beam with a diameter of 1 mm which equals an intensity of 1 mW/cm$^2$. Therefore, the ND filter must have 16% transmission or less in order to have an intensity of 160 µW/cm$^2$. To meet these specifications, we purchased a ThorLabs NE510B ND filter with a transmission of 14.5% at a wavelength of 780 nm. Figure 6.6 shows the spectroscopy system design flow chart, the most important part of which is that the beam power inside the minicell is 1.05 µW which yields an intensity of 132 µW/cm$^2$; a value comfortably below the 10% saturation intensity goal. Figure 6.6 illustrates the power flow design for the new spectroscopy system.
There is always some difference between the ideal design and the actual real-world system. After putting the system together, I measured the power levels of the beam. I measured the intensity at both the peak and trough of the wavelength scan since the wavelength is changed by a change in current, which also causes a change in probe intensity. While calibrating the power levels in our new spectroscopy system I did not have access to an optical power meter. Instead I used one of the photodiodes (Thorlabs DET36A) in conjunction with LabVIEW. The photodiode responsivity, obtained from the spec sheet, is 0.51 A/W. The photodiode was attached to a 5.6 kΩ load. The optical power was then calculated by measuring the voltage across the load resistor and plugging it into Equation (6.6),

\[
P_{\text{beam}} = \frac{V}{R} \times \frac{1}{R} = V_{\text{load}} \times \left(3.5 \times 10^{-4} \frac{W}{V}\right) \tag{6.6}
\]

Using this equation the following optical powers were measured. The laser output varied from 23 to 33 mW. It then passed through the ND filter that was supposed to have a transmission of 14.5% but was actually is 16%. The ThorLabs CM1-BS014 beam splitter is actually 55:45 split at 780 nm. The beam sampler transmission was 0.5%, which is precisely what the beam samplers are designed for. The 1% used in the design was based on what was measured in the physics lab. The sampling transmission is dependent on the beam sampler.
angle, and my original measurement must have been considerably far from the standard 90° incidence angle. Taking all this into account, it makes sense that beam power arriving at the vapor-cell varies from 0.33 to 0.51 µW which corresponds with intensities of 42 and 65 µW/cm², respectively. Considering the loss incurred via transmission through the glass 2 mL minicell wall, the intensity inside the vapor-cells varies from 38 to 58 µW/cm², which is almost two magnitudes of order below the saturation intensity. Being lower than our design goals because of the differences discussed, is not a bad thing; in fact, the lower the intensity the higher the accuracy of spectra. This lower probe beam intensity means that we should expect less than 1% error between the observed optical depth and the actual optical depth [63].

![Figure 6.7: Photo of final spectroscopy free-space optical system.](image)
6.3.2 Scanning calculations, pre-DAQ circuitry, and post-capture analysis

After the spectroscopy system was assembled and the correct probe intensity was set up, the next step was to design the circuitry to convert the detector current signal to a voltage at the DAQ input and figure out the required sampling rates.

In my first attempts I had problems with the load-resistor selection. Now that I was using a low intensity for my probe beam, I had to use a large load resistor to create a voltage high enough at the DAQ such that voltage resolution and noise levels were not a problem.
Unfortunately, this caused ghosting between my channels and limited the sampling rates that I could use. In the end I employed an operational amplifier (opamp). Opamps can amplify the signal to higher voltage levels and provide a low input resistance at the DAQ, thus eliminating ghosting. I used the Texas Instruments LM363 for my spectroscopy system. The current signal generated by the detectors is dropped across a 39 kΩ resistor to create a voltage signal at the input of the opamp that is configured for a gain of 100. The current generated by the photodetectors is generally in the 0.5 to 2 µA range, resulting in a DAQ input voltage range of 2 to 8 V.

In theory, when the input of an opamp is zero, the output of the opamp should be zero as well. However, for most opamps there is a small, non-zero voltage at the output even when the input is zero. This is called an offset voltage. Apart from the opamps internally generated offset, there was also input offset generated by dark current from the detector even when the probe laser was off. These offset voltages shifted the reference point at the DAQ and generated up to a 5% error in the spectroscopy calculations. The LM363 allows for offset trimming using a potentiometer (POT) in a resistive network. By adjusting the pot the output voltage can centered on the desired voltage. I set up this offset eliminated circuitry as described in the LM363 instruction manual. After adding the opamps to the pre-DAQ circuitry I was able to sample at high speeds without any ghosting and the random system noise was observed to be < 0.5% of a healthy minicell’s optical depth.

I started designing the system to have 75 sample points over the average D2 absorption dip at 1 mTorr. I did this to ensure an adequate resolution so that we could have confidence that our absorption dips were yielding accurate results. The Rb D2 lines at 1mTorr are ~600 MHz wide. All four of the transitions span about 8 GHz. I chose my scan window to be 12 GHz wide.
to ensure plenty of data points on the edges of the scan to help generate an accurate baseline. The total samples needed in one scan is determined as follows in Equation (6.7),

$$S_{tot} = \frac{75 \text{ samples}}{600 \text{ MHz}} (12 \text{ GHz/scan}) = 1500 \frac{\text{samples}}{\text{scan}}.$$  \hspace{1cm} (6.7)

![Circuit Diagram](image)

**Figure 6.9:** a) Illustration and b) photo of pre-DAQ circuitry.

Nothing set in stone about the 75 samples per absorption dip number; however, it provided an ideal target to shoot for. Numerous factors can limit your samples/scan capability such as number of channels, speed, signal strength, and data-analysis capabilities. I will discuss
this in detail at a later point. However, dropping below 50 samples/dip starts to limit the accuracy of the collected data, especially if probing for SAS or if EIT is being considered as a potential application.

As mentioned earlier in this section, the probe beam scans a 12 GHz spectral range at a rate of 17Hz. Even though the system uses only 5 channels, the DAQ supports 8 channels, and I designed the system such that all 8 channels could be used in case of future expansion. The system takes 1500 samples over the 12 GHz range per channel, resulting in a total of 12,000 samples per scan. The scans occur at a rate of 17 Hz meaning the DAQ sampling rate is 204,000 samples/second, well below the DAQ’s 250,000 samples/second limit.

I wrote a LabVIEW program to control the laser diode and the DAQ. The user specifies the bias current supplied to the diode, the temperature of the diode, the sampling rate per channel, the number of samples taken per scan, and the total consecutive number of scans desired. (Note: There are many behind-the-scenes settings hard-coded into the program that are specifically for the PH780DBR040T8 (Photodigm, Inc.) diode. That means that one should exercise caution before using this program on another photodiode with a different pin-out without first making sure that all the necessary changes to the LD controller are made.) The stand-alone waveform generator was not integrated into the LabVIEW software. Therefore the diode current waveform shape, frequency, and amplitude are controlled via the waveform generator itself. The LabVIEW program provides an ‘oscilloscope’ view of the signals captured on the eight channels of the DAQ. Each channel can independently be turned on or off. The oscilloscope functionality can be used without actively collecting any data. To collect the data, the user provides the ID of the device being tested along with the date and time. The user then sets the ‘Save Data’ button to ‘on’ and starts the scanning process for the desired number of scan
iterations. The LabVIEW program saves the data in a .txt file where each sample point is separated by a comma and every scan by a return. An individual file is created for each selected channel. For subsequent data analysis processes to work, the power reference and bulk cell reference channels always need to be selected.

Figure 6.10: Screen grab of LabVIEW spectroscopy program GUI showing the power reference channel (top) and the bulk cell reference channel (bottom).

After the LabVIEW program captures and saves the raw spectral data, a series of MATLAB programs help with post-capture data analysis. The first program centers and averages all the scans. For my experiments I captured 1,200 scans of each channel, each with 1,500 sample points. Each scan is a spectrum by itself. Multiple scans are taken and averaged to further reduce random noise in the spectrum. The action taken by my averaging program is to divide the power reference channel into all the other channels. This will (a) reduce any common
noise and (b) flatten the baseline. The scans cannot be directly averaged because of wavelength drift in the laser output. The laser diode center wavelength (a) has a noise component and (b) can slowly drift over time. If all the scans were to be averaged without first centering each scan, it could lead to artificial spectral broadening. Since we expect some of the cells to fail, we also expect the spectra of said cells to distort as they fail. As such we need a constant and consistent point of reference with which to compare our cells with. This is where the bulk cell reference (or spectral reference) channel comes into play. The averaging program finds the sample point (i.e., 1-1,500) with the lowest transmission and plots that across the scan iteration (i.e., 1-1,200) for each scan. For my scans, the lowest point (excluding noise) should always be at the center of the $^{85}\text{Rb} \ 5^2S_{1/2}(F=3) \rightarrow 5^2P_{3/2} (F=2,3,4)$ absorption peak. Since the bulk cell reference channel also experiences noise, we cannot center the spectra with the raw center values. A polynomial function is fit to sample point vs. scan iteration plot. That function is then used to provide a center sample point for each scan iteration of all the other channels. After the scans are aligned they are averaged for each channel leaving one-low noise spectrum per channel.

Figure 6.11: Flow chart of post-capture data analysis.
Follow-up MATLAB programs then flatten the spectrum baseline, normalize the y-axis, give the x-axis units of frequency, and finally measure the optical depth and FWHM linewidth of the D2 $^{85}$Rb $5^2S_{1/2}(F=3) \rightarrow 5^2P_{3/2} (F=2,3,4)$ absorption peak. These programs also automatically save and keep track of the data by device ID and the date and time of each measurement. I wrote other MATLAB scripts to allow me to quickly and easily pull up a specific spectrum or plot the optical depth and linewidth of a device over time. The scripts also identified the time-to-failure for each device based on a given failure criteria. I tried to make the data processing as automated as possible since I captured literally thousands of spectra; doing all the post-capture data analysis by hand would have taken a prohibitive amount of time. While the series of scripts I created might not be polished, I think they provided the best return on time-put-in. For documentation purposes, I have added the MATLAB scripts in Appendix B.2. With my multi-channel spectroscopy system setup and post-capture data analysis scripts finished, I started conducting accelerated lifetime testing of minicells en masse.

![Transmission Plot: EFEU8DC2](image)

Figure 6.12: Example of a minicell spectrum probed and analyzed on the new spectroscopy system.
7 OPTICAL VAPOR-CELL PERFORMANCE

7.1 Accelerated Lifetime Testing

The desired goal with accelerated lifetime testing is to obtain lifetime/reliability data in a short amount of time. This is especially important for devices that would take years to fail. This is done by putting a device through harsher operating conditions than the device would normally experience. The stressed operating conditions cause the device to experience premature or 'accelerated' failure. That accelerated failure data is then used to describe how long the device would last under normal conditions. For example, if a device was designed to last 10 years, the company producing the device could not realistically wait 10 years before publishing reliability information. Instead, the company designs an accelerated lifetime test with harsh operating conditions that causes the device to fail in weeks. They then use that data to estimate the reliability data under normal conditions, which they then publish at the same time they release the product to the market.

Early on in our research the ‘heat-cycle’ or ‘ramp’ test described in previous chapters served as a crude method of accelerated lifetime testing. However, during the search for the third-generation ARROW vapor-cell, a weakness was found in the ‘ramp’ testing method. The Houskeeper seal experiment revealed many materials (mostly metal) that seemed to be compatible with Rb, the most promising of which were indium and nickel. On account of these
findings we started using these two metals in our devices. Since then, periodical research collaborated with the Houskeeper experiments, extolling the excellent Rb compatibility properties of nickel. These findings were later substantiated via long-term Houskeeper minicell tests. Conversely, during my first forays into indium minicells, I noticed the accumulation of black dust and the eventual complete failure of the minicell, pointing toward a reaction between Rb and In. The ramp test did not expose this slow reaction because it took days at elevated temperatures before the effects were noticeable, whereas the ramp test lasts only a handful of hours. I learned two things at this point: (1) the ramp tests simply did not last long enough to gather the performance resolution of my better sealing methods, and (2) another test had to be developed to probe the long-term reliability of my next gen devices.

I want to quickly mention a phenomena that I observed in conducting our lifetime experiments. Most cells undergo a rapid small scale initial degradation during testing. Even the long-lasting Houskeeper cells drop a percent or two in atomic density during the initial hours of the testing before holding steady state for the remainder of the test. I have since concluded that this initial drop in the atomic density is caused by a variable amount of impurities that are not completely removed from the minicell during the cleaning, loading, and sealing procedures. While during my research I have found better ways to reduce these impurities via various cleaning procedures, I have never completely eliminated them. It is important to note that a small amount of initial signal degradation in the absorption spectrum is expected as any residual impurities are ‘cooked-out’. Because of the temporal brevity of the ramp tests, the initial impurity degradation ‘noise’ was overwhelming the small scale degradation caused by the better seals. Observing the long-term stability became more important for these materials than monitoring the initial drop. The ‘ramp’ tests were useful in providing a crude direction for our
research, but another testing method was required to fine tune our techniques. At this point I started researching common accelerated lifetime testing techniques.

7.1.1 The Arrhenius equation

One of the most common methods of accelerated life testing is the Arrhenius model, the back-bone of which is the Arrhenius equation. The Arrhenius equation was developed in the late nineteenth-century by the Swedish chemist Svante Arrhenius; it describes the relationship between temperature and a reaction rate constant. This relationship can be extended to describe the temperature dependence of many temperature dependent first order kinetic reactions and processes. These include material structural changes, chemical reactions, electrical carrier trapping, and diffusion coefficients. These processes are heavily dependent on the temperature because of the necessity of overcoming an activation energy [108]. Because of its relative simplicity and highly accurate description of these processes, the Arrhenius accelerated lifetime model is commonly used to describe the expected lifetime of many devices and materials. It was even commonly used in the early years of the electronics industry, but as electronics grew in complexity so did the variety of failure mechanisms, requiring the development of more complex accelerated lifetime testing techniques [109]. However, for the application at hand the Arrhenius model will provide an accurate lifetime prediction because the vapor-cell failure mechanisms fall into one of two categories: (1) the structural degradation of the various materials leading to the loss of a hermetic seal or (2) an adverse chemical reaction between two or more of the included materials that cause a degradation of the absorption spectrum.

The Arrhenius equation defines the reaction rate, \( k \), of a chemical as shown in Equation (7.1),
where \( E_a \) is the activation energy, \( T \) is the temperature, \( R \) is the gas constant, and \( A \) is a constant called the ‘prefactor’. In our application we are monitoring a catastrophic fail event, not monitoring a percentage of failure. If \( k \) is the reaction rate, then the ‘reaction’ being measured is a device failure. Therefore, \( k \) can be defined as \( 1/t \) where \( t \) is the time it takes for a device to fail.

Applying the new definition of \( k \) to Equation (7.1) yields the following equation,

\[
\frac{1}{t} = Ae^{-\frac{E_a}{RT}}. \tag{7.2}
\]

The Arrhenius can be used to predict failure by solving Equation (7.2) for \( t \) at a given temperature \( T \). However, Equation (7.2) contains two unknown constants, \( A \) and \( E_a \). These constants must be defined for the process in question before the equation becomes useful. Some algebraic manipulation of Equation (7.2) converts the Arrhenius equation into a more user-friendly format as represented by the follow equations,

\[
\ln \left( \frac{1}{t} \right) = -\frac{E_a}{R \cdot T} + \ln A, \tag{7.3}
\]

\[
y = \ln \left( \frac{1}{t} \right), x = \left( \frac{1}{T} \right), C = -\frac{E_a}{R}, D = \ln A, \tag{7.4}
\]

\[
y = Cx + D. \tag{7.5}
\]

Equation (7.5) describes the Arrhenius equation as a line with slope \( C \) and offset \( D \). With multiple \( x,y \) data sets, one can mathematically solve for \( C \) and \( D \). The \( x,y \) data sets are obtained empirically by monitoring device lifetimes (\( t \)) at multiple high temperatures (\( T \)). After fitting Equation (7.5) to the experimental results, \( C \) and \( D \) are used to solve for \( E_a \) and \( A \).
and $A$ back into Equation (7.3) yields a mathematical relationship, for the specific process, with which one can calculate the expected lifetime of a device at any given temperature.

That is the basic idea behind using the Arrhenius equation in accelerated lifetime tests. The import remaining factor is how failure is defined. It is important to keep the definition of failure constant across all groups in order to be able to compare the results. As I will explain later, the exact definition of failure did change between our generational testing. This happened as our understanding of the failure mode improved. In general however, failure data was collected from the atomic spectra of Rb vapor-cells. At this point I want to reiterate that all optical testing was conducted by our sister research group at UCSC for our first- and second-generation devices. However, for our third-generation devices, the optical lifetime testing was conducted by me at BYU.

7.2 Second-generation Performance

7.2.1 Lifetime performance

I conducted lifetime experiments on our second-generation vapor-cells to (a) see if we could learn anything from the results (i.e., quantify lifetime expectancy or gain a better understanding of the fail model) and (b) to set a standard to which all future generations would be compared. The minicells used in these tests were created utilizing the best performing epoxy, Aremco 2310, as discussed in detail in section 4.4. I fabricated the minicells using the method outlined in section 4.4.1, loaded them with 0.5g of Rb each, and shipped them to UCSC for testing.

At UCSC, the cells were evaluated by monitoring the Rb vapor density via the optical depth of the Rb spectrum. Specifically, the optical transmission about the $^{85}\text{Rb} \ D2 \ 5^2S_{1/2} \ F=2 \rightarrow$
$^5\text{P}_{3/2} F'=3$ transition was monitored using a spectroscopy system with a tunable laser centered around the 780 nm D2 wavelength [66]. This transition was chosen because of its being the second-most opaque transition in the D2 lines, providing a higher contrast between operational and failed minicells, and being isolated from the other transitions to minimize error caused by transition absorption peak mixing. A drop in vapor density indicated that the Rb was reacting with something in the cell. For these tests, failure was defined as a 50% drop in the maximum atomic density achieved during the testing process.

![Figure 7.1: Rb D2 line spectrum showing I, I0, and the linewidth $\Delta \nu_{\text{FWHM}}$.](image)

The atomic density was calculated by measuring the optical depth of the transition using the spectrum data probed by the laser. This is done by dividing the intensity of the light coming out of the vapor-cell, $I$, by the intensity of the light going into the minicell, $I_0$. 
This ratio gives the percentage of the light that was not absorbed by the atomic vapor in the cell,

\[ \text{Optical Depth} = \frac{I}{I_0} \]  

(7.6)

The optical depth can be used to calculate the atomic density in the vapor-cell by using equation (7.6). It is important to note that multiple considerations factor into this method of calculating an accurate atomic density. The first consideration is to know how many transitions are contributing to an absorption peak’s optical depth. The absorption peaks from our raw spectra actually contain multiple transitions. Doppler broadening has caused their individual peaks to combine into one large peak. Therefore, the optical depth of these peaks can actually contain contributions from multiple transitions. In order for the atomic density calculation to be correct, all of the transitions must be taken into account. Second the temperature and pressure of the cell must remain constant (or be independently monitored and taken into account). The absorption cross-section of the atoms is temperature and pressure dependent. For our tests we held temperature constant and assumed the pressure was constant.

My counterpart at UCSC, Bin Wu, kept the minicells I fabricated on hotplates at three temperatures: 70, 80, and 90°C. Once a day she would take the minicell off the hotplate and probe its spectrum at the same temperature it was being stored at. From the spectrum she would then calculate and log the atomic density. Figures (7.2) through (7.4) show the plotted results of these tests. Notice that the diamond point on each graph represents the point where the atomic density dropped by 50% of the original density. This, as you will recall, was what we defined as our failure point.
Figure 7.2: Aremco 2310 minicell 70 °C accelerated lifetime test.

Figure 7.3: Aremco 2310 minicell 80 °C accelerated lifetime test.
The results of these tests showed that the devices failed after 11.6 days at 70 °C, 5.7 days at 80 °C, and 3.1 days at 90 °C. I created some MATLAB code using the Arrhenius equations outlined in section 7.1.1 and used it to calculate the expected lifetimes of the vapor-cells at RT. The code used can be seen in appendix A.4. The code plots the empirically gathered data from the accelerated lifetime tests, \( t \) being days to failure and \( T \) being the temperature; the code then fits a line to the data as seen in Figure 7.5(a). The fitted line equation can then be used to solve for \( E_a \) and \( A \). The data from these experiments yielded an \( E_a \) of 0.71 eV and an \( A \) of \( 2.2 \times 10^9 \) days\(^{-1}\). Using equation (7.2) and solving for \( t \), the code then solves for the expected lifetime of the devices at any temperature, as shown in Figure 7.5(b). These experiments predict a room

![Figure 7.4: Aremco 2310 minicell 90 °C accelerated lifetime test.](image)
temperature device lifetime of 1.2 years, but an increase of just 10 °C cuts that lifetime by 60 percent.

The results of the accelerated lifetime test showed that our second-generation vapor-cells definitely had a limited lifespan. I was impressed with how well the data fit the Arrhenius model. The Arrhenius equations were specifically created to model chemical reactions, and the

Figure 7.5: (a) Fitted Arrhenius equation to empirically gathered lifetime vs. temperature data (b) Lifetime expectancy vs. temperature projection plot.
fact that my experimental data fit so well seems to verify my fail-mode hypothesis--that the Rb is undergoing a chemical reaction in the cell. This is especially apparent because the lifetime decreases as operating temperature increases, pointing at a chemical reaction with a rate that increases with temperature. Another piece of information gleaned from these tests is the importance of the cell geometry. The minicells remained viable for days at elevated temperatures while the Rb-loaded ARROW devices lasted only hours. This most likely points to the difference between the volume to epoxy surface area ratio. In short, while the second-generation seals were somewhat successful we had to search for another, longer-lasting seal and verify its performance using accelerated lifetime tests.

### 7.2.2 EIT and slow light experimental results

Even with an observed lifetime limitation caused by the epoxy seal, the second-generation sealing method was successfully applied to both macro-scale devices (minicells) and chip-scale devices utilizing our ARROW platform. Most significantly, these ARROW devices were the first integrated on-chip vapor-cells to demonstrate electromagnetically induced transparency and slow light [50, 66, 110]. These experiments were conducted at the UCSC Applied Optics lab by my counter-part, Bin Wu. The second-generation ARROW vapor-cells were created using the process outlined in section 4.4.5.

Figure 7.6 shows the experimental setup for probing EIT on an ARROW vapor-cell. The experiment is conducted while the ARROW vapor-cell is maintained at an elevated temperature of 80°C. Two external cavity diode lasers (ECDL) are used to generate the probe and coupling beams. The probe and coupling beams are both fed into an optical fiber that couples the light into the ARROW vapor-cell. An objective lens at the output of the ARROW vapor-cell collects the light and feeds it into a detector. The ARROW waveguide has a polarization preference in
the direction of propagation and automatically collimates the alignment with both probe and coupling beams. This eliminates two commonly used methods to separate the coupling and probe beams from each other. In order to separate the probe signal from the ARROW cell output modulation is employed. A chopper is used to provide a 1kHz modulated signal on the probe beam. A sample of the modulated probe beam and the output of the ARROW vapor-cell are fed into a lock-in amplifier, which then separates the probe beam signal from the combined output. A lambda EIT scheme is created by scanning the probe beam frequency around the $^{85}\text{Rb} \, D2 \, 5^2S_{1/2} \, F=2 \rightarrow 5^2P_{3/2} \, F'=3$ transition while the coupling beam frequency is locked onto the $^{85}\text{Rb} \, D2 \, 5^2S_{1/2} \, F=3 \rightarrow 5^2P_{3/2} \, F'=3$ transition. The coupling beam power is set at 18.9mW and the probe power is set to 1/5 of the coupling beam power.

![Figure 7.6: EIT experiment setup [50].](image)

The EIT experiments were quite successful and matched theory well as explained in section 3.3. In EIT experiments the probe beam is monitored as it is swept across a range of frequencies. Figure 7.7 shows the EIT spectrum with the coupling laser turned off. We can see the transmission dip caused by the probe being absorbed by the Rb D2 line transition. When the coupling beam is turned on, as shown in Figure 7.8, EIT occurs, and we can observe the
transmission spike in the center of the transition absorption dip. The highest transmission peak observed in an ARROW vapor-cell was 40% transparency.

![Graph of transmission vs. frequency](image)

**Figure 7.7**: EIT spectrum (probe signal) in Rb-loaded ARROW with coupling beam turned off.

![Graph of transmission vs. frequency](image)

**Figure 7.8**: EIT spectrum in Rb-loaded ARROW with coupling beam turned on.
As mentioned in section 3.4, observing EIT is an important precursor to slow light. In fact, they can be considered the same phenomenon, differing only in how the probe beam is monitored. In the EIT experiments the probe beam was swept over a range of wavelengths and the resulting spectrum was captured. In slow light the probe beam wavelength is centered on the transition wavelength while the beam of light is modulated temporally and the resulting temporal signal is captured. As such the experimental setup for slow light is very similar to that of EIT. In this case however, the probe beam is modulated with an acousto-optic modulator (AOM) that creates 20ns pulses at a repetition rate of 5 MHz. A reference signal is sampled from the modulated probe beam and sent to a separate detector while the remaining probe beam and coupling beam are coupled into the ARROW vapor-cell. The same lambda EIT scheme as before is created by centering the probe beam frequency on the $^{85}\text{Rb D2 } 5^2S_{1/2} \ F=2 \rightarrow 5^2P_{3/2} \ F'=3$ transition and locking the coupling beam frequency onto the $^{85}\text{Rb D2 } 5^2S_{1/2} \ F=3 \rightarrow 5^2P_{3/2} \ F'=3$ transition. The coupling beam power is set at 7.3mW and the probe power is set to 3.61mW.

![Figure 7.9: ARROW vapor-cell slow light experimental setup [50].](image)

Figure 7.10 shows the observed results of the slow light experiment. The time axis is centered on the moment the unperturbed probe pulse arrived at the detector. As theory predicts,
the steep slope of the index of refraction at the center of the EIT-generated transmission peak slows the group velocity of the signal propagating through the ARROW. As can be observed in Figure 7.10, this results in a 16ns delay in the pulse and a 12.5ns increase in the pulse width.

![Figure 7.10: Slow light experimental results. The blue dots comprise the unperturbed probe pulse while the green stars comprise the probe pulse after passing through the ARROW vapor-cell.](image)

The results from these experiments were an exciting achievement for me and the entire team. Not only was this the first time that we had probed such non-linear effects on our ARROW, but this was the first time that such effects had been reported on an integrated on-chip vapor-cell package. However, as mentioned before, the device lifetime was short and investigations were made to find a way to increase it.
7.3 Third-generation Performance

When experimenting with indium solder and the electroplated coated solders, the standard heat-cycle tests were not able to detect failure from the minicells. As such I relied on the Arrhenius-based accelerated lifetime testing. When I used these tests on the second-generation minicells I already knew that Aremco 2310 was the best-performing epoxy, and I was looking to quantify the device’s failure. With the third-generation minicells I actually needed these tests to determine which solders and metal coatings performed the best [106].

During my evaluation of the second-generation accelerated lifetime test results, I became certain that we were missing important information by not deliberately monitoring the spectral linewidth as well as the optical depth. Since the linewidth of the absorption dips in the probed spectrum depended heavily on the pressure inside the cell, there was some potentially important information that could be gathered. Also, I felt that testing the minicells at the temperature they were being stored at, as we did previously, was a mistake. The atomic density and spectral linewidth of the minicells change drastically with a change in temperature. This meant that the data collected from each temperature group could not be directly compared one with another. Since our definition of failure was normalized to each cell's individual performance I do not think this introduced a large error in our second-generation tests. However, in the interest of maintaining uniformity and reducing variance within our new third-generation data set, I tested all minicells at 46°C no matter what temperature they were being stored at.

As discussed in section 5.6.2, I used the Arrhenius accelerated lifetime tests to investigate the performance of minicells created with bare indium solder, bare tin/lead solder, copper-coated indium solder, copper-coated tin/lead solder, and nickel-coated tin/lead solder. Because the testing scheme and minicell geometries had changed since the second-generation tests, I included
new Aremco 2310 minicells created with similar geometries as the solder minicells to provide a comparison baseline to the tests. The minicells were created using the techniques outlined in section 5.7.1.

The vapor-cells were evaluated by monitoring the Rb spectral absorption peaks and their Voigt profile FWHM linewidths, $\Delta \nu_{\text{FWHM}}$, as seen in Figure 7.1 [64]. Specifically, optical transitions of the D2 lines in natural rubidium ($5^2S_{1/2} \rightarrow 5^2P_{3/2}$) were monitored using a tunable laser swept over a ~12 GHz range centered around 780.24 nm [66]. All optical tests took place when the cells were heated to 46°C, although they were stored for long periods at higher temperatures. Since I was not assuming that pressure was constant in these tests as in our second-generation tests, the atomic density could not be directly calculated. This is because the optical depth is dependent on both the pressure and the atomic density. As pressure increases more of the atomic population starts to absorb light to the sides of the center transition wavelength. Even if the atomic density is held constant, the optical depth starts to decrease as pressure increases. Since there is no way to independently monitor the pressure inside our cells, the atomic density and internal pressure become convoluted in the optical depth measurement. The only method to extract the atomic density from our data was to fit the data to a theoretical model. The large number of spectra being collected in this experiment combined with the long computing times of the fitting algorithm made calculating the atomic density for each individual spectrum impractical. Since this test is more comparative in nature than quantitative, I redefined cell failure as a 30% drop in the optical depth. Notice that this means the test does not differentiate between different failure modes. The failure could be caused by a drop in atomic density, an increase in pressure, or any combination of the two. Since all of these failures are undesirable the lack of distinction between failure mode in the lifetime predictions is acceptable.
Three or more minicells of each type (epoxy, Pb/Sn, indium, copper-coated indium, copper-coated Pb/Sn, and nickel-coated Pb/Sn) were stored at the following temperatures: 65 °C, 80 °C, and 95°C. The optical depth and FWHM linewidth of the combined Voigt profiles in the D2 $^{85}$Rb $^5S_{1/2}(F=3) \rightarrow ^5P_{3/2} (F=2,3,4)$ absorption peak were monitored at least once a day until failure. The collected failure data (average failure times for the minicells of each type stored at each temperature) can be seen in Table 6.

Table 6: Observed days to failure [mean and standard deviation (StdDev)] for tested minicells by material type and temperature. Also included are calculated $E_a$ and $A$ constants for minicells with measurable failure times.

<table>
<thead>
<tr>
<th>Type of Seal for Minicell</th>
<th>Epoxy</th>
<th>Pb/Sn</th>
<th>Indium</th>
<th>Pb/Sn w/Copper/Nickel Overcoat</th>
<th>Indium w/Copper Overcoat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Days to failure Mean (StdDev)</td>
<td>Days to failure Mean (StdDev)</td>
<td>Days to failure Mean (StdDev)</td>
<td>Days to failure Mean (StdDev)</td>
<td>Days to failure</td>
</tr>
<tr>
<td>95 °C</td>
<td>3.6 (1.3)</td>
<td>1.6 (0.6)</td>
<td>0.5 (0.2)</td>
<td>1.6 (1.4)</td>
<td>No failure 30+ days</td>
</tr>
<tr>
<td>80 °C</td>
<td>6.4 (3.2)</td>
<td>2.0 (1.1)</td>
<td>3.7 (1.9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>65 °C</td>
<td>15.2 (9.4)</td>
<td>5.8 (2.5)</td>
<td>5.6 (2.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_a$ &amp; $A$</td>
<td>0.520 J/mol 3.910 $\times 10^5$ s$^{-1}$</td>
<td>0.469 J/mol 1.947 $\times 10^6$ s$^{-1}$</td>
<td>0.871 J/mol 1.369 $\times 10^{12}$ s$^{-1}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Using the modified Arrhenius equations outlined in section 7.1.1, these experiments predicted a room temperature device lifetime of 161 days for epoxy, 45 days for bare Pb/Sn, and 413 days for bare indium. The goodness-of-fit values ($R^2$) between the gathered data and the lifetime estimates are 0.99, 0.90, and 0.85 for epoxy, bare Pb/Sn, and bare indium, respectively.

All the copper-coated solder minicells were stored at 95 °C. Testing was halted for the copper and nickel-coated Pb/Sn minicells since they appeared to be suffering from poor electroplated metal adhesion and their failure when stored at 95 °C was identical to the uncoated
Pb/Sn minicells. This seemed to indicate that Rb was penetrating beneath the Cu/Ni overcoat and reacting with the underlying Pb/Sn solder. However, the copper-plated indium seals were observed to last for over 30 days at 95 °C with no degradation in atomic density and no significant linewidth broadening. Since failure times could not be obtained at this temperature, it was assumed failure times would not be found at lower temperatures and so these tests were not performed.

It is important to note the evolution of the pressure and Doppler broadened spectral linewidth during the experiments. For the bare indium and copper-plated indium minicells, no noticeable increase in the linewidth occurred. However, for the epoxy and the Pb/Sn minicells the linewidth did increase, leading to the eventual merging of all four absorption dips in the Doppler broadened Rb D2 lines. Figure 7.11 compares the typical spectral linewidth response for epoxy, bare Pb/Sn, and copper-coated indium minicells. As mentioned earlier, this increase in the spectral linewidth is likely caused by a gaseous byproduct between the Rb and sealing material or, in the case of the epoxy, the outgassing of solvents, water, or carbon dioxide, a common occurrence for epoxies, even certified low-outgassing versions.

Figure 7.11: Voigt profile FWHM linewidth vs. time for copper plated indium (blue diamonds), epoxy (red squares), tin/lead (green triangles) minicells. These minicells were stored at 95°C and optically tested at 46°C.
While theoretical fitting to all our data was not possible, one of my counterparts at UCSC (Jennifer Black) fitted some of our spectra to a model and compared them to theoretical values. The theoretical model takes into account the two isotopes of naturally occurring Rb, all hyperfine energy transitions, Doppler broadening, and pressure broadening [59, 60, 63, 111]. This theoretical model was used to extract the atomic density and homogeneous linewidth via a least-squares fit.

Figure 7.12: Experimental (blue stars) vs. theoretical spectrum (purple solid line) for the 87Rb F=1 transition for a copper-coated indium cell.

The spectrum in Figure 7.12 shows experimental points plotted with a fitted theoretical curve for a minicell that was made using an indium solder and copper overcoat. The experimental points were gathered from optical tests performed at 46°C after the minicell had been stored at 95°C for 33 days. Based on the data gathered and the complete theoretical model,
the spectrum yielded a small homogeneous linewidth of $(55.56 \pm 24.69)\text{MHz}$ and an atomic density of $(7.41 \pm 0.16) \times 10^{10} \text{cm}^{-3}$, which matches the theoretical value of $7.37 \times 10^{10} \text{cm}^{-3}$. This means that the minicell was basically unaffected by the month-long exposure to high temperature as it closely matched the theoretical values for atomic density and spectral linewidth.

In stark contrast to the copper-coated indium minicell, Figure 7.13 shows a spectrum for an epoxy-sealed minicell that had been stored at $95^\circ\text{C}$ for only 15.5 days. To fit the measured points, the theoretical model had to include significant pressure broadening yielding a homogeneous linewidth of $(1046.00 \pm 15.13)\text{MHz}$. This most likely indicates a gaseous by-product of a chemical reaction. The atomic density for this cell is calculated to be $(5.01 \pm 0.33) \times 10^{10} \text{cm}^{-3}$, which is lower than the density for the cell measured in Figure 7.12, indicating that the Rb was reacting with some material in the cell and forming a product that reduced the overall concentration of pure Rb.

![Figure 7.13: Plot for a “dying” epoxy cell with a widened $^{87}\text{Rb} F=1$ transition and lower atomic density.](image-url)
After observing that Rb vapor-cells created with copper-plated indium solder maintain high atomic densities at 95 °C for over 30 days, I concluded that this method has no rubidium chemical reaction failure mode, resulting in vapor-cells with extremely long lifetimes. The sealing technique builds upon our previous success with the copper cold-weld sealed reservoir and adds a Rb neutral passivation coating over an indium seal. Due to the gentle nature of the indium solder process, I submit that the indium-copper combination provides the most versatility in packaging, especially when considering the drive to miniaturize vapor-cell technologies. The versatile nature of this method results from indium’s relatively malleable nature, which allows for low stress joints and make it acceptable to a wider array of materials and geometries.
8 CONCLUSION

8.1 Future Work

There is much more that can be done with the ARROW vapor-cell platform. The most logical development direction is to move toward multi-device integrated systems. The future of the technology lies in its potential ability to create entire monolithically integrated optical, microfluidic, and electrical systems on the same chip. Lab-on-a-chip (LOC) platforms have great potential of being ultra-portable, cheap platforms that can change the landscape of industries such as medicine, chemical detection, and forensics. ARROW technologies could allow for monolithic fabrication of electronics, microfluidics, and micro vapor system all on the same die. This could even include on-chip lasers and detectors. LOC technologies are currently in their infant stages, and most research is spent on developing individual pieces of the systems that may someday be fabricated in whole. My research up to this point really focused on successfully creating a single vapor-cell. The platform is integrated in that it combines the waveguiding and vapor-cell into one package, but it lacks the multi-device integration that this research is ultimately working toward. The next phase of the project, which is already underway thanks to the efforts of my colleague Matthieu Giraud-Carrier, is to create multi-input/output, multi-cell devices. This will require unique hollow-core configurations to allow a signal Rb reservoir source to populate multiple cells and the development of ridge waveguide coupling/splitting
capabilities. Utilizing these configurations many multi-cell devices will be possible. These devices include all optical Mach-Zehnder interferometers, buffers, multiplexers, and pulse-sequence generators. Such multi-cell devices will be a huge achievement in the drive for miniaturized application-oriented vapor-cell technologies and a big step toward lab-on-a-chip systems.

While the focus of the Air-core ARROW research will be heading down the multi-cell, non-linear optics route, a couple of other potential future projects can be beneficial to the research.

### 8.1.1 Multi-core atomic clocks

One idea that I had came about by thinking about was the quickest route the ARROW vapor-cell platform could take to become a commercially available product. One application that we often mention for our ARROW vapor-cells is that of an all-optical communication buffer/switch utilizing the slow light phenomenon. However, the fiber optic communication system utilizes wavelengths in the 1500 nm range which does not coincide with the alkali vapor transitions commonly used in non-linear experimentation. In order to use vapor-cells as buffers, the vapor would have to been changed to something else like acetylene gas [32] or the entire fiber-optic infra-structure would have to be switched back to 780 nm. I would imagine this would put out many of the senior telecommunication engineers. While I am not disputing the great potential the ARROW technology has for the telecommunications industry, I am saying it is a longer road. However, one application that atomic vapor-cell technologies are currently used for is atomic clocks. Atomic clocks using the small vapor-cells developed by NIST are already in use for land, sea, air, and space navigation and communication systems. These devices can have volumes as small as 17 cm³. In these devices the physics package (laser, optics, vapor-cell,
detector) is only about 1/3 of a cm$^3$. That is only 2% of the total device size. The rest of the package containing all the necessary support systems to make an atomic clock work is not so easily shrunk. Even if we could provide a smaller physics package than the NIST technology there is not that great of a benefit because of the size of the supporting systems. Looking to the future, someday ARROW technology could be monolithically integrated onto the same die as the laser, detector, and other supporting electronics, but we are not there yet. However, the ARROW vapor-cell platform still has a potential advantage, multi-cell capabilities.

Small atomic vapor-cells generally suffer from poorer performance than their large closet-sized brothers that reside in underground government bunkers. Small portable atomic clocks cannot afford to be super-cooled, and the small dimensions of the cell mean increased spin decoherence due to atom-wall interactions. These all contribute to less accuracy and a decrease in drift stability. However, there has been development of techniques that utilize ensembles of multiple less-accurate vapor-cells where an advanced algorithm ‘averages’ their outputs to result in much better performance [112]. To increase the number of vapor-cells with the NIST-based technology, one would have to replicate the entire physics package, meaning 2 vapor cells would take 2 times the size and power, 3 would take 3 times, etc. With ARROW-based vapor-cells, one could fit literally hundreds of cells in the space of one NIST cell. Using on-chip integrated waveguiding, one laser could be used to probe multiple vapor-cells and a CCD array could capture all the outputs. This could theoretically allow for more accuracy via multiple vapor-cells without drastically increasing the physics package volume or power consumption in a small and mobile platform.
8.1.2 Planar reservoir ARROW vapor-cells

The second idea I had has to do with a new planar sealing solution. Up to this point, the main approach to Rb introduction has been to create a 3D reservoir coming out of the top of the ARROW surface. There is another potential method to introduce Rb using techniques readily available in a typical MEMS foundry. One of the most limiting factors in our search for reservoir attachment methods has been that the reservoir has to seal over the fragile hollow-core ridge. Having a more robust, planar surface opens up several other options. To that end instead of accessing the hollow-core through the top of the ARROW, we could access the core through the bottom of the wafer. Through-wafer etching is not an uncommon process. There are two main ways to etch through a wafer: an RIE dry etcher or a KOH bath. The most readily available method at the IML is the KOH bath. Silicon nitride is very resistive to KOH baths with etch rates known to be less than 0.1 nm/hour at 120 °C [113]. The top layer of the bottom ARROW stack is silicon nitride; this layer could act as a KOH etch mask protecting the top of the silicon substrate from etching. A silicon nitride mask could also be grown on the bottom of the wafer and using photo lithography techniques through-wafer vias could be patterned into the silicon nitride on the bottom of the wafer and the vias themselves could then be etched by placing the wafer in a KOH bath. A tricky part of this method would be to align the vias etched through the back of the wafer with features on the top of the wafer. If the backside vias are the first patterns etched into the wafer, the next patterning step would be the creation of the sacrificial SU-8 hollow-core features. While backside alignment tools do exist, the bottom ARROW layer stack is relatively thin and the contrast between silicon substrate and the void created by the through-wafer vias should be optically visible for traditional top-side alignment. The sacrificial SU-8 hollow-core would be aligned to these vias. The rest of the ARROW fabrication flow would be
the same up until the core-expose process. Instead of etching through the top layers the wafer would be flipped over and the bottom ARROW stack would be etched with a dry-etch plasma. The silicon substrate would act as the mask and eliminate the need for another lithography step. The newly exposed SU-8 core would be chemically removed, resulting in a completed ARROW device with hollow-core access through the bottom of the wafer.

Figure 8.1: Illustration of proposed planar reservoir ARROW vapor-cell process flow.
As stated earlier this would allow for other types of reservoir attachment methods the most exciting of which would be anodic bonding. Anodic bonding can create hermetic seals between a flat silicon and flat glass substrate via ionic diffusion caused by heat and strong electrostatic forces. This can be done successfully at temperatures as low as 250 °C, which is within the ARROW heat-tolerance limit. An anodically bondable reservoir could be created by anodically bonding a second plain silicon wafer to a glass wafer with holes etched through it. The holes in the glass wafer could be populated with rubidium and then the glass wafer would be anodically bonded to the bottom of the ARROW wafer with the Rb-populated glass holes aligning with the hollow-core through-wafer vias. This concept is very similar to the NIST vapor-cell. Instead of a silicon wafer sandwiched between two glass wafers, it would be a glass wafer sandwiched between two silicon wafers, one of the silicon wafers having ARROW devices on the surface. Since the cells need to be evacuated and contain exposed Rb during the final seal, the anodic bonding process would have to take place under vacuum in a Rb-friendly environment. This could be done by installing a bell jar in the glovebox. Electrodes supplying the power necessary for anodic bonding and a heating pad could be fed into a bell jar attached to a vacuum system [10]. The planar nature of the Rb reservoir would ultimately allow for even more compact ARROW vapor-cell designs. While these ideas are over-simplified with these brief conceptual outlines and would undoubtedly pose many challenges, I do believe they have merit and are completely achievable.
8.2 Final Summary and Conclusion

The material in this dissertation describes the development of two generations of novel atomic vapor-cell construction methods. These methods were created with the intent to apply them on integrated on-chip ARROW-based vapor-cells. However, it is important to note that these construction methods are not limited to said ARROW packages and stand out as versatile methods applicable to vapor-cells made of a wide variety of materials and geometries.

This work included the development of the first functioning ‘minicell’ platform vapor-cell. These minicells were created using the novel second-generation sealing method that employed the use of high-temperature epoxy and copper cold-weld seals. While the minicell was intended only as a testing platform for ARROW development, in and of themselves they are no small accomplishment. They are cheap, small, easily repeatable vapor-cells, the best of which rivaled the performance of expensive, commercially available Rb reference cells.

This dissertation also outlines the construction and testing of the first-ever integrated on-chip vapor-cell to have successfully been probed for Rb absorption spectra, EIT, and slow light. This was done utilizing ARROW devices developed and fabricated on-site in the BYU IML laboratories and packaged using the techniques developed on the minicell platform. This marks an exciting development in the quest for small, fully integrated vapor-cell-based devices with applications in the communications, research, medical, navigation, and lab-on-chip industries.

These successful vapor-cell technologies were further improved by the development of a copper-coated indium solder sealing technique that has yielded better performance and longer lifetimes on the minicell platform. This long-lasting seal is critical to furthering the development of the ARROW vapor-cell-based devices. This will greatly improve our temporal performance
resolution, enhance our optimization efforts, and allow for the development of multi-cell based devices and experimentation.

There were other notable accomplishments along the way. One of these was the designing, building, and qualifying of a multi-channel atomic spectroscopy system. This includes the writing of a ‘software suite’ of LabVIEW and MATLAB code that allowed for the fast-paced simultaneous gathering, filtering, and analyzing of spectral results on multiple channels. This multi-channel aspect of both the hardware and software was a particularly uncommon attribute of the spectroscopy system and allowed for timely execution of a large quantity of spectral experimentation.

Along with the spectroscopy system, I also put together and developed an electroplating system and procedure. This system ultimately was designed to be able to plate two types of metals on both planar and more complex geometries. Electroplating rates, current densities, and surface properties were experimentally qualified to produce the desired effect. This system also includes MATLAB codes that help to determine electroplating settings based on desired device properties.

The work included in this dissertation also represents the coordinated efforts of 7+ assisting research assistants whom I trained and directed during my time as lead research assistant for the BYU Air-core ARROW team. I have worked with a great team, including my advisor, BYU faculty and staff, my colleagues at UCSC, and my fellow students. I am proud of the novel ideas, solutions, capabilities, and academic works that I have been able to contribute to this team and project. I look forward to the many developments that will continue to be made on this project.
REFERENCES


APPENDIX A. PUBLICATIONS

A.1 Journal Articles


A.2 Conference Proceedings

APPENDIX B. CODE FOR RESEARCH PROGRAMS

This appendix presents the MATLAB scripting code written to conduct various experiments in my research. As future ARROW Air-core researchers will be utilizing the same systems and techniques, I have included the critical pieces of code required for electroplating, post-capture spectroscopy data analysis, spectrum plotting, and accelerated lifetime Arrhenius calculations.

B.1 Electroplating Code

%Script Calculates time or current density for electroplating process of Ni or Cu
%Dr. Aaron Hawkins Slow Light Research
%Author John Hulbert April 26, 2012

clear all
close all
clc

%******** User Defined ************************************************************************
shape = 'arbitrary'; %choose between 'tube' or '3dr' or 'donut' or 'arbitrary'
thickOrTime = 'time'; %choose between 'time' or 'thick'
element = 'Cu'; %choose between 'Cu' or 'Ni'
numDevices = 2; %how many devices are being electroplated at once

time = 3600; %seconds
th = 3e-6; %electroplating thicknesss (meters)

%Current Density Limits Ni:3 to 11(4.3 is average) & Cu:3.7 to 5.4(4.6 is average) (mA/dm^2)
ampD = 3.7e-3; %Current Density(A/dm^2)
ampD = ampD * 100^2; %Current Density(A/m^2)
%initializing variables
Sanode = 0;

switch shape

case 'inChip'
    rIn = 1.5e-3; % inner radius (meters)
    h = 4e-3;  % height (meters)

    % calculate surface area of tube
    SInCyl = 2*pi*rIn*h;
    S = SInCyl; %total surface area (m^2)

case 'inMini'
    rIn = 4e-3; % inner radius (meters)
    h = 13e-3;  % height (meters)

    % calculate surface area of tube
    SInCyl = 2*pi*rIn*h;
    S = SInCyl; %total surface area (m^2)

    % calculate surface area of anode
    hanode = h;
    ranode = 1.5e-3;
    Sanode = 2*pi*ranode*hanode;

case 'charexp'
    % calculates device surface area for characterization experiments
    height = 7e-3;
    width = 14e-3;
    numStrip = 3;

    stripWs = [0.8,1.1,1.1,1,.9,1,1,1.5,1,1,.8,1,1,1,1,.8,1,1,.9,.9,.9,1,1,1.2,1,1,1,1.2,1,1,1,1.2,1,1,1,1.1,1,.8,.8,.9,1,1,.8,1,1.2,1,1.2]*1e-3;
    [dontWant,sizeSW] = size(stripWs);
    stripWidth = sum(stripWs)/sizeSW;

    S = width*height-(stripWidth)*height*numStrip;

case 'minicellTop'
    rOut = 11e-3; % outer radius (meters)
    rIn = 6e-3; % inner radius (meters)

    % calculate surface area of donut shape on top of minicell
    outsideCircle = pi*rOut^2;
    insideCircle = pi*rIn^2;
    donutS = outsideCircle - insideCircle %total surface area (m^2)

    % calculate surface area of silver epoxy wire attachment site
    % approximated as a 3D triangle
    protrusionHeight = 3e-3;
    width = 7e-3;
    height = 4e-3;
epoxyS = 
4*(1/2*width/2*protrusionHeight)+2*(sqrt((1/2*width)^2+protrusionHeight^2)*height)
S = donutS + epoxyS;
cool = (30e-3/S)/(100^2)

case 'tube'
%For 3/8" tubing: 4.763mm OR, 3.763mm IR
rOut = .004763; % outer radius (meters)
rIn = .003763; % inner radius (meters)
h = 6.35e-3;%6.35e-3; % height (meters)

%calculate surface area of tube
SoutCyl = 2*pi*rOut*h;
SInCyl = 2*pi*rIn*h;
SbottomCyl = pi*rOut^2 - pi*rIn^2;
S = SoutCyl + SInCyl + SbottomCyl; %total surface area (m^2)

case '3dr'
w = 4.5e-3; % Width (meters)
d = 0; % depth/thickness (meters)
h = 12e-3; % height (meters)

%calculate surface area of a right-angled parallelepiped or 3D rectangle(3dr)
frontBack = 2*w*h;
sides = 2*d*h;
bottom = d*w;
S = frontBack + sides + bottom; %total surface area (m^2)

case 'donut'
rOut = 5e-3; % outer radius (meters)
rIn = 1.5e-3; % inner radius (meters)
approxRadiusWire = 0.4e-3;
%calculate surface area of donut shape
%For now, estimating solder sites as the inner circle
outsideCircle = pi*rOut^2;
insideCircle = pi*rIn^2;
Wires = 2*pi*approxRadiusWire*1e-2; %circumference of wire * 1cm
in solution
S = outsideCircle + Wires; %total surface area (m^2)

case 'arbitrary'
S = 1e-4; %1 square centimeter test area

otherwise
    error('Not a valid shape.')</end

%check to see if anode or cathode surface area is current limiting factor
if S < Sanode || Sanode == 0
    Slimit = S;
else
    Slimit = Sanode;
end
I = Slimit*ampD*numDevices;
Elemental constants are selected based on material being electroplated

```matlab
switch element
    case 'Ni'
        rho = 8.908e6; %density of nickel (gm/m^3)
        M = 58.6934; %gm/mol of nickel (standard atomic weight)
        atomic weight
            electronPerAtom = 2; % Ni^(2+) + 2e^(-1) <--> Ni (electron/atom)
    case 'Cu'
        rho = 8.94e6; %density of copper (gm/m^3)
        M = 63.546; %gm/mol of copper (standard atomic weight)
        atomic weight
            electronPerAtom = 2; % Cu^(2+) + 2e^(-1) <--> Cu (electron/atom)
    otherwise
        error('Invalid element');
end

% Calculates the total amount of charge needed to create the total mass
totalMass = S*th*rho*numDevices; %gm
totalMol = totalMass/M; %mol of nickel
AvoNum = 6.022e23; %atom/mol
elecCharge = 1.602e-19; %Coulomb/electron
Q_perMol = AvoNum*elecCharge*electronPerAtom; %Coulomb/mol of EP Ni

% Charge equals product of current and time. (Q=I*t) Therefore, t = Q/I.
Q = Q_perMol*(totalMol);
t = Q/I;
if t/3600 < 1
    if t/60 < 1
        answer = ('For a thickness of ' num2str(th/1e-6) 'um, electroplate for ' num2str(t) ' seconds at ' num2str(I/1e-3) 'mA.');
    else
        min = fix(t/60);
        sec = rem(t,60);
        answer = ('For a thickness of ' num2str(th/1e-6) 'um, electroplate for ' num2str(min) ' minutes and ' num2str(sec) ' seconds at ' num2str(I/1e-3) 'mA.');
    end
else
    hrs = fix(t/3600);
    remhrs = rem(t,3600);
    min = fix(remhrs/60);
    sec = rem(remhrs,60);
    answer = ('For a thickness of ' num2str(th/1e-6) 'um, electroplate for ' num2str(hrs) ' hours, ' num2str(min) ' minutes, and ' num2str(sec) ' seconds at ' num2str(I/1e-3) 'mA.');
end
msgbox(answer,'Electroplating Recipe Answer')
```
B.2 Post Spectroscopy Data Analysis Code

% This program performs necessary post-spectroscopy data analysis. It calls
% the functions funcAverageNcenterSpectra and funcBaselineNfreqLabel.
% Author John Hulbert BYU 2012
close all
clear all
clc

%*****User Input**************************************************************************

%Test Time (Military i.e. 8:30am = 0830)
time = '0915';

%Date of test. Example: August 28 = 0828
day = '21';
month = '09';

%Year
year = '2012';
date = [year month day];

%Base folder is where the folders "averageSpectraSL, baselineSpectraSL and
%dataTrackSpectraSL" are located.
baseFolder = 'C:\Users\ecestudent\Dropbox\OpticsResearch\';

%The folder where the spectroscopy programs saves all the raw spectrum scans
rawFolder = 'C:\Users\ecestudent\Desktop\rawSpectraSL\';

%Bulk Cell Channel Number(Note: this program relies on having a Bulk Cell
%channel and power reference channel to work)
bulkChanNum = '5';

%Power Reference Channel Number
refChanNum = '7';

%Channel #'s that are used for testing devices. As opposed to the ref and
%bulk channels. Note: This is not asking for what channels are active,
%it's asking what channels are used for testing devices in teh spectroscopy
%setup. This is so it knows what channels to check for active status in
%the 'chInfo*.txt' file.
testChans = ['0','2','4'];

%Up to what order do you want polyfit?
order = 10;

%***********************************************************

%Setting Dialog Box properties, asks user if he wants to average and center
%the spectra.
options.Resize='on';
options.WindowStyle='normal';
options.Interpreter='none';
responseSaveData = inputdlg('Do you want to average and center the spectra?
(Y or N) [Q to quit]:','Run Average Function?',1,{'Y'},options);
%The user is asked if he wants to save the data incase there was an error.
switch responseSaveData{1,1}
    case {'q','Q'}
        disp('Program quit by user.')
        return
    case {'n','N'}
    case {'y','Y'}
        funcAverageNcenterSpectra(time, day, month, year, baseFolder, rawFolder, bulkChanNum, refChanNum, order);
    otherwise
        error('(Run Average Function?): Invalid Input')
end

%Setting Dialog Box properties, asks user if he wants to run baseline and frequency label function.
options.Resize='on';
options.WindowStyle='normal';
options.Interpreter='none';
responseSaveData = inputdlg('Do you want to run baseline and frequency label function? (Y or N) [Q to quit]:','Run Baseline Function?',{1,'Y'},options);

%The user is asked if he wants to save the data incase there was an error.
switch responseSaveData{1,1}
    case {'q','Q'}
        disp('Program quit by user.')
        return
    case {'n','N'}
    case {'y','Y'}
        close all
        clc
        funcBaselineNfreqLabel(time, day, month, year, baseFolder, testChans);
    otherwise
        error('(Run Baseline Function?): Invalid Input')
end

%Written August 30, 2011 --- John Hulbert ---Slow Light, Dr. Hawkins BYU
%Matlab Program Designed to average and center an array of Rb spectrum
%scanned with Dr. Hawkins spectroscopy setup in CB417.
function [] = funcAverageNcenterSpectra(time, day, month, year, baseFolder, rawFolder, bulkChanNum, refChanNum, order)

%%%Semi-User Input (Designed to match with test file naming protocol)**********
date = [year month day];

%Folder spectra scan files are located in
folder = [rawFolder date '\'];

%Folder to save averaged spectra in
folderSave = [ baseFolder 'averageSpectraSL\avg' date '\'];

%*************************************************************************

%***Bulk Cell and Array Alignment***
%Due to wavelength drift in the laser output over time, this program finds
%the center of the deepest absorption dip for each scan then fits a curve
%to estimate any wavelength drift. The program plots the fitted curve, rms,
%R^2, and spread values of multiple fits to help user to decide which fit
%is the best. The bulk cell is used for this alignment data since it is a
%stable reference. This program also needs a file that tells it which
%channels are 'selected\on'(which channels to process) and a file that
%contains each channels ID.

%Import power reference(ref) and bulk cell(bulk) data
ref = importdata([folder 'ch' refChanNum '_' date '_' time '.txt']);
bulk = importdata([folder 'ch' bulkChanNum '_' date '_' time '.txt']);

%Get dimensions of the data matrices
length = size(bulk,2);
height = size(bulk,1);

%set dimensions for various matrices and arrays
bulkRef = zeros(height,length);
bulkIndexOfMin = zeros(1,height);

for h = 1:height

    %Divide out the laser power output vs wavelength
    bulkRef(h,:) = bulk(h,:)./ref(h,:);

    %gets the index location of minimum for each scan
    [~,bulkIndexOfMin(h)] = min(bulkRef(h,:));

end

clear h bulk %since we are dealing with gigs of data its good practice to
clear unneeded data from memory

%Calculates the fit polynomial(bFit), an array of data points for that
%polynomial(bFitx), the rms value, the spread, and the R^2 value for a set
%of polynomial orders
spread = max(bulkIndexOfMin)-min(bulkIndexOfMin);
x = 1:1:height;
bFitx = zeros(order,height);

for n = 1:order

    bFit = polyfit(x,bulkIndexOfMin,n); %finds best fit poly of order n
    bFitx(n,:) = round(polyval(bFit,x)); %analyzes fitpoly for array x

    clear bFit

end

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Calculating R^2
ypred = bFitx(n,:); % predictions
devel = bulkIndexOfMin - mean(bulkIndexOfMin); % deviations - measure of spread
SST = sum(dev.^2); % total variation to be accounted for
resid = bulkIndexOfMin - ypred; % residuals - measure of mismatch
SSE = sum(resid.^2); % variation NOT accounted for
Rsq(n) = 1 - SSE/SST; % percent of error explained
clear ypred devel SST resid SSE

Calculating rms (kinda)
topRms = 0;
for h = 1:height
    topRms = topRms + (bFitx(n,h)-bulkIndexOfMin(h))^2;
end
rms(n) = sqrt(topRms/height);
spreadFit(n) = max(bFitx(n,:))-min(bFitx(n,:));
clear h topRms

gof factors vs. polyfit order
figure(1)
subplot(3,1,1)
plot(rms)
xlabel('Polyfit Order')
ylabel('RMS (want low)')
set(gca,'Xtick',1:1:order)
title(['Polyfit GOF data: ' month '/' day '/' year ' @ ' time 'hrs'])
subplot(3,1,2)
plot(Rsq)
xlabel('Polyfit Order')
ylabel('R^2 (want high)')
set(gca,'Xtick',1:1:order)
subplot(3,1,3)
plot(spreadFit)
xlabel('Polyfit Order')
ylabel('Polyfit Index Spread')
set(gca,'Xtick',1:1:order)

while exit == 0
    % Setting Dialog Box properties, asks user which polyfit order to use.
    options.Resize='on';
    options.WindowStyle='normal';
    options.Interpreter='none';
    responseOrder = inputdlg(['Which order would you like to use in polyfit(1-' num2str(order) ')? [Q to quit]:','Polyfit Order?','1',{''},options);
    userOrder = responseOrder{1,1};
    switch userOrder
    case 'Q'
        exit = 1;
    end
end
case {'q','Q'}
    disp('Program quit by user.')
    return

otherwise
    userOrder = str2double(userOrder);
    if isnumeric(userOrder) && (mod(userOrder,1)==0) && (userOrder >= 1) && (userOrder <= order)
        %making sure 'userOrder' is a number, an integer, and in
        %the right range
    else
        error('Polyfit Order?: Invalid input. Input must be integer
        within range of polyfit orders.')
    end
end

%Plots spectral minimum indeces & polyfits vs. scans
figure(2)
plot(x,bulkIndexOfMin,'b-',x,bFitx(userOrder,:),'r')
xlabel('Scan #')
ylabel('Array Index where Scan Min Occurs')
title(['Spectral Minium Index Location: ' month '/' day '/' year ' @ ' time 'hrs'])
legend('Actual','Polyfit')

%Setting Dialog Box properties, asks user if continue or if wants other
polyfit order.
    options.Resize='on';
    options.WindowStyle='normal';
    options.Interpreter='none';
    responseContinue = inputdlg('Continue? Y to continue or anything else to
select another polyfit order.','.Continue?','1',{'Y'},options);
    userContinue = responseContinue{1,1};

switch userContinue
    case {'y','Y'}
        exit = 1;
    otherwise
end
end
clear bulkIndexOfMin

clear responseOrder
close([1,2])

fitIndexOfMin = round(bFitx(userOrder,:));
clear bFitx

%Finds the two extremes of the minimums
minOfFitIndexOfMin = min(fitIndexOfMin);
maxOfFitIndexOfMin = max(fitIndexOfMin);

%***************Next section centers and averages the spectrum arrays for
%each channel********************
As we shift the arrays to align with the fitted minimum index polynomial, we will have overhang and underhang of data at the end. This clips off the overhang so each array is the same size and all arrays are filled with useful data.

```
%***Bulk Cell***
bulkAvg = zeros(1,length - (maxOfFitIndexOfMin-minOfFitIndexOfMin));
for h = 1:height
    % calculates where the array needs to be clipped on front and end for alignment
    lowIndex = 1 + fitIndexOfMin(h) - minOfFitIndexOfMin;
    highIndex = length - (maxOfFitIndexOfMin - fitIndexOfMin(h));

    % Adding each scan to calculate average and reduce noise effects
    bulkAvg = bulkAvg + bulkRef(h,lowIndex:highIndex);
end
clear h bulkRef
bulkAvg = bulkAvg/height; % average
dlmwrite(fullfile(folderSave 'avgbulk_' date '_' time '.txt'), bulkAvg, 'precision', 8, 'delimiter', '	', 'newline', 'pc');

%***Channels 0 through 5**************
chInfo = importdata(fullfile(folder 'chInfo_' date '_' time '.txt'),
chSelect = chInfo.data;
[dontcare, lengthchSelect] = size(chSelect);

j = 1;
for chNum = 1:lengthchSelect
    if chSelect(chNum) == 1 && chNum ~= (str2num(bulkChanNum)+1) && chNum ~= (str2num(refChanNum)+1)
        chActive = importdata(fullfile(folder 'ch' num2str(chNum-1) '_' date '_' time '.txt')); % read in data

        % creating matrices and arrays with correct dimensions
        chActiveRef = zeros(height,length);
        chActiveAvg = zeros(1,length - (maxOfFitIndexOfMin-minOfFitIndexOfMin));
        for h = 1:height
            chActiveRef(h,:) = chActive(h,:)/ref(h,:); % dividing out power variance
        end

        % calculates where the array needs to be clipped on front and end for alignment
        lowIndex = 1 + fitIndexOfMin(h) - minOfFitIndexOfMin;
        highIndex = length - (maxOfFitIndexOfMin - fitIndexOfMin(h));

        % Adding each scan to calculate average and reduce noise effects
        chActiveAvg = chActiveAvg + chActiveRef(h,lowIndex:highIndex);
```
end
chActiveAvg = chActiveAvg/height; %average

%saving averaged spectra
dlmwrite(fullfile('avgch' num2str(chNum-1) '_' date '_' time '.txt'), chActiveAvg, 'precision', 8, 'delimiter', '	', 'newline', 'pc');

%Saving averaged spectra for each channel and channel number for plot titles
chAvg(j,:) = chActiveAvg;
plotTitleNum(j) = chNum;
j = j + 1;

clear h chActive chActiveRef chActiveAvg
else
end
end
clear ref

%************************Plotting******************************

%number of channels on
numOch = sum(chSelect);

%this case statement allows the spectra plot to dynamically adapt to amount
%of channels that are on
switch numOch
    case {2}
        error('Not enough Channels.');
    case {3}
        dimx = 2;
        dimy = 1;
    case {4,5}
        dimx = 2;
        dimy = 2;
    case {6,7}
        dimx = 2;
        dimy = 3;
    case {8}
        dimx = 2;
        dimy = 4;
    otherwise
        error('Invalid number of channels')
end

%ploting spectra
figure(3)
subplot(dimy,dimx,1)
plot(bulkAvg)
title(['Bulk Cell: ' month '/' day '/' year ' @ ' time 'hrs'])

%plots only channels that are on
for n = 1:(numOch-2)
    subplot(dimy,dimx,(n+1))
    plot(chAvg(n,:))
    title(['Channel ' num2str(plotTitleNum(n)-1)])
function [] = funcBaselineNfreqLabel(time, day, month, year, baseFolder, testChans)

%*****Explaination of function inputs****************************************
%The inputs "time(military), day, month, & year" are all strings.
%Base folder is where the folders "averageSpectraSL, baselineSpectraSL and
%dataTrackSpectraSL are located.
%'testChans' is an array of strings containing the numbers of the channels
%set aside for the experiments. As opposed to the ref and bulk channels.
%Note: This is not asking what channels are active, it's asking what
%channels are used for testing devices in the spectroscopy setup. This is
%so it knows what channels to check for active status in the 'chInfo*.txt'
%file. This is asking, "For this spectroscopy system, which channels are
%set aside for the tests?" Example, right now our spectroscopy system uses
%channels 0, 2, and 4 as the testing channels. Therefore:
%testChans = ['0','2','4']
%**************************************************************************

%*****Semi-User Input (Designed to match with test file naming
% protocol)*****

date = [year month day];

%Default Frequency Label
freqLabel = '650,1017,3.035e9';

%Folder Averaged and Centered(Drift Compensated) spectra scan files are
%located in
folder = [ baseFolder 'averageSpectraSL\avg' date '\'];

%Folder to save Baseline & Frequency labeled spectra in
folderSaveBaseline = [ baseFolder 'baselineSpectraSL\' ];
folderSaveDataTrack = [ baseFolder 'dataTrackSpectraSL\' ];

%**************************************************************************

format long

%Imports channel names\indentifiers
fullnumofChan = size(testChans,2);
chInfo = importdata([folder 'chInfo_' date '_ ' time '.txt'], '\t', 1);
chIden = chInfo.colheaders;
chSelect = chInfo.data;
numofChan = 0;
for n = 1:fullnumofChan
    fullcellIden{n} = chIden{str2num(testChans(n))+1};
    if chSelect(str2num(testChans(n))+1) ~= 1
    else
        numofChan = numofChan + 1;
        chanNum(numofChan) = testChans(n);
        cellIden{numofChan} = fullcellIden{n};
    end
end

% Import bulk cell (bulk) and channel data
bulk = importdata(fullfile('avgbulk_','_','_','txt'));
for n = 1:numofChan
    chan(n,:) = importdata(fullfile('avgch','chanNum(n)_'','_','_','txt'));
end
length = size(bulk,2);
x = 1:1:length;

%**** plots the bulk cell spectra and the raw 'chan/minicell' spectra for
% comparison
num2Plot = numofChan + 1; % bulk plus num of chan

% this case statement allows the spectra plot to dynamically adapt to amount
% of channels that are on
switch num2Plot
    case {2}
        dimx = 1;
        dimy = 2;
    case {3}
        dimx = 2;
        dimy = 2;
    case {4}
        dimx = 2;
        dimy = 2;
    otherwise
        error('Invalid number of channels')
end

figure(1)
subplot(dimy,dimx,1)
plot(bulk)
xlabel('Scans')
ylabel('Absorption Ratio')
title([' Bulk Cell ' month '/' day '/' year ' @ ' time 'hrs'])
for n = 1:(numofChan)
    subplot(dimy,dimx,(n+1))
    plot(chan(n,:))
xlabel('Scans')
ylabel('Absorption Ratio')
title(cellIden{n})
end
%********
%***Defining the 'fit regions' for bulk and all the chan
userFitRegion = [30,80,length-60,length-10];

xFit = x(userFitRegion(1):userFitRegion(2));
xFit = [xFit,x(userFitRegion(3):userFitRegion(4))];

baseFitBulk = bulk(userFitRegion(1):userFitRegion(2));
baseFitBulk = [baseFitBulk,bulk(userFitRegion(3):userFitRegion(4))];

for n = 1:numofChan
    dummybaseFitChan = chan(n,userFitRegion(1):userFitRegion(2));
    dummybaseFitChan = [dummybaseFitChan,
        chan(n,userFitRegion(3):userFitRegion(4))];
    baseFitChan(n,:) = dummybaseFitChan;
    clear dummybaseFitChan
end

%******

baseLength = size(baseFitChan(1,:),2);
%***adjusting all arrays to chop off edge data that the fit polynomial wont take
%into account(edges are usually very messy especially at high order fits)
bulk = bulk(userFitRegion(1):userFitRegion(end));
for n = 1:numofChan
    newchan(n,:) = chan(n,userFitRegion(1):userFitRegion(end));
end
chan = newchan;
length = size(bulk,2);
x = x(userFitRegion(1):userFitRegion(end));
%****

%***Calculates the fit polynomial(bFit) and an array of data points for that polynomial(bFitx): This is calculating the baseline

for n = 1:numofChan
    bFit = polyfit(xFit,baseFitChan(n,:),1); %finds best fit poly of order n
    bFitx(n,:) = polyval(bFit,x); %analyzes fitpoly for array x
    %normalizes baseline on chan with selected polyfit function
    baseChan(n,:) = chan(n,:)./bFitx(n,:);
    clear bFit
end

bFit = polyfit(xFit,baseFitBulk,1); %finds best fit poly of order n
bFitxBulk = polyval(bFit,x); %analyzes fitpoly for array x
%normalizes baseline on chan with selected polyfit function
baseBulk = bulk./bFitxBulk;
clear bFit
%***

%*********plots fitting segments of chan and the selected polyfit
figure(2)
subplot(dimy, dimx, 1)
plot(xFit, baseFitBulk, x, bFitxBulk)
xlabel('Scan #')
ylabel('Absorption (V)')
title(['Baseline Fit: Bulk ' month '/' day '/' year ' @ ' time 'hrs'])
legend('Fit Spectra', 'Baseline')

for n = 1:numofChan
    subplot(dimy, dimx, n+1)
    plot(xFit, baseFitChan(n,:), x, bFitx(n,:))
    xlabel('Scan #')
    ylabel('Absorption (V)')
    title(['Baseline Fit: ' cellIden{n} ' ' month '/' day '/' year ' @ ' time 'hrs'])
    legend('Fit Spectra', 'Baseline')
end

%****plots all of chan and the selected polyfit
figure(3)
subplot(dimy, dimx, 1)
plot(x, bulk, x, bFitxBulk)
xlabel('Scan #')
ylabel('Absorption (V)')
title(['Absorption Spectra Baseline: Bulk ' month '/' day '/' year ' @ ' time 'hrs'])
legend('Absorption Spectra', 'Baseline')

for n = 1:numofChan
    subplot(dimy, dimx, n+1)
    plot(x, chan(n,:), x, bFitx(n,:))
    xlabel('Scan #')
    ylabel('Absorption (V)')
    title(['Absorption Spectra Baseline: ' cellIden{n} ' ' month '/' day '/' year ' @ ' time 'hrs'])
    legend('Absorption Spectra', 'Baseline')
end

%****plots the bulk cell and baseline compensated chan
figure(4)
subplot(dimy, dimx, 1)
plot(baseBulk)
xlabel('Scans')
ylabel('Absorption Ratio')
title(['Bulk Cell Spectra ' month '/' day '/' year ' @ ' time 'hrs'])

for n = 1:numofChan
    subplot(dimy, dimx, n+1)
    plot(baseChan(n,:))
    xlabel('Scans')
    ylabel('Absorption Ratio')
    title(cellIden{n})
end

%****
% This next section sets the x-axis to frequency values (instead of scan #)
% and asks for the location of the absorption minimum.
% The user will enter 4 data entries separated by commas. The first two
% will be two locations on the spectra (scan #) separated by the frequency
% value provided as the third data entry. The fourth data entry is the
% location of the minimum on 'chan' that will be analyzed as the absorption
% point. It should be noted that the minimum will be used as the 0
% frequency. The first three data points should generally come from the bulk
% cell plot since its spectra should be more trustworthy than the minicells.

% Setting Dialog Box properties, asks user to label x axis and choose minimum location.
options.Resize='on';
options.WindowStyle='normal';
options.Interpreter='none';
responseFreqLabel = inputdlg('Enter two locations on the bulk spectrum and the delta frequency between them. [Q to quit]:','Frequency X-axis Labeling & Minimum',1,{freqLabel},options);

switch responseFreqLabel{1,1}
  case {'q','Q'}
    disp('Program quit by user.')
    return
  otherwise
    userFreqLabel = str2num(responseFreqLabel{1,1});
    regionLength = size(userFreqLabel, 2);
    if isnumeric(userFreqLabel) && (regionLength == 3) &&
     (mod(userFreqLabel(1,1) == 0) && (mod(userFreqLabel(2,1) == 0)
        else
        error('(FrequencyLabel): Invalid Input')
  end

% based on user input, calculates frequency separation between each scan point
freqPerScan = userFreqLabel(3)/(userFreqLabel(2)-userFreqLabel(1));

% creates a new frequency x-axis
nonCenterxFreq = 0:freqPerScan:((length-1)*freqPerScan);

% closing unwanted figures
close all

for n = 1:numofChan
% creates frequency axis centered around minimum locations on each spectrum.
\[
[\text{minChanVal, minChan}] = \min(\text{baseChan}(n,:));
\]
\[
\text{xFreq} = \text{nonCenterxFreq} - \text{nonCenterxFreq}(\text{minChan});
\]

% based on the value of the provided minimum location on 'chan' calculates % the value of FWHM of the absorption dip
\[
\text{halfMax} = \text{baseChan}(n,\text{minChan}) + (0.5)*(1-\text{baseChan}(n,\text{minChan}));
\]

% The following two loops look for the frequency location of the two % pMax intercepts % The first loop checks to the left or negative x direction % and the second goes right or positive x direction
\[
\text{stillLooking} = 0;
\]
\[
l = \text{minChan};
\]
\[
\text{while stillLooking == 0}
\]
\[
\text{if baseChan}(n,l) == \text{halfMax}
\]
\[
\text{law} = \text{xFreq}(l);
\text{sillLooking} = 1;
\]
\[
\text{elseif baseChan}(n,l) < \text{halfMax} && \text{baseChan}(n,l-1) > \text{halfMax}
\]
\[
\text{y2L} = \text{baseChan}(n,l);
\text{x2L} = \text{xFreq}(l);
\text{y1L} = \text{baseChan}(n,l-1);
\text{x1L} = \text{xFreq}(l-1);
\]
\[
\text{BL} = (\text{x2L}\times\text{y1L}-\text{y2L}\times\text{x1L})/((\text{x2L}-\text{x1L})
\text{AL} = (\text{y2L}-\text{BL})/\text{x2L};
\]
\[
\text{yFL} = \text{halfMax};
\text{xFL} = (\text{yFL}-\text{BL})/\text{AL};
\]
\[
\text{law} = \text{xFL};
\text{sillLooking} = 1;
\]
\[
\text{else}
\]
\[
\text{l} = \text{l} - 1;
\]
\[
\text{end}
\]
\[
\text{end}
\]
\[
\text{stillLooking} = 0;
\]
\[
r = \text{minChan};
\]
\[
\text{while stillLooking == 0}
\]
\[
\text{if baseChan}(n,r) == \text{halfMax}
\]
\[
\text{raw} = \text{xFreq}(r);
\text{sillLooking} = 1;
\]
\[
\text{elseif baseChan}(n,r) < \text{halfMax} && \text{baseChan}(n,r+1) > \text{halfMax}
\]
\[
\text{y2R} = \text{baseChan}(n,r+1);
\text{x2R} = \text{xFreq}(r+1);
\text{y1R} = \text{baseChan}(n,r);
\text{x1R} = \text{xFreq}(r);
\]
\[
\text{BR} = (\text{x2R}\times\text{y1R}-\text{y2R}\times\text{x1R})/((\text{x2R}-\text{x1R})
\text{AR} = (\text{y2R}-\text{BR})/\text{x2R};
\]
\begin{verbatim}
yFR = halfMax;
xFR = (yFR-BR)/AR;

rsw = xFR;
stillLooking = 1;
else
    r = r + 1;
end

%Full Width Half Max
FWHM = rsw - lsw;

%plots the baseline compensated 'chan' spectra and the locations of
%FWHM
figure(n)
plot(xFreq,baseChan(n,:),'-bl',[lsw,rsw],[halfMax,halfMax],'--
rx',xFreq(minChan),minChanVal,'kd',xFreq(userFreqLabel(2)),minChanVal,'go',xFreq(userFreqLabel(1)),baseChan(n,userFreqLabel(1)'),'ms'
xlabel('Frequency')
ylabel('Absorption Ratio')
title(['Normalized Spectra: ' cellIden{n}'    month '/' day '/' year ' @ ' time 'hrs'])

%calculating absorption ratio and percentage
absorption = 1 - baseChan(n,minChan);
absorpPercent = 100*absorption;

absorpPercent

%The following section saves spectrum data. There are two files. The
%file
%whos filename starts with 'base' contained the baseline compensated
%spectra and the date the spectra was taken. Note that the file format is
%alternating rows of dates and spectra. The second file starting with
%'data' saves the date(matlab serial date format), the absorption ratio,
%the spectral width(FWHM), and the date again(excel serial date format in
%case the data will be analyzed in excel)[I later added a 5th it is the
%distance between user defined bulk spectrum min and user defined cell
%spectrum min]. Each of these data points are
%entered on one row in there own comma seperated column. The data is
%appended to the file after each run

%Setting Dialog Box properties, asks user to if he wants to save/write
data to file.
options.Resize='on';
options.WindowStyle='normal';
options.Interpreter='none';
responseSaveData = inputdlg('To you want to save spectrum data to file?.
(Y or N) [Q to quit]:','Save data?',1,{'Y'},options);

%The user is asked if he wants to save the data incase there was an
error.
switch responseSaveData{1,1}
\end{verbatim}
case {'q','Q'}
    disp('Program quit by user.')
    return

case {'n','N'}

case {'y','Y'}

    dataToWrite =
        [datenum(str2num(year),str2num(month),str2num(day),str2num(time(1:2)),str2num(time(3:4)),00),
        (datenum(str2num(year),str2num(month),str2num(day),str2num(time(1:2)),str2num(time(3:4)),00))-
        datenum('30-Dec-1899'),
        absorption,FWHM,xFreq(minChan)-xFreq(userFreqLabel(2))];
    dlmwrite([folderSaveBaseline cellIden{n} '\base' cellIden{n} ' ' 
        date '_' time '.txt'],[xFreq;baseChan(n,:)],'precision',8,'delimiter', '\t',
        'newline', 'pc');
    dlmwrite([folderSaveDataTrack 'data' cellIden{n} 
        '.txt'],dataToWrite,'-append','precision',8,'delimiter', '\t',
        'newline', 'pc');
otherwise
    error('(SaveData): Invalid Input')
end
end
end

B.3 Spectra Plotting Code

% loads baseline spectrums for figure creation

clear all
close all
clc

%***User Input (Designed to match with test file naming protocol)**************
% Cell Identity
cellIden = 'CI95C9';

% Date (yyyyymmdd)
date = '20120824';
time = '1205';

% Folder where file is
folder = 'C:\Users\ecestudent\Dropbox\OpticsResearch\baselineSpectraSL';

% X-Axis Label
xlabelUser = 'Frequency';

% Y-Axis Label
ylabelUser = 'Transmission';

% Title
titleUser = ['Transmission Plot: ' cellIden];
spectra = importdata(['folder cellIden ' base' cellIden '_' date '_' time '.txt']);
frequency = spectra(1,:);
spectrum = spectra(2,:);

figure
plot(frequency, spectrum)
axis([-9e9 4e9 0.2 1.1])
xlabel(xlabelUser)
ylabel(ylabelUser)
title(titleUser)

%Calculates and displays lifetime Spectral Data Collected from Lifetime Spectroscopy tests.
%Dr. Hawkins Slow Light Research
%Author John Hulbert April 26, 2012

clear all
close all
clc

%***User Input (Designed to match with test file naming protocol)**********
%Cell Identity
%cellIden = {'CI95C9','E95C3','S95C2','I95C1'};

%ultimate vs rest 95C
%cellIden = {'CI95C4','E95C3','S95C2'};

%65C comparison
%cellIden = {'E65C2','S65C8','I65C1'};

%80C comparison
%cellIden = {'E80C3','S80C5','I80C2'};

%95C comparison
%cellIden = {'E95C3','S95C2','I95C1'};

%epoxy
%cellIden = {'E95C3','E80C3','E65C2'};

%Pb/Sn
%cellIden = {'I95C1','I80C2','I65C1'};

%indium atomic density
%cellIden = {'I95C1','I80C2','I65C1','E95C3'};

%indium linewidth
%cellIden = {'I95C1','I80C2','I65C1','E95C3'};

%Folder where file is
folder = 'C:\Users\ecestudent\Dropbox\OpticsResearch\dataTrackSpectraSL';

%In what form do you want the y-axis data? Choices are 'atomic'(atomic density) or 'absorption' (percent absorption)
yDataType = 'atomic';

nonlinOnOff = 0; %1 for on, 0 for off
fitOnOff = 0; %1 for on, 0 for off

%Fail Point (Percentage of Maximum value)
failPoint = 50;
[dren, numSpectra] = size(cellIden);

for ijk = 1:numSpectra

    % Load spectrum data from file
    spectra = importdata(fullfile('data' cellIden{ijk} '.txt'));
    time = spectra(1:end,1);
    absorption = spectra(1:end,3);
    linewidth = spectra(1:end,4);
    centerShift = spectra(1:end,5);
    clear spectra

    % Normalize dates to days
    days = time - time(1);
    clear time

    % Convert percent absorption to Pin/Pout
    PinPout = 1./(1 - absorption);

    % Atomic Density Calculation Data
    % Atomic Cross-section
    sigma = 1.2457e-9; % cm^2
    % Length of atomic cell
    length = 1; % cm

    switch yDataType
        case 'absorption'
            % The absorption data is already normalized
            data2Plot = absorption*100; % makes absorption a true percentage plot
            data2Fit = absorption;
            norm2orig = 100; % makes absorption a true percentage plot
            xaxisLabel = 'Days';
            yaxisLabel = '% Absorption';
        case 'atomic'
            % The non-linear fitting function requires the data to be normalized
            atomDensity = log(PinPout)/(sigma*length); % 1/cm^3
            atomDensityNorm = atomDensity./atomDensity(1,1);
            norm2orig = atomDensity(1,1);
            data2Plot = atomDensity;
            data2Fit = atomDensityNorm;
            xaxisLabel = 'Days';
            yaxisLabel = 'Atomic Density (atoms/cm^3)';
        otherwise
            error('Not a valid yDataType value.');
    end
    clear atomDensity atomDensityNorm absorption PinPout

    % Maximum Alignment (MA) some cells take a day or two to 'warm up' to maximum absorption. So that the fit function isn't messed up this excludes data points before the maximum absorption point in the fit.
    [C, maxI] = max(data2Fit);
    maxI = 2;
    data2FitMA = data2Fit(maxI:end,1);
    daysMA = days(maxI:end,1);
%x-axis data points for fitted plot
fitDays = linspace(min(daysMA), max(daysMA), 100);

if nonlinOnOff == 1
  %*************Non-linear Fit
  %Non-linear Fit function
  modelFun = @(p,days) p(1) + p(2)*exp(p(3)*days);
  %Non-Linear Fit
  paramEsts = nlinfit(daysMA, data2FitMA, modelFun, [0.5;0.5;-0.5]);
  nonlinFitPlot = modelFun(paramEsts,fitDays)*norm2orig;
  %Plot non-linear fit
  figure(1)
  subplot(2,3,1)
  plot(days,data2Plot,'o',fitDays,nonlinFitPlot,'-')
  title([cellIden{ijk} ' Non-Linear Fit'])
  xlabel(xaxisLabel)
  ylabel(yaxisLabel)
else
derase nonlinFitPlot
end
clear nonlinFitPlot

%*************PolyFit
for n = 1:5
  polyfitFit = polyfit(daysMA,data2FitMA,n);
  polyfitFitPlot(n,:) = polyval(polyfitFit,fitDays)*norm2orig;
  subplot(2,3,n+1)
  plot(days,data2Plot,'o',fitDays,polyfitFitPlot(n,:),'-')
  title([cellIden{ijk} ' PolyFit #' num2str(n)])
  xlabel(xaxisLabel)
  ylabel(yaxisLabel)
end
clear polyfitFit polyfitFitPlot fitDays

%*************Extract Fail Point Data
if fitOnOff
  %Setting Dialog Box properties, asks user which fit function to use.
  options.Resize='on';
  options.WindowStyle='normal';
  options.Interpreter='none';
  responseOrder = inputdlg('Which fit function would you like to use?
  (enter 1-5 for polyfit functions or nonlinear) [Q to quit]:','Fit
  Function?','1',['nonlinear'],options);
  userReply = responseOrder{1,1};
else
  userReply = '1';
end
%clear up memory
close(1)
clear polyfitFitPlot nonlinFitPlot

% get higher resolution fit data so that failpoint data can be more accurate
fitDaysHD = linspace(min(daysMA), max(daysMA), 1000);
switch userReply
    case 'nonlinear'
        FitPlotHD = modelFun(paramsEsts, fitDaysHD) * norm2orig;
    case '1'
        polyfitFitHD = polyfit(daysMA, data2FitMA, 1);
        FitPlotHD = polyval(polyfitFitHD, fitDaysHD) * norm2orig;
    case '2'
        polyfitFitHD = polyfit(daysMA, data2FitMA, 2);
        FitPlotHD = polyval(polyfitFitHD, fitDaysHD) * norm2orig;
    case '3'
        polyfitFitHD = polyfit(daysMA, data2FitMA, 3);
        FitPlotHD = polyval(polyfitFitHD, fitDaysHD) * norm2orig;
    case '4'
        polyfitFitHD = polyfit(daysMA, data2FitMA, 4);
        FitPlotHD = polyval(polyfitFitHD, fitDaysHD) * norm2orig;
    case '5'
        polyfitFitHD = polyfit(daysMA, data2FitMA, 5);
        FitPlotHD = polyval(polyfitFitHD, fitDaysHD) * norm2orig;
    case {'q', 'Q'}
        disp('Program quit by user.')
        return
    otherwise
        error('Not a valid response. (Fit Function?)')
end

clear polyfitFitHD data2FitMA daysMA

% find the fail point indece location and calculate failpoint day and value
ind = find(FitPlotHD < data2Fit(maxI, 1) * norm2orig * failPoint/100, 1, 'first');
xfailP = fitDaysHD(ind);
yfailP = FitPlotHD(ind);

pdays{ijk,} = days;
plinewidth{ijk,} = linewidth;
pcenterShift{ijk,} = centerShift;
pfitDaysHD{ijk,} = fitDaysHD;
pFitPlotHD{ijk,} = FitPlotHD;
data2Plot{ijk,} = data2Plot;
pxfailP{ijk,} = xfailP;
pyfailP{ijk,} = yfailP;

clear days linewidth centerShift fitDaysHD FitPlotHD data2Plot xfailP yfailP data2Fit n
end

if numSpectra == 1

% ************Plot linewidth and center shift plots
figure(2)
plot(pdays{1,:}, pcenterShift{1,:}, 'ok', 'Markersize', 10, 'Linewidth', 2)
title([cellIden{1} ' Center Absorption Dip Shift with respect to Bulk Cell'])
xlabel('Days', 'fontSize', 11, 'fontWeight', 'bold')
ylabel('Shift (Hz)', 'fontSize', 11, 'fontWeight', 'bold')
set(gca,'fontWeight','bold', 'LineWidth', 2, 'TickLength', [0.025; 0.05])

figure(2)
plot(pdays{1,:},plinewidth{1,:},'ok', 'Markersize', 10, 'LineWidth', 2)
set(gca, 'FontSize', 11, 'FontWeight', 'bold')

elseif numSpectra == 2

%*************Plot linewidth and center shift plots
figure(2)
plot(pdays{1,:},pcenterShift{1,:},'-sk', pdays{2,:},pcenterShift{2,:},'-sk', 'Markersize', 10, 'LineWidth', 2)
set(gca,'FontSize','11','FontWeight','bold')

figure(3)
plot(pdays{1,:},plinewidth{1,:},'-sk', pdays{2,:},plinewidth{2,:},'-sk', 'Markersize', 10, 'LineWidth', 2)
set(gca,'FontSize','11','FontWeight','bold')

%*************Plot Failure Analysis Data
figure(4)
plot(pdays{1,:},pdata2Plot{1,:},'ok', pdays{2,:},pdata2Plot{2,:},'ok', 'Markersize', 10, 'LineWidth', 2)
set(gca,'FontSize','11','FontWeight','bold')

225
elseif numSpectra == 3

%************Plot linewidth and center shift plot
figure(2)
plot(pdays{1,:},pcenterShift{1,:},'--xk', pdays{2,:},pcenterShift{2,:},'--xk', pdays{3,:},pcenterShift{3,:},'--xk', 'Markersize', 10, 'Linewidth', 2)
%title(['Center Absorption Dip Shift with respect to Bulk Cell'])
xlabel('Days', 'fontSize', 11, 'fontWeight', 'bold')
ylabel('Shift (Hz)', 'fontSize', 11, 'fontWeight', 'bold')
set(gca,'fontWeight','bold', 'LineWidth', 2, 'TickLength', [0.025; 0.05])
legend('Cu/In', 'Epoxy', 'Pb/Sn', 'fontSize', 11, 'fontWeight', 'bold')
legend(cellIden{1}, cellIden{2}, cellIden{3}, 'fontSize', 11, 'fontWeight', 'bold', 'Location','East')

figure(3)
plot(pdays{1,:},plinewidth{1,:},'--xk', pdays{2,:},plinewidth{2,:},'--xk', pdays{3,:},plinewidth{3,:},'--xk', 'Markersize', 10, 'Linewidth', 2)
%title(['Linewidth vs. Time'])
xlabel('Days', 'fontSize', 11, 'fontWeight', 'bold')
ylabel('Linewidth (Hz) [FWHM]', 'fontSize', 11, 'fontWeight', 'bold')
set(gca,'fontWeight','bold', 'LineWidth', 2, 'TickLength', [0.025; 0.05])
legend('Cu/In', 'Epoxy', 'Pb/Sn', 'fontSize', 11, 'fontWeight', 'bold')
legend(cellIden{1}, cellIden{2}, cellIden{3}, 'fontSize', 11, 'fontWeight', 'bold', 'Location','East')

%***************Plot Failure Analysis Data
figure(4)
plot(pdays{1,:},pdata2Plot{1,:},'--xk', pdays{2,:},pdata2Plot{2,:},'--xk', pdays{3,:},pdata2Plot{3,:},'--xk', 'Markersize', 10, 'Linewidth', 2)
%title(['Failure Analysis Plot (Fail Point @ ' num2str(failPoint) ' Max)'])
xlabel(xaxisLabel, 'fontSize', 11, 'fontWeight', 'bold')
ylabel(yaxisLabel, 'fontSize', 11, 'fontWeight', 'bold')
set(gca,'fontWeight','bold', 'LineWidth', 2, 'TickLength', [0.025; 0.05])
legend('Cu/In', 'Epoxy', 'Pb/Sn', 'fontSize', 11, 'fontWeight', 'bold')
legend(cellIden{1}, cellIden{2}, cellIden{3}, 'fontSize', 11, 'fontWeight', 'bold', 'Location','East')
pdays{1,:}
pdata2Plot{1,:}
pdays{2,:}
pdata2Plot{2,:}
pdays{3,:}
pdata2Plot{3,:}

elseif numSpectra == 4

%***************Plot linewidth and center shift plots
B.4 Arrhenius Lifetime Predictive Code

% Arrhenius Lifetime Prediction Calculations

figure(2)
plot(pdays{1,:},pcenterShift{1,:},'-ok', pdays{2,:),pcenterShift{2,:},'-dr', pdays{3,:},pcenterShift{3,:},'-xb', pdays{4,:),pcenterShift{4,:},'--sm', 'Markersize', 10, 'Linewidth', 2)
%title(['Center Absorption Dip Shift with respect to Bulk Cell'])
xlabel('Days', 'FontSize', 11, 'FontWeight', 'bold')
ylabel('Shift (Hz)', 'FontSize', 11, 'FontWeight', 'bold')
set(gca, 'FontSize', 16,'FontWeight','bold', 'LineWidth', 2, 'TickLength', [0.025; 0.05])
legend('In w/Cu', 'Epoxy', 'Pb/Sn', 'In', 'FontSize', 11, 'FontWeight', 'bold', 'Location', 'East')

figure(3)
plot(pdays{1,:},plinewidth{1,:},'-ok', pdays{2,:),plinewidth{2,:},'-dk', pdays{3,:),plinewidth{3,:},':-xk', pdays{4,:),plinewidth{4,:},'-sk',
'Markersize', 10, 'Linewidth', 2)
%title(['Linewidth vs. Time'])
xlabel('Days', 'FontSize', 16, 'FontWeight', 'bold')
ylabel('Linewidth (Hz) [FWHM]', 'FontSize', 16, 'FontWeight', 'bold')
set(gca, 'FontSize', 16,'FontWeight','bold', 'LineWidth', 2, 'TickLength', [0.025; 0.05])
legend('In w/Cu', 'Epoxy', 'Pb/Sn', 'In', 'FontSize', 16, 'FontWeight', 'bold', 'Location', 'East')

%************Plot Failure Analysis Data
figure(4)
plot(pdays{1,:},pdata2Plot{1,:},'-ok', pdays{2,:),pdata2Plot{2,:},'-dk', pdays{3,:),pdata2Plot{3,:},':-xk', pdays{4,:),pdata2Plot{4,:},'-sk',
'Markersize', 10, 'Linewidth', 2)
%title(['Failure Analysis Plot (Fail Point @ ' num2str(failPoint) ' % Max)'])
xlabel(xaxisLabel, 'FontSize', 16, 'FontWeight', 'bold')
ylabel(yaxisLabel, 'FontSize', 16, 'FontWeight', 'bold')
set(gca, 'FontSize', 16,'FontWeight','bold', 'LineWidth', 2, 'TickLength', [0.025; 0.05])
legend('In w/Cu', 'Epoxy', 'Pb/Sn', 'In', 'FontSize', 16, 'FontWeight', 'bold', 'Location', 'East')
%legend(cellIden{1}, cellIden{2}, cellIden{3}, cellIden{4}, 'FontSize', 11, 'FontWeight', 'bold')
graphSave = figure(3);
print(graphSave, '-dtiff', '-r300', 'linewidth')
graphSave = figure(4);
print(graphSave, '-dtiff', '-r300', 'atomicDensity')

else
error('Not a valid number of spectra')
end
clc
close all
clear all

%*********************User Input**************************

%Definition of failure (% of max value)
failPoint = 70;  % (%)

%Temperature at which failure data was collected (highest first)
tempCalc = [95, 80, 65] + 273.15;

%Select test series(In, Pb/Sn, epoxy)
testSeries = 'Pb/Sn';

%Time when failure occurred for each temperature in days. (Match with
%tempCalc temperature locations)
timeCalc = [1, 5, 8];

%********************************************************

%**********Compile Test Data (Semi User Dependant)******
%selects the lifetime data for the high(tH), medium(tM), and low(tL)
%temperatures based on test series(indium, lead/tin, epoxy)
switch testSeries
    case 'In'
        tH = [0.47, 0.43, 0.32, 0.69];
        tM = [4.47, 5.50, 1.15, 3.84, ];
        tL = [6.82, 2.71, 7.33];
    case 'Pb/Sn'
        tH = [1.60, 2.18, 1.48, 1.93, 0.97, 2.35, 0.57];
        tM = [3.27, 3.32, 1.33, 2.08, 2.07, 3.10];
        tL = [0.90, 1.32, 2.07, 2.49, 12.94, 5.00, 16.07];
    case 'epoxy'
        tH = [4.92, 3.28, 2.45];
        tM = [4.03, 10.08, 5.01];
        tL = [27, 16.38, 13.11, 4.20];
    otherwise
        error('Not a valid testSeries value.');
end

%Averages out all of the test samples for each temperature
[dren, lengthtH] = size(tH);
tHavg = sum(tH) / lengthtH;

[dren, lengthtM] = size(tM);
tMavg = sum(tM) / lengthtM;

[dren, lengthtL] = size(tL);
tLavg = sum(tL) / lengthtL;

%places all of those averages in one array
timeCalc = [tHavg, tMavg, tLavg]
%*********************************************************
%Constants
k = 8.6e-5; %eV/K
titleCalc = [num2str(failPoint),'% Absorption Drop Fail Condition'];

%Setting temperature range for lifetime projection
failTempC = [95,90,80,70,65,60,50,40,30,25,20]; %Temperature to calculate fail time (Celsius)
failTemp = failTempC+273.15; %Temperature to calculate fail time (Kelvin)

%****Calculating and plotting Arrhenius equation in linear form to extract Ea
lnInvt = log(1./timeCalc);
invT = 1./tempCalc;

polyFitData = polyfit(invT,lnInvt,1)

Ea = -polyFitData(1) * k
prefactorA = exp(polyFitData(2))
polyFitLine = polyval(polyFitData,invT);

subplot(1,2,1)
plot(invT,lnInvt,'+k',invT,polyFitLine,-k', 'Markersize', 10, 'Linewidth', 2) %
xlabel('1/T  (1/Kelvin)')
ylabel('ln[1/t]  (t=days)')
%title(['Calculating Ea']) % with ',titleCalc])
legend('Experimental Data', 'Fit Function')
%axis([2.75e-3 2.95e-3 -2.5 -1])

%*******Projecting failure times at different temperatures with Arrhenius Equ
failTime = 1./(prefactorA*exp(-Ea./(k*failTemp)))

subplot(1,2,2)
semilogy(failTempC,failTime,-k', 'Linewidth', 2, 'Markersize', 18)
ylabel('Days to Failure')
xlabel('Temperature  (C)')
%title(['Projected Lifetime']) % with ',titleCalc])
%axis([20 90 1 1000])